

Fabrication and Characterization of Novel Core-shell Structured Metastable Intermolecular Composites

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 dissertation comprises of 7 chapters. Shina Maini was the sole author of Chapters 1, 2, 3 and 7, which were written under the guidance of Dr. John Z. Wen and were not written for specific publications. Following are the details of the collaborative research work presented in Chapters 4, 5 and 6.

Research presented in Chapters 5 and 6

Both Chapter 5 and Chapter 6 include the first-author publications from the peer-reviewed journals. Shina Maini and Anqi Wang were the primary co-investigators of these studies. The research was conducted at the University of Waterloo under the supervision of Dr. John Z. Wen. The conceptualization of these studies was framed by Dr. Wen, while the design of experiments was co-created by Shina Maini and Anqi Wang. The data analysis was done in partnership with Dr. Wen and Dr. Anqi Wang.

As the lead author of these two chapters, I was responsible for contributing to conceptualization of the research design, carrying out experiments, data collection and analysis, and drafting manuscripts. My co-authors provided advice at each step of the study and provided feedback on drafts of manuscripts. The citations for these two chapters are the following:

- Maini, S., Wang, A., & Wen, J. Z. (2024). Characteristics of Gasless Combustion of Core–Shell Al@ NiO Microparticles with Boosted Exothermic Performance. *ACS Omega*.
- Maini, S., Wang, A., & Wen, J. Z. Fluctuating Flame from Suspending Ferrimagnetic Core/Shell Al@ Fe₃O₄ Nanoparticles in a Magnetic Field. *Advanced Materials Interfaces*, 2400328.

Exceptions to sole authorship of material are as follows

Research presented in Chapter 4

This research was conducted by Dr. Anqi Wang and me, under the supervision of Dr. John Z. Wen. The project was conducted at University of Waterloo. Anqi designed the research apparatus under the guidance of Drs. John Wen and Jean-Pierre Hickey. Shina Maini contributed to conducting the experiments to find the activation energy and prove the repeatability. Each author provided intellectual input on the manuscript draft.

Citation:

- Wang, A., Maini, S., Hickey, J. P., & Wen, J. Z. (2022). Solution synthesis of core-shell n-Al@ CuO based on electrostatic self-assembly for enhanced energetic performance. *Chemical Engineering Journal Advances*, 11, 100323.

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Abstract

The advancement in micro-electromechanical systems (MEMS) and other engineering applications demands highly efficient, responsive, and controllable energetic materials. Metastable Intermolecular Composites (MICs) consisting of an energetic blend of reducing and oxidizing particles in either a nano or microscale, have thus gained an immense limelight in the past few years. The reducing and oxidizing component of an MIC is also referred to as a fuel and an oxidizer, respectively. MICs belong to the broader category of thermites. Within the MIC family, classifications include conventional metal-based nanothermites, innovative core-shell configurations, 3D ordered macroporous structures (3DOM), layer-by-layer nanolaminates and ternary nanocomposites. Through specialized fabrication methods, it is possible to create any of the above-mentioned architecture to realize enhanced combustion performance while allowing precise control over ignition characteristics and safety measures. Amongst different geometries, the core-shell arrangement, in particular, stands out as a promising microstructure, offering a self-contained reactive system comprising fuel and oxidizer housed within a single assembly. It is however challenging to construct a perfect core-shell assembly wherein each fuel particle is uniformly and completely covered by the oxidizer particles. Therefore, this thesis puts forward, three wet-chemistry synthesis methods for fabricating three novel core-shell structured MICs, namely Al@CuO, Al@NiO and Al@Fe₃O₄, whereupon Al forms the core and CuO, NiO and Fe₃O₄ particles form the shell inside the core-shell unit respectively. Wet-chemistry synthesis is shown to overcome the obstacles associated with traditional manufacturing processes, such as incomplete mixing of fuel and oxidizer and phase separation across samples to some extent. These core-shell structured MICs are shown to exhibit significantly enhanced thermochemical behaviors, reduced ignition delay, and homogeneous combustion, which are critical for applications requiring precise energy delivery and minimal disturbance, such as in micro-initiators and welding.

The first project embodying this research work was the development of the fabrication process and establishing the properties of spherical core-shell Al@CuO MICs. This study revealed that synthesis parameters, especially ammonia content, critically influenced the structure of the final product. This manipulation allowed the transition between a well-mixed nanocomposite and individual nanosized core-shell spheres at NH₃/Cu ratio of 6.0. Notably, these Al/CuO core-shell nanoparticles demonstrated a reduction in both onset and peak combustion temperatures by 8 °C and 20 °C respectively, alongside a decreased activation energy by 20 kJ/mol when compared to physically mixed counterparts, indicating improved efficiency and reactivity due to the optimized proximity between fuel and

oxidizer. The second project focused on application of a similar wet-chemistry based one-pot synthesis process to Al/NiO duo. The Al@NiO MIC was found to be relatively easier to fabricate since the core-shell structure was not found to be as sensitive to the synthesis parameters and showcased the initiation temperature and the content of energy release from the reaction between Al and NiO was in the same ballpark for various samples of different equivalence ratios and NH_3/Ni ratios. These composites showed exceptional ability to be combusted without a significant delay to ignition after the laser was triggered. This could be attributed to the efficient thermite and subsequent alloy-formation reactions facilitated by the core-shell configuration. This structure not only reduced the activation energy for the thermite reaction but also enabled a rapid and complete combustion, outperforming physically mixed composites. For both Al@CuO and Al@NiO, electrostatic force was deduced to be the driving force behind the formation of these core-shell assemblies.

Then the research was further advanced to Al@Fe₃O₄ MICs since magnetite (Fe₃O₄) was hypothesized to serve a dual role as an oxidizer and a functional ferrimagnetic component, thereby imparting an extra degree of freedom to the resulting composite that could be leveraged in unique applications. The previous wet-chemistry route was found to be inapplicable in this case since Fe did not form a coordination complex ion with NH_3 to trigger a core-shell assembly around the negatively charged Al particles. A novel fabrication process leveraging the process of crystallization was invented. Fe₃O₄ shell was constructed by initiating the decomposition of Fe-salt into Fe₃O₄ crystallites that used Al nanoparticles as seed to nucleate upon. The fabricated core-shell structure resulted in a significant decrease in activation energy and a shorter ignition delay compared to physically mixed samples. The magnetic nature of these composites allowed for controlled transport and delivery, enhancing their application scope.

Collectively, these studies highlighted the potential of core-shell structured MICs in refining the performance of energetic materials for industrial as well as engineering utilizations. The findings demonstrated that wet-chemistry synthesis routes can effectively produce advanced energetic materials with superior combustion properties, offering a promising avenue for the development of more efficient and reliable energetic systems.

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I extend my sincere gratitude to my supervisor, Dr. John Z. Wen, for generously providing me with the invaluable opportunity to conduct research in his esteemed laboratory. Under his guidance, I have gained profound insights into the realms of combustion, nano energetics, technical writing, and scientific analysis, shaping me into a more adept researcher.

I am deeply appreciative of the dedicated members of my committee, Drs. Fiona Kelly, Peng Peng, Kevin Musselman, and Yuning Li, who invested their time and expertise in reading my thesis and offering constructive feedback. Their valuable contributions have significantly enriched the quality of my work.

I would like to express my heartfelt thanks to all my research colleagues who have been instrumental in shaping my academic journey over the past four years. A special acknowledgment goes to Dr. Anqi Wang, whose insightful discussions about experiments and analysis have been instrumental in shaping the trajectory of my research.

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Finally, I owe a debt of gratitude to my parents, siblings and husband, whose unwavering support and belief in me have been a constant source of strength. Their presence, encouragement, and willingness to be a sounding board in both triumphs and challenges have been the cornerstone of my perseverance.

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List of abbreviations

MEMS	Micro-electromechanical systems
MICs	Metastable intermolecular composites
3DOM	3D ordered macroporous structures
SHS	Self-propagating high temperature synthesis
ARRM	Arrested reactive milling
P4VP	Poly (4)-vinyl pyridine
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis
ACS	American Chemical Society
ER	Equivalence ratio (Φ)
PM	Physically-mixed
TEG	Tri-ethylene glycol
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
XPS	X-ray photoelectron Spectroscopy
EDS	Energy Dispersive X-ray Spectroscopy
XRD	X-ray Diffraction
PTFE	Polytetrafluoroethylene
CVD	Chemical vapor deposition
PVP	Polyvinylpyrrolidone
PDA	Polydopamine
EPD	Electrophoretic deposition
JCPDS	Joint Committee on Powder Diffraction Standards
IONPs	Iron oxide nanoparticles
FTIR	Fourier Transform Infrared Spectroscopy
STEM	Scanning transmission electron microscopy

Chapter 1

Introduction

1.1 Short Background and Research Gap

Thermite is a pyrotechnic composition of a reductive fuel, such as aluminum (Al) [1], magnesium, silicon, boron etc. and an oxidizer like a metal oxide [2, 3]. The types of the fuel and the oxidizer can be selected in such a way that their redox reaction can produce either a substantial amount of heat or a sharp pressure change, which can be leveraged in many applications [4, 5]. With the boom of nanotechnology, nanothermites comprising of at least one component in nanoscale dimension, are becoming an emerging frontier in areas of propulsion and energetics, because of high energy densities (2100-4800 J/g) [6, 7], high propagation velocities(<300m/s) [7] and small diffusion path between reacting components. Out of all nanothermites, Al-based nanothermites have been widely favored and investigated due to the commercial availability of stable Al nanopowders, with narrow particle size distribution and well-defined metal/oxide content, combined with a high oxidation enthalpy and an abundance on earth [8, 9, 10]. Over the past two decades, researchers have shown that structure-control over nanothermites prompts improved material properties, combustion performance and multifunctionality. This revelation has led to the development of various structure-controlled nanothermites [11] like powder mixtures with homogeneously distributed reactants, layer-by-layer, 3DOM and core-shell structured composites by applying special fabrication approaches [12]. Among these, the core-shell structure increases the surface area of contact between the fuel and the oxidizer. Either fuel or oxidizer in different shapes can be employed as the core material, which is then fully covered by the other component to form a core-shell structure. It is worth noting that most of the studies regarding core-shell nanothermites are, in fact, recent and supremely focused on Al/CuO core-shell nanothermites [13, 14, 15, 16] capitalizing on micron-sized Al particles. A well-controlled core-shell structured thermite harnessing nano-Al hasn't been fabricated yet. Additionally, Al/CuO pair (in stoichiometric composition), despite exhibiting large energy density (20.8 kJ/cm³) [6] and high reactivity in the form of low activation energy and low temperatures of onset and peak of reaction, is faced with one major short coming that limits its application universally in the field of energetics. The

thermite reaction of Al/CuO pair is so explosive that it results in very high flame temperature which consequentially decomposes Cu(II) oxide to Cu(I) oxide releasing oxygen gas and eventually, vaporizing the Cu metal formed after the thermite reaction. Literature quotes the gas production of around 0.54 moles gas/100 g thermite [6, 17, 18] While this gas production is necessary for its application in the realms of MEMS, airbags, gas generators, and microthrusters, it is highly undesirable in the field of microinitiators and welding [17] where the produced gas and its pressure can induce vibrations in the mechanical system or disturbances in flow. For such scenarios, there is a requirement of the generation of a high heat output without production of gas accompanying the thermite reaction. A careful review of the literature [6,17] reveals that Al/NiO and Al/Fe₃O₄ display an excellent merit in this regard with the gas product amounting to ~2% and ~10%, respectively, of the gas generated during the thermite reaction of Al/CuO pair. Shockingly, the data on the fabrication of these core-shell nanothermites is scarce in the literature. Although there are a few scattered studies [19, 20, 21] reporting on the synthesis and characterization of Al/NiO composites, none of them constructed 0D(spherical) core-shell nanothermites. Interestingly enough, structured Al/Fe₃O₄ nanothermites have not been actualized yet. Fe₃O₄ is particularly fascinating. Thanks to its ferrimagnetic nature, it is widely exploited in medical applications like delivery of a drug to a target, magnetic resonance imaging (MRI), and in hyperthermia [22]. Nonetheless, it has never been researched for its energetic attributes when combined with Al. Thus, the fabrication and thermochemical characteristics of these core-shell nanothermites require a thorough investigation. If conducted successfully, this research can open unique arenas of applications, for example, welding and joining in places faced with constraints pertaining to equipment, energy production and human resources namely in space, underwater, Arctic, and Antarctic extreme environments [23]. Al/Fe₃O₄ core-shell nanothermites can be transported to such locations with the aid of magnetic field.

1.2 Research Objectives

The primary objectives of this research work are:

1. Development of a process of fabricating core-shell structured Al@CuO, Al@NiO and Al@Fe₃O₄ nanothermites.
2. Characterization of these synthesized core-shell nanothermites for morphology, chemical elemental composition, thermos-chemical behavior, and combustion performance.

3. Proposing a formation mechanism behind the construction of the core-shell structure of each of these nanothermites
4. Proposing a reaction mechanism or the steps involved in the thermochemical response of these energetic composites upon slow heating.
5. Determination the apparent activation energy of the fabricated composites in comparison to their physically-mixed counterparts.
6. Since Al@Fe₃O₄ MIC is expected to be magnetic in nature, one unique attribute of this thesis is showcasing a novel application for Al@Fe₃O₄ nanothermite exploiting its magnetic property.

1.3 Thesis Organization

This thesis is organized into six chapter. The big picture of this thesis is displayed in Figure 1.

- Chapter 1 begins with an outline of the area of research via a short background, treading towards the research gap that this thesis is aiming to fill in and describes the goals of the study. Chapter 1 lays the foundation for the wide-ranging review of literature presented in the following chapter.
- Chapter 2 encompasses all literature that was read and found relevant to the broad subject of nanothermites, going in depth regarding various synthesis methods being followed by the researchers worldwide. Then, the debate regarding the reaction mechanism of aluminothermic reactions in nanothermites is stated, followed by the traditional and novel proposed applications of nanothermites.
- Chapter 3 outlines the methodology used in fabricating core-shell structured Al@CuO, Al@NiO and Al@Fe₃O₄ nanothermites. The experimental and characterization procedures have been highlighted and a discussion is made with respect to different uncertainties arising in the measurements.
- Chapter 4, 5 and 6 form the heart of this thesis. These three chapters have culminated into three journal publications. Thus, these chapters hold the detailed review of literature for each of the Al/CuO, Al//NiO and Al/Fe₃O₄ duos, along with the results that perpetuated from all the experimental studies done in that regard.

- Chapter 7 contains the summary of the major conclusions from various projects that form this thesis. This chapter also lists the limitations of this research and provides recommendations for future work.

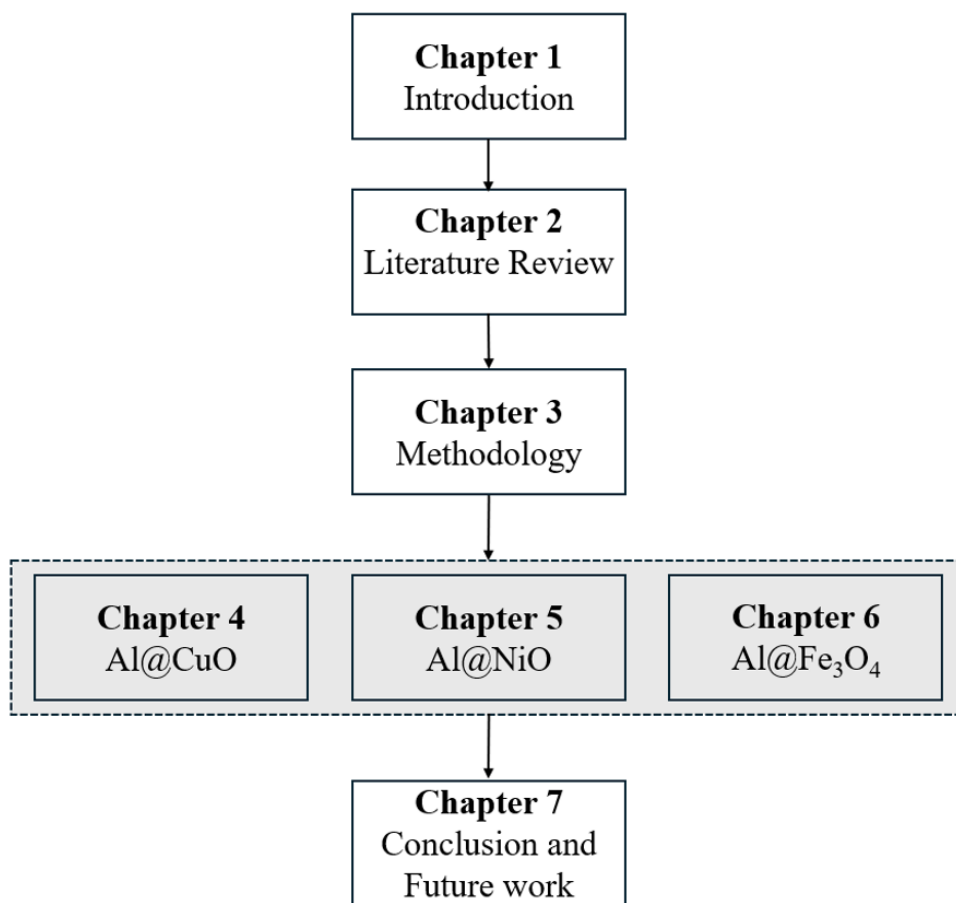


Figure: 1.1: An overview of the structure of this thesis.

Chapter 2

Literature Review

This chapter presents an overview of the general information and relevant literature concerning nanothermite synthesis, thermite reaction mechanism, and applications. Initially, a small overview of energetic materials is provided, and the focus is shifted towards nanothermites by highlighting the shortcomings of the other classes of energetic materials. Following this, the thermite reaction is introduced, and a foundation is laid for the subsequent chapters. Then, the distinctions between nanoscale and bulk-scale thermite are delineated. Subsequently, the advantages of imposing a structure-control are mentioned and the superiority of the core-shell structure is highlighted. Finally, literature concerning different synthesis processes, thermite reaction mechanism and the potential applications of nanothermites are reviewed.

2.1 Energetic Materials and Their Shortcomings

Energetic materials cover a diverse array of substances like propellants, pyrotechnics, and explosives [24] which can release a significant amount of contained chemical energy upon getting triggered by an external factor like impact, friction, or shock. Conventionally, the term “energetic materials” is used for military explosives which are monomolecular organic chemicals, generally consisting of nitro, hydrazine and azido groups in their molecular structure. At the atomic level, these materials are majorly made up of four kinds of atoms: carbon C, nitrogen N, oxygen O and hydrogen H. Some notable examples of energetic materials in this category are RDX, HMX, TNT, TATB, and CL20 [24]. The molecular structures for RDX, HMX and CL-20 are shown in Figure 2.1. [25] When these materials combust, the O from nitro, hydrazine and azido groups transfers to C and H atoms to form CO, CO₂ and H₂O. Therefore, it is safe to say that the enthalpy of formation of the reaction products, CO₂ and H₂O when the oxidation is complete, limits the maximum heat of combustion for any monomolecular compound. Since both oxidizing and reducing components for the reaction are present within the same molecule, the exothermic reaction is enabled very rapidly. The rate of this reaction is primarily controlled by the reaction kinetics of decomposition of the molecule. [26]. Another fascinating caveat about the combustion of monomolecular energetic materials is the fact that they detonate, i.e., they

display supersonic combustion which characterized by an extremely violent reaction accompanied by a shock wave travelling through the material at a speed exceeding the speed of sound [27]. Since detonations are usually destructive, this pushes the applications of these materials for destructive purposes like mining etc.

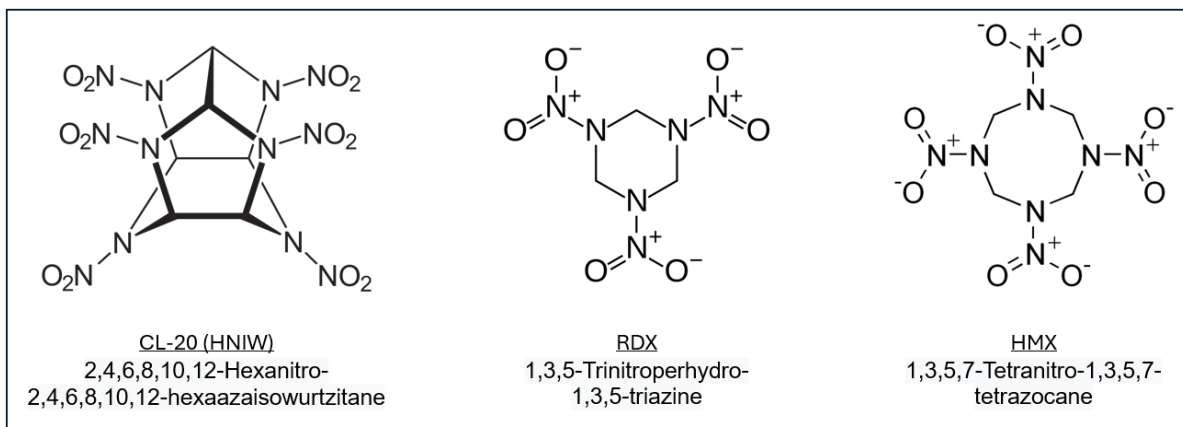


Figure 2.1: Molecular structures of RDX, HMX and CL-20, reproduced/adapted with permission from Ref. [25]. 2015, Yang, Z.

Despite the rapid reaction rates, monomolecular compounds exhibit challenges in modifying their material properties for tuning the sensitivity and improving the storage conditions [28], thereby compelling researchers to shift focus to other energetic materials such as the metal-based nanocomposite. For instance, Figure 2.2 illustrates the maximum enthalpies of reaction per unit mass and volume for some metals and monomolecular compounds. Metals, as fuels, clearly out-perform the monomolecular compounds with enthalpies as high as 138 kJ/cm^3 as compared to $\sim 10\text{--}30 \text{ kJ/cm}^3$ for the monomolecular compounds. [29]

Metal-based fuels usually incorporate elements such as Ti, Zr, Al, Mg, and B, among others. These metals (fuel), typically in powder form, result in a slower and a more manageable rate of reaction relative to that of monomolecular energetic materials. This is because metals need an external oxidizer to combust, unlike monomolecular energetic materials. This is also the reason why metals do not detonate, they deflagrate. Metal combustion is characterized by subsonic combustion with relatively

low or no pressure release. [27, 30] In the last 20 years, there has been increasing interest in metal-based energetic materials within both the scientific population and civil industry, owing to their ability to create localized gas, thermal energy, and power [31].

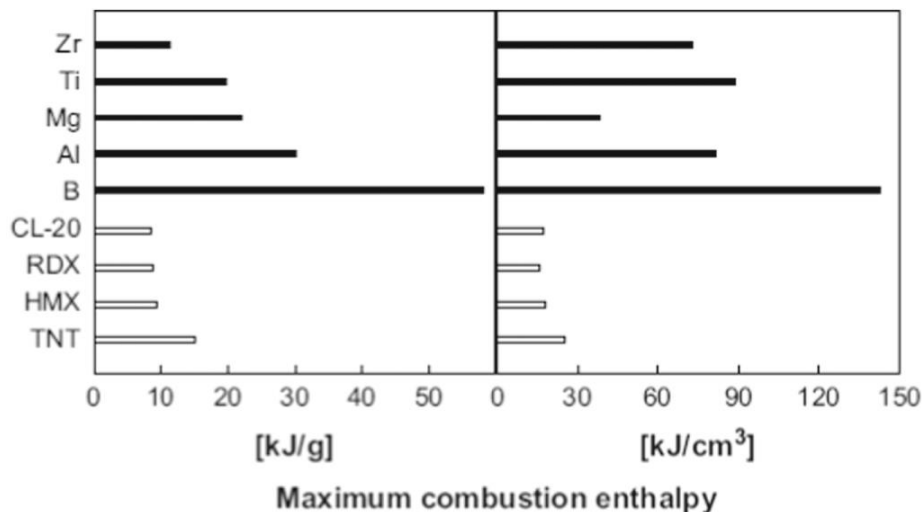


Figure 2.2: A comparison of enthalpy of combustion of monomolecular energetic materials and metal fuels, reproduced/adapted with permission from Ref. [24]. 2009, Dreizin, E. L.

2.2 Thermites and Thermite Reactions

In 1908, Goldschmidt first coined the term thermite [32] while attempting to extract metals from its ores. The term “thermite” refers to an amalgamation of materials which can rapidly release the great amounts of chemical energy stored within by virtue of a chemical reaction. This chemical reaction is usually termed as thermite reaction describing an oxidation-reduction reaction between metal/fuel and oxidizer. The oxidizer gets reduced in the process, while the fuel/metal gets oxidized. Metals that can be used as a fuel include silicon, magnesium, aluminum, titanium, zinc, or boron. Amongst these, aluminum is a widely used fuel component [33] because of its affinity to oxygen and high energy-density per unit volume. In addition, aluminum is abundantly present on planet Earth, and it retains the properties of being highly reactive while producing mostly benign products. Due to its affinity to oxygen, aluminum spontaneously reacts with atmospheric air and forms an aluminum oxide shell around it, which acts as a passivation layer and further prevents Al from getting oxidized, thereby

facilitating safe storage. As far as the oxidizer component of a thermite composite is concerned, elemental oxides like cupric oxide (CuO) [34-36], nickel oxide (NiO) [31,37], iron oxide (Fe₂O₃) [38-40], tungsten oxide (WO₃) [41], and molybdenum oxide (MoO₃) [41, 42, 43] are some of the choices.

Table 2.1 shows the energy production from the thermite reactions between different fuel/oxidizer pairs. It is obvious that some metal/metal oxide pairs can reach adiabatic temperatures of beyond 3000K. A typical thermite reaction is shown in Equation 1.1:



where AO is the oxidizer; M is the metal/fuel component; MO is the newly produced thermodynamically more-stable oxidizer; A is the metal, and ΔH is energy released during reaction. Table 2.1 also shows that the characteristics of a thermite reaction are highly material dependent. [44] Figure 2.3 provides a qualitative and quantitative judgement of the heat of reaction and thermal diffusivity of various aluminothermic formulations in comparison to monomolecular energetic compounds. While Al/MnO₂ is seen to be highly energetic, it also produces a lot of gas. Al/CuO hits quite a sweet spot with high energy and moderate gas production. Al/NiO and Al/Fe₃O₄ are the only two duos that produce moderate energy with negligible gas production. The structured core-shell Al/CuO, Al/NiO and Al/Fe₃O₄ form the bulk of this thesis.

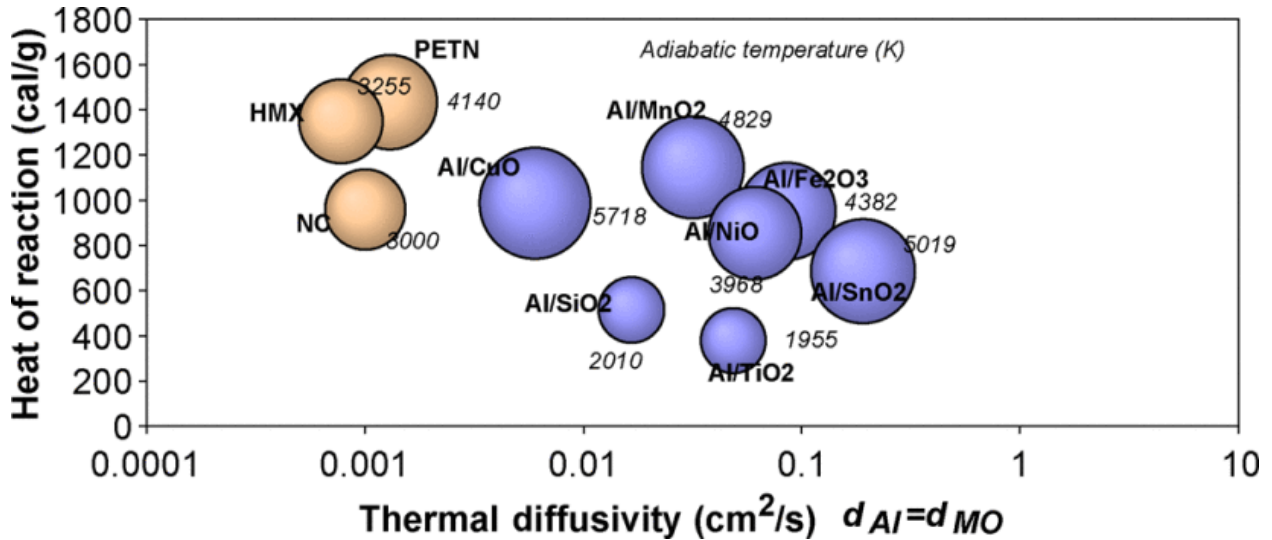


Figure 2.3: Heat of reaction versus thermal diffusivity for different nanothermite systems, reproduced/adapted with permission from Ref. [31]. 2007, Rossi, C.

Table 2.1: Properties of some thermite pairs, reproduced from Fischer et al. [44]

Constituents	Adiabatic flame temperature (K)	State of products		Gas formed/100 g	Energy release	
	With phase change	State of oxide	State of metal	Moles gas/100g	-Q, cal/g	-Q, cal/cm ³
2Al + 3CuO	2843	liquid	l-g	0.5400	974.1	4976
2Al + Fe ₂ O ₃	3135	liquid	l-g	0.1401	945.4	3947
8Al + 3Fe ₃ O ₄	3135	liquid	l-g	0.0549	878.8	3747
2Al + 3NiO	3187	liquid	l-g	0.0108	822.3	4288
2Al + MoO ₃	3253	l-g	liquid	0.2425	1124	4279
2Al + WO ₃	3253	l-g	liquid	0.1434	696.4	3801
4Al + 3WO ₂	3253	l-g	solid	0.0662	500.6	4047
4Al + 3MnO ₂	2918	liquid	gas	0.8136	1159	4651

2.3 Nanothermites vs Conventional Thermites

An inherent limitation of employing metal fuels lies in their relatively sluggish reaction rates upon ignition [45]. This lethargy arises from the elongated diffusion pathways for both mass and thermal energy, resulting in micron sized powders exhibiting prolonged delay in ignition as compared to monomolecular energetic compounds. Consequently, a protracted period of self-sustained combustion ensues between micron metal-powders and oxygen [46]. Furthermore, micron sized metal fuels fail to undergo complete consumption during the reaction, curtailing their potential for their installation in energy intensive applications of explosives, propellants, and pyrotechnics. The kinetics of the thermite reaction are impeded by (i) time required for oxygen to reach the surface of the metal; (ii) its rate of diffusion through Al₂O₃ passivation layer [47].

Conventional thermites contain micro-sized fuel and oxidizer particles [31] and exhibit high energy density per unit volume and affinity to oxygen. Difficulties in powder mixing hinders the net interfacial contact are between reacting components, thereby altering the reactivity. Although conventional thermite composites comprise of components with amplified interfacial contact, thereby facilitating tunable thermite reactions, this does not alleviate ignition delay or notably augment reaction rates.

According to the diffusion-control reaction mechanism which is widely accepted for micro-sized thermites, ignition delay predominantly stems from oxygen diffusion through the innate Al_2O_3 passivation layer [47]. Despite the unique mechanism of reaction between Al-fuel and metal oxide, the oxygen supplied by the oxide merely marginally influences the diffusion of oxygen. Moreover, as the reaction progresses, the Al_2O_3 passivation layer thickens, prolonging the diffusion path for oxygen. This delayed reaction kinetics, coupled with protracted heat dissipation, may induce a quenching effect in certain applications, markedly affecting consistency in thermite utilization for MEMS applications.

To minimize the ignition delay and maximize the rate of reaction, the emergence of nanotechnology has facilitated the production of nanothermites—mixtures of fuel and/or oxidizers with nanoparticles—exploiting their high specific surface area, marking a transition to nanoenergetic materials [31]. Going from micron to nano size increases the surface area, specifically the surface/volume ratio, which consequently raises the surface energy. Moreover, the small particle size enhances the area of contact and component distribution in the mixture, which consequentially results in upgraded reactivity [46] with enhanced rate of propagation and potential for easier thermal ignition [31, 48, 49] as compared to conventional thermites. All these assets make nanothermites promising contenders for applications such as microchip-initiators or solid propellant ignition. Their speedy reaction kinetics and elevated energy release offset the heat dissipation effects in micro-applications and ignition of alternative propellant types.

It should be mentioned here that the extended surface area offered by the nanoparticles does not always translate into the anticipated performance enhancement. Nanothermites are faced with certain inherent limitations like incomplete mixing, or heterogeneous phase distribution between fuel and oxidizer, which not only diminishes the surface area of contact and rates of reaction drastically, but also induces reactive sintering of agglomerated particles, nullifying the benefits of increased surface area.

To circumvent these challenges, researchers have discovered various structural designs and synthesis routes. For instance, magnetron sputtering has been utilized to deposit multi-layers of alternating fuel and oxidizer to form nanolaminates, which consequentially lowered the reaction temperatures and enhanced safety measures by mitigating loose MICs powder during synthesis. However, this method is primarily suitable for small-scale production with limited combustion rates. Self-assembly has

emerged as a promising approach for bulk fabrication of nanothermite composites, offering improved homogeneity and heightened reactivity of the final product. Various additives, such as surfactants [50, 51], graphene oxide [52], and DNA [53], have been utilized to induce assembly. The resulting self-assembled nanothermite exhibits superior homogeneity and augmented surface contact between fuel and oxidizer, thereby enhancing reactivity.

Among the diverse array of structures, the core-shell structure stands out for maximizing surface contact between fuel and oxidizer, thereby enhancing energetic performance. Additionally, a well-coated metal oxide shell diminishes the potential participation of gaseous oxygen in the energetic reaction, fostering a more uniform and consistent reaction as the density of nanoenergetic materials fluctuates.

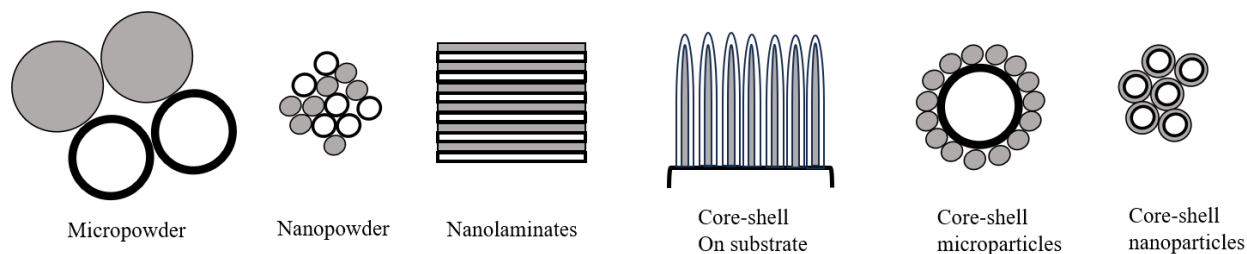


Figure 2.4: Comparison of different structures of thermites, reproduced/adapted with permission from Ref. [15]. 2019, Zhang, Y.

2.4 Synthesis Methods

MICs are prepared using several different methods, each with a different approach and with both advantages and disadvantages. Factors that influence choice of method include the following: simplicity of the process [31, 54]; safety of the process [31]; process temperature [31]; cost of the process [31]; ability for the products to be tailored [24, 31]; homogeneity of the product [24, 31, 54]; agglomeration ability of the product [54]; concentration of product impurities [31]; thermal conductivity of the product [54, 55]; and reaction energy and rate of the product [31, 54].

The following paragraphs describe numerous methods used in literature to prepare MIC composites.

Ultrasonication: Ultrasonication is a prevailing approach wherein an ultrasound bath is used to prepare reactive nanomaterials involving blending nanostructures of reactants. In this technique [56, 57] the reactant particles i.e. metal and metal oxide particles are subjected to mixing in a bath of solvents like

alcohols (ethanol, hexanol etc.), alkanes (hexane etc.), or any other liquid using an intensified ultrasound actuator. Subsequently, the liquid is removed via evaporation at low temperatures, resulting in the attainment of a dry powder. This method has an inherent challenge of the quality of the mixing process. A review indicates that most assessment techniques for mechanically mixed nanopowders rely on scanning and viewing a limited region of the mixed composite sample, necessitating repeated scanning across various parts of the sample powder for a dependable assessment. The significance of mixing quality becomes more pronounced when dealing with nanopowders of varying morphologies. Typically, oxide nanopowders exhibit shapes like nanorods or flakes, making it challenging to capture an image that accurately represents the mixture, especially when bigger particles in the form of some complex geometries like flakes may obstruct the view of the relatively smaller particles. Ultrasonication is a type of mechanical mixing method and although an effective method on a laboratory scale, scaling it up poses difficulties as the mixing quality tends to decrease with an increase in batch size. Despite all these factors, ultrasonication remains the standard method of producing nanothermites.

Sol-gel method: This method [24, 31] is a wet-chemistry method involving two steps: hydrolysis and condensation. Many researchers consider the sol-gel as a substitute to other mechanical mixing methods. In general, it offers a process where an oxide material matrix is formed with metal nanoparticles filling its pores. The general procedure for creating a reactive nanomaterial via this process is as follows. First the metal salts, also termed as the precursor, are made to react with water and this step of this process is called hydrolysis. Then, a gelation agent is added into the mix. The main function of the gelation agent is to convert the colloid solution into gel like network. This is followed by the addition of metal nanoparticles with an intent that the particles get trapped in the gel like network created with the aid of gelation agents like silica, alumina, titanium oxide, propylene oxide etc. Subsequently, the fluid from the gel is extracted out with slow evaporation, leaving behind an energetic MIC. While this process achieves a very intimate mixing, it does come with drawbacks such as unnecessarily highly porous final product, which is undesirable towards certain purposes. Additionally, the materials that possess the capability to be gelled are limited, and scalability poses challenges due to the requirement for precise introduction of the metal nanopowder at a specific stage in the process. The process (Figure 2.5) usually produces either an aerogel, a lightweight porous material, or a xerogel,

a dense form in which the pores have collapsed, also called cryogel [54, 58]. To prepare MICs, a metal oxide aerogel is produced, and the metal particles are embedded in the pores of the aerogel [24].

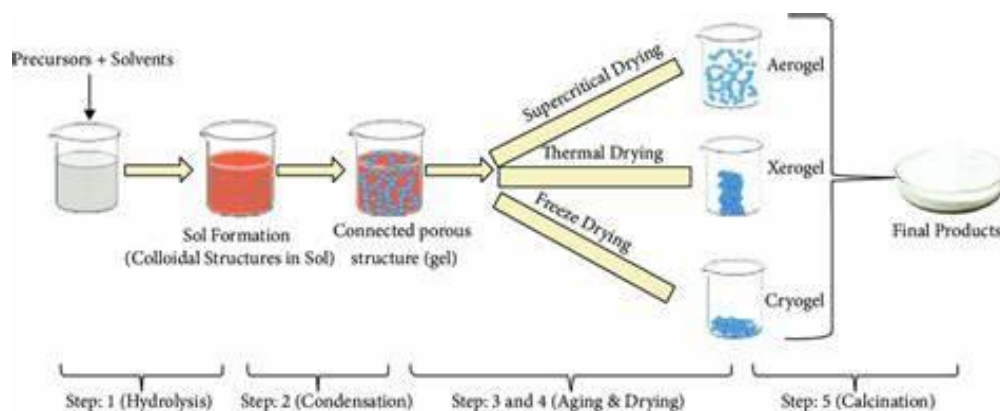


Figure 2.5: The sol-gel process showing different stages: from a precursor to an aerogel, reproduced/adapted with permission from Ref. [59]. 2021, Bokov, D.

Layered vapour deposition: An intriguing approach to nanothermite synthesis involves creating a composite through stacking subsequent nano-layers of individual components with the aid of vacuum. [60, 61]. In that effect Al/Ni multilayer films were made by Yang et al. [62] with thickness of each layer ranging from 60-300 nm. The Al and Ni are evaporated alternately with the help of electron beam and are consequently deposited over a substrate made of glass which has been pre-coated with a photoresist at a certain pressure. The photoresist is removed in the end after dissolving leaving behind independent Al/Ni layers. Upon initiation, a SHS reaction was observed and Al_3Ni_2 , Al_3Ni , and Al were found in the reaction products within layers. This method was subsequently patented by T. W. Barbee and T. Weihs with systematic development, and extensive research followed. Subsequent research efforts led to the development and characterization of Al/CuO multilayer foils.

Arrested reactive milling: ARRM stands out as the exclusive top-to-bottom approach for the preparation of thermite nanocomposites [63, 64]. In this technique, big granular particles of reactant are mixed, and ball milled. While milling, the reactants get ignited because of the mechanical energy from the balls and that triggers a self-sustained exothermic reaction. To obtain an energetic MICs, the self-sustained reaction is halted prior to its onset. It is critical to determine this time of stopping the reaction and it has been estimated in literature by preliminary experimentations with small samples and running modelling & simulations for large batches numerically [65, 66]. The outcome of this

method is the formation of compact composite comprising dense microparticles mixed with nanoparticles. The onset time of the reaction in this approach becomes a crucial factor for effectively mixing the reactants, and this time is influenced by variables of the milling process such as the ratio $\frac{\text{mass of reactants}}{\text{balls in the milling vessel}}$, the size of the batch and the temperature. In addition to all these factors, the properties of the composites prepared by ARRM are also affected by solvents used in the process. The solvents are sometimes referred to as process control agents used during milling. The process control agents serve three purposes: (i) as a lubricant; (ii) as a cooling agent; (iii) to functionalize surface of the prepared mixtures. Figure 2.6 shows the schematic of ARRM method used by Mursalat et. al [67] to study the effect of polar and nonpolar liquid solvents on properties of thermites. The two process control agents used in this study were acetonitrile and hexane. Figure 2.6 represents these agents in yellow and blue as immiscible solvents.

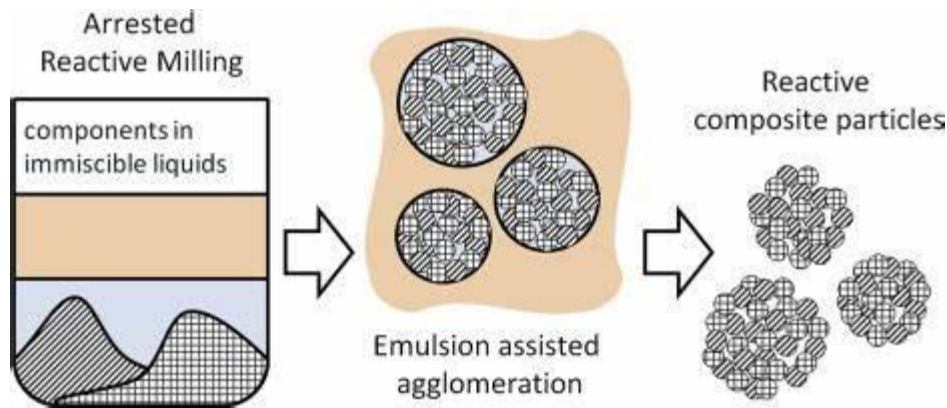


Figure 2.6: Schematic diagram of ARRM, reproduced/adapted with permission from Ref. [67]. 2020, Mursalat, M.

Self-assembly: In recent years, an alternative approach has emerged: the self-assembly of metal particles on functionalized metal oxide particles. This is usually achieved by installing either difference of electrostatic charges on the metal and metal oxide particles or by using additives like polymers or surfactants to direct a close-knit assembly. Self-assembly has the potential to yield ordered structures with better performance characteristics when compared with traditional mixed powders. For instance, the polymer P4VP can be used to functionalize CuO nanorods [68, 69] and an Al + CuO nanocomposite can be built by mixing Al into it. Subsequently, P4VP functionalizes the nanorods and aluminum particles self-assemble over those nanorods, resulting in ordered and ornamented nanorods. Similarly,

micelle sol-gel synthesis process was harnessed to create a porous iron oxide and an Al-Fe₂O₃ MIC was developed by adding surfactants [70]. The use of surfactants led to an ordered structure of pores in Fe₂O₃. In contrast, a reference sample synthesized without surfactants exhibited less ordered pores. The fabricated structured composite exhibited a superior rate of combustion, showcasing an improved control of properties of reaction properties. Cheng et al. [70] conducted a comparison of kinetics of the reaction of Al and Fe₂O₃ nanothermites formed using a self-assembly process versus ones prepared by mechanical mixing. They concluded that the self-assembly significantly amplified the chemical kinetics as compared to physically mixed counterparts. This enhancement was attributed to the increased intimacy between the metal and metal oxide, leading to superior rate of flame propagation. However, it should be pointed out that this method comes with some shortcomings. For example: the cost to prepare the oxide is high; the resulting material is highly porous and the presence of an additive/functionalization agent within the reactants reduces the specific energy output from the thermite reaction.

Overall, the fabrication processes are divided into two big blocks: physical & chemical. The processes like ultrasonication, arrested reactive milling, vapour deposition etc. fall under the umbrella of physical methods. And the processes like sol-gel method, self-assembly comes under the bracket of chemical methods. Generally speaking, physical methods usually have high costs and low yields, preventing them from being used for bulk production. Physical methods result in non-homogeneous/phase separated MICs. Chemistry methods, sometimes referred to as solution-based wet chemistry methods or bottom-up approach, are fairly novel. They have been considered a promising method of bulk fabrication of MICs with improved homogeneity, thus increasing the reactivity of the final product. Various additives have been utilized to trigger the assembly, such as surfactants, graphene oxide, and DNA, but these additives act as a dead mass between the fuel and the oxidizer. These structure-controlled MICs have demonstrated better homogeneity and enhanced fuel-oxidizer surface contact, improving reactivity of the fabricated MICs.

2.5 Mechanism of Reactions

A thermite reaction involves the oxidation of Al and the reduction of metal oxide. The oxidation of Al is a complicated process because it involves various variables. A stand-alone Al particle bears a core-

shell structure with active Al as core and the peripheral alumina (Al_2O_3) as shell. [71] This core-shell structure strongly influences Al oxidation process. The Al_2O_3 shell acts as a hinderance between the active Al core and the oxidizing component and therefore, limits the reactivity of Al. In addition to the spontaneous Al_2O_3 shell on top of the Al particle, the extra Al_2O_3 which is formed as a product from the combustion reaction, further wraps around the leftover active Al core, further deterring the combustion reaction, leading to incomplete combustion and lower energy release. Extensive research has been done to resolve the problem of Al_2O_3 shell hampering Al oxidative capability and combustion efficiency. Researchers have proposed three mechanisms to explain Al ignition and combustion process:

- The oxidant diffusion mechanism
- The Alumina phase transformation mechanism
- The Al-core melt-dispersion mechanism

The following paragraphs provide a brief description of these mechanisms one by one.

The oxidant diffusion mechanism: The contact between the oxidizer and the active Al is crucial for the thermite reaction to happen. Zachariah [72-74] proposed a three-step reaction mechanism (Figure 2.7) based on the “shrinking core” model for the spherical particles wherein the reaction front moves inwards radially leading to the formation of completely reacted by-products (ash) as an outer layer. Step 1 involves the transport of the oxidizer molecules through the Al_2O_3 shell layer, i.e., the diffusion of molecules to reach ash layer. The speed of this step is dictated by Al_2O_3 shell resistance. Step 2 is the diffusion of oxidizer molecules through the ash layer to reach the active Al core. This step is affected by ash resistance. And the last step comprises of the chemical reaction between the active/unreacted Al core and the oxidizer. This step is governed by the chemical reaction resistance. The experiments in the research database have shown that Al_2O_3 shell resistance is minimal since alumina keeps forming spontaneously and the ash resistance is the dominating resistance. Therefore, the rate limiting step is the diffusion of oxidant through the ash layer to meet with Al core.

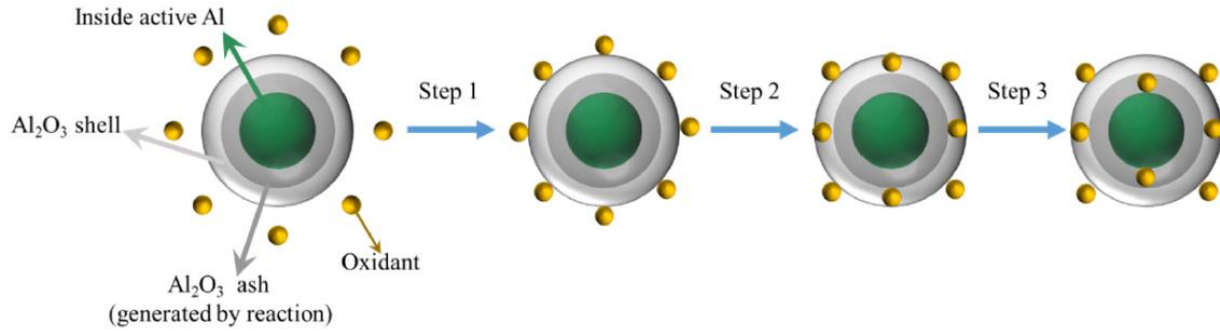


Figure 2.7: Zachariah's three step mechanism of oxidation of Al, reproduced/adapted with permission from Ref. [75]. 2022, Wang, D.

The Alumina phase transformation mechanism: This reaction mechanism was proposed by Trunov et. Al [76] based on the coexisting growth and crystal transformation of the Al_2O_3 layer on the outside of Al particle. Al oxidation process is split into four stages (Figure 2.8). In 1st stage, the amorphous Al_2O_3 slowly grows thicker, and Al cations diffusing outwards control the rate of reaction [77]. In the 2nd stage, the amorphous alumina shell transitions into γ phase when the temperature is necessarily high. Since the γ - Al_2O_3 is denser than the amorphous Al_2O_3 , the shell cracks to let the inside active Al to get in direct contact with the oxidizer molecules to speed up the oxidation of Al. As temperature rises, the γ - Al_2O_3 starts healing and thickening, eventually forming a polycrystalline continuous layer on top of Al by the end of 2nd stage. In the 3rd stage, the γ phase transforms into δ or θ - Al_2O_3 . Since the density of this phase is not much different from the γ phase, the shell layers stay intact, not affecting the rate of reaction much. In this stage, however, the oxidation is taking place because of the inward grain-boundary diffusion of oxidizer's anion molecules. [78] By the end of this stage, a homogeneous shell of α - Al_2O_3 forms around the Al particle. In the last stage of Al oxidation, the α - Al_2O_3 becomes denser to such an extent that the path of diffusion of any ions across it is completely blocked, thereby decreasing or halting the reaction.

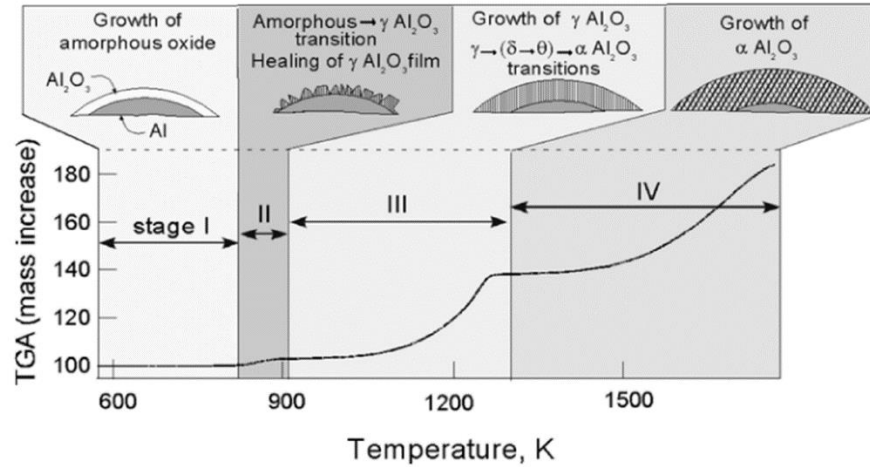


Figure 2.8: The transformation of Al_2O_3 shell during the oxidation of Al particle, reproduced/adapted with permission from Ref. [76]. 2006, Trunov, M. A.

The Al-core melt-dispersion mechanism: This mechanism has been proposed by Levitas [79], specially to address the Al oxidation during rapid heating rate. He proposed that the fast heating melts the inside Al core. The molten Al expands by 6% in volume, pushing against the Al_2O_3 shell. Ultimately the Al_2O_3 shell spalls, leading to the flow to molten Al to meet nearby oxidant for the thermite reaction to take place. Figure 2.9 illustrates this reaction mechanism.

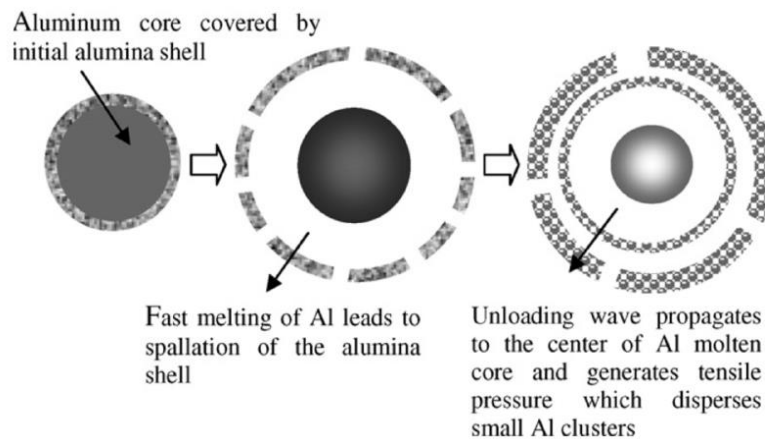


Figure 2.9: The melt and dispersion of Al during the oxidation of Al at rapid heating rate, reproduced/adapted with permission from Ref. [80]. 2009, Levitas, V. I.

In summary, it can be said that the diffusion of the oxidant, the crystallization and the growth of the Al_2O_3 shell, and the melting and dispersion of the internal active Al, are all pivotal towards the oxidation process of Al. However, the reaction mechanism is dictated by two leading factors: particle size and the heating rate of Al. Different conditions lead to different oxidation process. This is elaborated in the next three points.

- Slow heating rate and nano-Al: The diffusion of the oxidiser molecules plays a principal role and Al conforms to Zachariah's [72-74] three-step oxidation process.
- Slow heating rate and micro-Al: The transformation and growth of the Al_2O_3 shell have the most influence on the oxidation process. Al adheres to Trunov's [76] Al_2O_3 shell transformation and growth mechanism.
- Fast heating rate and nano-Al: The melting and dispersion of the inside Al-core govern the oxidation process Al, so Levitas' [79] melting diffusion mechanism is followed.

Thermite reaction can be initiated via triggering through variety of means, including laser radiation [81], electrical power, impact, or the propagation of a flame front of a chemical reaction [82, 83]. In addition to the above three factors, the ignition capability of a thermite is also affected by the reactants' stability, both chemically and physically. Chernenko et al. [84] categorized oxide reactants in 2 groups on the basis of stability: chemically-stable and chemically-unstable oxides. Within chemically stable category, extra classification reveals physically-stable oxides, which remain inert until ignition, and physically-unstable oxides, which decompose by either melting or subliming below the threshold of ignition temperature, potentially enhancing reaction rates. Volatile oxides in the latter category can lead to reactions with aluminum vapor upon heating. Chemically unstable oxides can decompose upon heating, releasing oxygen that initiates combustion. For instance, chromium trioxide decomposes at 170°C , releasing oxygen and sparking ignition. Additionally, certain oxides, like iron oxide and copper oxide, further oxidize in air, releasing heat that may elevate temperatures to the ignition point.

To outline the reaction mechanism of aluminum-based thermites, both Al and the metal oxide play a crucial role in the redox reaction. From Aluminum standpoint, the particle size and the heating rate strongly influence the reaction. From the metal oxide side of things, it is the stability and thermal decomposition of the oxide that maneuver the reaction steps. Therefore, all these causes need to be

considered to explain the reaction mechanism of the thermite reaction and combustion of the MICs in the context.

2.6 Applications

Primitive thermites were mostly used for welding. The classic example of this is the use of $\text{Al}/\text{Fe}_2\text{O}_3$ powder mixtures for railway welding [85]. The property that allows for such utilization is the substantial heat coming from the thermite reaction that melts the Fe and Al_2O_3 product which flows into the area of welding because of gravity and the difference of density. A major advantage of choosing $\text{Al}/\text{Fe}_2\text{O}_3$ powder mixtures for welding is the minimal gas generated from the thermite reaction. The pictogram of the traditional welding process is shown in Figure 2.10. The thermites can be further applied to the low-oxygen and vacuum environments because they do not require any external oxygen for the thermite reaction to take place and evolve heat. Therefore, MICs can be employed in under water construction, such as wet-welding and thermal boring and spacecraft maintenance.

Another area where modern-day MICs can be exploited is in the automobile industry. The automobile airbag system (Figure 2.11) is prevalent micro-pyrotechnical technology which was invented in the early 1970s. [86] It was designed to decelerate the motion of the car occupants within milliseconds in case of a collision to avoid injury. [87, 88]. The airbag inflator is an essential, gas-generating part of the airbag system. It houses gas-generating mixtures which, upon activation, ignite to produce enough gas to eventually inflate the airbag. Most of the inflating chemicals developed so far rely on propellants, like sodium azide (NaN_3) and potassium nitrate (KNO_3), which decompose [89] to produce N_2 that fills up the airbag.

There are two inherent problems with the current airbag systems:

- i. Metallic azides are extremely noxious. [90] If the combustion is incomplete, the products of the decomposition of azides are also toxic. Azides have been replaced by high N_2 -producing non-azide compositions like guanidine nitrate, ammonium nitrate etc. [91, 92] to reduce the toxicity. In fact, Takata utilized ammonium nitrate as a gas generator for inflating airbags from the beginning of 2001. And over 16 million vehicles were recalled from across the globe due to this serious safety concern [94, 95].

- ii. When the heat generation upon activation is inadequate, there isn't enough energy available to decompose the gas-generating materials completely. Hence, the desirable volume of the N_2 gas to fill an airbag is not fully attained which eventually can lead to serious failures of the automobile's airbag system. [96].

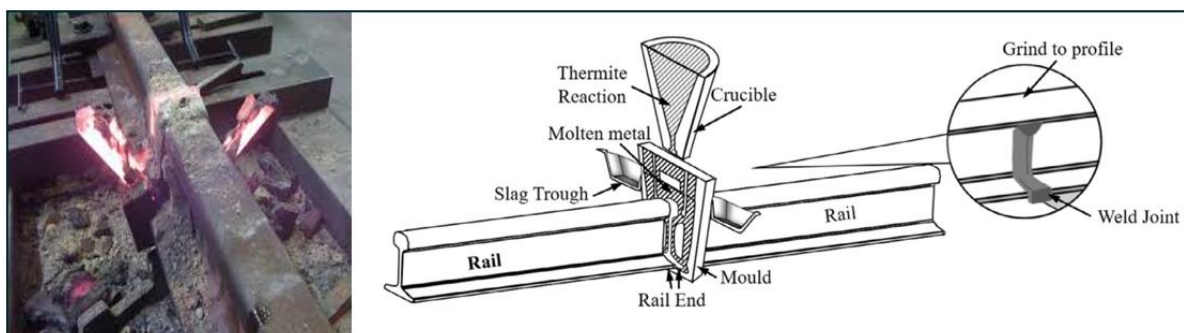


Figure 2.10: Traditional thermite welding and thermite welding setup, reproduced/adapted with permission from Ref. [83]. 2021, Liu, Y.

Hence, most of the automobile safety community has been on the hunt for a better inflating chemical or technology or a lesser harmful alternative. One solution to the abovementioned problems is using hybrid mixtures of nanothermites and the existing gas-generating chemicals. If the nanothermite itself produces gas (like Al/CuO system), it can contribute towards additional gas for inflating the airbag. If the nanothermite is gasless (like the Al/NiO and Al/Fe₃O₄ system), it can act as a heat source and ensure complete combustion of the existing gas-generating chemicals.

Adding to this, MICs can be exploited based on their gas producing capability. The more the gas produced via thermite reaction, the greater is the explosivity of the thermite. In that regard, the Mg/CuO thermite system can be classified as highly explosive since significant gas is produced when Mg and CuO react. Such a material is more fitting for pyrotechnic/fireworks and propellant applications rather than for welding/joining usage since the gas will result in bubbling in the weld/joint. Therefore, the gas production from the thermite reaction is necessary for its application in the realms of MEMS, airbags, gas generators, and microthrusters. However, it is highly undesirable in the field of microinitiators [17] and welding where the produced gas and its pressure can induce vibrations in the mechanical system or disturbances in flow. It is in such systems, where the novel core-shell Al/NiO and Al/Fe₃O₄ systems can be exploited.

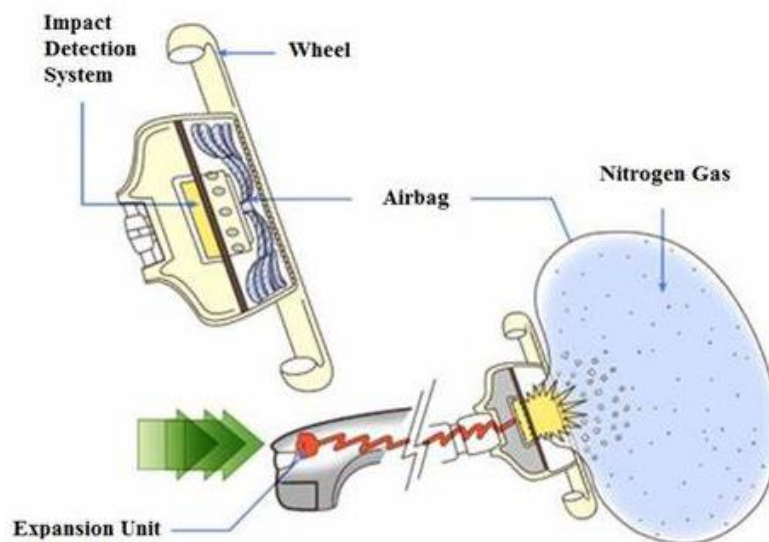


Figure 2.11: Schematic of an automobile airbag system reproduced/adapted with permission from Ref. [87]. 2000, Shaout, A, © 2024 Inderscience Enterprises Ltd.

Amongst the three oxidizers explored in this research work, Fe_3O_4 bears a unique characteristic. Fe_3O_4 is ferrimagnetic in nature. Therefore, at a nanoscale level, $\text{Al}/\text{Fe}_3\text{O}_4$ will also be magnetic. This magnetic nature is a distinctive feature of this thermite system. By virtue of this, $\text{Al}/\text{Fe}_3\text{O}_4$ MICs can be transported and put to use, by the aid of magnetic field, in the areas faced with human resources and equipment constraints, e.g., space, underwater, Arctic, and Antarctic extremum environments.

Chapter 3

Methodology

This chapter provides the details about design of experiments towards fabricating and characterizing the novel core/shell structured Al@CuO, Al@NiO and Al@Fe₃O₄ MICs. There are three sections in this chapter:

- i) *Fabrication*: All the experimental procedures followed to synthesize the core-shell structured MICs are contained in this section. This section also details various parameters that were varied during fabrication and how it affected the morphology and performance of the resulting composite.
- ii) *Characterization*: This section elaborates on the characterization methods which were harnessed to examine these materials' chemical and physical characteristics.
- iii) *Uncertainty analysis*: This section discusses different potential sources of error in the measurements from this study. In this section, various arguments are made in the context of establishing confidence in the outcomes from this study.

3.1 Fabrication

3.1.1 Al@CuO MIC

Al (100 nm diameter) and CuO nanoparticles (80 nm diameter, as a reference oxidizer sample for performance comparison) were acquired from US Research Nanomaterials, Inc. The active percentage of Al nanoparticles was determined to be at 83% by DSC-TGA. Cu(NO₃)₂·2.5H₂O, ACS reagent of 98% purity and ammonia water solution of concentration of 28 – 30% were bought from Sigma-Aldrich (St. Louis, MO).

In a typical synthesis, 50 mg Al particles were disseminated in 15 mL ethanol and mixed via ultrasonication for 2 hours, while a copper ammonia complex suspension was prepared by adding the desired amount of ammonia solution into Cu(NO₃)₂·2.5H₂O solution in 10 mL ethanol. After the 2-hour sonication, the copper ammonia complex (Cu-NH₃ complex) suspension and an extra 25 mL ethanol were poured into the Al dispersion. After stirring for 1 hour, the mixture was filtered harnessing

vacuum filtration. The solid was collected and annealed at 230 °C for 3 hours to obtain the final Al/CuO core-shell product.

Two variables, the equivalence ratio (Φ) and ammonia to copper ratio (NH₃/Cu ratio) were investigated to find out how they affect the formation and energetic performance of the final product. The nominal equivalence ratio of the Al/CuO final product was calculated using the molar amount of active aluminum core and copper nitrate, assuming Al to Cu ratio does not change much during the fabrication process, as shown in Equation 3.1. Ammonia to copper ratio was calculated by the molar amount of ammonia and copper nitrate used to obtain the Cu-NH₃ complex suspension. The concentration of ammonia used in the calculation was 30%. Samples with equivalence ratios of 1.5, 2.0, 2.5, 3.0, and 4.0, and ammonia to copper ratios of 4, 6, 8, and 16 were prepared and analyzed. NH₃/Cu ratio at 4 is the stoichiometric value of forming the complex coordination ion of Cu(NH₃)₄²⁺. Considering the concentration of ammonia was between 28 – 30%, the actual NH₃/Cu ratio was slightly lower than the calculated amount. Therefore, for the samples with NH₃/Cu ratio of 4, the copper was in excess. The amounts of raw materials are listed in **Error! Reference source not found..**

$$\Phi = \frac{(n_{Al}/n_{CuO})_{actual}}{(n_{Al}/n_{CuO})_{stoichiometry}} = \frac{(n_{Al}/n_{Cu(NO_3)_2})_{actual}}{(n_{Al}/n_{CuO})_{stoichiometry}} \quad \text{Equation 3.1}$$

Table 3.1. Detailed amounts of raw materials of each sample.

Φ	NH ₃ /Cu ratio	Al powder	Cu(NO ₃) ₂ ·2.5H ₂ O	30% ammonia
1.5	6	50 mg	360 mg	540 µL
2.0	6	50 mg	269 mg	405 µL
2.5	6	50 mg	215 mg	328 µL
3.0	6	50 mg	180 mg	270 µL
4.0	6	50 mg	135 mg	203 µL
1.5	4	50 mg	360 mg	360 µL
1.5	8	50 mg	360 mg	720 µL
1.5	16	50 mg	360 mg	1440 µL
2.0	4	50 mg	269 mg	270 µL
2.0	8	50 mg	269 mg	540 µL
2.0	16	50 mg	269 mg	1080 µL

2.5	4	50 mg	215 mg	215 μ L
2.5	8	50 mg	215 mg	430 μ L
2.5	16	50 mg	215 mg	865 μ L
3.0	4	50 mg	180 mg	180 μ L
3.0	8	50 mg	180 mg	360 μ L
3.0	16	50 mg	180 mg	720 μ L
4.0	4	50 mg	135 mg	135 μ L
4.0	8	50 mg	135 mg	270 μ L
4.0	16	50 mg	135 mg	540 μ L

Two Cu-NH₃ complex samples at NH₃/Cu ratios of 4 and 16 were prepared by adding the calculated amount of ammonia aqueous solution to Cu(NO₃)₂·2.5H₂O/ethanol solution. The precipitation was filtered and dried at 70 °C overnight to obtain the target product.

Five reference Al/CuO samples of the corresponding equivalence ratios were prepared using ultrasonication as a set of standard samples to compare with the core-shell samples. Two dispersions; 50 mg aluminum nanoparticles in 2 ml ethanol and the calculated amount of 80 nm CuO nanoparticles in 2 mL ethanol; were prepared by the aid of ultrasonication for 2 hours. These dispersions were then mixed and dispersed ultrasonically for an additional hour. All ethanol was removed by drying the resulting mixture for 4 hours at 70 °C in the oven.

3.1.2 Al@NiO MIC

US Research Nanomaterials, Inc. provided one micron Al and 15-35 nm NiO particles (used as a reference oxidizer to prepare the physically mixed sample for performance comparison). The active percentage of Al microparticles was determined to be 97% by DSC-TGA. Sigma-Aldrich provided Nickel (II) nitrate hexahydrate, Ni(NO₃)₂·6H₂O of 99.999% purity and ammonia water solution (28 – 30% by NH₃ weight). The ethanol (ACS grade) used during the experiment contained water content less than 0.1% as per the manufacturer and was stored with molecular sieves to avoid contamination by moisture.

The fabrication procedure (Figure 3.1) and the design of experiments for Al@NiO MIC was similar to that of Al@CuO. In brief, the synthesis process began with sonicating 50 mg Al microparticles

dispersed in 15 mL ethanol for 2 hours, along with preparing a Ni-NH₃ intermediate by adding the desired amount of ammonia solution into Ni-salt solution prepared with 10 mL ethanol. Post sonication, the Ni-NH₃ suspension and an extra 25 mL ethanol was poured into the Al dispersion and stirred magnetically for 1 hour before being filtered. The solid, thus collected on the filter paper was then annealed at 230 °C for 3 hours to obtain the final $\mu\text{Al}@\text{NiO}$ core-shell product.

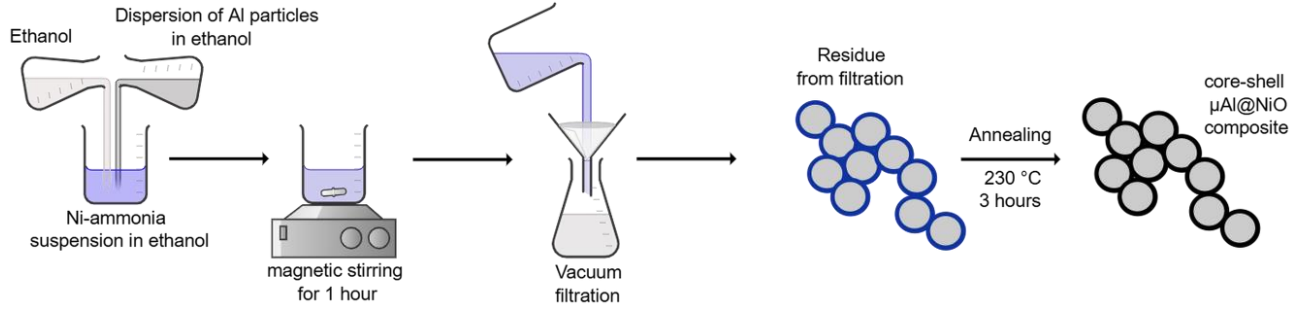


Figure 3.1. Schematic of fabrication process

Two variables, the equivalence ratio (Φ) and ammonia to nickel ratio (NH₃/Ni ratio) were investigated to find out their effect on the formation and energetic performance of the final product. The nominal equivalence ratio of the Al/NiO final product was calculated using the molar amount of active aluminum core and nickel nitrate, assuming Al to Ni ratio does not change much during the fabrication process, as shown in Equation 3.2.

$$\Phi = \frac{(n_{\text{Al}}/n_{\text{NiO}})_{\text{actual}}}{(n_{\text{Al}}/n_{\text{NiO}})_{\text{stoichiometry}}} = \frac{(n_{\text{Al}}/n_{\text{Ni(NO}_3)_2})_{\text{actual}}}{(n_{\text{Al}}/n_{\text{NiO}})_{\text{stoichiometry}}} \quad \text{Equation 3.2}$$

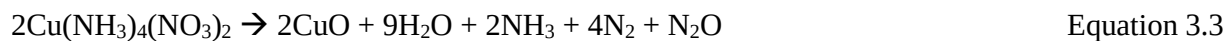
NH₃/Ni ratio was calculated by the molar amount of ammonia and nickel nitrate used to obtain the Ni-NH₃ intermediate suspension. The concentration of ammonia used in the calculation was 30%. Samples with equivalence ratios of 2.0, 2.5, 3.0, 3.5 and 4.0, and ammonia to nickel ratios of 4, 6, 8, 10 and 12 were prepared and analyzed. NH₃/Ni ratio at 6 is the stoichiometric value of forming the complex coordination ion of Ni(NH₃)₆²⁺. Considering the concentration of ammonia was between 28 – 30%, the actual NH₃/Ni ratio was slightly lower than the calculated amount. Therefore, for the samples with NH₃/Ni ratio of 6, the nickel was in excess. The amounts of raw materials are listed in Table 3.2.

Table 3.2. Amounts of raw materials of the sample

ER	NH ₃ /Ni ratio	Al powder	Ni(NO ₃) ₂ •6H ₂ O	Ammonia 30%
2.0	6	50 mg	403.9 mg	524.7 µL
2.5	6	50 mg	323.1 mg	419.8 µL
3.0	4	50 mg	269.3 mg	233.2 µL
3.0	6	50 mg	269.3 mg	350 µL
3.0	8	50 mg	269.3 mg	459 µL
3.0	10	50 mg	269.3 mg	583 µL
3.0	12	50 mg	269.3 mg	688.5 µL
3.5	6	50 mg	230.8 mg	302.2 µL
4.0	6	50 mg	202 mg	264.7 µL

A reference PM μ Al/NiO sample of the equivalence ratio 3.0 was prepared using ultrasonication as a standard sample to compare with the corresponding core-shell sample. Two dispersions were prepared: (i) 50 mg aluminum nanoparticles in 2 mL ethanol; (ii) the calculated amount of 15-35 nm NiO nanoparticles in 2 mL ethanol; using ultrasonication mixing for 2 hours. These dispersions were then mixed and dispersed ultrasonically for an additional hour. All ethanol was removed by drying the resulting mixture for 4 hours at 70 °C in the oven.

For both Al@CuO and Al@NiO, the last step of the fabrication process involves annealing the Al@Cu(NH₃)_x(H₂O)_y(NO₃)₂ and Al@Cu(NH₃)_x(H₂O)_y(NO₃)₂ respectively. The x and y in the chemical formula relies on the metal ion's coordination number, amount of ammonia used during fabrication and the pH of the reaction solution. During annealing, the coordination complex loses NH₃ and H₂O to the ambient and the nitrate ion decomposes into N₂, N₂O, NO, etc. leaving behind oxide ion with the metal. For instance, Southern et. al [97] reported the following equation (Equation 3.3) for the decomposition of tetra-ammine copper nitrate coordination complex. A likewise equation (Equation 3.4) has been put forward by Migdał-Mikuli et. al [98]. Hence, the coordination complex gets converted to CuO and NiO.



3.1.3 Al@Fe₃O₄ MIC

Al nanoparticles of 100 nm diameter and magnetite (Fe₃O₄) nanoparticles of 15-20 nm diameter was sold by US Research Nanomaterials, Inc. The active percentage of n-Al was found to be 83% by using DSC-TGA. Iron (III) acetylacetonate, (Fe(C₅H₇O₂)₃, abbr. Fe(acac)₃), the precursor for iron oxide, was acquired from EMD Millipore Corporation (Billerica, MA). TEG was used as a solvent for the polyol method and was bought from Sigma-Aldrich Co (St Louis, MO). Commercially available analytical grade ethyl acetate and ethanol were bought locally.

The synthesis procedure employed was as follows. 2 mmol of Fe(acac)₃ and the desired amount of n-Al (based on Φ) were firstly dispersed in 10 ml of TEG in two separate vials in the sonication bath for 2 hours. After the 2 hours of sonication, both the dispersions and an extra 10 ml TEG were poured into a two-neck round bottom flask immersed in an oil bath equipped with a condenser, magnetic stirrer, and a provision for continuous flow of nitrogen (Figure 3.2). This concoction, while being magnetically stirred under the atmosphere of nitrogen, was subjected to a temperature program. The oil bath was first slowly heated (heating rate around 3.4 °C/min) to 180 °C and kept at that temperature for 30 minutes. It was then quickly heated (heating rate around 14 °C/min) to 280 °C, the reflux temperature of TEG, and kept at that temperature under reflux for 1 hour. At the end of the 1-hour mark, the resulting solution in the flask was a black homogeneous colloidal suspension of Al@Fe₃O₄ core-shell nanoparticles in TEG. This mixture was then allowed to cool to room temperature. The particles were subsequently separated by flocculating them together by adding 10 ml ethanol and 20 ml ethyl acetate into the mixture, followed by sedimentation under the influence of a magnetic field. The black precipitated particles were then washed and separated three more times utilizing the same procedure. Consequently, the collected precipitation was dried in an oven at 70 °C for 15-30 minutes to vaporize all the wash solvents. The powder product, thus obtained, consisted of Al@Fe₃O₄ core-shell nanoparticles with some remnant TEG strongly adhering to the surface of the nanoparticles. It has been reported that TEG plays an extremely important role in the polyol procedure of forming Fe₃O₄ nanoparticles [99]. A dense solvation layer of TEG is formed on the surface of the fabricated Fe₃O₄ nanoparticles, helping with its monodispersed size and dispersion. However, this solvation layer cannot be removed easily by washing with other solvents and acts as a dead mass and a barrier if left in the sample. In order to acquire the solvent-free core-shell Al@Fe₃O₄ nanoparticles, an additional removal

step of prolonged annealing the particles under an atmosphere of nitrogen in a tube furnace at 270 °C (near the boiling point of TEG (280 °C) for 3 hours, was added to the synthesis process.

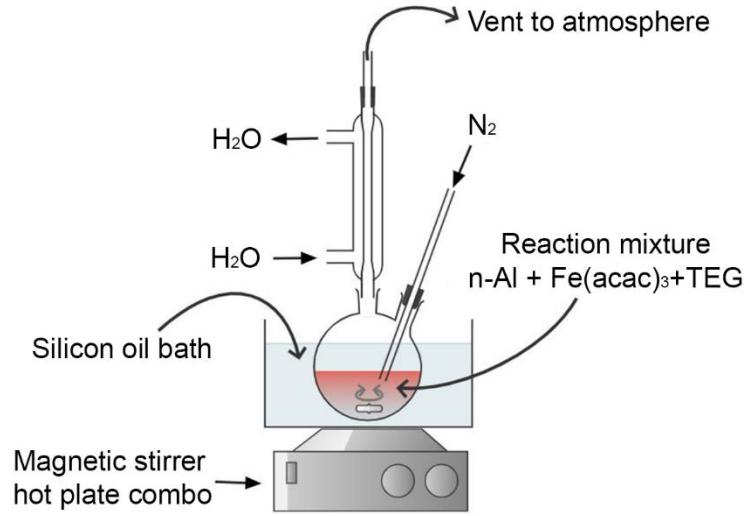


Figure 3.2: Experimental setup for the fabrication of core-shell Al@Fe₃O₄ composite.

The effect of the equivalence ratio (Φ) on the morphology and energetic performance of the final product was investigated. The equivalence ratio is the ratio of the actual fuel-to-oxidizer ratio to the stoichiometric fuel-to-oxidizer ratio. As this study accounts for the oxidizer's quantity indirectly based on the amount of oxidizer's precursor (Fe(acac)₃) used for the synthesis, it is the nominal equivalent ratio in consideration. The nominal equivalence ratio of the Al@Fe₃O₄ final product was calculated using the moles of active aluminum core. Since 3 mmole of Fe(acac)₃ reduce to give 1 mmole of Fe₃O₄, a factor 3 was accounted for in Equation 3.5 assuming the entire Fe from Fe(acac)₃ gets converted to Fe₃O₄ during the fabrication process. Four samples were prepared and analyzed corresponding to the equivalence ratios of 2.0, 3.0, 4.0, and 5.0, considering the fact that fuel-rich samples, around Φ 3.0, are usually optimal for best core-shell structure and overall performance as indicated by our previous research. The detailed amounts of raw materials corresponding to these equivalence ratios are listed in Table 3.3.

$$\Phi = \frac{(n_{Al}/n_{Fe_3O_4})_{actual}}{(n_{Al}/n_{Fe_3O_4})_{stoichiometry}} = \frac{(n_{Al}/(n_{Fe(acac)_3}/3))_{actual}}{(n_{Al}/n_{Fe_3O_4})_{stoichiometry}} \quad \text{Equation 3.5}$$

Table 3.3: Amount of raw materials of the samples

Equivalent ratio (Φ)	Fe(acac) ₃ (mg)	Al nanoparticles (mg)
2.0	706.34	115.66
3.0	706.34	173.50
4.0	706.34	231.33
5.0	706.34	289.16

A reference sample of n-Al+Fe₃O₄ nanoparticles matching the equivalence ratio of 3.0 was prepared by the aid of ultrasonication, as a standard sample (referred to as the “physically mixed” sample in the following text) to compare with the parallel core-shell sample. 50 mg of 100 nm diameter n-Al and the calculated amount of 10 nm Fe₃O₄ nanoparticles were dispersed in 2 mL ethanol for 2 hours, respectively. The two dispersions were then mixed and sonicated for another hour before drying in an oven at 70 °C for 4 hours to remove all the ethanol.

3.2 Characterization

When a new material is synthesized in the world of material science, it is imperative to establish its structure and properties. Characterization is the process by which the structure and behavior of the material is probed and ascertained [100, 101]. Three types of characterizations are usually performed over newly engineered materials:

1. Microscopy: Microscopic characterization techniques involve probing and mapping the surface and sub-surface structure of a material. To collect information about the sample’s structure across various length scales, these techniques involve the use of electrons, ions, photons, or physical cantilever probes. This type of characterization technique paints a picture of the morphology of the material. SEM and TEM are most commonly exploited microscopy characterization techniques for MICs.
2. Spectroscopy: Spectroscopic characterization techniques employ various principles to uncover the properties of the materials after exposure to electromagnetic radiation. The data related to the elemental composition, distribution, crystal lattice arrangement and photoelectric properties of materials, etc., can be extracted out of these techniques. XPS, EDS are some of the spectroscopy techniques that are utilized in the context of MICs.

3. Macroscopy: Macroscopic properties of materials of MICs are usually characterized by TGA and DSC.

The following paragraphs describe the characterization techniques employed in this research in little more detail.

3.2.1 SEM

SEM is a microscopy technique using electron beams in a vacuum environment. It is used to study surface morphology of the samples at both micro and nano level. When electrons strike the sample's surface, each topological change is manifested in the form of different intensities and contrast on the resulting high-resolution images. Two types of electrons are detected by the detector: secondary electrons coming directly out of the atoms of the sample and the back-scattered electrons which are just the reflected-back primary electron beams. For core-shell structured MICs, SEM is a very powerful tool to estimate the coating of the shell material over the core material. The heavier elements show up bright while the light elements show up dark (because of more back-scattered electrons). Such differences provide insights into ordering of the elements and coating quality. SEM is usually used in tandem with EDS to substantiate the element distribution across samples. For this research study, a Zeiss field emission simultaneous SEM-EDS was utilized.

3.2.2 TEM

TEM is the most powerful of all the microscopy tools available for characterization of advanced materials. It can show up the finest of the details of the surface of the material that can get missed in SEM since it uses electrons with smaller De Broglie wavelengths. As a result, TEM images of the samples are much sharper and higher resolution than the SEM images. Hence, TEM is usually the preferred choice for microscopy when the samples contain ultra-small nanoparticles that can't be viewed by SEM. As the name suggest, TEM is based on transmittance of electron beams through the samples. Hence samples need to be deposited as an ultrathin layer on the substrate for the electron beams to penetrate, which demands ultrasonication of the nanoparticle samples in a solvent to break the agglomerates before they are deposited on a substrate.

3.2.3 XRD

Crystalline structure of the material and the atomic spacing is another property that can be investigated to characterize a material. XRD is the most used technique for such a purpose. In this technique, the sample is hit with a monochromatic beam of X-rays which is then scattered by the electrons revolving around the nucleus of the atoms constituting the sample. Each set of lattice planes in the sample scatters this beam at specific angles. The constructive interference of these scattered X-rays produces a diffraction pattern which is governed by a fundamental equation given by the Bragg's Law:

$$n\lambda = 2d \sin \theta$$

Here: n represents an integer and reflects the order of diffraction, λ represents wavelength of an incident wave, d represents distance between two crystalline planes in the crystal lattice structure of the sample under investigation and θ is the angle of incidence of the X-ray striking the crystal plane. The powder sample is scanned from multiple directions i.e. through the wide ranges of angle of incidences for the X-ray with an intention of obtaining all possible diffraction patterns of the crystal lattice. The detector keeps recording the intensities of the peaks and the software translates this data into a plot of peak intensities versus angle of incidence. This plot can then be compared against the reference XRD patterns for standard materials (which serve as fingerprints) available in various databases (e.g. JCPDS) and elements or compounds existing within the material of inspection can be identified. The d spacing, is another characteristic property of a material and λ , the wavelength and θ , the incident angle is used to calculate its value and identify its corresponding material by comparison with the database.

3.2.4 XPS

XPS is a material characterization tool for accessing material's surface up to a thickness of 20 nanometers of the materials and provides a spectrum from which the element constituents of the material can be deduced. It enables acquisition of information regarding the chemical and electronic state of the elements along with the empirical formula of the compound. Typically, XPS reveals the presence of the primary element and its bonding with other elements. After exposure of the material's surface to the incident beams of X-rays, the software generates the data that graphically shows the recorded kinetic energy and the quantity of electrons that have flown are subsequently analyzed. XPS spectrum presents the relative frequencies of these electrons' binding energies in electron-volts (eVs).

The elements to which the peaks correspond are identified using binding energies. This thesis utilizes XPS to differentiate the valency of the metal ion of the metal oxide and ascertain the extent of oxidation during the production of MICs.

3.2.5 EDS

EDS is another characterization tool to detect the elements contained in the materials. The idea behind the energy dispersive spectroscopy is the excitation of the core electrons of the elements with the incoming electron beam. The core electrons are the electrons that are in the inner shells i.e., not the outermost shell. As a result of excitation, the core electron is ejected out of the material, leaving behind a hole which ends up getting filled by the electrons from the higher-energy orbitals. This sort of electron jump is accompanied by the release of an X-ray which are recorded by the detector. A further post processing of the spectrum created by these X-rays provide with the information about the identity and the relative content of different elements in the material. EDS mostly provides qualitative results but can provide semi-quantitative results as well. For this research, a simultaneous SEM-EDS instrumentation was harnessed that allowed the mapping of elements present in the features seen by SEM. In the simultaneous SEM-EDS equipment, the morphology is obtained from the signals generated by the secondary and backscattered electrons; and the chemicals present in the sample, are identified and quantified using the signals generated by the emitted X-rays.

The current work contains the EDS results of various MICs. These results in combination with the SEM images provide various insights into the relative ordering of the components with respect to different tweaks in manufacturing process.

3.2.6 TGA-DSC

TGA is a tool to analyse wherein a sample's mass in response to a set temperature program with respect to time or temperature. Any change in mass is said to have come from a physical or a chemical change. The rate of change of mass is immensely useful when describing the steps involved in the reactions and in determining the reaction kinetics like the order of reaction and reaction mechanism. This research work exploits TGA to determine temperatures at which the thermite reaction begins and ends by looking at the start and the end of the mass loss curve. It can also be used to identify any phase transitions in the oxidizer with temperature. DSC is a method of characterization wherein a plot of energy vs time/temperature is recorded in a thermal equilibrium environment. The sample is heated or

cooled with respect to a set temperature program and energy of the sample relative to that of an empty crucible is recorded. Any chemical reaction or phase change manifests in the form of peaks on the plots from which the data like heat of reaction, peak temperature, onset temperature, activation energy etc. can be quantitatively extracted out.

For this research, SEM of the samples was carried out using a Hitachi SU5000. All images were taken using 10 kV acceleration voltage in high vacuum mode. EDS was measured using an Oxford detector coupled with SEM. STEM – EDS was performed using a Talos 200X coupled with an X-FEG source with an acceleration voltage at 200 45 kV. XRD spectra were measured by a PANalytical X'Pert Pro MPD Powder XRD with a 2θ value from 10° to 80° at a step size of 0.017° . The instrumentation employed for XPS was the Thermo Scientific ESCALAB 250. DSC-TGA runs were carried out using a NETZSCH STA 449F3 wherein the samples were heated from ambient temperature to 1200°C at a constant rate of heating of $20^\circ\text{C}/\text{min}$ under the flow of argon gas flowing at the rate of $40\text{ mL}/\text{min}$. Each measurement was carried out with 5-6 mg samples. At least 3 measurements were carried out for each sample to reduce the error.

3.2.7 Combustion tests

A combustion chamber coupled with a fast camera is used for carrying out the combustion tests to figure out critical combustion parameters of the materials (in this case, the physically-mixed and the as-produced core-shell composite), such as ignition delay and burning rate. A scheme of this setup is shown in Figure 3.3A. An acrylic tube (5 cm long, 1/8-inch ID, 3/8-inch OD) with the bottom end fixed by a glued metal screw was used as the sample holder (Figure 3.3BI). For the in-house facility, the ignition tests are made using a 5W continuous wave 532 nm laser. The laser was kept on for a duration of 400 ms at 75-90% output power. The samples (for Al-CuO pair, 10 mg of the as-prepared core-shell and physically-mixed Al/CuO samples were used; for Al-NiO and Al-Fe₃O₄ pairs, 20 mg of physically-mixed and core-shell were used) are loosely loaded into the sample holder and ignited (Figure 3.3B I) to compare the performance between core-shell and a reference physically mixed sample. For Al-Fe₃O₄ pair which displayed magnetism, an additional set of combustion tests are conducted to demonstrate this magnetic property. A standard alnico horseshoe magnet with a max pull of 5 lb (2.2 kg) is glued outside of the tube that serves as a sample holder to magnetically suspended

the as-prepared core-shell Al@Fe₃O₄ particles in the center of the tube (Figure 3.3B II) to demonstrate the ability of the sample to be located at a certain position and ignited. The combustion is recorded using Phantom v2012 high-speed camera (recording at 200,000 fps for Al-CuO pair and 80,000 fps for Al-NiO and Al-Fe₃O₄ pair) with 285 ns exposure time. Both laser and fast camera are triggered simultaneously by a Tektronics AFG1022 function generator. These tests are repeated three times for each sample to ensure the repeatability of the results.

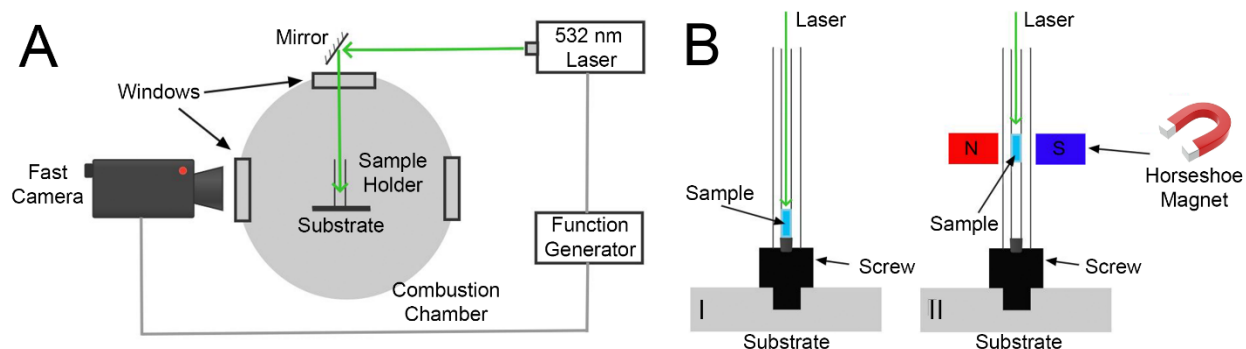


Figure 3.3: Filming setup for the combustion tests (A). Sample holder with sample assembly (B) for combustion test of samples in the absence (I) and presence (II) of a horse-shoe magnet.

3.3 Uncertainty Analysis

Every research study has some limitations attached to it. Uncertainty analysis is the method of recognizing these limitations in the scientific data and assessing their implications on scientific deductions. Uncertainties and errors can arise due to multitude of factors and are of three broad categories: random, systematic and environmental. Any unpredictable variation arising in the measurements due to unpredictable factors is a random error. For instance, variation in mass and volume measurements stemming from different technique of making the measurement or handling the samples is an example of random errors. These errors scatter the data around the true value. Systematic errors are consistent and repeatable errors. Any flaw in the experimental setup, equipment, or procedure introduces systematic errors in the measurements. These errors result in measurements being consistently off from the true value in the same direction, either too high or too low. Examples of systematic measurements are mis-calibrated instruments like the hot plate, oven or the tube furnace, consistent bias in measurement techniques, incorrect assumptions or models used in data analysis. Environmental errors are disparities caused by changes in the external environment where the

experiment is conducted. These factors are beyond the control of the experimenter and may influence the results of the experiment. Examples include changes in ambient temperature, pressure, or humidity affecting the measurements.

In this research work, the effect of random and environmental errors on the measurements has not been studied and form a limitation of this study. The systematic errors were reduced to a minimum by calibrating the mis-calibrated instruments and using well-calibrated and maintained equipment. These errors were considered in the form of standard deviation from mean by repeating the TGA/DSC measurements and combustion tests thrice. These standard deviations are reported in the following chapters.

One systematic error that forms a major shortcoming from this research is the yield of product. The manufacturing process involves vacuum filtration and thermal decomposition. Assumptions were made regarding no loss of the product in the filtrate or the wash solvents. However, the checks were not made to ensure no loss of product. This, perhaps, forms a part of future work and can be confirmed by performing SEM-EDS on the filtrate and wash solvent to visualize and detect any loss of product.

Chapter 4

Fabrication and characterization of core-shell Al@CuO MICs

This chapter constitutes the research work conducted by Dr. Anqi Wang, under the supervision of Dr. John Z. Wen. Dr. Wang designed this research work in consultation with Drs. John Wen and Jean-Pierre Hickey who also contributed to the data analysis. Dr. Wang drafted the manuscript and Shina Maini contributed to conducting the experiments to find the activation energy and prove the repeatability. Each author provided intellectual input on manuscript drafts. The content of this chapters has been re-produced from the following citation:

Citation [102]:

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4.1 Introduction

Metal fuels with a high energy density are desirable in many applications such as pyrotechnics, propellant, and as raw materials to produce hydrogen. [96] Some of these fuels can be ignited and combusted with solid-state oxidizers, making them useful in oxygen-depleted environments such as vacuum, space, and underwater conditions. [103] The mixture of metal fuels with solid-state oxidizers is usually referred to as MICs, or thermites. Commonly used metal fuel includes aluminum (Al) [1], magnesium [104], silicon [105], boron [106], while metal oxides [2, 3] and halogen composites [107-109] can be used as the oxidizer. When fuel reacts with an oxidizer, the redox reaction between the two generates large quantities of heat and pressure, which are leveraged in many applications. [4, 5] Among different MICs composites, aluminum-based MICs have been widely studied and favored due

to the high oxidation enthalpy, abundance on earth, and relatively low cost of production of aluminum. [8, 9] With the advances in nanotechnology, aluminum-based nanoscale MICs have gained great interest. Compared to traditional micron-sized or larger MICs, nanoscale MICs material features a greater surface area of aluminum fuel and oxidizer nanoparticles, enhancing the surface contact while reducing the path of diffusion between the two reacting components, thus shortening the ignition delay. [5, 110]

However, the extended surface area does not always result in the expected performance enhancement due to some drawbacks occurring in MICs composites. The incomplete mixture, or phase separation, between aluminum fuel and oxidizer not only significantly reduces the surface contact area and the reaction rate [66, 111], but also causes reactive sintering of the agglomerated aluminum nanoparticles, leading to the loss of the advantage of increased surface area arising from the nanoscale dimensions of Al particles. [112, 113]. Additionally, the Al_2O_3 shell that spontaneously forms on the surface of Al particle, prevents the oxidizer to come in contact with Al core directly. This increases the energy barrier for triggering the reaction. [107] The presence of an inert shell between aluminum fuel and oxidizer also significantly complexifies the reaction mechanism of aluminum-based MICs, which is yet to be confirmed. [47] Moreover, the extreme sensitivity of aluminum nanoparticles to external stimuli including electrical static discharge and mechanical shock, limits the bulk production, transportation, and safe application of MICs. [1]

Researchers have developed various structures and synthesis routes to overcome the drawbacks of MICs. Marin et al [114] applied magnetron sputtering to deposit multi-layered Al/CuO nanolaminates with reduced reaction temperature and enhanced safety measures by avoiding loose MICs powder during the synthesis. However, the process is only good for the production of a very small quantity with a limited combustion rate. Self-assembly has been considered a promising method of bulk fabrication of MICs with improved homogeneity, thus increasing the reactivity of the final product. Various additives have been utilized to trigger the assembly, such as surfactants [39], graphene oxide [115], and DNA [41]. The self-assembled MICs have demonstrated better homogeneity and enhanced area of contact between reactants, thereby improving the reactivity of the fabricated MICs.

Among different types of MICs, the core-shell structure maximizes the surface contact between fuel and oxidizer with an increased energetic performance. The well-coated metal oxide can also reduce

the participation of gaseous oxygen in the energetic reaction, possibly leading to a more homogeneous and consistent reaction when the density of the nanoenergetic materials changes. [116-118] Various core-shell structured MICs, such as Al/PTFE [119], $\text{Co}_3\text{O}_4/\text{Al}$ [103], and $\text{NiCo}_2\text{O}_4/\text{Al}$ [120] have been developed by physical fabrication methods, such as CVD and magnetron sputtering. However, these physical methods usually have high costs and low yields, preventing them from being used for bulk production. Chemistry methods used to synthesize core-shell energetic materials have also been developed but are mostly restricted to micron-scale thermite materials. Deng et al. reported a precipitation method and a displacement method to synthesize closely packed, well-distributed, and core-shell micron-Al/CuO MICs composite. [121] In previous research, we also reported on a one-pot synthesis process, based on wet chemistry method, to prepare spherical micron-Al/CuO with a core-shell structure. [15] A copper ammonia complex layer was first formed onto the surface of Al micron-sized particles and then calcinated to obtain a CuO shell, producing well-coated Al/CuO core-shell particles. It has been challenging to synthesize nano-scale core-shell energetic materials via a chemistry method since the Al and metal oxide nanoparticles tend to self-agglomerate in the solvent. Researchers have tried to apply polymers and surfactants between Al and metal oxide nanoparticles, such as PVP [39] and PDA [122], which indeed helped the formation of core-shell nanostructures but also contributed to the addition of dead-mass between the reacting components, reducing the reactive susceptibility of the final product. Therefore, a surfactant-free synthesis route of core-shell structured Al-metal oxide nanoparticles with enhanced energetic performance is desired.

This project focuses on developing a core-shell synthesis procedure for nano-sized Al spherical particles without using polymers. We conducted a comprehensive study on the fabrication process of nanosized core-shell Al/CuO product by XRD, SEM, EDS, and evaluated its potential as a MIC material using simultaneous DSC-TGA and laser combustion. By controlling the process parameters, we show that the formation mechanism is driven by the electrostatic force of Al nanoparticle and Cu-NH_3 complex, which is discussed in detail. By tuning the ratio of components of the synthesis process, the final product can be switched between a core-shell nanoparticle microstructure and a well-mixed nanoparticle composite. DSC-TGA test results revealed the relationship and controllability between the nanostructure of Al/CuO core-shell nanoparticles and their energetic performance, as well as confirming that the activation energy of core-shell Al/CuO was reduced by 10% compared to its physically mixed counterpart. More interestingly, the combustion experiments not only verified that

the core-shell structure helped to reduce the ignition delay but also changed the reaction pathway. It is hypothesized that the participation of gaseous oxygen in the reaction is eliminated, and the reaction mechanism is simplified, which is out of the scope of this piece of work but definitely worth more investigations in the future.

4.2 Result and Analysis

4.2.1 Structural properties of as-fabricated Al/CuO core-shell particles

The formation mechanism of Al/CuO core-shell particles is of great interest as it provides insight into the design and large-scale synthesis of Al/oxidizer core-shell nanoparticles. Notably, a hypothesized mechanism was proposed in a previous study [15], while no detail or measurement was provided to verify its validity. In this study, we describe the following detailed process of Al/CuO MICs formation during wet chemistry synthesis. Based on the varying optical property (color) and corresponding chemical composition and microstructures of the intermediates and final product, the formation of the Cu-NH₃ complex on Al particles is believed as the key step to the fabrication of the core-shell structure. Upon addition ammonia to copper nitrate solution in ethanol, a complexation reaction occurred between ammonia molecules and copper ions, forming Cu-NH₃ complex, or Cu(NH₃)₄(H₂O)₂²⁺, which dissolves well in water, forming a dark blue solution. However, the copper ammonia complex does not dissolve well in ethanol, giving a suspension with cyan flocculent precipitation, as shown in Figure 4.1. The precipitate is hypothesized to contain [Cu(NH₃)_x(OH)_y]²⁺ with x and y depending on NH₃/Cu ratio, For instance, for ammonia rich solution, x and y are expected to be 4 and 0 respectively, making the major cation of the precipitate to be [Cu(NH₃)₄]²⁺.

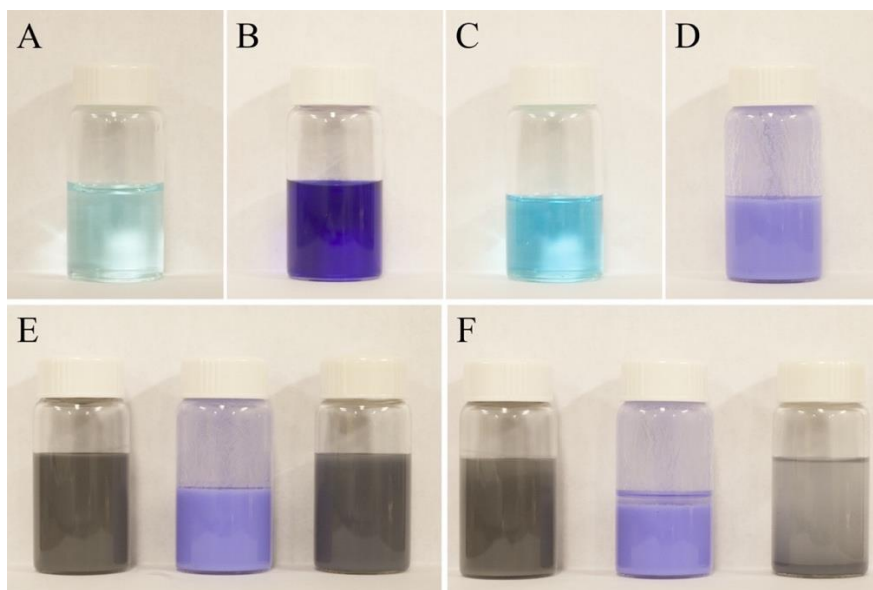


Figure 4.1. $\text{Cu}(\text{NO}_3)_2$ aqueous solution (A), $\text{Cu}(\text{NO}_3)_2$ aqueous solution after adding ammonia (B), $\text{Cu}(\text{NO}_3)_2$ ethanol solution (C), $\text{Cu}(\text{NO}_3)_2$ ethanol solution after adding ammonia (D), (from left to right) Al dispersion in ethanol, Cu-NH_3 complex suspension in ethanol and Al/ Cu-NH_3 complex mixture (ER2.0, NH_3/Cu ratio = 8) in ethanol before (E) and after resting for 1 hour (F).

The assembly to core-shell Al/ Cu-NH_3 complex structure then occurred after mixing Al dispersion with Cu-NH_3 complex suspension. Figure 4.1E shows the immediate condition of Al dispersion after sonication, Cu-NH_3 complex, and Al/ Cu-NH_3 mixture after stirring, in which all appeared well-dispersed. However, after resting for an hour, a clear difference was found between the samples. Al dispersion started to show a concentration gradient as Al nanoparticles precipitated, although one hour was not long enough for Al nanoparticles to fully separate from ethanol, leaving an uneven dark gray dispersion. Unlike Al, the Cu-NH_3 complex suspension showed a clean boundary between the cyan flocculent precipitation and clear supernatant. However, the separation between the precipitation and supernatant was not complete and the flocculent precipitation seemed to have a low density. The Al/ Cu-NH_3 mixture, however, precipitated quickly with an almost clear supernatant. There was no significant concentration gradient, caused presumably by a slow precipitating process or low-density flocculent material, indicating that the formation of a denser solid in the mixture between all the Al nanoparticles and Cu-NH_3 complex resulted from a self-assembly process. The formation of such precipitation and a clear supernatant were found in most samples. However, when Cu was not in excess

(NH_3/Cu calculated ratio at 4), the precipitating process of the Al/Cu- NH_3 complex mixture was much slower, and the supernatant was not clear for a few days. Therefore, the amount of ammonia also significantly changed the self-assembly process and could change the structure as well as the energetic properties of the final composite. For NH_3/Cu ratio of 16, Al/Cu- NH_3 complex mixture is hypothesized to contain $\text{Cu}(\text{NH}_3)_4(\text{NO}_2)_2$ as a major constituent and for NH_3/Cu ratio of 4, the mixture is believed to contain $\text{Cu}(\text{OH})_3\text{NO}_3$, predominantly. This has been proved by XRD and the results are presented on page 64 of this thesis.

SEM imaging and EDS mapping were taken to characterize the microstructure of Al/CuO core-shell MICs and understand how it was affected by the NH_3/Cu ratio, as shown in Figure 4.2. Al nanoparticles, as shown in FigureA, were mostly around its labeled 100 nm diameter (60 – 200 nm), with some impurities, such as large particles of around 1 micron. The uncoated Al nanoparticles were nearly perfectly spherical and demonstrated a very smooth surface. The Al/CuO core-shell nanocomposite, on the other hand, exhibited a completely different morphology, as shown in FigureB-F. FigureB and C show the Al/CuO nanocomposite synthesized when Cu was slightly in excess (NH_3/Cu calculated ratio at 4). Many small nanoparticles existed in the sample, indicating the formation of CuO, which was confirmed by the correspondence of EDS mapping results of Cu and O in Figure 4.3A-E. The formed CuO nanoparticles were smaller than the Al nanoparticles roughly between 20 – 60 nm, as shown in FigureA. The CuO nanoparticles formed some irregular clusters, possibly due to self-aggregation among the nanoparticles. Meanwhile, the coating of CuO on Al nanoparticles was unsatisfactory. Only a small fraction of Al nanoparticles was well-coated (green), while a large fraction of Al nanoparticles was left only partly coated (orange) or even un-coated (red), as shown in FigureC. The EDS result in Figure 4.3A-E confirmed an even distribution of Al and CuO throughout the sample. The Al-rich regions indicated in Figure 4.3C were due to some larger bare Al particles ($\sim 1 \mu\text{m}$) that were left uncoated. Therefore, instead of an Al/CuO “core-shell” nanoparticle, this sample was better described as a well-mixed Al/CuO nanocomposite synthesized via the wet-chemistry when copper was slightly excessive compared to ammonia in the complex. FigureD-F show the SEM of the core-shell Al/CuO nanocomposite when ammonia was excessive (NH_3/Cu calculated ratio at 16). Different from FigureB, there was no sign of CuO clusters formed as shown in FigureD, there was an even distribution of Al and CuO particles in the composite, which was also confirmed by the EDS mapping in Figure 4.3F-J. Moreover, compared to FigureC, the formation of “core-shell”

Al/CuO was much better in FigureE where a higher NH_3/Cu ratio was used. Indeed, there are still some Al left uncoated (red), while there was a large part of Al particles that were either well-coated (green) or partly coated (orange). FigureF shows a close-up of some of the well-coated Al/CuO core-shell nanoparticles. FigureE and FigureF, both show that the CuO nanoparticles were also smaller than the Al nanoparticles, allowing them to assemble onto the surface of Al and form a shell. Therefore, it can be concluded that an excessive amount of NH_3 would facilitate the formation of core-shell structured Al/Cu-NH₃ complex, leading to better Al/CuO core-shell nanostructures after calcination. EDS statistics in Table 4.1 also indicate the actual equivalence ratio in the final products was very close to the nominal value calculated using the amounts of raw materials after the wet chemistry synthesis process.

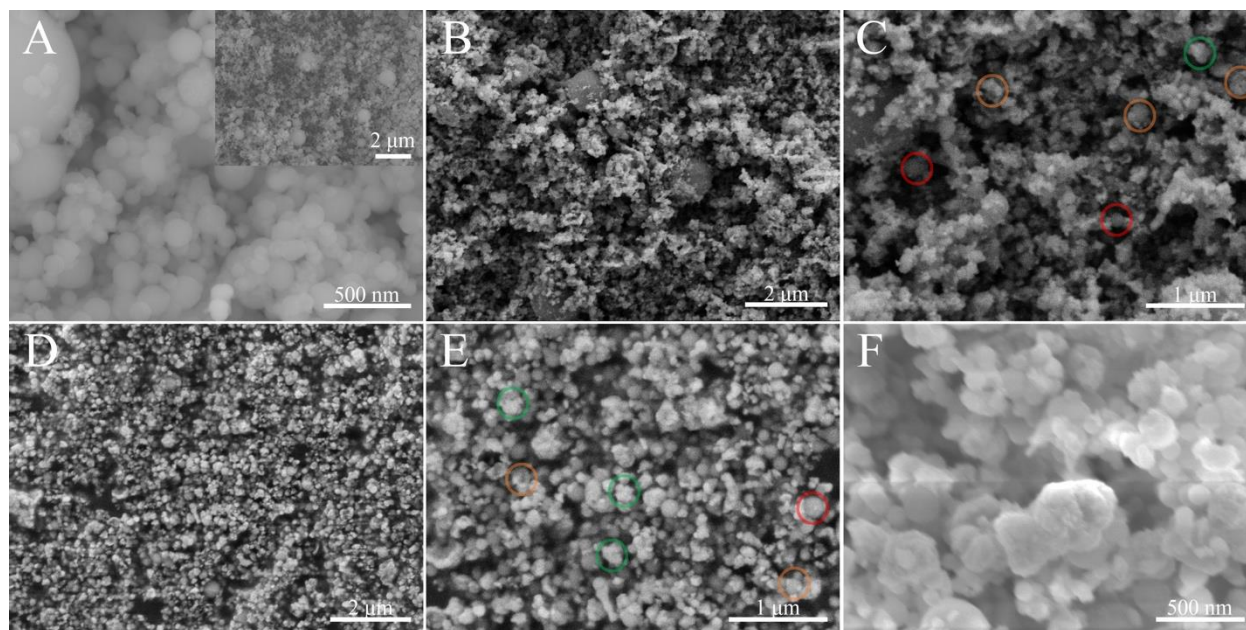


Figure 4.2. SEM images of pure Al nanoparticles (A), Al/CuO core-shell nanocomposite at ER=2.5, NH_3/Cu ratio = 4 (B, C), Al/CuO core-shell nanocomposite at ER=2.5, NH_3/Cu ratio = 16 (D, E, F).

[102]

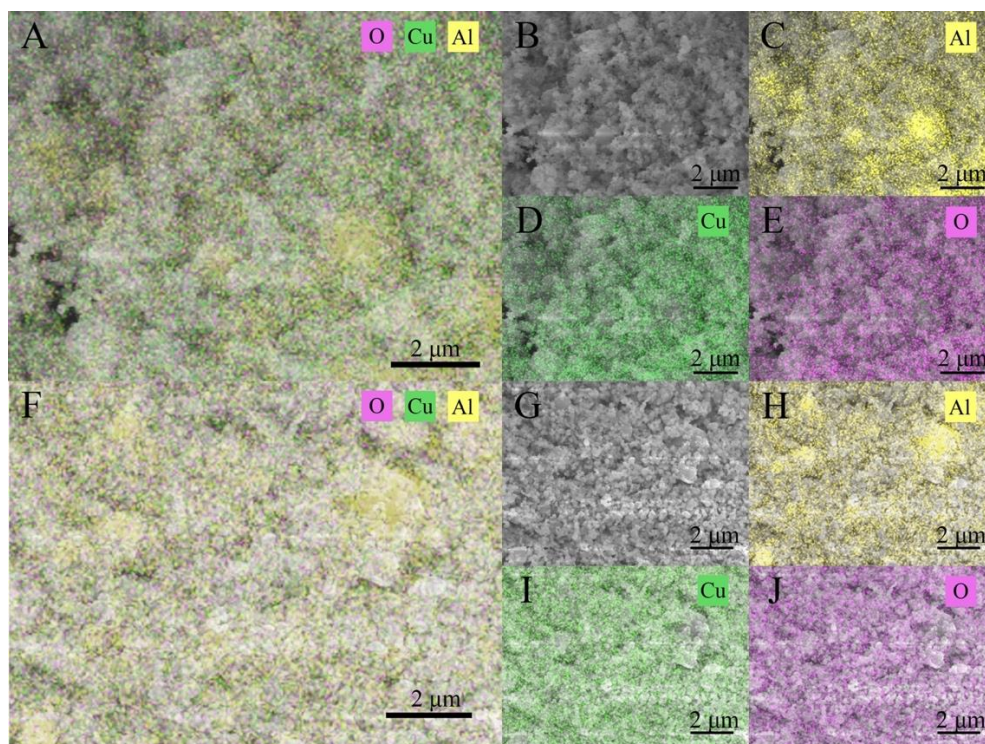


Figure 4.3. EDS mapping of Al/CuO core-shell nanocomposite at ER=2.5, NH_3/Cu ratio = 4 (A-E), Al/CuO core-shell nanocomposite at ER=2.5, NH_3/Cu ratio = 16 (F-J).

Table 4.1. EDS statistics of Al and Cu in samples with ER at 2.5 and 1.5.

ER	Al atomic%	Cu atomic%	Al/Cu	Al/Cu (theory)
1.5	31.5%	30.6%	1.029	1.000
2.5	43.1%	25.8%	1.671	1.667

It was anticipated that the different Al/CuO structures in the final nanocomposites, produced from different NH_3 to Cu ratios, resulted from the different Cu- NH_3 complex structures deposited onto the surface of Al nanoparticles. XRD of two dried Cu- NH_3 complex samples was taken to compare the crystalline structures of the Cu- NH_3 complex precipitations formed from different NH_3 ratios at 4 and 16, as shown in Figure 4.4. The two curves in Figure A exhibit peaks at about the same 2θ value, but with drastically different intensities, indicating more than one composite was present in the Cu- NH_3 complex. Two kinds of copper composites correspond well to both XRD data and experiment procedure: $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ (shilovite) [123], and $\text{Cu}(\text{OH})_3(\text{NO}_3)$ (rouaite) [124]. By comparing the

characteristic peaks at $2\theta = 12.8^\circ$ (rouaite), 15.2° , 21.3° , and 31.0° (shilovite), the ammonia-rich sample (NH_3/Cu ratio = 16) was found to contain more shilovite ($\text{Cu}(\text{NH}_3)_4\text{NO}_3$) and the ammonia poor sample (NH_3/Cu ratio = 4) should contain more rouaite ($\text{Cu}(\text{OH})_3(\text{NO}_3)$). It can be explained by a competitive reaction of Cu(II) with either NH_3 or OH^- when ammonia was poured into the $\text{Cu}(\text{NO}_3)_2$ solution, as shown in Equation 4.1. As per the Le Chatelier principle, excess NH_3 shifts the equilibrium to the right, encouraging the formation of Cu- NH_3 coordination complex where all ligands are replaced by NH_3 . In addition, according to the spectrochemical series of ligands, NH_3 is a stronger ligand as compared to OH^- and bears a stronger ability to stabilize the metal-ligand bond.

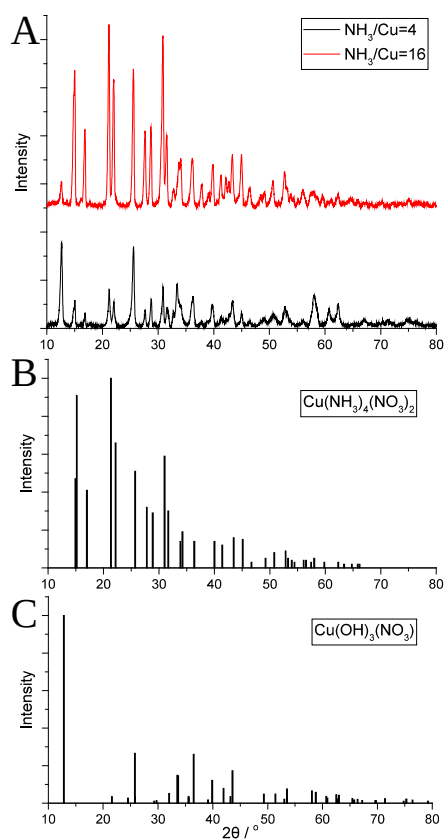
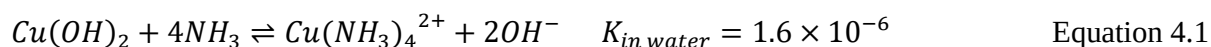


Figure 4.4: XRD spectra of Cu- NH_3 complex with NH_3/Cu ratio at 4 and 16 (A), standard XRD spectra of $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ (B) [115] and $\text{Cu}(\text{OH})_3(\text{NO}_3)$ (C) [116]. [102]

When ammonia was in excess, the $\text{Cu}(\text{NH}_3)_4^{2+}$ formation was favored in the precipitate. Figure 4.1D also showed that when ethanol is used as solvent (unlike water), Cu(II) forms the precipitate with

excess ammonia. However, when the ammonia concentration was low, the competing reaction between Cu^{2+} and OH^- in a less acidic or alkaline environment became more important. To further confirm the formation and structure of core-shell Al/CuO (ER=2.5, $\text{NH}_3/\text{Cu} = 8$) at a higher resolution, STEM-EDS of local particles was carried out, as shown in Figure 4.5. The STEM image shows two particles. On the left, it can be clearly seen that numerous brighter CuO nanoparticles of the size smaller than 30 nm are attached to the surface of the darker Al nanoparticle with a diameter of about 150 nm. Most of this Al particle was covered by CuO, but there was still a small part that was not covered. Therefore, the Al/CuO on the left was an imperfect core-shell nanoparticle. However, the particle on the right side showed a surface fully composed of CuO nanoparticles, while the EDS mapping confirmed the existence of an Al nanoparticle inside, indicating the formation of a perfect core-shell Al/CuO nanoparticle. The EDS elemental mapping of the as-prepared composite also indicated the formation of tiny CuO particles on the relatively larger aluminum nanoparticles, forming an oxidizer shell on Al core. Therefore, confirming the successful synthesis of the core-shell Al/CuO.

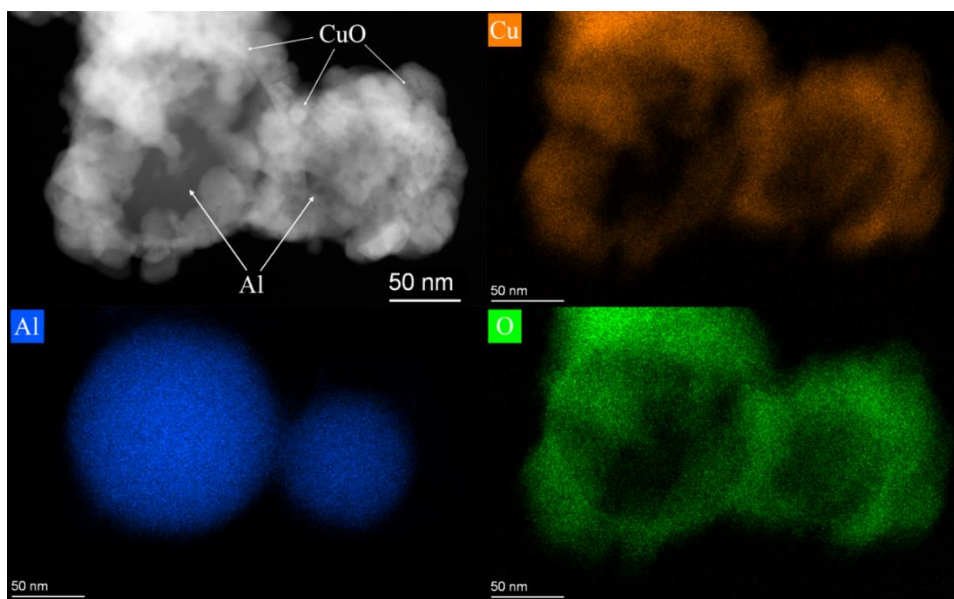


Figure 4.5: STEM image and corresponding EDS results of an assembly of core-shell Al/CuO nanoparticles. The order of EDS mapping from top to bottom is Al, Cu, and O. [102]

4.2.2 Mechanism of the formation of Al/CuO core-shell nanocomposite

When copper ammonia complex suspension was added to the Al/ethanol dispersion, two different types of suspended substances, Al particles, and Cu-NH₃ complex, co-existed in the mixture and both tended to precipitate. However, instead of precipitating separately, these two precipitants assembled into a core-shell structure of the Al/Cu-NH₃ complex (Figure 4.1), which is here hypothesized to be driven by the solubility equilibrium of the Cu-NH₃ complex in ethanol, as well as the electrostatic force between Al particles and Cu-NH₃ complex. In a typical solubility equilibrium of ionic compounds, the dissolution process of the solid precipitations and the precipitation of the dissolved ions occur at the same time and reach a dynamic equilibrium state when the dissolution and precipitation rates are equal, which occurred for the Cu-NH₃ complex in ethanol as shown in Figure 4.1D. However, the precipitation process was different when Al particles co-existed with Cu-NH₃ complex precipitation in ethanol.

Dispersed Al nanoparticles in ethanol have a near-neutral surface charge due to the oxidized shell of Al particles. [115] When the solution was alkaline due to the addition of ammonia aqueous solution, it turned negative, especially when pH > 9 [125, 126] as confirmed by Zeta potential analysis shown in Figure 4.6 and Table 4.2. The ammonia added to the Al dispersion for Zeta potential analysis indicated the “excess” amount of ammonia, assuming each Cu²⁺ ion consumes 4 NH₃ molecules. It helps to elucidate different structures of the final core-shell Al/CuO MIC as observed in the SEM images. Al nanoparticles were dispersed in ethanol under sonication and presented a near-neutral surface charge before the Cu-NH₃ intermediate was added. When the addition occurred, the components that co-existed in the mixture can be seen in Table 4.3. When the mixture was ammonia lean, for instance, at the NH₃/Cu ratio of 4, the mixture was less alkaline with an insufficient amount of NH₃ available to fully react with Cu²⁺. Therefore, the Al maintained a near-neutral surface charge, while the Cu²⁺ formed more Cu(OH)_n instead of Cu(NH₃)₄²⁺. Therefore, there was no significant electrostatic force between Al and Cu-NH₃ intermediate. The Al and Cu-NH₃ intermediate mixture was then filtered and calcinated, forming a well-mixed Al-CuO nanocomposite. However, when the mixture was ammonia-rich, for instance, when the NH₃/Cu ratio was 16, the mixture was more alkaline. As a consequence, Al nanoparticles showed a more negative surface charge around -30 mV and Cu²⁺ reacted more with ammonia and mainly formed Cu(NH₃)₄²⁺ in the precipitation. Therefore, the electrostatic force between negative Al nanoparticles and dissolved positive Cu(NH₃)₄²⁺ triggered the self-assembly

between the components, forming a core-shell Al/Cu-NH₃ intermediate structure, which was then calcinated to obtain the final core-shell Al@CuO nanostructure. When the NH₃/Cu ratio was 6 or 8 in other samples, Al also presented a negative surface charge as shown in Figure 4.6, while the percentile of Cu(NH₃)²⁺ may not be as high. With that being said, NH₃ was still excessive compared to Cu²⁺ and the Al/Cu-NH₃ intermediate were able to precipitate within a few hours. Therefore, the products were considered closer to core-shell Al@CuO in these samples, as illustrated in Figure 4.7.

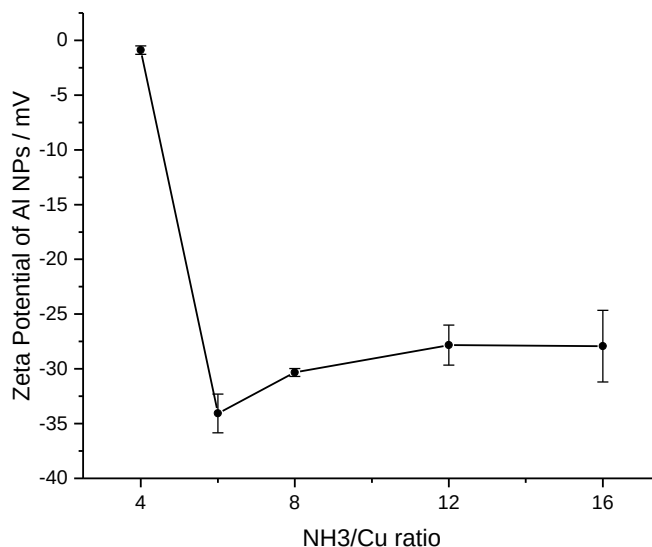


Figure 4.6. Zeta potential of Al nanoparticles (0.002 mg/mL) in ethanol with the addition of excess ammonia simulating the environment of different NH₃/Cu ratios at ER 2.5.

Table 4.2. Amounts of ammonia (“excess” ammonia) added to ethanol for Zeta potential measurement.

Al concentration	Ethanol volume	Simulating NH ₃ /Cu ratio	Ammonia amount based on NH ₃ /Cu ratio (ER 2.5)	“Excess” ammonia
0.002 mg/mL	50 mL	4	215 µL	0
		6	325 µL	110 µL
		8	430 µL	215 µL
		12	645 µL	430 µL
		16	860 µL	645 µL

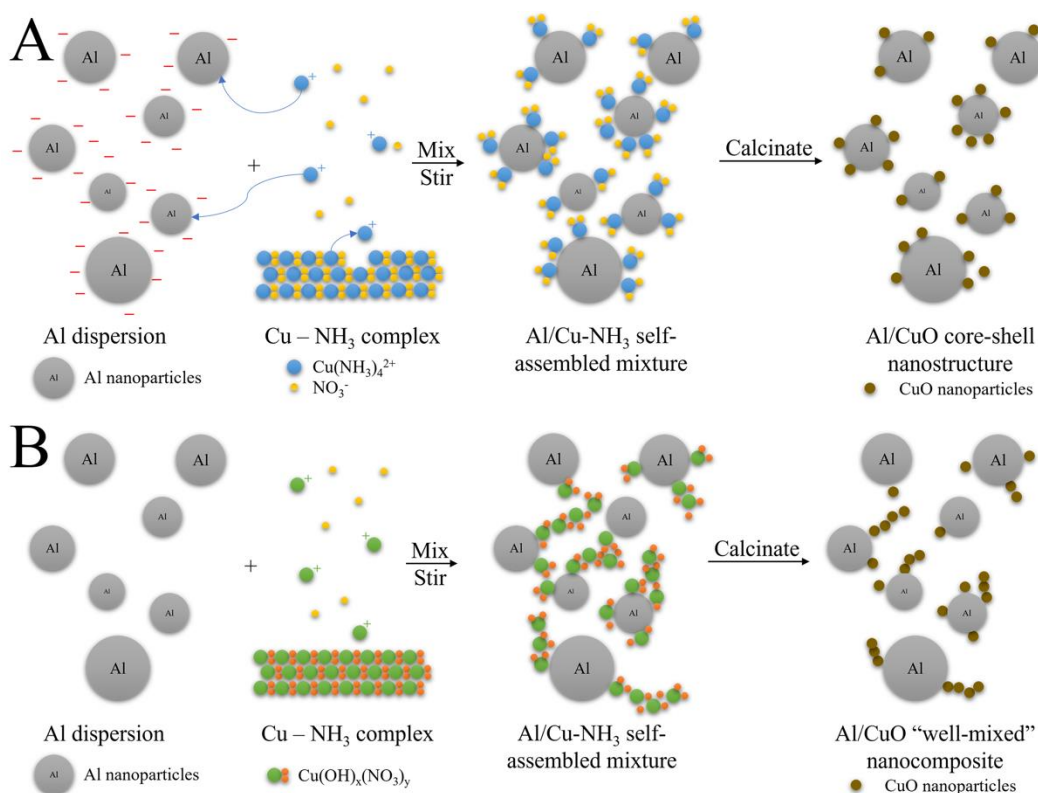


Figure 4.7: Scheme of the self-assembly of Al/Cu-NH₃ complex when ammonia is in excess (A), and when ammonia is insufficient. [102]

Compared to micron-sized Al particles, Al nanoparticles had a much higher surface area and were much harder to disperse into single particles, even with the help of sonication. Therefore, more uncoated Al nanoparticles were found compared to Al microparticles. [15]

It is fair to say that the major driving force behind the formation of the core-shell structure is the electrostatic force between the Al nanoparticles and Cu-NH₃ complex. Moreover, the structure of the final product can be switched between core-shell and homogeneous nanoparticle mixture by changing the amount of ammonia solution used during synthesis, allowing a design and good control of the morphology as well as the energetic performance of the final product.

Table 4.3: Characteristics of Al/Cu-NH₃ complex mixture.

Mixture	Component	Characteristics
Ammonia poor	Al	Near neutral surface charge
	Cu	Cu(OH)_n (major) Cu(NH ₃) ₄ ²⁺ (minor)
Ammonia rich	Al	Strongly negative surface charge
	Cu	Cu(NH₃)₄²⁺ (major) Cu(OH) _n (minor)

4.2.3 Energetic Properties of the as-fabricated Al/CuO core-shell material

DSC measurements of all the produced Al/CuO samples with different ER and NH₃/Cu ratios were carried out to analyze the energetic reaction pathways and potentials, as shown in Figure 4.8. Note that energy release in Figure 4.8 corresponds to a single case and not an averaged value. The key parameters of the main reaction, including the onset temperature, peak temperature and amount of energy released from the reaction, are of interest as they assist in determining the energetic reaction pathway and composite structure. Table 4.4 list the exact values of these parameters.

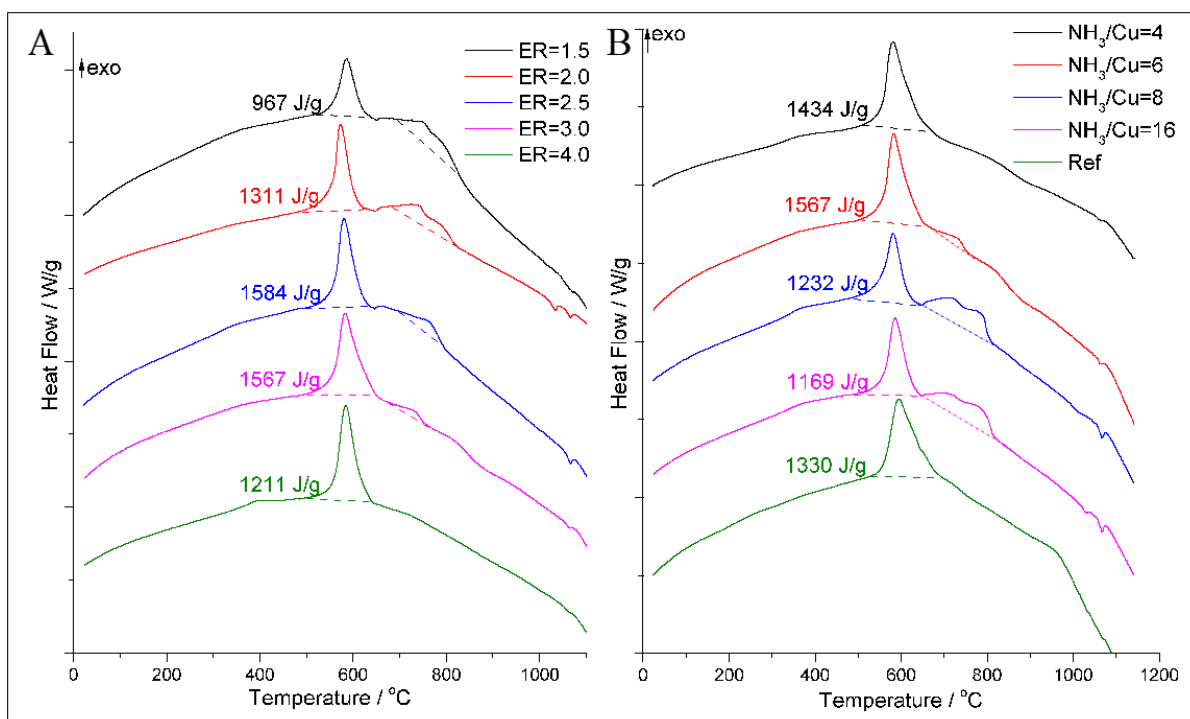


Figure 4.8: DSC results of Al/CuO core-shell nanocomposite with different ER ($\text{NH}_3/\text{Cu} = 6$) (A), core-shell Al/CuO nanoparticles with different NH_3/Cu ratios compared to ultrasonication mixed Al/CuO ($\text{ER}=3.0$) (B). The units on the y-axis (W/g) belong to each individual plots, however, the scale is arbitrary for these stacked plots.

Table 4.4. Energy release, onset temperature, and peak temperature of the core-shell Al/CuO MIC and ultrasonication mixed Al/CuO.

Φ	NH_3/Cu ratio	Energy release	Onset temperature	Peak temperature
1.5	4	$901 \pm 14 \text{ J/g}$	$558 \pm 0 \text{ }^\circ\text{C}$	$588 \pm 1 \text{ }^\circ\text{C}$
1.5	6	$967 \pm 8 \text{ J/g}$	$556 \pm 3 \text{ }^\circ\text{C}$	$582 \pm 3 \text{ }^\circ\text{C}$
1.5	8	$966 \pm 33 \text{ J/g}$	$557 \pm 3 \text{ }^\circ\text{C}$	$585 \pm 1 \text{ }^\circ\text{C}$
1.5	16	$915 \pm 14 \text{ J/g}$	$560 \pm 2 \text{ }^\circ\text{C}$	$591 \pm 3 \text{ }^\circ\text{C}$
2.0	4	$1215 \pm 75 \text{ J/g}$	$558 \pm 1 \text{ }^\circ\text{C}$	$584 \pm 1 \text{ }^\circ\text{C}$
2.0	6	$1249 \pm 78 \text{ J/g}$	$552 \pm 3 \text{ }^\circ\text{C}$	$574 \pm 1 \text{ }^\circ\text{C}$
2.0	8	$1226 \pm 5 \text{ J/g}$	$559 \pm 6 \text{ }^\circ\text{C}$	$578 \pm 2 \text{ }^\circ\text{C}$
2.0	16	$1122 \pm 9 \text{ J/g}$	$557 \pm 2 \text{ }^\circ\text{C}$	$581 \pm 2 \text{ }^\circ\text{C}$
2.5	4	$1357 \pm 34 \text{ J/g}$	$559 \pm 2 \text{ }^\circ\text{C}$	$584 \pm 2 \text{ }^\circ\text{C}$

2.5	6	1566 ± 80 J/g	556 ± 3 °C	578 ± 2 °C
2.5	8	1318 ± 75 J/g	556 ± 1 °C	579 ± 3 °C
2.5	16	1163 ± 55 J/g	556 ± 1 °C	583 ± 3 °C
3.0	4	1434 ± 66 J/g	552 ± 2 °C	579 ± 2 °C
3.0	6	1562 ± 39 J/g	555 ± 2 °C	576 ± 4 °C
3.0	8	1219 ± 60 J/g	555 ± 1 °C	581 ± 1 °C
3.0	16	1209 ± 29 J/g	559 ± 1 °C	582 ± 1 °C
4.0	4	1054 ± 49 J/g	552 ± 2 °C	571 ± 2 °C
4.0	6	1245 ± 86 J/g	558 ± 2 °C	580 ± 1 °C
4.0	8	943 ± 17 J/g	560 ± 2 °C	581 ± 3 °C
4.0	16	967 ± 50 J/g	554 ± 2 °C	575 ± 1 °C
1.5 (Ref)	N/A	1116 J/g	563 °C	600 °C
2.0 (Ref)	N/A	1331 J/g	563 °C	600 °C
2.5 (Ref)	N/A	1578 J/g	563 °C	598 °C
3.0 (Ref)	N/A	1330 J/g	561 °C	595 °C
4.0 (Ref)	N/A	1322 J/g	564 °C	600 °C

Figure 4.8A compares the representative curves of the samples with different ER at a fixed NH_3/Cu ratio of 6. The peak of the main reaction was present between 520 to 660 °C for all the curves. The main reaction happened below Al's melting point (660 °C), implying that the reaction occurred in condensed phase. [127] The detailed reaction pathway is not yet clear, but it is here hypothesized to be triggered by the diffusion the oxide ions across the Al_2O_3 shell towards the inside active Al core. As the temperature rises, at ~600°C, Al ion diffuses out of the Al_2O_3 shell through the cracks formed during its crystallization from the amorphous phase to γ phase at 350 °C. [128] In addition, the redox reaction consequentially creates local hot spots and further promotes the diffusion of ions, thus, accelerating the reaction. The samples with ER at 2.5 and 3.0 gave the highest energy release, similar to the reference Al/CuO sample mixed using ultrasonication. In samples with lower ER, a second exothermal reaction shoulder can be found between 680 to 800 °C, possibly resulting from the reaction between the excessive CuO with the as-produced co-oxidizer. The second reaction was very small compared to the main reaction peak, indicating most of the material reacted prior to the melting of Al.

Figure 4.8B shows the different NH_3/Cu ratios at a fixed ER of 3.0. For the regular ultrasonically mixed samples, the reaction continued until about 690 °C, which indicated that part of the reaction took place after the melting of Al nanoparticles due to the physical distance between Al and CuO nanoparticles, which is also confirmed by Figure 4.9.

However, the main reaction peak shown in the DSC curves of Al/CuO core-shell nanoparticles in Figure 4.8A and B were all completed prior to the melting of Al at 660 °C, indicating a condensed-phase reaction between Al and CuO for its main reaction. The sample prepared using slightly excessive ammonia (NH_3/Cu) showed the highest energy release as compared to the other samples for same ER at 3.0, which also occurred for samples with other ER, as shown in Figure 4.9 and Table 4.4. When ammonia was slightly excessive compared to copper, Al and $\text{Cu}(\text{NH}_3)_4^{2+}$ presented enough surface charge to self-assemble into core-shell structures, while there was not too much water to react with and deactivate the Al nanoparticles. When the NH_3/Cu ratio was too high, the water from the ammonia aqueous solution could result in a partial deactivation of the aluminum core during synthesis. Therefore, with an NH_3/Cu ratio of 6, a good core-shell Al/CuO nanocomposite was formed while the deactivation of Al was minimal, leading to its highest energy release. A discrete second peak can be seen in Figure 4.8B when NH_3/Cu ratio is high for Al/CuO core-shell samples. The reaction possibly resulted from the reaction between the unreacted CuO and the Al-Cu co-oxidizer after the main reaction, or between the unreacted CuO and the unreacted Al core, which was trapped inside the thickened Al_2O_3 shell caused by excess water during synthesis.

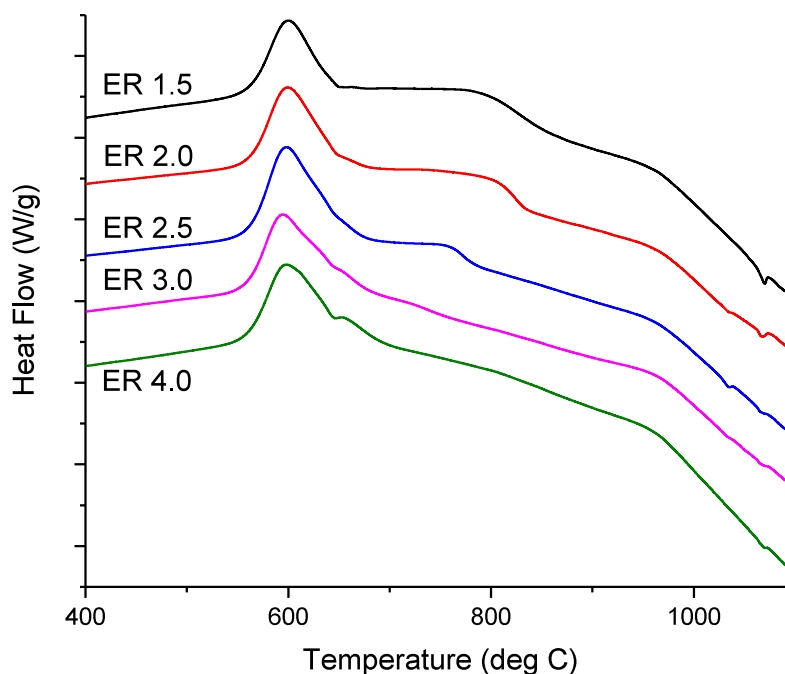


Figure 4.9. DSC curves of ultrasonication mixed Al/CuO at different equivalence ratios. The units on the y-axis (W/g) belong to each individual plots, however, the scale is arbitrary for these stacked plots.

Compared to Al/CuO mixed by ultrasonication, the core-shell Al/CuO nanocomposite did not result in a higher energy release, as shown in Table 4.4. However, the characteristic temperature of the reaction did change significantly. Apart from the complete temperature of the main reaction, which was discussed earlier, the onset and peak temperatures of the main reaction were also reduced. The decrease of onset temperature was relatively minor, only about 3 – 10 °C, indicating that the triggering mechanism of the exothermal reaction remained unchanged. However, due to the proximity of fuel and oxidizer in the core-shell arrangement, the peak temperature of the reaction decreased significantly. Once the diffusion of Al occurred, the reactive fuel could easily get into contact with the oxidizer without traveling a longer distance, resulting in a reduction of the peak temperature by 10 – 25 °C. Although a better core-shell structure was formed when ammonia was in excess, it did not conclusively result in lower onset or peak temperature. This could be arising from the fact that ammonia that was used during the fabrication process was in the form of solution. Therefore, it contained water. Since, Al is present higher up in the electrochemical series when compared to H^+ ion, Al can react with water

to release hydrogen. In other words, the extra water from the ammonia deactivated part of the Al, thickening the Al_2O_3 shell and increasing the onset and peak temperatures.

The reaction parameters of the main reaction of the as-fabricated core-shell Al/CuO nanostructure are compared to other Al/CuO structures, as shown in Table 4.5. The as-fabricated Al/CuO core-shell nanoparticle in this work showed the second-lowest onset and peak temperature, only higher than the first peak of another similar structure stated by Shi et al. [129] The reaction began at a lower temperature because of the close proximity between the fuel and oxidizer in the core-shell structure. Moreover, most reactions showed multiple exothermal peaks, indicating the occurrence of different reaction pathways during heating, which resulted from either the inhomogeneity of the sample or the large Al particles. However, the core-shell Al/CuO presented here and in our previous research [15] both show a single dominant exothermal peak that ends before the melting of Al, indicating the construction of a homogeneous core-shell structure and condensed-phase reaction between fuel and oxidizer.

When micron-Al particles were physically mixed with CuO nanoparticles, the separation between these two particles was too significant to allow an exothermal reaction to occur in DSC-TGA. [130] However, when a core-shell structure was formed between the two, a significant reaction was seen in DSC, giving energy release over 800 J/g, confirming the fact that the core-shell microstructure allows a more significant reaction between fuel and oxidizer by allowing improved intermixing and surface contact. [15, 129] When Al nanoparticles were chosen as fuel in a physically-mixed sample, the energy release was just barely higher than core-shell micron-Al/CuO, again due to the separation distance between fuel and oxidizer. Self-assembly using additives or CuO with different morphologies was tried with Al nanoparticles. However, these processes could not maximize the surface contact between fuel and oxidizer. Al could not fully react with CuO before its melting. In terms of total energy release, the core-shell Al/CuO shown in this research is equivalent to the highest reported numbers in literature but uniquely occurred in one exothermic reaction at a condensed phase.

Table 4.5: Comparison of onset, peak, end temperature, and energy release of Al/CuO with different structures and synthesis methods. The symbol “~” indicates the number was not directly given in the paper and was measured based on the DSC curve. [102]

Structure / Synthesis method	Onset temperature	Peak temperature	End temperature	Max total energy release
Physical Mixture Al(1.5 μm)/CuO(200 nm) & Al(100 nm)/CuO(200 nm)[130]	No significant exothermal reaction peak (Micro-Al)			
	~570 °C (Nano-Al)	630 °C (Nano-Al)	~700 °C (Nano-Al)	949.5 J/g (Nano-Al)
Physical Mixture Al(30-100 nm)/CuO(nanorod) [131]	~550 °C ~750 °C	604 °C ~795 °C	657 °C ~830 °C	1835 J/g (two peaks)
Assembled Al(~100 nm)/CuO(nanorod) with graphene [132]	~580 °C	595 °C 680 – 710 °C	695 – 725 °C	1679 J/g (two peaks)
Assembled Al(100 nm)/CuO(50 nm) with peptide [133]	~550 °C	663 °C	750 °C	2070 J/g (two peaks)
	582 °C (rod)	620 °C (rod)	660 °C (rod)	1977 J/g (rod)
Sputtered core-shell CuO-nanorod/Al & CuO-nanotube/Al [134]	582 °C (tube) 730 °C (tube)	625 °C (tube) 730 °C (tube)	660 °C (tube) 770 °C (tube)	2281 J/g (tube) (two peaks)
Spherical core-shell Al(1 μm)/CuO [15]	~580 °C	~620 °C	655 °C	807 J/g
Spherical core-shell Al(0.5-5 μm)/CuO [129]	~520 °C ~700 °C	~560 °C ~730 °C	~800 °C	832 J/g
Spherical core-shell Al(100 nm)/CuO (this work)	555 $\pm$ 5 °C	580 $\pm$ 10 °C	655 °C	1566 J/g

The activation energy (E_a) is another differentiating characteristic parameter confirming the formation of core-shell nanoparticles. The apparent activation energy is commonly used to describe the energy

threshold to overcome before the initiation of the chemical reaction. [135] A lower E_a indicates a smaller energy input to trigger the ignition between fuel and oxidizer for energetic materials. The Kissinger equation, as shown below, is usually used to calculate the activation energy using the peak temperature of the reaction at different heating rates. [136]

$$\ln \frac{\beta}{T_p^2} = -\frac{E_a}{RT_p} + \ln \left(\frac{AR}{E_a} \right)$$

Where R is the universal gas constant, A is the pre-exponential factor, β indicates the heating rate, and T_p represents the peak temperature at the given heating rate. The activation energy (E_a) can be calculated from the slope of the fitting curve of a series of discrete points of $\ln (\beta/T_p^2)$ against $1/T_p$.

In this work, multiple DSC runs with heating rates of 5, 10, 15, 20, and 25 K/min were carried out for the calculation of the activation energy of core-shell (ER=2.5, $\text{NH}_3/\text{Cu}=6$) and physically mixed (ER=2.5) Al/CuO samples, as shown in Figure 4.10. Generally, the core-shell Al/CuO showed a reduction of around 20 °C in peak reaction temperature of the main reaction peak compared to the physically mixed Al/CuO at all different heating rates, as shown in Figure 4.11. Figure 4.11 also shows the uncertainties attached to the onset, peak temperatures and energy release values from all the core-shell and reference samples. The calculated activation energy is 237.6 ± 7.1 kJ/mol for core-shell Al/CuO, and 258.4 ± 10.4 kJ/mol for physically mixed Al/CuO. Note that similar to the DSC curves in Figure 4.8, all the main exothermal peaks of core-shell Al/CuO terminated before the melting point of Al, confirming the domination of solid-state reaction between fuel and oxidizer in core-shell Al/CuO. The reduction of activation energy was likely due to the proximity between Al and CuO nanoparticles, shortening the diffusion length between the fuel and the oxidizer and thus reducing the energy barrier for the energetic reaction to trigger.

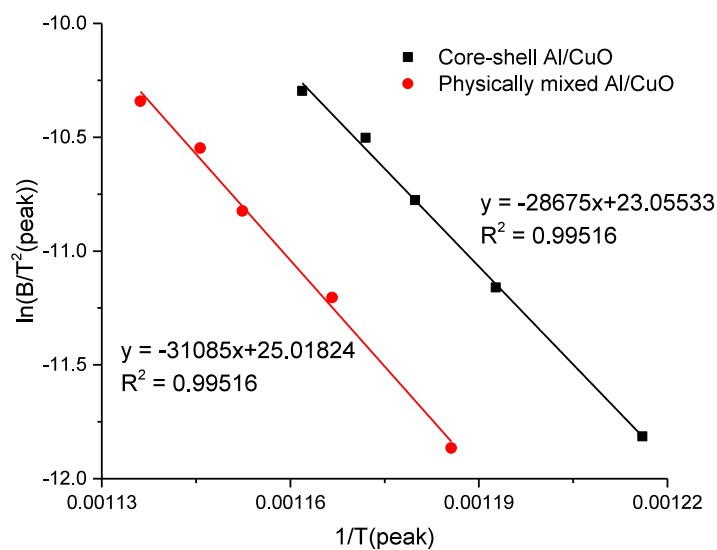


Figure 4.10: Linear fitted plot of $\ln(\beta/T_p^2)$ against $1/T_p$.

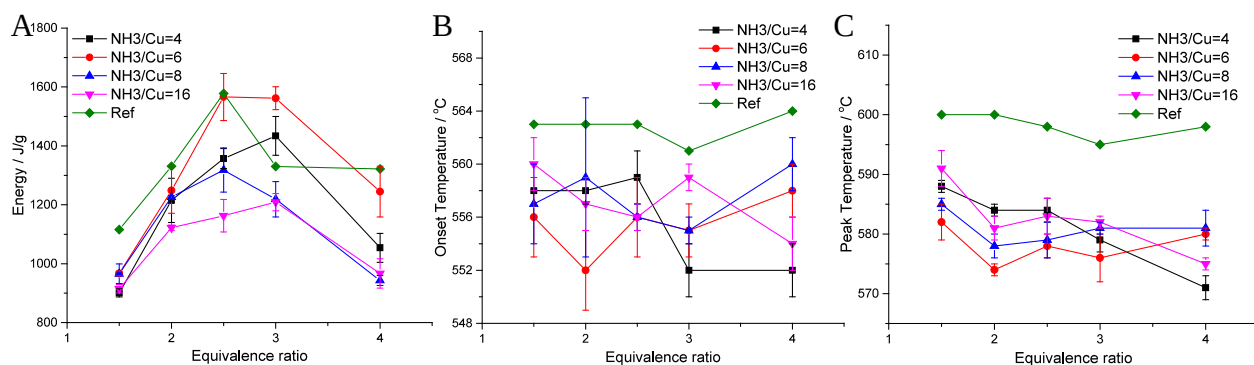


Figure 4.11. Characteristic DSC results of Al/CuO core-shell nanoparticles with different ER and NH_3/Cu ratios compared to ultrasonication mixed Al/CuO, including energy release, onset temperature, and peak temperature of the major exothermic peak.

The comparison of combustion behaviors between core-shell (ER=2.5, $\text{NH}_3/\text{Cu}=6$) and physically mixed (ER=2.5) Al/CuO was carried out using a high-speed camera at 200,000 fps. Note that the fast camera and the laser were triggered simultaneously by a function generator (at time = 0). Some important frames of the fast video of the combustion are shown in Figure 4.12A and B. The inner diameter of the tubes used was 1/8" and the length of the tubes was 5 cm. It should be noted that the

core-shell composite had a lower TMD% than the physically mixed sample. The top surface of the samples was irradiated and heated up by a high-power laser, shown as the small bright dot in the first few frames in Figure 4.12A and B, which then became the initiation of the ignition for both samples. In both samples, the flame first propagated upwards, away from the nanoenergetic material, before propagating downwards and igniting the rest of the sample. Figure 4.12C shows the evolution of the flame propagation, calculated frame by frame, which highlights some key differences between the combustion of core-shell and physically mixed Al/CuO. The upward flame of core-shell and physically mixed Al/CuO presented a very close exit speed at the end of the tube at 777 ± 27.7 and 833 ± 23 m/s. The exit speed of the flame is determined by the gas generation, the thermodynamic state of the product, and the heat release of the combustion. [2, 137] Note that the 10 mg nanothermite completely combusted before the flame reached the opening of the tube. Although the microstructure was different between core-shell and physically mixed Al/CuO, the close energy release, same composition, and same equivalence ratio resulted in nearly identical reaction product and heat generation between the two samples. Therefore, both core-shell and physically mixed Al/CuO gave very close exit speed. However, the processes of combustion of the core-shell and physically mixed Al/CuO samples behaved quite differently. The core-shell Al/CuO showed a much shorter ignition delay at 60 ± 14 μ s compared to the physically mixed Al/CuO at 155 ± 14 μ s, which was probably caused by its lower activation energy and more homogeneous structure. The behavior of the combustion after ignition was more interesting. In core-shell Al/CuO, once the top surface was ignited by the laser, the flame propagation started to accelerate instantly, reaching a velocity of 200 m/s within only 17 ± 4.5 μ s, while the nanothermite beneath the surface started reacting about 20 μ s after the surface ignition. However, it was different in physically mixed Al/CuO. After the flame appeared on the surface of the sample, it propagated at a relatively low speed (below 100 m/s for over 100 μ s), and the sample beneath did not combust until 130 μ s after the ignition on the surface. Therefore, the combustion of physically mixed Al/CuO was clearly a two-stage process, with the first stage happening on the top surface before the occurrence of the second stage into the sample. The thermite reaction can be initiated either from diffusion of oxygen from a solid-state oxidizer, availability of oxygen gas from surrounding environment, or oxygen gas coming from the decomposition of the oxidizer. [116, 138, 139] Compared to core-shell Al/CuO, the surface of Al particles in the physically mixed Al/CuO were significantly more exposed to the atmosphere, leading to a heterogeneous reaction between fuel and oxygen gas in

the first stage. In the second stage, however, the physically mixed Al/CuO showed similar behavior to the core-shell Al/CuO, accelerating quickly and reaching its highest propagation speed before exiting the tube. It is notable that the heterogeneous combustion was absent in core-shell Al/CuO despite its lower TMD% and higher porosity, indicating a single-step reaction entirely between Al and CuO during combustion.

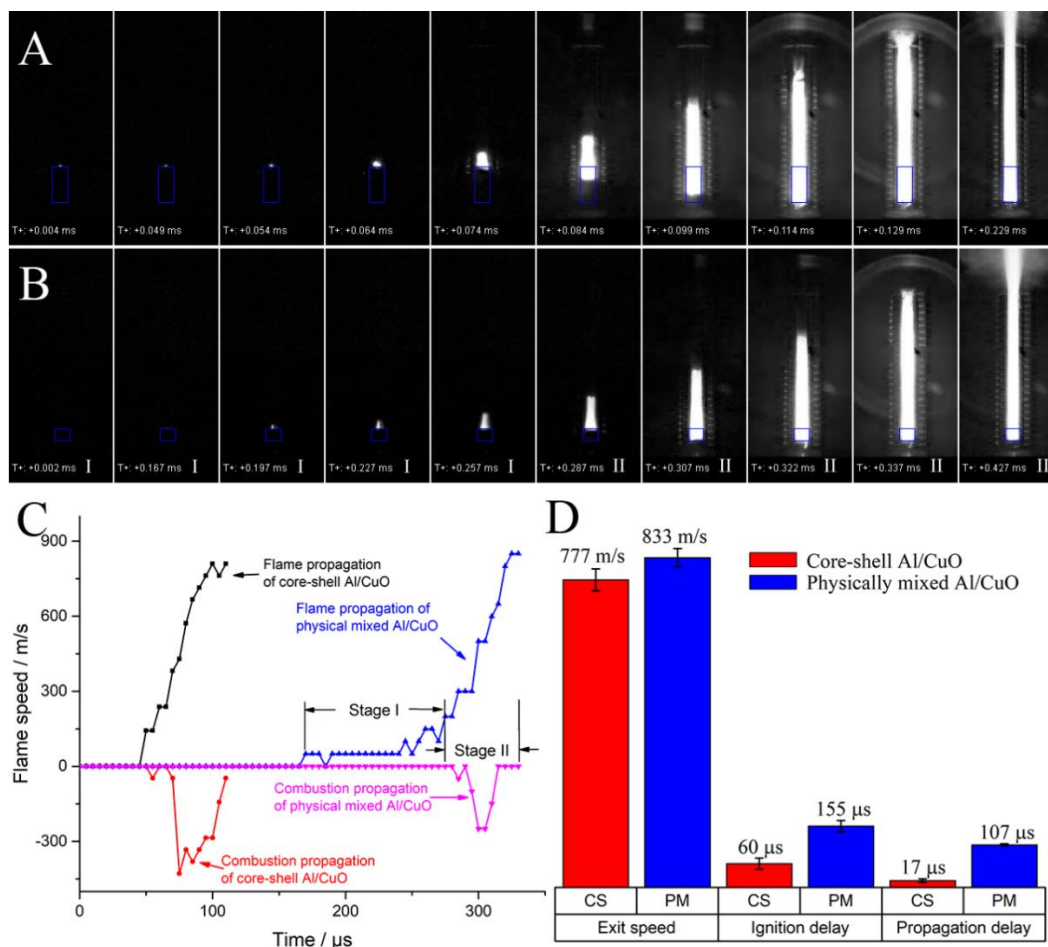


Figure 4.12: Important frames from the fast video of the combustion of 10 mg core-shell (A) and physically mixed (B) Al/CuO samples, the propagation speed of flame (upwards) and combustion in the sample (downwards) with time (C), and the comparison of key results between core-shell and physically mixed Al/CuO samples (D). The position of the loaded samples is highlighted in (A) and (B). The labels “I” and “II” in (B) correspond to the label “Stage I” and “Stage II” in (C). CS stands

for core-shell and PM stands for physically mixed, the propagation delay indicates the lag between the ignition of the sample and the moment when flame propagation rate reached 200 m/s. [102]

4.3 Conclusion

Nano-sized core-shell Al/CuO MIC was successfully fabricated via a wet chemistry method. Coverage of the coating CuO layer on Al nanoparticles relies on the opposite electrostatic force tuned by the amount of ammonia added during synthesis. By varying the ammonia to copper ratio, the target product can be “switched” between a well-covered Al/CuO core-shell nanostructure and a well-mixed Al/CuO nanoparticle composite. This key control factor together with the proposed formation mechanism of MICs particles can help guide the future design and large-scale synthesis of self-assembled nanostructures with similar properties in core-shell or simple mixture. Compared to physically mixed Al/CuO, the core-shell particles reduced onset temperature by 5 °C, peak temperature by 20 °C, and completed its energetic reaction before the melting of Al while maintaining about the same energy release, resulted from the closely packed Al fuel and CuO oxidizer in core-shell structure. The activation energy was also reduced by about 21 kJ/mol from 258.4 ± 10.4 kJ/mol for physically mixed Al/CuO to 237.6 ± 7.1 kJ/mol for core-shell. Additionally, the material also showed a highly tunable energy release which can be tuned not only by equivalence ratio but also by the amount of ammonia used. Upon laser heating, the fabricated core-shell Al/CuO showed a much shorter delay of ignition and a single-step combustion mechanism, which performed quite differently from physically mixed Al/CuO nanoparticles characterized by a surface combustion stage and a volume burning stage, due to the maximized surface contact between reactants. We will conduct future research on this topic to better correlate the structure of nanothermite with combustion mechanism and behavior. In summary, the fabricated core-shell Al/CuO nanostructure eliminated the phase separation problem of physically mixed Al/CuO nanocomposite, leading to enhanced, consistent, and controllable energetic performance. The wet-chemistry method does not require any special equipment, making it a promising candidate to bulk produce Al/CuO MICs with various but controllable structures and performances.

Chapter 5

Fabrication and characterization of core-shell Al@NiO MICs

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5.1 Introduction

The past two decades have seen a rise in the demand for developing novel energetic materials, including nanothermites which are often referred to as a green alternative to replace primary explosives such as lead azide and lead styphnate [141]. Nanothermites have made their place in applications related to propellants, pyrotechnics, and explosives [142], gas generation [117], micro-propulsion [143, 144], heat and impulse production in MEMs [145], and in micro-scale welding [23]. Nanothermites are reactive composites containing nano-sized fuel or oxidizer components. It has been shown that increasing the intimacy between the fuel and oxidizer components can enhance performance of nanothermites. This can be achieved either through decreasing the particle sizes or by increasing the contacting areas of these particles. Most recently, the fabrication of a variety of core-shell nanothermite structures has enabled extensive research on new combustion properties coupled with a tunable chemical reactivity. Nevertheless, thanks to the metastable and heterogeneous nature of nanothermites, energy input and chemical processing should be strictly controlled during fabrication, in order to keep the desirable energy density and reduce the by-products.

A popular type of nanothermites is based on aluminum [40, 146, 147] mixed with oxidizers which take the form of CuO [15, 102, 148], Fe₂O₃ [149, 150], and MoO₃ [151], etc. Other oxidizers like fluoropolymers [152], halogen oxides [153] and metal-organic framework (MOFs) [154] have been also developed. Reactions of nanothermites can generate gases, from possible sources of metal vapor production at high temperatures, release of oxygen gas from decomposition of oxidizers, and other chemical non-thermite reactions. While this gas production is sought-after in applications such as gas generators and micro-thrusters, it is highly undesirable where thermal energy generation is critical, e.g., during welding and in production of heat using a micro-ignitor [23]. Amongst various Al/metal-oxide systems shown in Table 2.1, the Al/NiO system produces the least gas. Thermodynamically, the gas production from an Al/NiO mixture is only ~7.7% of the gas generated from Al/Fe₂O₃ and ~2% of the gas released during Al/CuO reaction. A previous study reported on successful joining of 250 μ m thick silicon wafers using Al/NiO nanothermite composites and with a 30 μ m thick aluminum foil interlayer. A two-step energy release allowed for the achievement of a superior joint quality when Al micropowder was added to the nanothermite. The joined zone exhibited a micro-hardness of 129.3 ± 15.5 HV and the localized yield strength of 350.6 ± 17.8 MPa [155]. The direct transit of the reactive components over the conducting surface within the Al/NiO composite highlights the condensed phase reaction pathways, which govern the majority of the reaction mechanism of layered Al and NiO nanoparticles [156].

There are two major methods for fabrication of nanothermites. The physical methods include physical mixing with sonication, magnetron sputtering, atomic layer deposition, and ball milling etc. [157, 158, 6]. Dong et al. [20] developed a polymer assembly method to prepare the Al/NiO nanocomposite with enhanced thermal properties. It was discovered that the addition of P4VP significantly suppressed the agglomeration of nanoparticles, resulting in consistent contact and adequate interfacial area between Al and NiO nanoparticles. Wen et al. [159] used hydrothermal technique to create NiO nanowires, which they subsequently combined with nano-Al using sonication. They discovered that the onset temperature of the observed thermite reaction was independent of the NiO nanowire mass in the composite, however, the quantity of energy release was a strong function of varying NiO ratios. Zhang and Li [19] fabricated a n-Al/NiO thin film by EPD. Zhang et al. [37] were able to produce a nano-honeycomb Al/NiO composite by depositing Al through thermal evaporation on top of the oxidized Ni layer. Yu et al. [17] made a 3DOM Al/NiO nanothermite by incorporating a colloidal crystal template

and magnetron sputtering. Most recently, Wang et al. [160] mixed Al nanoparticles with NiO hollow nanospheres which were prepared by enhanced-absorption template method. Notably, these physical methods are effective in shortening the diffusion distance between reactants. However, many heterogeneities exist in chemical components across the samples and most nanoparticles are agglomerated into larger sizes. In addition, physical methods usually require sophisticated equipment for large-scale production, ending up being a costly and energy-ineffective process [102]. Contrarily, chemical methods such as sol-gel [161] and solution-based wet-chemistry methods [15, 16, 102] are based on interfacial chemistry, being efficient and flexible, without using of expensive equipment such as magnetron sputtering machines. Considering the merit of increased interfacial areas and shortened diffusion distance of reactive species within the layer-by-layer, 3DOM and core-shell nanothermite structures, it is desired to fabricate the similar structures for Al-NiO nanothermites. Interestingly in the literature, such fabrication methods have been rarely reported. In fact, if a core-shell particle can be fabricated with the fuel (Al) as the core and the oxidizer (NiO) as the shell, the homogeneity of the chemical composition in the composite can be significantly improved, not to mention the direct contact between the reactive species within the same particle. Both factors will increase the completion of the thermite reaction and facilitate the ignition, meaning the increased specific energy release and a reduced initiation temperature [134, 157, 162]. Most importantly, the core-shell particle acts like a complete reactive cell which is ready to be delivered to a target location for localized heat production. The major objective of this work is to develop a wet chemistry method for producing such core-shell Al@NiO particles with satisfying energetic properties. If produced successfully, the as-synthesised core-shell particles must exhibit an energy release from the thermite reaction either more or at least at par with the other values reported in literature for structured Al/NiO composites. Take for example, Sui et al. [156, 163] reported an energy release of 1.01-1.512 kJ/g with carbon nanotubes added into Al (40 - 60 nm)/NiO(50 nm) layers. Wen et al. [159] reported a number of 1000 J/g as the energy release for the composite prepared by mixing NiO nanowires with Al nanoparticles. Bai et al [164] used tremella NiO spheres which were synthesized in ethylene glycol by alcohol-thermo-mediated self-assembly and tested the nanothermite produced via ultrasonic mixing. They reported for 100 nm Al and 500 nm NiO, the observed energy release is 1172.8 J/g for ER = 1.4. Zhang et al. [33] stated a number of 931.1 J/g for Al(50 nm)/NiO(30 nm) mix. Wang et al [160] detailed a value of 1275-1410 J/g for the mix of Al nanoparticles with hollow NiO spheres.

We report on a fabrication process of core-shell structured $\mu\text{Al@NiO}$ nanothermite particles using an additive-free facile wet-chemistry based approach. Conceptually, the attempt has been made to instill opposite electrostatic charges on the fuel (Al) and the precursor to the oxidizer (Ni-salt) respectively, to let them self-assemble in the core-shell fashion. This approach naturally eliminates the need for additives such as polymers and surfactants to guide the assembly process. The resulting product is comprehensively characterized for (i) morphology by SEM and EDS; (ii) composition by XRD and XPS; (iii) its potential as an energetic material by simultaneous TGA) and DSC and laser ignited combustion tests. Two process parameters (the nominal equivalence ratio and NH_3/Ni ratio) were varied to quantify their effects on the energetic performance.

5.2 Results and Discussion

5.2.1 Microstructures of the as-prepared core-shell $\mu\text{Al@NiO}$ MICs

Figure 5.1 displays the SEM and EDS of the core-shell structured $\mu\text{Al@NiO}$ MICs corresponding to the ER 2.0, 3.0 and 4.0 (Figure 5.1A, B, and C respectively). Al microparticles were seen to be well coated with n-NiO particles in all three samples. It appeared as if ER 4.0 displayed the coating multiple layers thick (Figure 5.1C), while ER 2.0 showcased an uneven coverage (Figure 5.1A). However, this finding is not conclusive and requires additional characterizations. The exact size of NiO particles was difficult to be concluded due to the low resolution of SEM, nevertheless a further zooming in at ER 4.0 sample gave a rough estimate of ~ 40 nm (Figure 5.2A). One major distinction amongst samples was that ER 2.0 and 4.0 presented distribution of NiO particles across the sample even where Al is absent, ER 3.0, on the other hand, disclosed the presence of μAl and NiO particles in tandem. The core-shell structure was visible in samples of all ERs and was further verified by the accompanying EDS images.

The mechanism of making of the core-shell $\mu\text{Al@NiO}$ MICs is proposed to follow an identical route as Al/CuO, reported in previous studies. [15, 102] The nickel salt forms a green solution with ethanol. When aqueous ammonia solution is added into it, a purplish-blue precipitate is formed. It is worthwhile to mention that Ni^{2+} forms $[\text{Ni}(\text{NH}_3)_6]^{2+}$ with concentrated ammonia and the resulting solution becomes clear inky-blue. The absence of clear inky-blue solution and the formation of purplish-blue precipitate signified the formation of $[\text{Ni}(\text{NH}_3)_4]^{2+}$. Meanwhile, it has been shown by Zeta potential analysis that

passivated Al particles bear a negative charge in alkaline solutions [102]. So, when nickel salt plus aqueous ammonia (i.e. purplish-blue precipitate solution with extra spare ammonia) solution was poured into Al dispersion in ethanol, the alkalinity of the solution induced this negative charge on Al. Because of the opposite charge, there exists an electrostatic force between the Al and Ni-NH₃ complex ion which provokes them to self-assemble in a core-shell fashion. After filtration and upon calcination, the Ni-NH₃ complex decomposes into NiO and $\mu\text{Al@NiO}$ core-shell MIC is born.

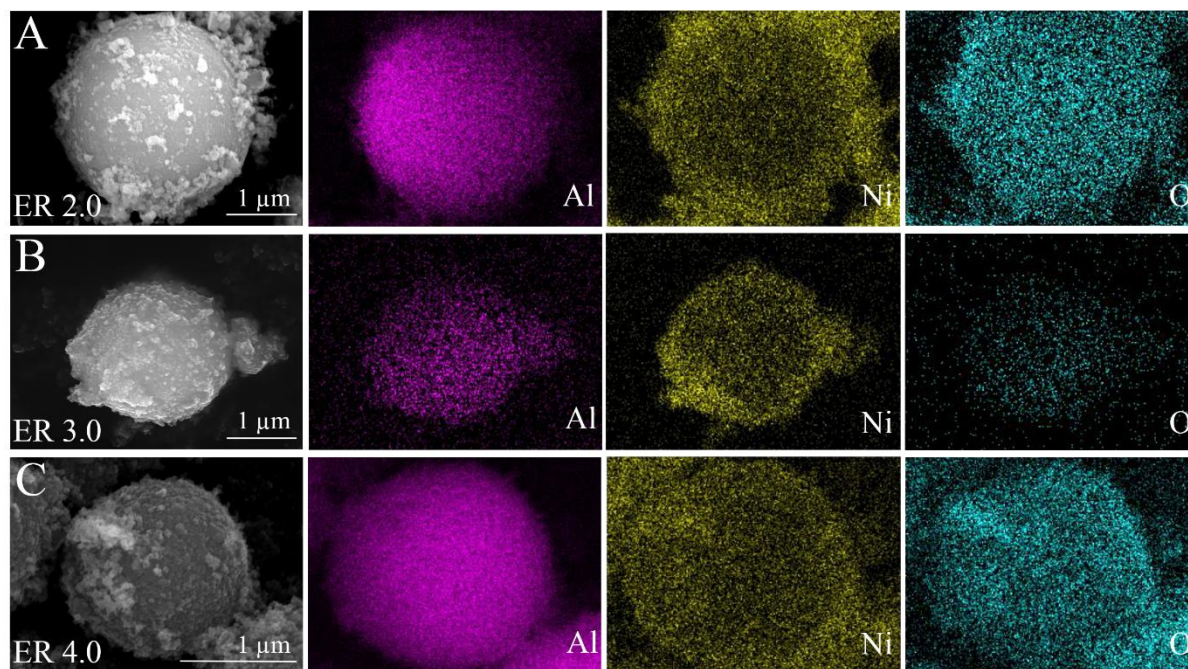


Figure 5.1: SEM and EDS of core-shell $\mu\text{Al@NiO}$ MIC for equivalence ratio of 2.0 (A), 3.0 (B) and 4.0 (C).

5.2.2 Microstructures of the products post reaction

Following the heating of each sample from ambient temperature to 1500°C, it was interesting to analyze the morphology of the products under SEM. In ER 2.0 post reaction, as visible in Figure 5.2C and 5.2E, many ball-like spheres were seen across the sample. Through ab initio molecular dynamics simulation, Wen et al [159] had predicted the creation of certain metallic liquid spheres from the thermite reaction.

EDS analysis (Al, Ni and O mapping following Figure 5.2E) showed these spheres to be solely composed of Ni. Since Ni melts at 1455°C, it is believed that the liquid Ni drops formed at 1455°C, solidifies into this ball upon cooling the equipment to room temperature before the samples were drawn out to be taken for conducting SEM. An effort was made to identify intermetallic alloy products from the reaction, but without success. A further close-up on the sample (Figure 4.3B) also showed a typical Al₂O₃ fiber-like structure which hinted at the reaction mechanism of $\mu\text{Al@NiO}$ thermite reaction. In lieu of the fact that the Al₂O₃ fibers appeared “stretched” and “straight”, it was tempting to deduce that $\mu\text{Al@NiO}$ pursued the melt dispersion mechanism wherein the Al melted and flies out of the cracked Al₂O₃ shell around each Al particle, consequentially encountering oxygen from the NiO on the way, thus forming Al₂O₃ fibers. However, the melt-dispersion mechanism could not be concluded because after the slow heating reaction in DSC, the literature overwhelmingly supports the Trunov’s [76] Al₂O₃ shell transformation and growth mechanism for μAl . Therefore, the Al₂O₃ fibers observed on SEM need further investigations.

For drawing the comparison, SEM was performed on the as-synthesized core-shell $\mu\text{Al@NiO}$ of ER 4.0 post reaction (Figure 5.2D and 5.2F) and the samples displayed not as many ball-like spheres i.e. the separate Ni-phase formed post thermite reaction most likely reacted further to form an alloy with Al but did not manifest as a ball inside of the products. In this sample, contrary to ER 2.0, the intermetallic alloy compounds were easily found at certain locations.

5.2.3 XRD and XPS

The XRD and XPS pattern (Figure 5.3A and 5.3B) was obtained for the as-fabricated core-shell $\mu\text{Al@NiO}$ for ER 3.0 to determine the composition and crystalline phase of NiO across samples. NiO displayed the XRD diffraction peaks at the 2θ values of 28.7°, 37.3°, 43.2°, 62.9°, 75.4° and 79.3° which indexed well to the characteristic peaks matching the crystal planes of (110), (111), (200), (220), (311) and (222) of the standard NiO (JCPDS NO. 47-1049 and 04-0835) [165, 166]. The diffraction pattern simultaneously reflected the XRD peaks at 2θ of 38.48°, 44.74°, 65.10°, 78.24°, and 82.42° which agreed well with the standard XRD pattern face-centered cubic (fcc) form of Aluminum (JCPDS NO. 04-0787) [167, 168]. The high-resolution Ni 2p XPS spectrum was described in order to comprehend the surface oxidation state of NiO (Figure 5.3B). It was possible to distinguish two edge splits caused by spin-orbital coupling of Ni 2p_{3/2} and Ni 2p_{1/2}. The Ni 2p spectrum of NiO was

deconvoluted into six peaks. Two strongest doublet peaks were identified belonging to $2p_{1/2}$ and $2p_{3/2}$ of Ni^{2+} at 871.4eV and 855.6eV, respectively.

Two other peaks were found at the binding energies of 878.8eV and 861eV and were recognized as the associated shakeup satellite peaks $2p_{1/2}$ and $2p_{3/2}$ of Ni^{2+} , respectively. Two additional peaks centered at 873.2 and 855.6 eV were related to Ni^{3+} implying the co-existence of two oxidation states (2^+ and 3^+) for Ni in the core-shell $\mu Al@NiO$ thermite. This non-stoichiometry detected on XPS comes from Ni^{2+} vacancies that are apparently detected as localized holes in the crystal lattice to NiO creating Ni^{3+} ions [169]. These findings demonstrated the existence of NiO and agreed well with the results reported in literature [169, 170].

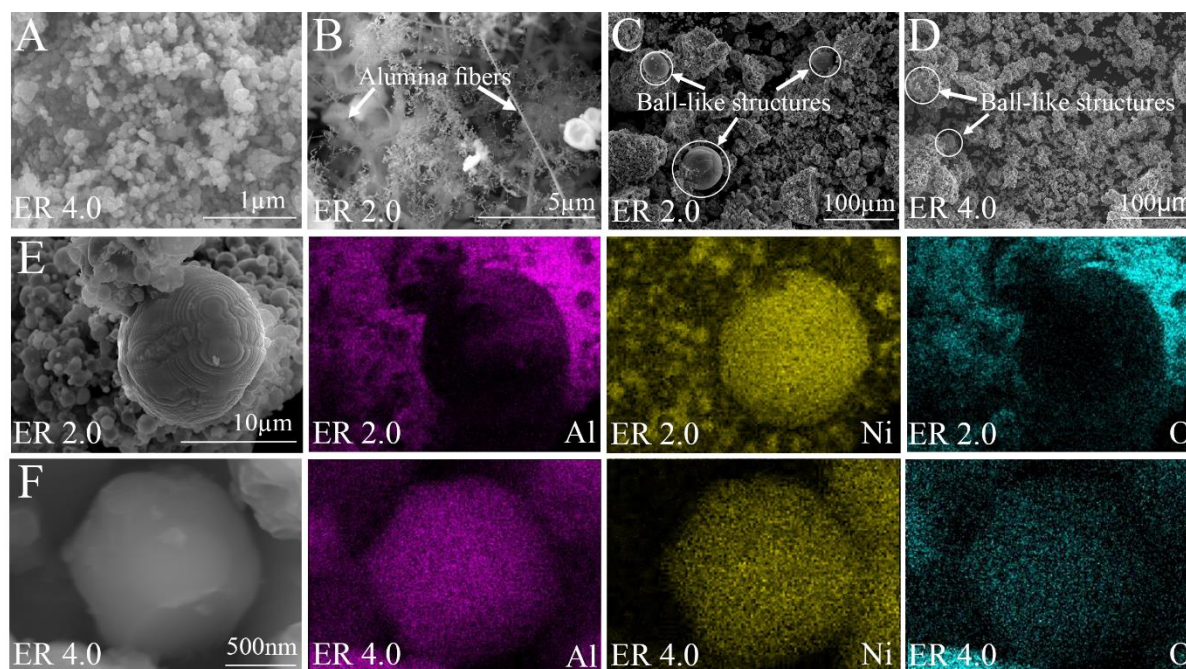


Figure 5.2: SEM of NiO nanoparticles (A) from core-shell $\mu Al@NiO$ MIC (ER 4.0 and NH_3/Ni 6.0); alumina fibers (B) found in core-shell $\mu Al@NiO$ MIC (ER 2.0 and NH_3/Ni 6.0) post reaction; ER 2.0 (C and E) and ER 4.0 (D and F) post reaction.

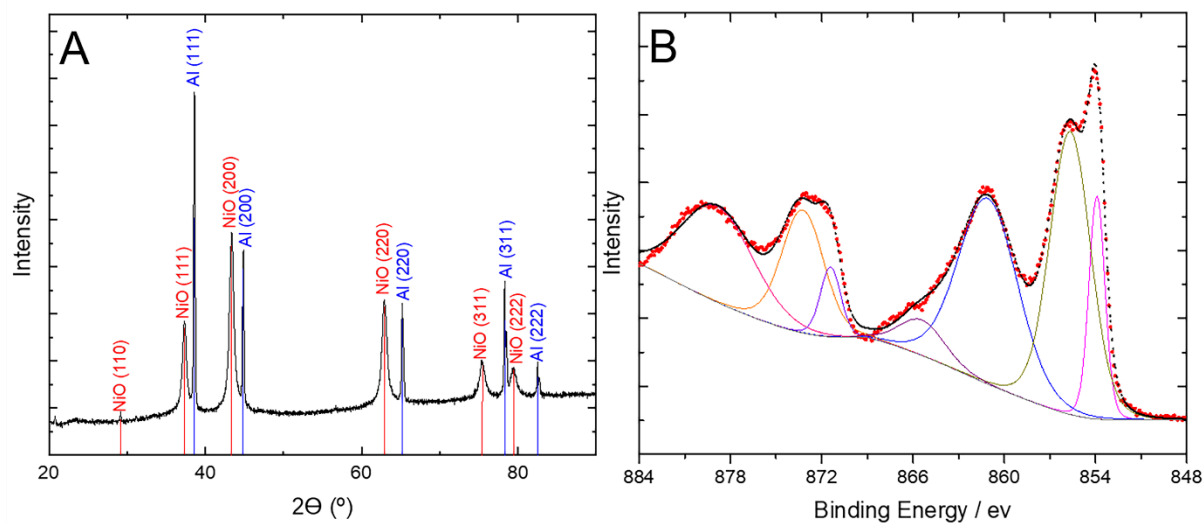


Figure 5.3: XRD spectra of $\mu\text{Al@NiO}$ MIC (ER 3.0 and NH_3/Ni 6.0) (A) and Ni 2p XPS spectrum (B)

5.2.4 Onset and energy release

All samples, with different ERs ($\text{NH}_3/\text{Ni}=6.0$) and different NH_3/Ni ratios (ER 3.0) were subjected to slow heating in an inert atmosphere to characterize their thermal behavior. The results, displayed in Figure 5.4 show that $\mu\text{Al@NiO}$ react after the Al completely melts and diffuses out of the cracks developed on Al_2O_3 shell during its phase transition temperature (at $< 300^\circ\text{C}$) to encounter NiO for the thermite reaction to take place.

All samples paraded an endothermic Al-melting peak at 660°C , an exothermic peak coming from the thermite reaction, followed by another relatively small exothermic peak coming from the alloy-formation reaction (Figure 5.4). The reaction's onset temperature was found to be inversely proportional to the equivalence ratio, with the onset of PM (ER 3.0) similar to the onset of core-shell for ER 2.0 and 2.5. The initiation temperature observed for these composites was in line with the molecular dynamics' inferences from Zhang et al. [161], Fathollahi & Azizi-Toupkanloo [171, 172]. Different alloys/intermetallics were expected based on the discoveries from Mameri et al [173] and Vrel et al [174]. It was suspected that the alloy formed from each sample depended on the Al content of the thermite. ER 2.0 (Al-lean/Ni-rich) exhibited another small endothermic peak at 1379.56°C [175] coming from the melting of AlNi_3 alloy. ER 3.5 and 4.0 samples (Al-rich/Ni-lean) exhibited a small exothermic peak at the melting point of Al_3Ni alloy at 1144.8°C [175]. ER 2.5 and 3.0 did not display

an additional alloy-melting peak between 1100-1450°C. However, it is suspected that these samples, on account of being neither Al-rich nor Al-lean, form a stoichiometric AlNi alloy which has a melting point of 1638°C [175] which is outside of the maximum operating temperature of the equipment. It is to be noted that the PM sample displayed the same trend as that of core-shell composites, however, the energy-release registered was 388.90 J/g lower than that of core-shell $\mu\text{Al}@\text{NiO}$ (ER 3.0) possibly due to the increased proximity between reactants. A thorough review of writings from literature provided a variety of numbers for energy released from the thermite reaction of Al-NiO duo. The comparison of content of energy release from this work to previously reported data is summarized in Table 5.3. All this to say is that the energy release from the core-shell composites built in this research is found to be on the higher end of this band. The reaction parameters of the main reaction of the as-fabricated core-shell $\mu\text{Al}@\text{NiO}$ MIC and PM are comprehensively tabulated in Table 5.1. The standard deviation from the error for these measurements is shown in Figure 5.5.

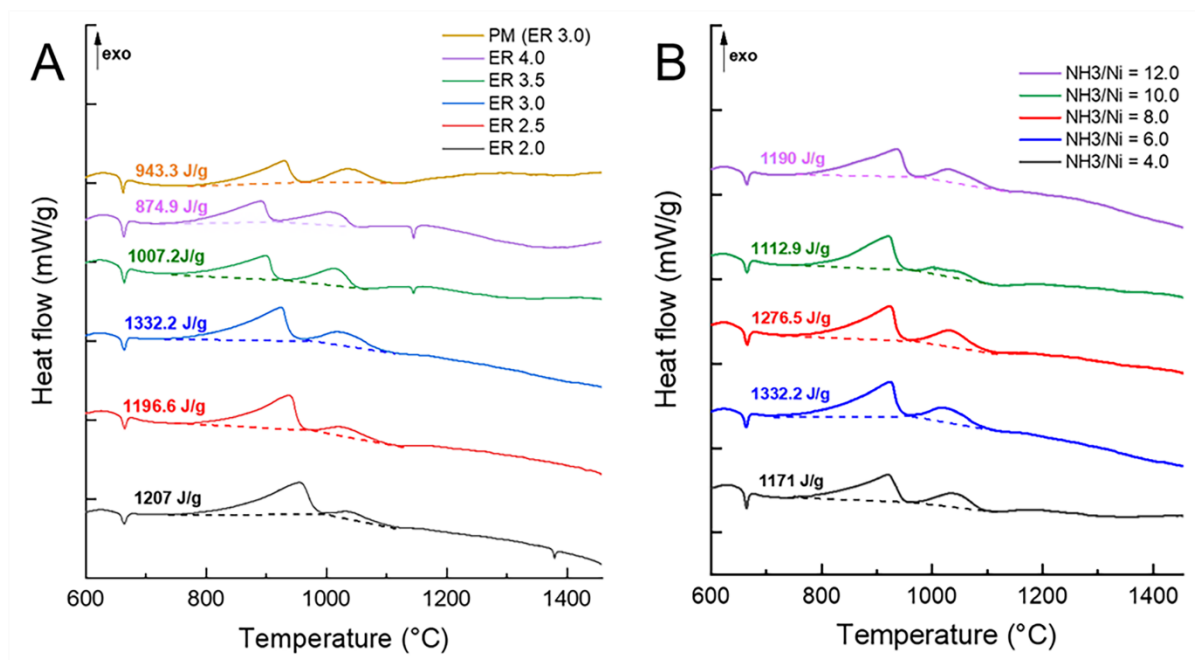


Figure 5.4: DSC results of $\mu\text{Al}@\text{NiO}$ core-shell nanocomposite with different ER (NH₃/Cu = 6) (A), $\mu\text{Al}@\text{NiO}$ core-shell nanoparticles with different NH₃/Ni ratios compared to ultrasonication mixed $\mu\text{Al}/\text{NiO}$ (ER=3.0) (B). The units on the y-axis (W/g) belong to each individual plots, however, the scale is arbitrary for these stacked plots.

Table 5.1: Onset, endothermic and exothermic peak temperatures, and energy release of $\mu\text{Al@NiO}$ composites with different ERs ($\text{NH}_3/\text{Ni} = 6.0$)							
		ER 2.0	ER 2.5	ER 3.0	ER 3.5	ER 4.0	PM
		$\text{NH}_3/\text{Ni}=6.0$					
Onset Temperature	($^{\circ}\text{C}$)	846.20 $\pm$ 1.28	840.40 $\pm$ 3.14	830.40 $\pm$ 1.48	813.40 $\pm$ 4.69	795.20 $\pm$ 2.11	840.30 $\pm$ 5.52
Exothermic peaks	($^{\circ}\text{C}$)	961.23 $\pm$ 3.96, 1033.31 $\pm$ 2.53	942.93 $\pm$ 2.81, 1017.72 $\pm$ 1.28	927.84 $\pm$ 1.72, 1013.43 $\pm$ 1.49	903.79 $\pm$ 3.11, 1012.16 $\pm$ 2.45	893.61 $\pm$ 1.67, 1008.04 $\pm$ 4.31	932.04 $\pm$ 3.32, 1037.33 $\pm$ 3.57
Energy released	(J/g)	1207.22 $\pm$ 38.91	1196.61 $\pm$ 5.50	1332.27 $\pm$ 10.76	1007.25 $\pm$ 2.06	874.93 $\pm$ 14.67	943.31 $\pm$ 12.85
Endothermic peaks	($^{\circ}\text{C}$)	660.0, 1379.56	660.0	660.0	660.0, 1144.88	660.0, 1144.95	660.0

Considering ER 3.0 outperformed for $\text{NH}_3/\text{Ni}=6.0$ as far as the overall energy released is concerned, ER 3.0 was selected for further experiments to determine an optimum NH_3/Ni ratio. Upon varying the NH_3/Ni ratio, it was observed that all samples exhibited similar trends with similar reaction parameters (summarized in Table 5.2), with the only difference in the content of energy released from the overall reaction which peaked for NH_3/Ni ratio of 6.0.

It can be deduced from correlating the DSC results with SEM/EDS that $\mu\text{Al@NiO}$ MIC, unlike its competitors like Al/CuO and Al/ Fe_3O_4 , does not require fine tuning when it comes to fabrication. It is not very sensitive to the fabrication parameters like ERs and NH_3/Ni ratio.

Table 5.2: Onset, endothermic and exothermic peak temperatures and energy release of $\mu\text{Al@NiO}$ composites with NH_3/Ni ratios (ER = 3.0)						
		$\text{NH}_3/\text{Ni}=4.0$	$\text{NH}_3/\text{Ni}=6.0$	$\text{NH}_3/\text{Ni}=8.0$	$\text{NH}_3/\text{Ni}=10.0$	$\text{NH}_3/\text{Ni}=12.0$
		ER = 3.0				
Onset Temperature	($^{\circ}\text{C}$)	826.70 $\pm$ 1.24	830.40 $\pm$ 1.48	830.50 $\pm$ 2.12	823.12 $\pm$ 2.69	825.24 $\pm$ 1.51

Exothermic peaks	(°C)	926.44 ± 2.66, 1033.58 ± 3.01	927.84 ± 1.72, 1013.43 ± 1.49	926.97 ± 2.69, 1033.56 ± 3.27	924.92 ± 4.31, 1034.42 ± 3.07	939.68 ± 3.85, 1031.61 ± 4.47
Energy released	(J/g)	1171.34 ± 19.42	1332.27 ± 10.76	1276.52 ± 5.86	1112.93 ± 25.29	1190.02 ± 40.35
Endothermic peaks	(°C)	660.0	660.0	660.0	660.0	660.0

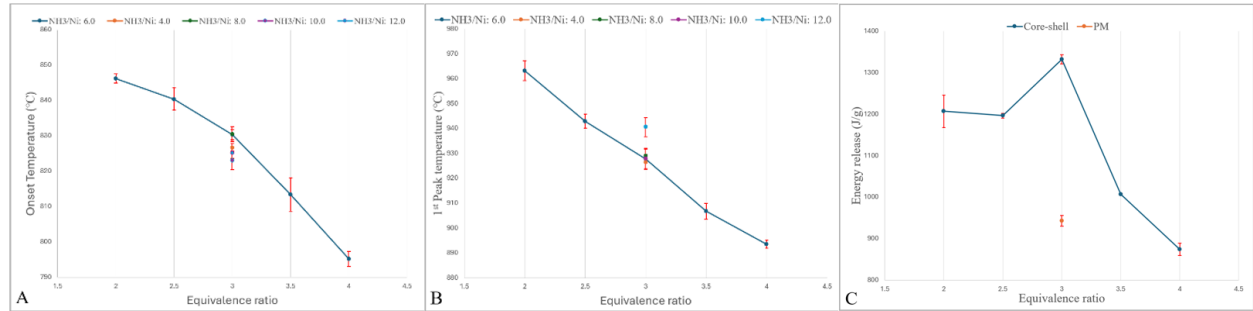


Figure 5.5: Onset temperature (A), 1st peak temperature (B) versus equivalence ratio for various NH₃/Ni ratios and Energy released versus equivalence ratio (C) for the core-shell and PM composite.

5.2.5 Activation energy

The core-shell structure was additionally confirmed by calculating the activation energy (E_a) for the as-produced $\mu\text{Al@NiO}$ composites vs the PM $\mu\text{Al/NiO}$ counterpart. The apparent activation energy is the characteristic reaction parameter that describes the threshold of energy to be surpassed for a chemical reaction to be initiated [176]. A lower E_a specifies a smaller energy threshold i.e. input to set off the redox reaction between the components for energetic materials. The activation energy can be estimated by Kissinger equation (Equation 5.1), as shown below, by taking into account the peak temperature of the reaction at different heating rates [136].

$$\ln\left(\frac{b}{T_p^2}\right) = -\frac{E_a}{RT_p} + \ln\left(\frac{AR}{E_a}\right) \quad \text{Equation 5.1}$$

where b is the heating rate, T_p indicates the temperature of the peak of the reaction at the chosen heating rate, A and R represent the pre-exponential factor and the universal gas constant, respectively. A series of discrete points of $\ln(b/T_p^2)$ versus $1/T_p$ can be fitted linearly whose slope is used to determine E_a .

In this research, multiple DSC runs were carried out at the heating rates of 5, 10, 15, 20, and 25 K/min to calculate the activation energy of core-shell (ER=3.0, NH₃/Cu=6) and PM (ER=3.0) μ Al/NiO samples, as shown in Figure 5.6.

Generally, the core-shell μ Al@NiO showed a reduction of around 5°C in peak reaction temperature of the main reaction peak compared to the PM μ Al/NiO at all different heating rates. The calculated activation energy is 274.01 ± 3.27 kJ/mol for core-shell μ Al@NiO, and 283.25 ± 4.98 kJ/mol for PM μ Al/NiO. For the sake of comparison (Table 5.3), activation energies reported for various Al/NiO system of differing component sizes, geometries or assemblies reported thus far are 193.87-224.44 kJ/mol [160], 195.17 kJ/mol and 283.04 kJ/mol [164], 178.6 kJ/mol [177], and 277 kJ/mol [178]. Given the fact that all of these studies use Al nanoparticles, the apparent activation energy showed by core-shell μ Al@NiO composite is pretty marvelous. One may argue that a reduction of 9.24 ± 8.25 kJ/mol obtained by engineering the assembly is insignificant. Nonetheless, it would be unreasonable to expect a drastic decrease in activation energy since the thermite reaction mechanism does not change evidenced by the similar DSC trend for core-shell and PM thermite. The reduction of activation energy is likely due to the tight condition between Al and NiO nanoparticles, shortening the diffusion distance between reactants and thus reducing the energy barrier for the energetic reaction to trigger. Note that NiO nanoparticles used for the preparation of physically mixed reference sample were 15-35 nm which are way smaller than the NiO (~40 nm) found in the SEM results (Figure 5.2A). Along those lines, a greater decrease in activation energy is conceivable if similar sized NiO were used to prepare the reference sample.

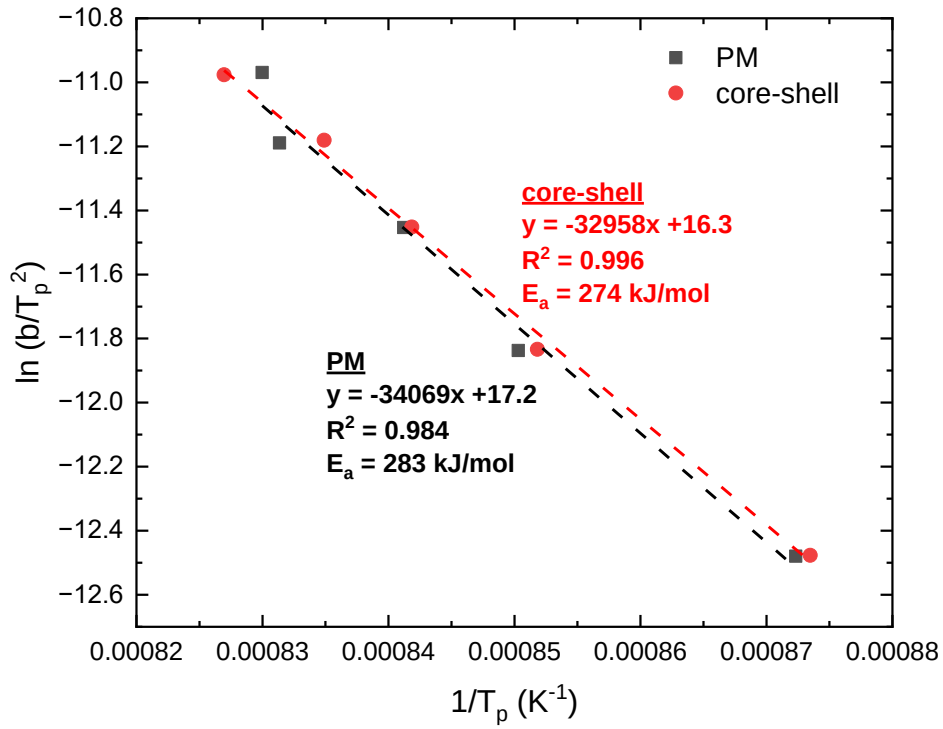


Figure 5.6: Plotting $\ln(b/T_p^2)$ against $1/T_p$ using a linear fit.

Components of NT	Size	ER	Synthesis method	Energy release (J/g)	Activation Energy (kJ/mol)	Reference
AlNiO nanowires	50-120 nm/20 nm diameter, > several μms	3.5	PM	1000	214.5-216.3	[159]
Al/NiO	50 nm/30 nm	1.23	EPD	931.1	-	[19]
Al/double shell or hollow spheresNiO	50 nm/140-200 nm	1.8	PM	1275-1410	184.6	[160]
(Al+CNT)/NiO Al/(NiO+CNT)	40-60 nm/50 nm	0.79	EPD	1268 1512	-	[163]
Al/NiO	40-60 nm/50 nm	0.79	EPD	1010	-	[156]

Al@Trameller NiO	100 nm/500 nm	1.4	PM	1172.8	195.17	[164]
Al/NiO	100 nm/500 nm	1.4	PM	-	283.04	[164]
Al/NiO & Milled Al/NiO	-/140 nm) -/42 nm)	1.0	Un-milled & Ball-milled(20hrs)	-	277 & 150	[178]
Al/Al/NiO	40 nm/5 μ m/50 nm	2.0	EPD	-	332.96 $\pm$ 8.22	[155]
Al/Al/NiO	40 nm/1 μ m/50 nm	2.0	EPD	-	696.09 $\pm$ 3.26	[155]
Al/NiO	40 nm/50 nm	2.0	EPD	-	663.81 $\pm$ 7.40	[155]
Al@NiO (this work)	1 μ m/40-50 nm	3.0	Core-shell	1332.27 $\pm$ 10.76	274.01 $\pm$ 3.27	

5.3 Combustion Dynamics

The thermal analysis results have well corroborated that μ Al@NiO conforming to ER 3.0 has better energy performance than other ERs and PM μ Al/NiO. To further strengthen the aforementioned results on the augmented energy output performance of the core-shell structure over the physically mixed counterpart, a high-speed camera was employed in the combustion chamber to record the combustion videos of the two composites (μ Al@NiO vs μ Al/NiO) in the atmospheric environment. Figure 5.7 shows the side-by-side comparison of the two and clearly depicts a stark difference in the combustion of the two composites. It is obvious that core-shell μ Al@NiO MIC could be ignited successfully (Figure 5.7A) and achieved a self-sustained combustion. On the other hand, the PM sample could not be ignited at all (Figure 5.7B).

For the core-shell composite, upon ignition by the laser, the flame appeared within 2.33 ms and was seen to spread swiftly in the vertical direction, reaching the top of the tube at 4.51 ms (in < 2 ms from ignition) and then combusting violently, accompanied by a thud. The entire sample was consumed within 6.5 ms. The intensity of combustion was observed to be maximum at the time of the thud at 6.24 ms. Such intensive and luminous combustion reaction was also recorded by Wang et al. [160] for Al (50 nm) +double-shell hollow NiO spheres (140-200 nm), however their samples displayed an ignition delay of >3.5 ms despite the smaller size of reactants, hence highlighting a major advantage of a tailored assembly over physical mixing. Same observation was put forward by Bai et al. [164] for the nanothermites built with tremella NiO (750 nm) and Al nanoparticles. Figure 5.7A distinctly

displays the potential of a tailored Al/NiO system for quickly releasing the chemical energy from the thermite reaction.

Similar to the combustion of Al@CuO reported in the previous study [102], $\mu\text{Al@NiO}$ also demonstrated two stages of combustion: surface combustion (2.55–5.88 ms) followed by the bulk combustion (5.88–9.05 ms). It was observed that once ignition began at the top surface of the core-shell thermite, the flame, thus formed, at first propagated up, away from the sample (the first-stage of combustion, marked as ‘I’ on Figure 5.7), and then propagated downwards when enough energy has been released from the first-stage combustion, igniting the rest of the material (the second-stage of combustion, marked as ‘II’ on Figure 5.7). For the PM composite (Figure 5.7B), a very dim flame appeared around 2ms. This miniscule flame keeps oscillating at its initial spot within the scale of 5-10 mm until 35-36 ms. It is to be noted that a proper flame never got developed for physically mixed MIC. The procession of the sample consumption during combustion is shown in the form of blue and red rectangles for core-shell and PM thermite (Figure 5.7A and 5.7B) respectively. The length that the flame travels inside the combustion tube for both $\mu\text{Al@NiO}$ and $\mu\text{Al/NiO}$ is illustrated in Figure 5.8A. Parallel to Figure 5.8A, a brightness plot representing the optical intensity observed in each frame of combustion video is plotted against time in Figure 5.8B. Both plots (Figure 5.8) clearly depict the initiation of combustion at 2.55 ms for the core-shell thermite. The length of the flame versus time plot is shown in Figure 5.8A. It is clear from the slope of the plot that the flame drifts at the speed of 33.46 m/s in the first-stage of combustion between 2.55-3.5 ms. The intensified flame is seen when the flame enters the second-stage at 5.88 ms, shown as the second hump of length versus time plot and the peak of brightness vs time plot (Figure 5.8A and 5.8B). The flame starts to die out after 7.5 ms as was seen by the diminishing intensity in Figure 5.7A and the downward slope in Figure 5.8A. The flame gets extinguished at around 15ms as seen by the termination of red peak in Figure 5.8B. Meanwhile, the physically mixed thermite did not get combusted enough to demonstrate any conspicuous features, although the intensity of the diminutive flame after 35 ms was captured in the brightness plot (Figure 5.8B) between 38-48 ms.

At this point, it is noteworthy to mention that Wang et al. [102] reports a probable involvement of atmospheric oxygen in the two-staged combustion of Al@CuO thermite in a similar setup. However, for $\mu\text{Al@NiO}$ or $\mu\text{Al/NiO}$ thermites, the involvement of oxygen seemed highly unlikely. Had atmospheric oxygen been involved in ignition, the PM $\mu\text{Al/NiO}$ should have at the very least ignited,

if not completely combusted (violently) as it majorly contained uncoated, heterogeneously distributed Al particles (differing from the coated, less accessible Al particles of the core-shell composite) which were easily accessible to oxygen inside combustion chamber. This boosted combustion performance of the core-shell $\mu\text{Al}@\text{NiO}$ MIC against the ultrasonically prepared $\mu\text{Al}/\text{NiO}$ mix in the atmospheric settings, undoubtedly, stemmed from the intimate bonding between μAl and NiO at nanoscale, which not only avoided additional oxidation of Al, but also shortened the path of heat transfer.

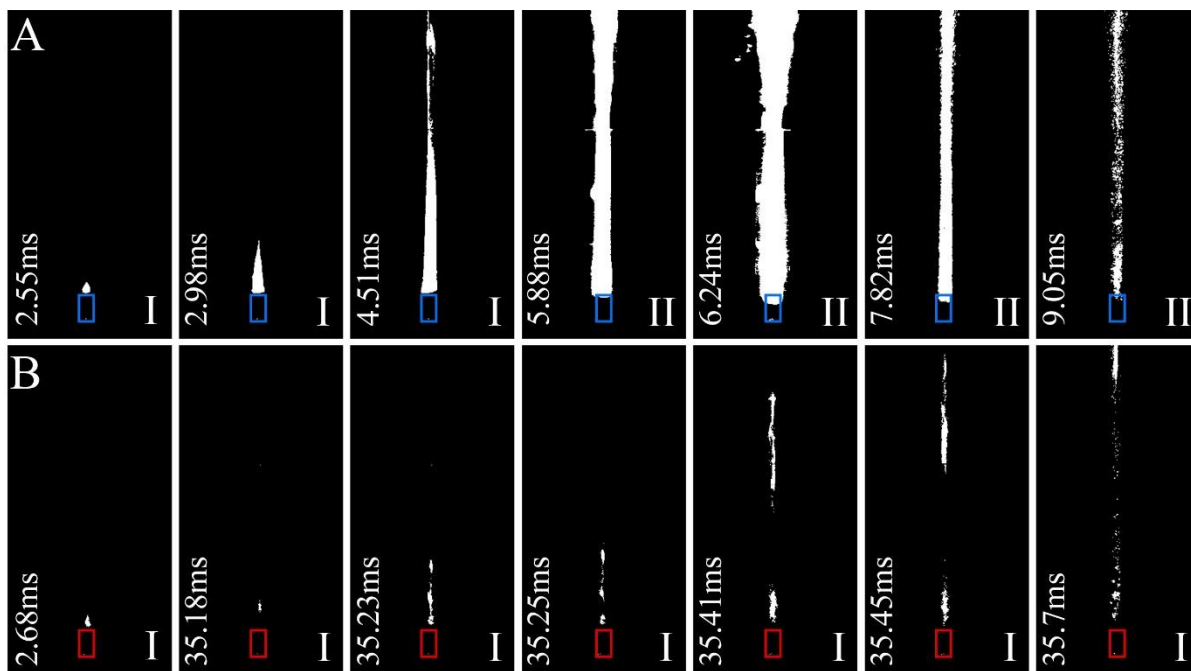


Figure 5.7: Important frames from the fast video of the combustion of 10 mg core-shell $\mu\text{Al}@\text{NiO}$ (A) and physically mixed $\mu\text{Al}/\text{NiO}$ (B) samples.

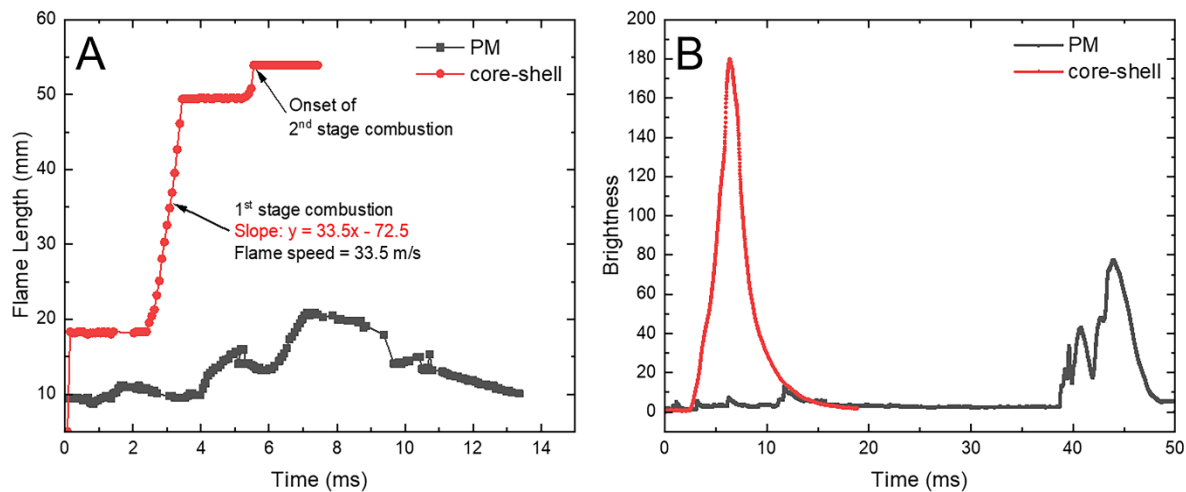


Figure 5.8: Flame length vs time plot (A) and Brightness vs time plot (B) for core-shell $\mu\text{Al@NiO}$ vs physically mixed $\mu\text{Al@NiO}$ MIC.

5.4 Conclusion

In summary, the core-shell $\mu\text{Al@NiO}$ MICs were successfully fabricated by wet chemistry method. The construction of the core-shell structure was steered by the electrostatic attraction between Al, bearing a negative charge and Ni-NH₃ complex bearing a positive charge. Different composites were prepared with different equivalence ratios and NH₃/Ni ratios. The core-shell structure was acknowledged amongst SEM/EDS of all equivalence ratios. Contrary to what was observed for the Al/CuO [102], the fabrication process or the final product was not as sensitive to either the equivalence ratio or NH₃/Ni ratio. Despite that, ER 3.0 displayed the lowest onset temperature and the highest energy release during slow combustion. The apparent activation energy was estimated to be 274.01 kJ/mol for core-shell $\mu\text{Al@NiO}$, and 283.25 kJ/mol for the physically mixed $\mu\text{Al@NiO}$ matching the equivalence ratio of 3.0. The core-shell assembly, however, increased the quantity of energy released from the overall reaction by 388.90 J/g. Upon laser combustion, the core-shell $\mu\text{Al@NiO}$ MIC ignited within 2.55 ms and got completely consumed within 6.5 ms. The combustion was also accompanied by a violent thud and extreme luminosity. The physically mixed composite on the other hand, could not be ignited at all.

Chapter 6

Fabrication and characterization of core-shell Al@Fe₃O₄ nanoparticles

The contents of this chapter are reproduced from the following citation:

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6.1 Introduction

MICs or nanothermites have lately been investigated for rapid energy and power generation in various domains, such as actuating MEMS, welding, joining, and propulsion [9, 23, 31, 142]. Typical MICs embody a reactive fuel – oxidizer formulation. Traditionally, metals like aluminum or magnesium [1, 104] and metal oxides such as CuO, Fe₂O₃, and Bi₂O₃ [15, 117, 180, 181] have been used as the fuel and the oxidizer component of the MIC respectively. Out of all the fuels, aluminum is extensively researched due to its high enthalpy of oxidation, abundance on earth, and relatively low cost of production. Recently, research has been focused on the use of novel oxidizers in MICs, including fluoropolymers, halogen oxides, halogen acids [119, 182, 183] and their combinations. Various physical and chemical properties were characterized with these oxidizers including reactivity and combustion properties, which can lead to promising applications such as biocidal capabilities by iodine or silver oxidizer [184, 185], enhanced thrust performance by ammonium perchlorate and nitrocellulose [186, 187], and possibilities for additive manufacturing when polymers are used [188, 189]. Another way to tune the reactivity is via fabrication of engineered structures to enhance the interfacial area of contact between the reactive components and reduce the oxygen's path of diffusion.

Recently physical and chemical methods were developed to synthesize core-shell MICs. Physical methods such as physical vapor deposition [181], and atomic layer deposition [158] are unsuitable for mass production due to its high energy consumption and low production rate. Chemical methods including the in-situ polymerization [7], sol-gel method [161], and self-assembly [129, 190], on the other hand, offer an alternative way for fabricating composites in bulk and with enhanced homogeneity and reactivity. Use of additives in these methods, especially surfactants [191], is however debatable and should be avoided, due to their existence in the final product as an inert mass and a barrier for the effective migration of reactive ions which hinders the reactivity. Nevertheless, *in situ* growth and crystallization of oxide nanoparticles on nano- and micro- sized Al particles has been proved to be a promising chemical method for fabrication of colloid core-shell Al@oxidizer structures [102].

An interesting candidate for choosing the metal oxide in MICs is Fe_3O_4 , or magnetite. Bulk Fe_3O_4 is ferrimagnetic, while single-domain Fe_3O_4 nanoparticles demonstrate a superparamagnetic nature [192]. Thanks to its magnetic nature, magnetite has been widely exploited for its medical applications such as in delivery of a drug to a target, MRI, and hyperthermia [193-195]. As per Fischer and Grubelich's research on energetics, the formulation of Al/ Fe_3O_4 exhibits an elevated combustion temperature of 2862 °C, a moderate heat of reaction of 15.74 kJ·cm⁻³, and the minimal gas production [44]. In fact, gases produced from the reaction of the aluminothermic mixture with Fe_3O_4 is approximately ~10% of gases from the mixture of Al/CuO [37], thereby making Al/ Fe_3O_4 MICs an ideal candidate for developing micro-initiators and welding/joining, where the produced-gas pressure and subsequent vibration is undesirable [23, 196, 197].

One of the major disadvantages of Al/ Fe_3O_4 , when compared to typically used energetic composites such as Al/ Fe_2O_3 , Al/CuO, Al/ Bi_2O_3 , and Al/ MoO_3 , is its rather low reactivity. Li et al. reported a slow propagation velocity (less than 5 mm/s) of a pellet made of 180 nm Al and 40% of 10 μm Fe_3O_4 [198]. The research performed by Wu et al. showed that Al/ Fe_3O_4 nanothermite mixture had very limited reactivity and its combustion could not even propagate when ignited by laser [199]. It is therefore essential to increase the reactivity of Al/ Fe_3O_4 MICs, especially through the aforementioned methods. In literature, a polyol method was developed to synthesize IONPs in organic solvents, forming nanoparticles with a narrow size distribution from 4 nm to up to 500 nm [200-202]. These nanoparticles, if fabricated successfully on the dispersed Al particles in the solution, could be used to produce reactive core-shell structures.

This work employs a solution-based, surfactant-free, wet-chemistry fabrication process, with the modification of synchronous addition of n-Al to the reaction mixture to produce functional magnetic Al@Fe₃O₄ core-shell nanothermites. Products with different nominal equivalent ratios (Φ) are prepared and characterized for morphology via SEM and for their energetic performance by simultaneous TGA-DSC. Consequentially, the building mechanism of the tailored-composite is proposed and the best-performing Φ i.e., the optimized product, is determined. Further characterizations of the optimized product are performed by utilizing TEM, EDS, and XPS. The calculation is made for the activation energy of the core-shell MICs to differentiate its reactivity from the physically mixed counterpart. The combustion performance of the MIC is evaluated by analyzing high-speed footage of the laser-ignited samples, and a demonstration of energy release through combustion of suspending composites in an external magnetic field.

6.2 Results and Discussion

6.2.1 Morphology of the as-fabricated core-shell Al@Fe₃O₄ MIC

Macroscopically, the Al@Fe₃O₄ MICs were found to be black in color and exhibit magnetism as demonstrated in Figure 6.1.

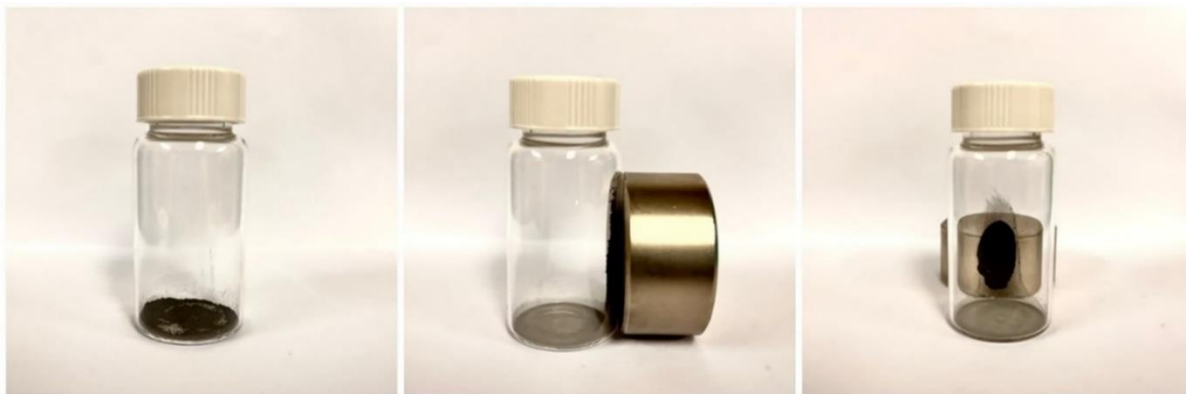


Figure 6.1: Macrostructure of the as-fabricated core-shell Al@Fe₃O₄ MIC

The significance of the last step of the fabrication experiment involving annealing the samples in the tube furnace at 270°C for 3 hours in the atmosphere of nitrogen was noticed in the TGA curves. Theoretically, thermite reactions display zero mass change during thermogravimetric analysis,

however, the as-prepared Al@Fe₃O₄ MICs, before the heat-treatment, showed quite significant mass loss before the thermite reaction when upon getting heated from the ambient temperature to 1000°C hinting at: (i) the presence of remnant TEG within particles; (ii) a possible delay in the ignition of the components. Figure 6.2 presents the mass loss observed for Φ 2.0 and Φ 5.0, both without and with the annealing process. Φ 2.0, before annealing, shows a total mass loss of 12.52%, whereas Φ 5.0, only shows a mass loss of 6.54% before annealing. After the annealing process, the mass loss was reduced to 6.39% and 3.54% for Φ 2.0 and Φ 5.0 respectively. Notably, mass loss occurs in steps. The first mass loss takes place until 400°C and it is hypothesized by many researchers that this mass loss comes from the evaporation of strongly adhered TEG from the nanoparticles. The second mass loss around 600°C is mostly from the phase change of Fe₃O₄ to FeO [124] TEG, in the polyol process, serves three purposes: (i) reducing agent for the metal salt; (ii) high boiling solvent; (iii) stabilizer for the nanoparticles [202]. One important observation from the TGA results of Figure 6.2 was that larger the amount of Al in the reaction mix (i.e. more Al seeds for IONPs to adhere to), smaller the role of TEG as a stabilizer and hence less TEG adherence in the Φ 5.0 samples.

An additional FTIR was conducted to check for the presence of TEG in the samples before and after heating. There was a stark difference between the FTIR spectrum of the samples before and after annealing. For the sake of straight-forward comparison, the region between the wavenumber 2750 cm⁻¹ and 3750 cm⁻¹ (between two blue dotted vertical lines) is focused on the plot in Figure 6.3. The FTIR spectrum of untreated samples was majorly dominated by the spectrum of standard TEG [203]. The peaks at wavenumber > 3500 cm⁻¹ (first green circle from left) come from -OH bonds of TEG and the peaks at wavenumber < 3000 cm⁻¹ (second green circle from left) come from -CH bonds of TEG. These peaks are absent in the heat-treated/annealed sample. The annealed sample simply displays the peaks corresponding to moisture (H₂O) and CO₂ from the atmosphere.

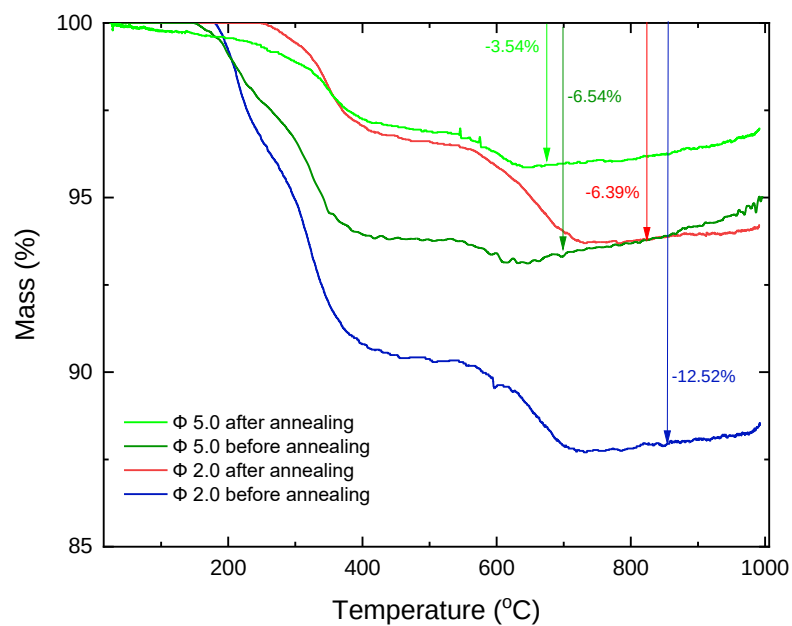


Figure 6.2: TGA of Φ 1.0 and Φ 5.0 samples before and after annealing.

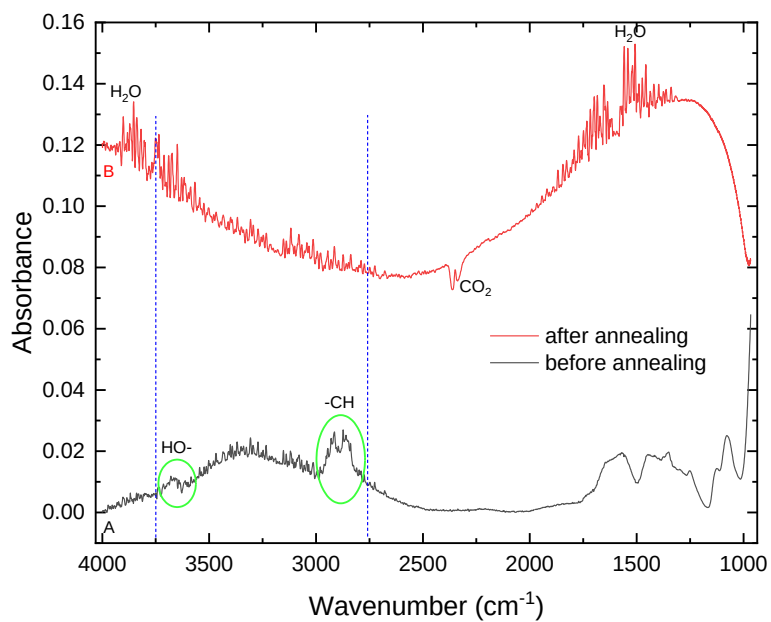


Figure 6.3: FTIR spectra of the as-fabricated core-shell Al@Fe₃O₄ MIC before and after annealing.

The TEM of core-shell nanoparticles with $\Phi = 3.0$ is illustrated in Figure 6.4A and C. It evidenced Al nanoparticles of diameter around 100 nm covered by many relatively tiny nanoparticles, which are considered IONPs formed from the decomposition of the precursor $\text{Fe}(\text{acac})_3$. A further zoomed-in image as shown in Figure 6.4B clearly shows IONPs with a diameter around 7 nm decorating a spherical Al core with an amorphous alumina shell of roughly 4 nm thickness. A simultaneous STEM-EDS was carried out to authenticate the distribution of the elements in core-shell Al/IONPs nanoparticles. Figure 6.5A showed the STEM images of the same particles, depicting a large number of IONPs bound to the surface of the Al nanoparticle. A clear and continuous circular oxygen shell can be seen on the surface of n-Al, as seen in Figure 6.5D, indicating the spontaneously formed amorphous Al_2O_3 shell, protecting n-Al from being further oxidized during the reaction. On top of that Al_2O_3 shell, the small particles showed composition of iron and oxygen, confirming the formation of IONPs, and thus confirming the formation of a core-shell structured $\text{Al}@\text{Fe}_3\text{O}_4$ reactive system.

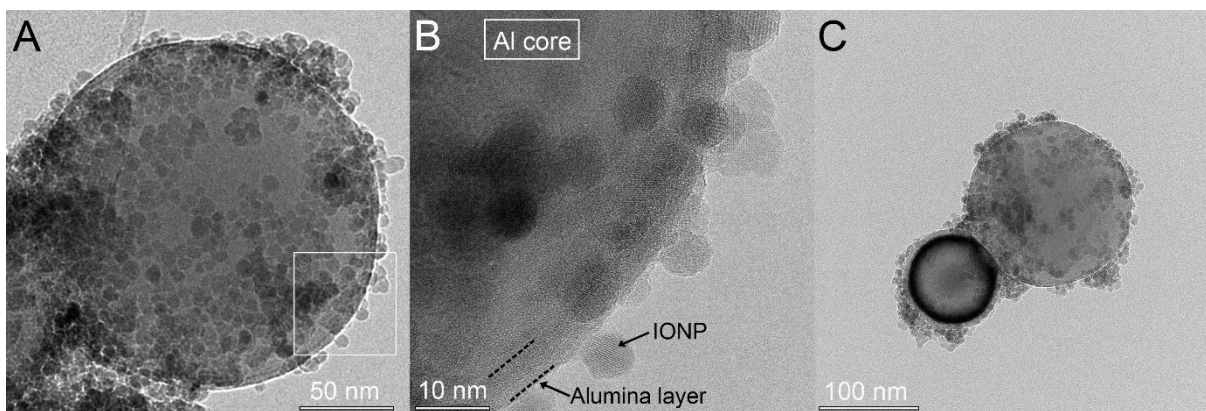


Figure 6.4: TEM images of an assembly of core-shell $\text{Al}@\text{Fe}_3\text{O}_4$ nanoparticles (A, C) and a zoomed in area of A at the interface (B).

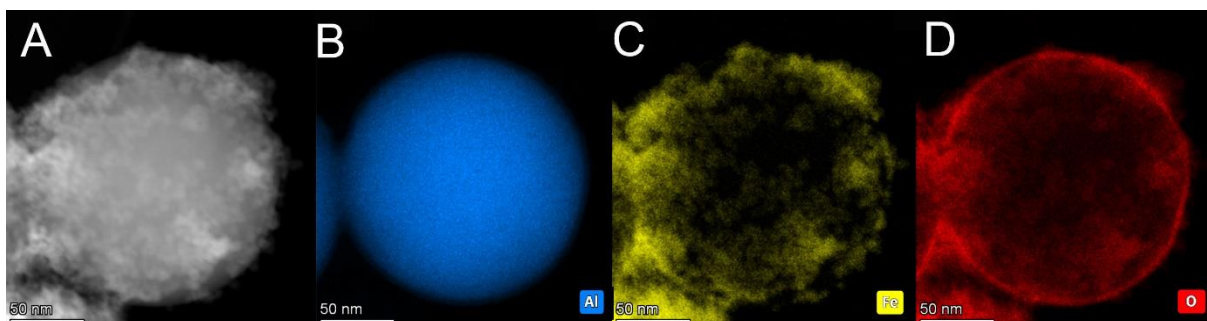


Figure 6.5: STEM image and corresponding EDS results of an assembly of core-shell Al@Fe₃O₄ nanoparticles. The order of EDS mapping from left to right is Al, Fe, and O

6.2.2 Composition of the as-fabricated products

An annealing process was facilitated during the fabrication process for the complete removal of TEG remaining in the composite after the reaction. FTIR measurements of the as-fabricated Al@Fe₃O₄ nanoparticles were done both before and after annealing to qualitatively vouch for the adherence and removal of the remnant TEG respectively. The release of TEG upon heating, was also confirmed by TGA results of the core-shell samples before and after the tube-furnace treatment.

The as-synthesized pure IONPs (fabrication without the addition of Al) and the core-shell Al@Fe₃O₄ MIC were examined to check their chemical composition. Figure 6.6 shows three XRD diffractograms corresponding to the standard Fe₃O₄, fabricated IONPs, and as-prepared core-shell Al@Fe₃O₄ nanoparticles. For the fabricated IONPs (Figure 6.6B), five major diffraction peaks were seen at $2\theta = 30.2^\circ, 35.5^\circ, 43.2^\circ, 57.1^\circ,$ and 62.9° coordinating with (220), (311), (400), (511), and (440) crystalline planes of magnetite phase, respectively [204, 205]. This pattern agreed well with the standard XRD pattern of the bulk Fe₃O₄ displayed in Figure 6.6A. With Al in the reaction mixture, the final product exhibited a number of dominant peaks of Al (shown with “▲”) alongside the major peaks for IONPs (shown with “x”) clearly shown in Figure 6.6C.

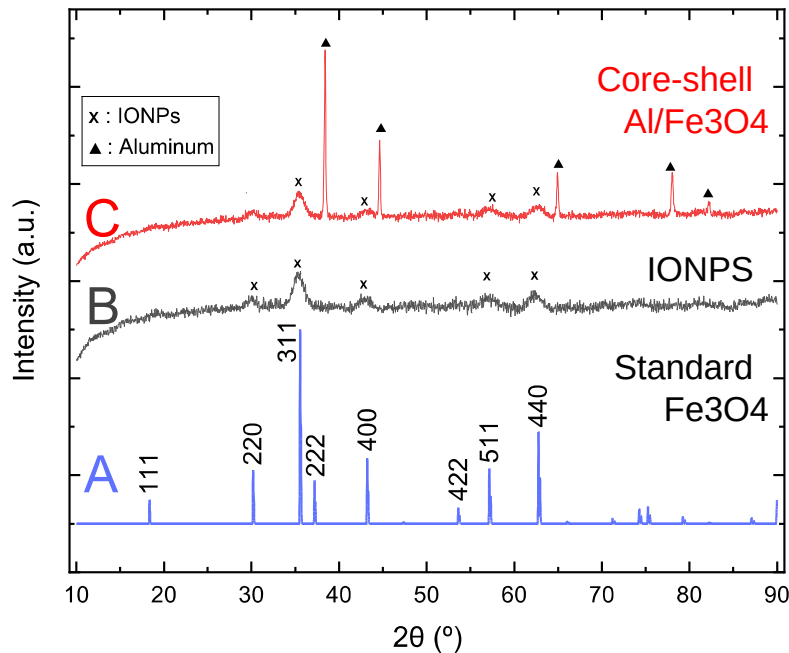


Figure 6.6: XRD Diffractograms for a) standard Fe_3O_4 ; b) fabricated IONPs; c) core-shell $\text{Al}/\text{Fe}_3\text{O}_4$ MIC.

It is notable that $\beta\text{-Fe}_2\text{O}_3$ (maghemite) has very similar XRD peaks like magnetite (Fe_3O_4). Therefore, the phase of the as-produced IONPs was further investigated by Rietveld refinements. Due to the small size of the crystal and nearly overlapped XRD patterns of maghemite and magnetite, determining the exact content of each phase in the IONPs is, however, difficult. Nevertheless, optimized curve fitting results indicated that Fe_3O_4 (magnetite) and maghemite coexist in the final IONPs, with Fe_3O_4 being the major phase which accounts for more than 60% of the final product. Therefore, all discussions below use Fe_3O_4 to represent IONPs. Please note both Fe_3O_4 and Fe_2O_3 are energetic when reacting with Al.

To further characterize the composition of the fabricated IONPs, the oxidation states of Fe were established using XPS. Figure 6.7 shows the deconvolution of the Fe 2p spectrum of the IONPs. The experimental data is represented by the red dots. The signature of Fe^{3+} species was found in the form of two spectral bands located at 725.3 eV, 711.7 eV, belonging to 2p_{1/2} and 2p_{3/2} orbits respectively. The signature of Fe^{2+} species was observed as other two peaks at 723.6 eV and 710.0 eV belonging to 2p_{1/2} and 2p_{3/2} orbits, respectively [197, 198]. The leftover small peaks at the binding energies of 714

eV and 719 eV were identified as the shakeup lines. This survey spectrum implied the coexistence of Fe^{2+} and Fe^{3+} . Combining with the XRD results, it is reasonable to claim the successful formation of the Fe_3O_4 in the fabricated IONPs as the main phase.

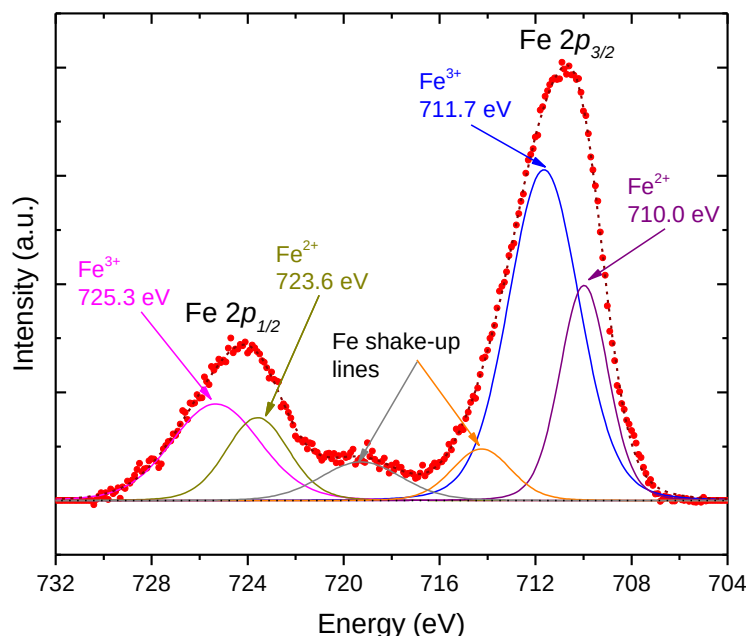


Figure 6.7: XPS of Fe 2p of IONPs.

6.2.3 The effect of the nominal equivalence ratio

The effect of the nominal equivalence ratio, Φ , on the structure of the final core-shell product was investigated. It is notable that the Φ of the final core-shell product may vary from the nominal equivalence ratio of the raw materials, but there is a positive correlation between the two numbers. SEM images were used to analyze the morphological differences among different samples. As seen in our previous publications, the as-purchased n-Al are smooth spheres [15, 102]. For the as-prepared $\text{Al@Fe}_3\text{O}_4$ nanocomposites, on the other hand, this smooth surface was not visible due to the coverage by IONPs. For small $\Phi = 2.0$, the sample appeared chunky with separated phase of iron oxide (highlighted in white circles in Figure 6.8A and 6.8B). The SEM of the sample of $\Phi = 2.0$ even exhibited some crystallographic planes shown with white arrows in Figure 6.8B. For $\Phi = 3.0$ and above, the samples appeared free of large iron oxide crystals and contained only small particles. (Figure 6.8C-F). Despite the limited resolution of the SEM images, some clusters of the core-shell $\text{Al@Fe}_3\text{O}_4$

nanoparticles were also discovered for $\Phi > 3.0$. As shown in Figure 6.8D, the cluster seemed to consist of multiple smaller particles that appeared like core-shell particles. However, it was difficult to establish the precise size and location of IONPs because of the agglomeration of the particles and the resolution of the SEM results. Nevertheless, they were seen to be much smaller as compared to Al.

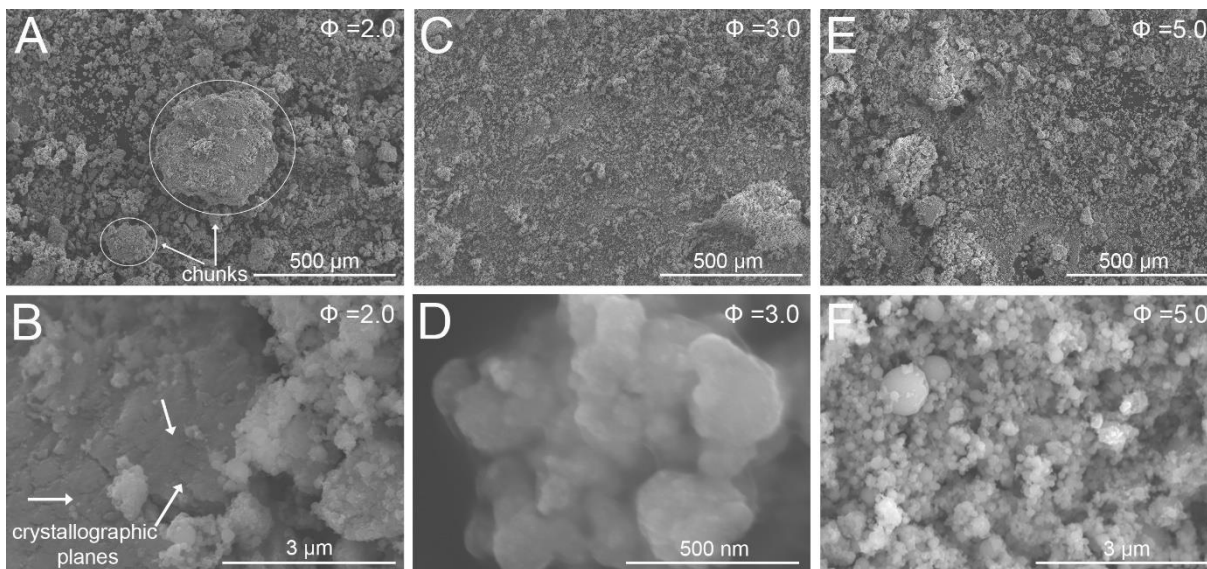


Figure 6.8: SEM images of core-shell Al@Fe₃O₄ MIC for $\Phi = 2.0$ (A and B), 3.0 (C and D) and 5.0 (E and F).

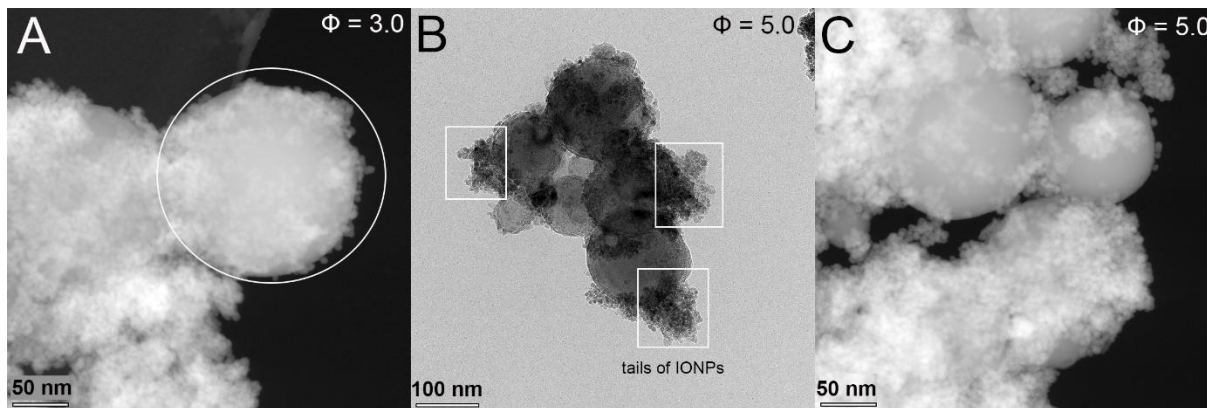


Figure 6.9: STEM image of core-shell Al@Fe₃O₄ MIC for $\Phi = 3.0$ (A); TEM and STEM image of core-shell Al@Fe₃O₄ MIC for $\Phi = 5.0$ (B and C) respectively.

To achieve high-resolution images, TEM and STEM were utilized to further differentiate the samples of $\Phi > 3.0$. Figure 6.4A and 6.9A shows the sample with $\Phi = 3.0$ illustrating a near-perfect shell

formation around the Al core composed by small Fe_3O_4 nanoparticles. For samples with $\Phi > 3.0$, for example, 5.0, presented in Figure 6.9 (B and C), two main observations were made: (i) the samples consisted of many partially coated Al, as seen in Figure 6.9C; (ii) IONPs preferentially grew on top of each other forming tails over Al nanoparticles (emphasized as white rectangles in Figure 6.9B), thereby reducing the interfacial area of contact between the metal and metal oxide making thermite system.

The findings from these results provide an insight into the building mechanisms of these core-shell $\text{Al}@\text{Fe}_3\text{O}_4$ MICs. It is postulated that the core-shell structure is formed via seed-mediated crystal growth [206, 207]. There are two stages that make up a typical crystal growth process. First is the generation of seed nanoparticles, also referred to as nucleation. Second is the subsequent growth of the crystal in growth solutions. Generally, the active components of the growth solutions are the reducing agents, precursors to the metal, and reagents to direct some shape. In the seed-mediated crystal growth process [206, 207], preformed seeds (in present case, Al nanoparticles) are added to the growth solution (in present case, $\text{Fe}(\text{acac})_3$ in TEG) to isolate the nucleation and crystal growth process into two distinct steps. This is only possible due to the fact that it is easier for the metal salts to get reduced to metal oxides and then to metals on the surface of preformed seeds as compared to reduction and attachment on seed particles getting formed in the growth solution i.e., homogeneous nucleation. [207] Hence, pre-existing seeds facilitate the autocatalytic growth of crystals on their surface [207]. In the current case, the Al nanoparticles act as a seed for IONPs to nucleate and grow upon. At a time, two competing processes take place in the reaction mixture: (i) Heterogeneous nucleation and crystal growth via atomic addition on the surface of seeds (Al nanoparticles); (ii) Homogeneous nucleation and crystal growth amongst the IONPs. Homogeneous nucleation is the favorable process in cases when there is fewer deposition sites provided by the seed than there are atoms derived from the precursor reduction. When the produced nanoparticles from the precursor reduction are small (as compared to the seed particles) and many in number, they tend to provide greater sites for homogeneous nucleation to take place if compared to the deposition sites provided by the seeds. In that context, the structural changes observed earlier with respect to the nominal equivalent ratio can be explained.

When $\Phi < 3.0$, Al nanoparticles provide deposition sites to promote heterogeneous nucleation to favor the formation of core-shell nanoparticles. However, for smaller Φ , there are barely enough seeds in the mix and to allow for perpetual heterogeneous nucleation. Due to this limited surface area on n-Al

particles, homogeneous nucleation starts to happen both spontaneously and simultaneously, leading to the formation of big chunks or crystals of IONPs as was witnessed in Figures 6.8A and 6.8B.

When $\Phi > 3.0$, although enough surface area should be provided for the nucleation and formation of IONPs, a new problem emerges. Because of the excess amount of Al in the reaction mix, Al seeds tend to remain agglomerated and are unable to disperse homogeneously. As a result of which, while there are many Al seeds to let the heterogeneous nucleation thrive throughout the reaction time, the Al agglomerates, there comes a limit when the produced IONPs (which are smaller in size) tend to provide greater deposition sites as compared to the partially covered Al agglomerate seeds. At this point, homogeneous nucleation becomes dominant, and it manifests as IONPs tails in the samples of high Φ , as seen in Figures 6.9B and 6.9C.

At $\Phi = 3.0$, there seem to be just enough Al seeds in the mix to stimulate near-uniform attachment of IONPs on the surface of aluminum particles to form the core-shell structured nanoparticles. Both homogeneous and heterogeneous nucleation coexist, but one does not overpower the another. Therefore, neither big chunks/crystals of IONPs, nor tails of IONPs were observed in the SEM or TEM-STEM images of samples with $\Phi = 3.0$ (Figures 6.4A, 6.5A, 6.8C, 6.8D and 6.9A)

6.2.4 Thermochemical properties of as-fabricated Al@Fe₃O₄ core-shell material

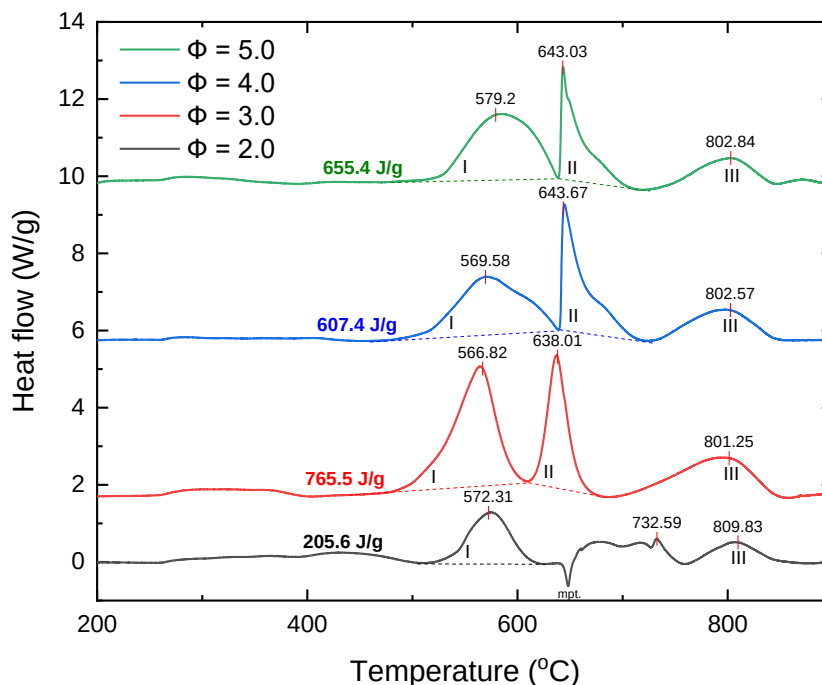


Figure 6.10: DSC results of Al@Fe₃O₄ core-shell nanocomposite with Φ 2.0, 3.0 and 4.0. The units on the y-axis (W/g) belong to each individual plots, however, the scale is arbitrary for these stacked plots. The values corresponding to the energy release (J/g) are calculated by integration of the area under the peaks and are the true values from the raw data.

The energetic behavior of the thermite reaction of the as-fabricated core-shell MICs was studied using DSC. All composite samples of different Φ were heated from the ambient state to 1000 °C at a constant rate of heating of 20 °C/min in an atmosphere of argon. The reaction parameters like the temperatures of onset and peak, and the amount of energy released from the reaction were determined in order to identify the thermite reaction pathway and its correlation to the composite structure described above. Figure 6.10 shows the DSC measurements of all samples of different Φ . The peaks are labelled as I, II and III and are stated as peak I, peak II and peak III respectively in the following paragraphs.

The peak I of the DSC curves of all Φ values depicted an exothermic condensed-phase thermite reaction taking place between Al and IONPs much below 660 °C, the melting point of aluminum

following the reaction R1. An occurrence of this reaction at a temperature below 600 °C is corroborated by Botta et al. who researched the thermal behavior of Al–Fe₃O₄ mixtures which were mechanochemically activated and mixed in the molar ratio of 2.67:1 [208]. This reaction is postulated to be initiated by the phase change of alumina layer from amorphous to crystalline (γ -Al₂O₃) followed by the diffusion of oxygen and aluminum atoms, in the solid-state, across the Al/Al₂O₃ interface [128, 209-211]. Inevitably, the thickness of alumina layer keeps increasing as reaction between Al and metal oxide progresses, hence, slowing down the diffusion processes and eventually bringing them to a halt. This entire reaction completes before the melting of Al.



For $\Phi = 2.0$, an endothermic peak at 660 °C is speculated to come from melting of leftover Al core. After this temperature (660 °C), two probable reactions take place: (i) reduction of Fe₃O₄ to FeO (spanning from 660 °C to 750 °C) ; (ii) Alloy formation (peak III) coming from the contact between the melted Al (flowing out through the cracks of γ -Al₂O₃) and Fe metal (at 809.83 °C) from the first reaction [212] following the reaction R2



These two reactions transpiring in series were also reported by Chung et al while they studied the two-step displacement reaction between Al and Fe₃O₄ taking place during sintering [213]. The exact temperatures reported for these two reactions were ~720 °C and ~840 °C respectively, which are reasonably close to what was observed in our results [213]. Also, when the temperature is greater than 800 °C, FeO predominantly converts to Fe, prompting the formation of Al-Fe alloy [214].

For $\Phi > 3.0$, the peak I (at 566.8 °C, 569.6 °C and 583.7 °C for $\Phi = 3.0, 4.0$ and 5.0 respectively) in the core-shell structured samples, as mentioned earlier, is hypothesized to come from reaction 1 stated earlier for the proximate Al and Fe₃O₄ particles, which is significantly more than the sample of $\Phi = 2.0$ due to the enhanced surface contact caused by the elimination of large chunks of iron oxide. Since the energy released from the first peak of the samples with $\Phi \geq 3.0$ is significantly larger than that of the sample with $\Phi < 3.0$, this energy creates hot spots [215] within the sample and triggers the reduction of leftover Fe₃O₄ $\rightarrow$ FeO (way earlier than for the samples with $\Phi < 3.0$) which immediately reacts with the rest of Al following the reactions R4 and R5 as shown below:





It is to be noted that the temperature at which Fe_3O_4 gets reduced to FeO strongly depends on the crystal size of IONPs nanoparticles [216]. The morphology showed that the crystal size of IONPs decreased with an increase in Φ . Since smaller crystal size (as was seen in samples of $\Phi \geq 3.0$) directly translates to thinner shell around n-Al core, there's only limited amount of Al that can be completely consumed by this shell. Hence the leftover Al participates in the reaction later. A careful analysis of the TGA curves (Figure 6.2) for two extreme Φ showed that the reduction of Fe_3O_4 to FeO completed by 600 °C for $\Phi = 5.0$ and 750 °C for $\Phi = 2.0$.

To explain the variability of the DSC results for $\Phi = 2.0$ sample, , it is postulated that the oxygen released from Reaction R3 gets ample time to escape the DSC system because of the gradual nature of the release until 750 °C and the absence of hot spots in the sample resulting from small first exothermic reaction prior to 660 °C, the melting point of Al. As an aftermath, reaction 4 does not take place, reaction 5 is further slowed down and is expressed as a broad second exothermic peak spanning from 660 °C to 750 °C with a subsequent the alloy formation reaction (Reaction R2) at ≈ 800 °C. Principally, the phase separation and difference in structure bring about the difference in the DSC curves of this sample when compared to higher Φ values.

For $\Phi \geq 3.0$, the oxygen release (Reaction R3) is larger and rapid, and it manifests in the form of significant solid-gas reaction between aluminum and gaseous oxygen, leading to a sharp vertical line portion of the peak 2. For higher Φ values of 4.0 and 5.0, an additional shoulder (670 °C - 700 °C) is observed trailing the end of peak II. This shoulder supposedly comes due to an excessive amount of Al appearing as separated phase across the sample. This shoulder is absent in the DSC curve of $\Phi = 3.0$, most likely because of the optimal contact between the reactants to only prompt the solid-solid condensed-phase reaction. $\Phi = 3.0$ presented minimal to no phase separation to manifest a dragging shoulder.

The qualitative reaction mechanism presented here is supported by Durães et al. [217] and Wang et al [218] wherein they conducted the characterizations of the intermediate and final products from the DSC runs for the stoichiometric and Al-rich mixes of Al/ Fe_2O_3 . used when the reaction mechanism for stoichiometric and Al-rich composites of Al/ Fe_2O_3 was proposed. It is reasonable to believe Al/ Fe_3O_4

will yield a similar mechanism since the suggested first-step of reaction of Al/Fe₂O₃ is the reduction of Fe₂O₃ to Fe₃O₄ and FeO and the successive steps are the reactions of Fe₃O₄ and FeO with Al.

The key parameters of the thermite reaction of various Φ values are summarized in Table 6.1. The core-shell samples corresponding to $\Phi = 3.0$ demonstrated the lowest onset and peak temperatures pointing towards the maximum intimacy and thus, shortest diffusion length between the constituents. $\Phi = 3.0$ thereupon, also released the maximum energy upon reacting. This thermochemical behavior tied well with the SEM, TEM and STEM results mentioned earlier in terms of no chunks and tails seen in the morphology of $\Phi = 3.0$.

Table 6.1: A summary of the onset temperature, peaks temperature, and energy released for different Φ values and a comparison of core-shell MIC with physically mixed ($\Phi = 3.0$)					
Φ		Onset temperature (°C)	First peak temperature (°C)	Second peak temperature (°C)	Overall energy released. (J/g)
2.0	As-produced core-shell	534.74 ± 2.31	572.32 ± 3.11	732.27 ± 5.42	205.61 ± 13.95
3.0		519.29 ± 1.05	566.83 ± 1.98	636.91 ± 1.34	765.54 ± 27.43
4.0		519.71 ± 1.21	569.58 ± 0.97	644.33 ± 3.32	607.43 ± 64.85
5.0		529.37 ± 2.33	583.74 ± 1.14	643.24 ± 3.25	655.37 ± 11.31
3.0	Physically mixed	540.02 ± 3.08	578.59 ± 2.96	793.66 ± 1.78	455.62 ± 42.69

Based on the aforementioned results, $\Phi = 3.0$ was made the focus of the rest of the research for showcasing an optimal morphology and an excellent energetic performance. For this best-performing nominal equivalent ratio, comparisons were also made with the physically mixed sample and are displayed in Figure 6.11. In physically mixed Al/Fe₃O₄, two widely separated exothermic reactions were seen. The condensed phase reaction only provided about 99.5 J/g of energy release, while the second peak around 793.6 °C had an energy release of 356.1 J/g. Overall, compared to core-shell, the energy potential of the physically mixed sample was poor due to the lack of good assembly of the particles. The core-shell sample reduced the temperature of onset of the thermite reaction by more than 20 °C and reduced the peak temperature of the first and the second exothermic peak by 13.8 °C and 157.2 °C respectively. In addition, it improved an overall energy release from the reaction by 68%. The detailed reaction parameters and the comparisons are mentioned comprehensively in Table 6.1.

Figure 6.11 provides the DSC curves for the core-shell Al@Fe₃O₄ sample vs the physically mixed sample of Φ 3.0. Figure 6.12 displays the standard deviation from mean for onset, peak temperatures and the energy released for different equivalence ratios.

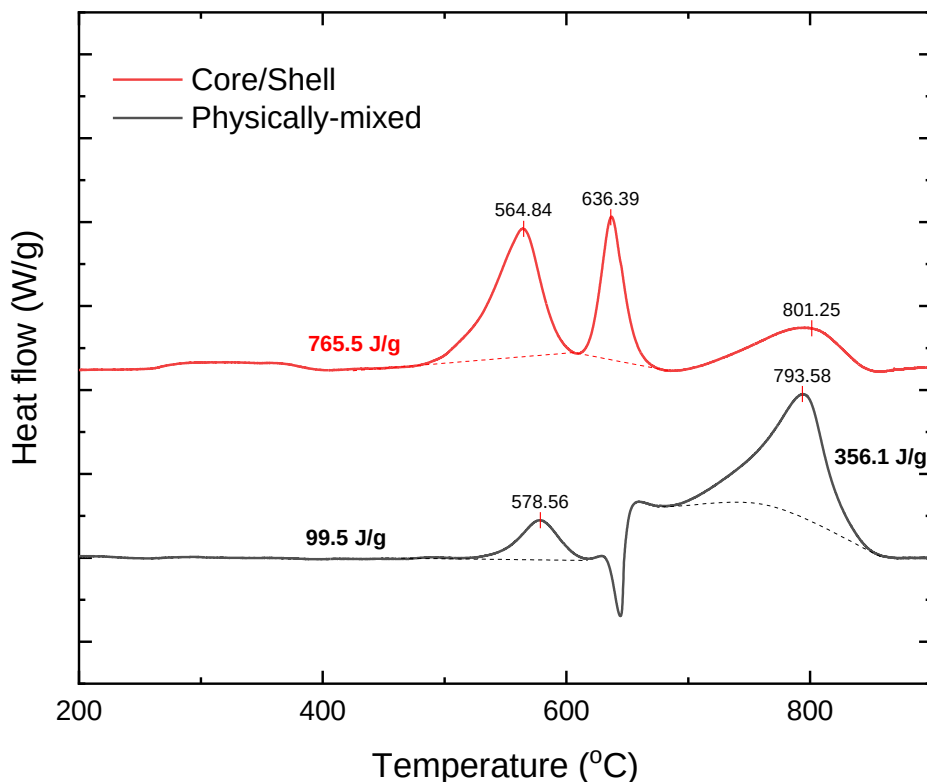


Figure 6.11: Comparison of the DSC results of Al@Fe₃O₄ core-shell nanocomposite vs the physically mixed sample for $\Phi = 3.0$.

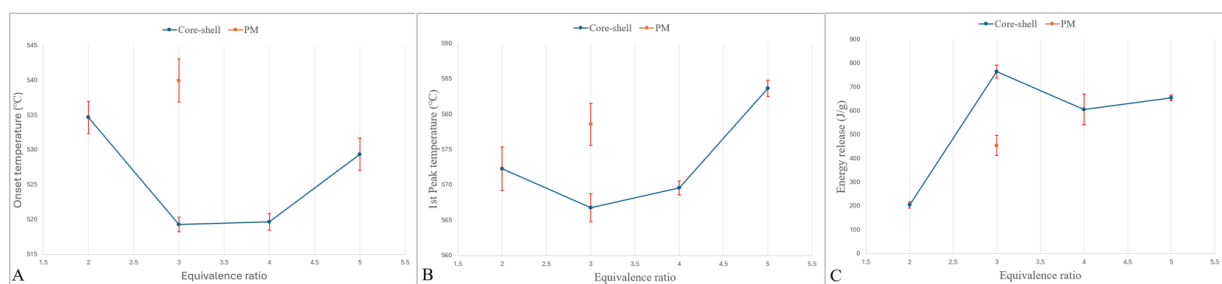


Figure 6.12: Onset temperature, 1st peak temperature and energy released vs equivalence ratios for core-shell and physically-mixed composite.

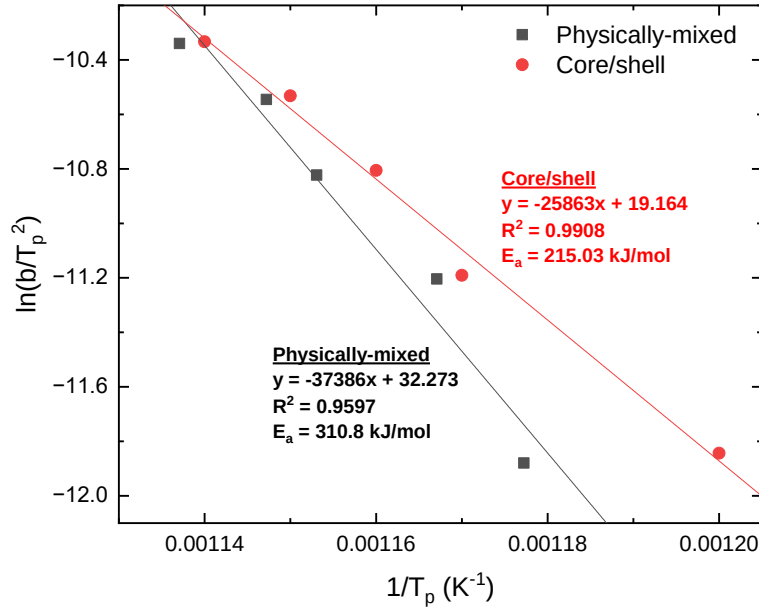


Figure 6.13: $\ln(\beta/T_p^2)$ versus $1/T_p$ plot.

To confirm the development of the core-shell structure and to compare the reactivity of the tailored-composite with the physically mixed, apparent activation energy (E_a) was used as another distinguishing characteristic parameter. The apparent activation energy is the minimum amount of energy required for a chemical reaction to occur i.e. before the initiation of the reaction. For energetic composites, a smaller value of E_a implies the lower energy input needed to prompt the ignition between fuel and oxidizer. In this work, the Kissinger equation (Equation 6.1) was used to calculate the apparent activation energy using peak temperatures of the reaction at different heating rates [136].

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\left(\frac{E_a}{RT_p}\right) + \ln\left(\frac{AR}{E_a}\right) \quad \text{Equation 6.1}$$

where R represents the universal gas constant, A is the pre-exponential factor, β denotes the rate of heating, and T_p indicates the temperature at which the reaction peaks for a given rate of heating. The E_a is extracted from the slope of the curve of $\ln \frac{\beta}{T_p^2}$ vs $\frac{1}{T_p}$. For the current case, multiple DSC runs were carried out for five different heating rates of 5, 10, 15, 20, and 25 °C/min for both core-shell and physically mixed Al/Fe₃O₄ samples of $\Phi = 3.0$, as shown in Figure 6.13. The apparent activation energy was calculated to be 215.03 ± 7.98 kJ/mol for core-shell Al@Fe₃O₄ and 310.82 ± 8.84 kJ/mol for the physically mixed counterpart. If the last data point for physically mixed sample is omitted, the slope of the plot changes from -37386 to -29611, which changes the value of activation energy to 246.19

kJ/mol, which is yet higher than that of the core-shell composite. In general, greater differences were detected in the peak temperatures of the core-shell and the physically mixed samples at slow rates of heating of 5 and 10 °C/min. The difference was minimal at fast rate of heating of 20 and 25 °C/min. The as-fabricated composite showcased a significantly lower (95.77 kJ/mol) activation energy proving the increased proximity between aluminum and IONPs and the decreased diffusion length between the components of the thermite reaction. Similar to the DSC curves in Figure 6.11, all DSC curves for the core-shell demonstrated two consecutive exothermic peaks while that of physically mixed illustrated two separated exothermic peaks.

6.2.5 Combustion behaviors

It is important to investigate how the core-shell Al@Fe₃O₄ sample combusts and what is the influence of an external magnetic field on its process. These combustion tests were arranged in an acrylic tube and visualized using a high-speed camera at 80,000 fps. A laser was used to initiate the chemical reaction, and its power was triggered by a function generator at time = 0. Figures 6.14 and 6.15 demonstrate the critical frames of the fast videos to show the combustion process with and without a magnetic field, and Figure 6.16 present the flame speed calculated by tracking the movement of the flame front from its first appearance to the time it reaches the exit of the tube.

The PM sample, as displayed in Figure 6.14A, presented a clear two-stage combustion process. The ignition of the sample started at 6.18 ms, and the flame steadily propagates upwards away from sample at an average speed of 11.98 m/s and a maximum speed of 15 m/s. The curve in Figure 6.16 clearly indicates a slow but very stable propagation. However, as the flame propagated towards the top of the tube, the combustion of the sample did not propagate downwards a lot, indicating a reaction limited to the surface of the sample, which is considered Stage I. The first stage of combustion continued until 17.98 ms as the bulk of the sample started to burn, labelled as Stage II. The transition process from surface burning to volume burning was smooth and barely conspicuous. The combustion of the bulk of the sample was also smooth and slow compared to other types of nanothermite materials. It took more than 50 ms for the 20 mg of physically mixed Al/Fe₃O₄ to complete the combustion. Overall, a smooth and homogeneous reaction with a slow flame and combustion propagation was observed with an overall exposure of the flame never becoming particularly high.

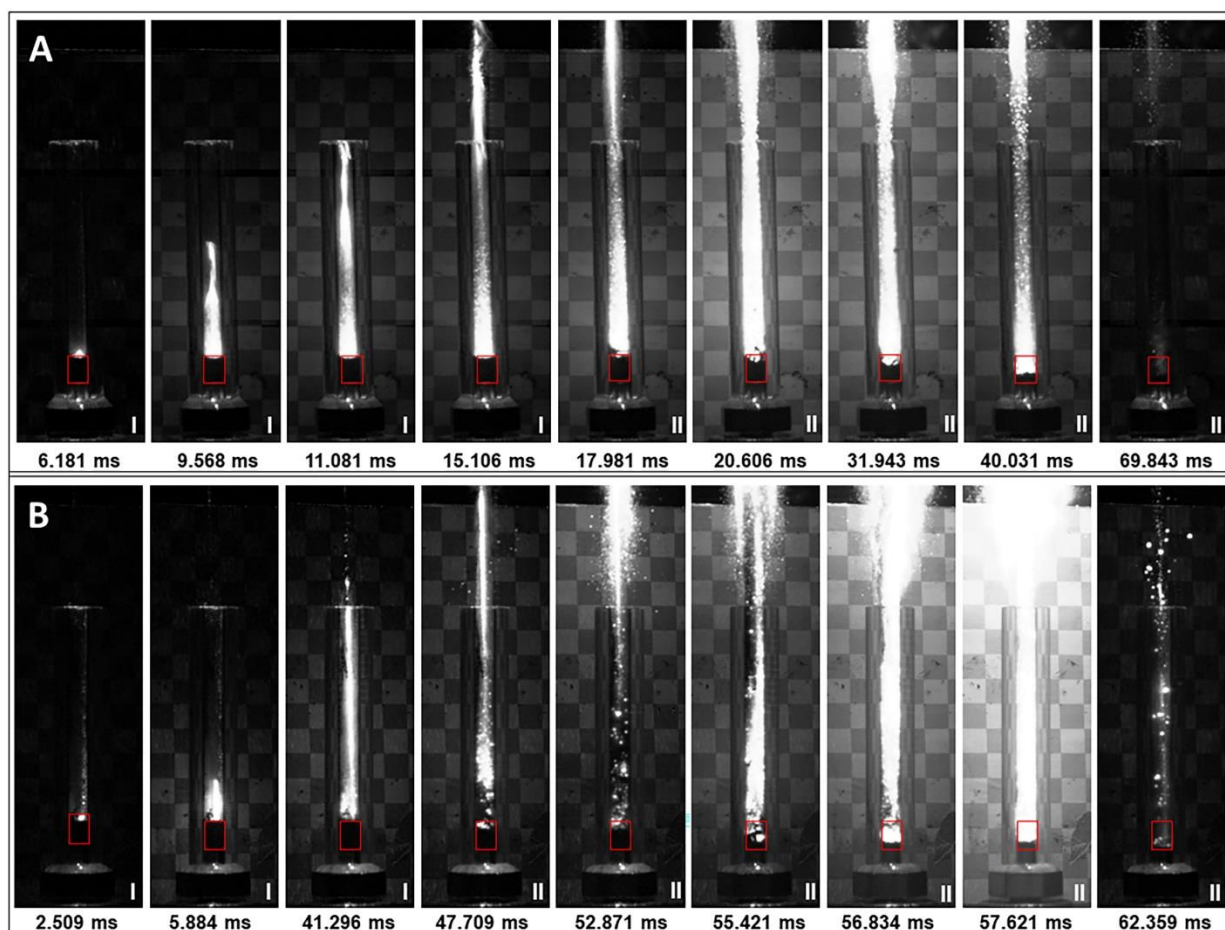


Figure 6.14: Important frames from the fast video of the combustion of 20 mg physically mixed (A) and core-shell (B).

The core-shell sample also resulted in a continuous combustion process after the sample was ignited. However, the process was drastically different from the physically mixed sample. Two distinct stages of combustion were clearly observed from the videos, accompanied by the burning of dispersed particles in the gas products. At the first stage, core-shell powders near the top surface of the specimen were heated by the laser and subsequently ignited with a smaller ignition delay of 2.509 ms. The reaction was restricted to the surface for an astonishing 45 ms. This stage was featured by the burning particles on the top surface and splashed particles from this surface to gas phase. However, as shown in Figure 6.16, unlike the steady flame propagation in physically mixed sample during surface combustion of Stage I, the propagation velocity of flame decreased after about 8 ms. Therefore, the surface combustion of core-shell $\text{Al@Fe}_3\text{O}_4$ was significantly inhibited. The volume combustion,

however, did not start until 47 ms. The long transition stage between 8 to 47 ms is hypothesized as a transition stage, where the formation of solid combustion product helped accumulate energy at the powder layer near the top surface, which eventually resulted in a flame propagation along the packed volume of the specimen. At Stage II of the combustion, a flame appeared near the top surface of the packed sample and then moved downwards through the sample volume (55.4 ms to 62.3 ms). During this process, huge energy was produced from the thermite reaction, accompanied by a production of hot gases which filled the tube. The second stage lasted for about 10 ms, which is much shorter than the first stage. At this stage, a long fire plume was formed in the tube with high-enthalpy gases escaping from the top exit of the tube. Worthwhile to note, due to use of the loose powders in these tests, some core-shell particles, whether burning or unburned, were lifted with the gaseous product and combusted in the gas. This phenomenon was visible for all stages of the combustion, but especially evident during the volume combustion (around 55 ms), as some of the sample was seen to be propelled out as a result of the energy accumulated from combustion. Once the reaction propagated beneath the surface i.e., beginning of the Stage II of combustion, the leftover sample reacted rapidly, accompanied by an extraordinary illumination in the combustion tube, displaying a reactivity far higher than the physically mixed. The entire sample got consumed within 14.65 ms. The flame speed reached a maximum of 23.4 m/s after the end of the transition stage when the combustion was ramping up to enter Stage II of bulk combustion.

As the core task of this study, the ferrimagnetic nanoparticles were suspended in the middle of the combustion tube, 2 cm from the bottom, using of a permanent magnet and the energetic event was recorded and shown Figure 6.15.

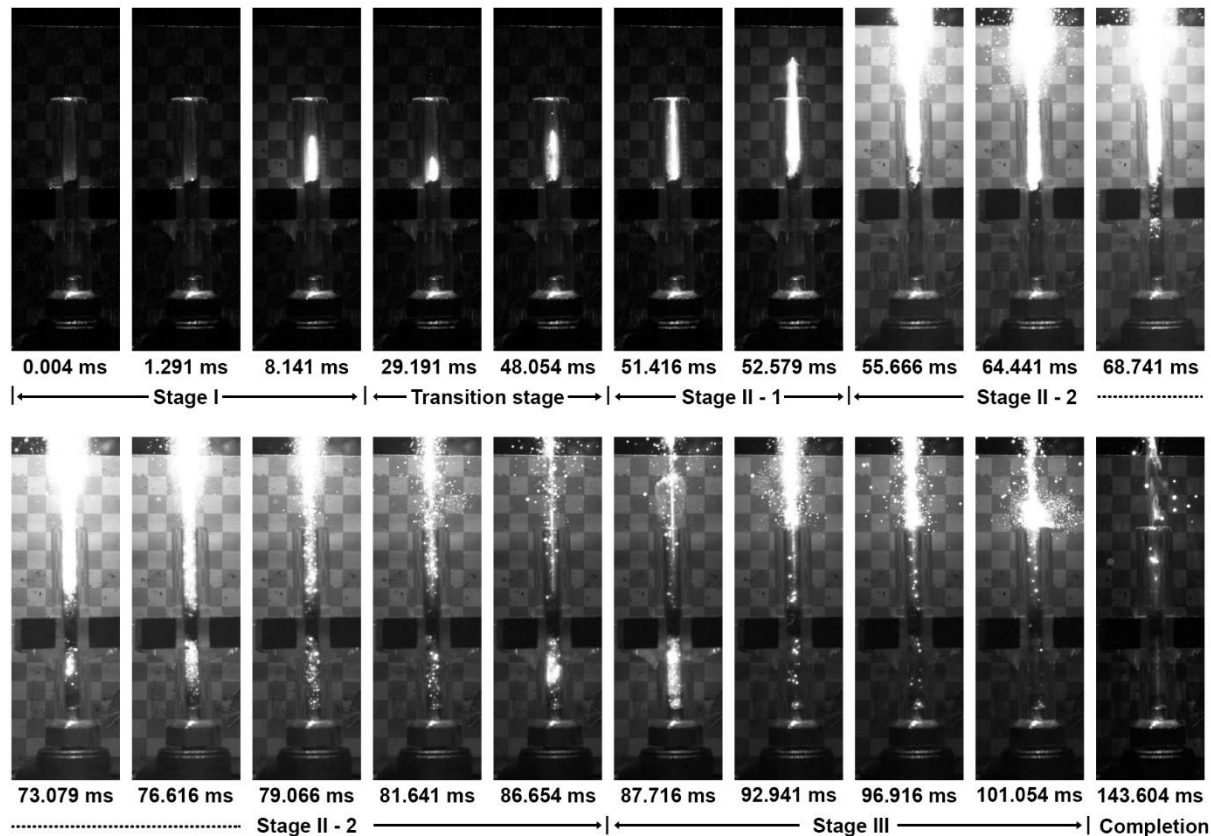


Figure 6.15: Important frames from the fast video of the combustion of 20 mg core-shell composite.

The packing density of the floating sample was estimated to be 0.25 g/cm^3 . Similar to the samples placed on the bottom of the tube, combustion of particles and ablation of burning particles were first observed on the top surface of the sample. The floating core-shell composite displayed an ignition delay of 1.291 ms with the flame traveling back and forth in the tube during the first stage. Similar to the combustion of core-shell $\text{Al@Fe}_3\text{O}_4$ at the bottom of the tube, Stage I lasted over 50 ms before Stage II of the combustion of the bulk sample initiated. Stage II of the bulk combustion can be further separated into two small parts. In the first few milliseconds of the bulk combustion, the propagation of the sample combustion, downwards into the sample, was clearly seen and the flame steadily raised. Stage II – 1 is considered as the volume burning of the sample, resulted by the advective heat transfer of the accumulated heat from the surface reaction into the powder volume leading to propagation of combustion. After a few more milliseconds into Stage II, the brightness of the image significantly increased, indicating a drastically increased rate of combustion, which can be separated as Stage II –

2. During this period, the violent reaction caused the ejection of particles, both reacted and unreacted. After part of the nanocomposite was consumed, the ejections occurred in both top and bottom surface of the suspended sample. This Stage II – 2 of dual burning is the main combustion process of this sample. Stage II of volume burning lasted about 30 – 35 ms. As the Al nanoparticles reacted, the reaction clearly lost its kinetics. However, between 87 to 101 ms in Figure 6.15, some firework-like combustion was observed at the exit of the sample holder. It is hypothesized that it is the oxidation of the iron particles, generated from thermite reaction between Al and Fe_3O_4 that showcase this firework-like combustion. The gaseous oxygen in the tube has mostly been consumed or ejected during the main combustion of Stage II. Once the hot iron particles were ejected out of the tube, they reacted with atmospheric oxygen immediately and gave the firework-like effect. Finally, the combustion was completed, and the system started to cool down.

Compared to the core-shell samples being combusted without the effect of a magnetic field, the overall ignition delay and combustion period are similar. However, an interesting flame grow-and-shrink phenomenon was observed during Stage I. In addition, the ejection of unburned particle and its subsequent combustion out of the tube, which was observed in Figure 6.14B during Stage II, was not present in combustion of the core-shell samples with the magnetic field. It was reported that 4.9-nm-diameter Fe_3O_4 nanoparticles have a Curie temperature of 854 K [218], slightly lower than that of bulk Fe_3O_4 at 858 K and very close to the peak temperature of the exothermic reaction of the composite (around 850 K). On the other hand, the product of the redox reaction, Fe, has a much higher Curie point of 1043 K. Therefore, it can be anticipated that the magnetic properties of core-shell $\text{Al}@\text{Fe}_3\text{O}_4$ particles are highly related to the progress of the exothermal reaction. During Stage I, the exothermic reactions are limited to the surface and as a result, the temperature increases near the top surface of the sample. Once the flame containing burning particles propagates upwards (i.e., flame grows), the temperature at its top is cooled down, causing the newly produced Fe particles to be drawn back by the magnet (flame shrinks). As the flame moved downwards, more energy is accumulated near the surface of the sample, accelerating the redox reaction. Temperature increases significantly and, at some point, exceeds the Curie point of Fe particles. These particles become paramagnetic and are not attracted to the magnet any longer. Thus, the flame grows again. The dependence of the magnetic properties of Fe particles on the flame temperature may explain the unique grow-shrink-grow phenomenon seen in Figure 6.15. As the energy accumulates, reaction enters Stage II, the bulk reaction is triggered. During

the rapid bulk reaction, the unreacted particles are instantly heated up over the reaction threshold temperature and get combusted. Once the bulk combustion initiates, the significant heat release and temperature-increase assure that the magnetic field is no longer be effective in restraining the movement of the high-temperature particles, allowing the ejection of hot materials to provide energy to the environment. It is fascinating to note the analogous effects of the magnetic field on the combustion of the powder at the bottom of the sample where a back-shooting flame is visible.

Table 6.2: Summary of characteristic parameters of combustion for the physically mixed, core-shell and the floating core-shell nanoparticles for $\Phi = 3.0$.

Parameters	Ignition delay	Duration of the first and transition stage of combustion	Maximum flame speed observed during combustion	Duration of the second stage of combustion
Core-shell	2.509 ms	47.7 ms	23.4 m/s	14.6 ms
Physically mixed	6.181 ms	12 ms	15 m/s	52 ms
Floating core-shell	1.291 ms	51 ms	26.25 m/s	24 ms

Unlike other physically mixed and core-shell counterparts that have similar combustion behavior (with minor differences in delay and velocity), physically mixed Al/Fe₃O₄ and core-shell Al@Fe₃O₄ presented notably different combustion behavior within the two stages. This behavior is likely related to the combined effects of various reaction mechanisms occurring at different stages of the reaction. The Stage I reaction was seen to be restricted to the sample surface. Considering that the experiment was done in atmosphere, it can be reasonably hypothesized that there was an involvement of atmospheric oxygen in the ignition process. During this stage, gas-solid reactions play a crucial role in increasing the temperature of flame front. Both the physically mixed and core-shell samples were in the form of loose powder, leading to a low density and a high porosity for trapping atmospheric oxygen with pores, which significantly promotes the first-stage reaction [116, 138]. In physically mixed Al/Fe₃O₄, a great portion of the surface of n-Al particles was accessible to gaseous oxygen trapped in these pores. In contrast, in the core-shell composite, n-Al particles were covered by IONPs which acted as a barrier. Hence, the aluminum surface had limited access to atmospheric oxygen. As a consequence, the physically mixed Al/Fe₃O₄ demonstrated a much more significant gas-solid reaction than the core-shell Al@Fe₃O₄ during the first reaction stage at lower temperatures. This difference caused by the

participation of gaseous oxygen led to a higher average combustion propagation rate for the physically mixed $\text{Al}/\text{Fe}_3\text{O}_4$ (11.98 m/s vs. 6.77 m/s for the core-shell $\text{Al@Fe}_3\text{O}_4$, as demonstrated in Figure 6.16) for the first-stage reaction, and also a much smoother combustion for physically mixed $\text{Al}/\text{Fe}_3\text{O}_4$ compared to the back-and-forth moving combustion in core-shell $\text{Al@Fe}_3\text{O}_4$. A much shorter combustion time was subsequently observed for the physically mixed sample (~ 12 ms vs. ~ 48 ms for the core-shell $\text{Al@Fe}_3\text{O}_4$). However, as the surface combustion proceeded and increased, the runaway reaction starts to travel beneath the surface, consuming the leftover sample, irrespective of the availability of gaseous oxygen.

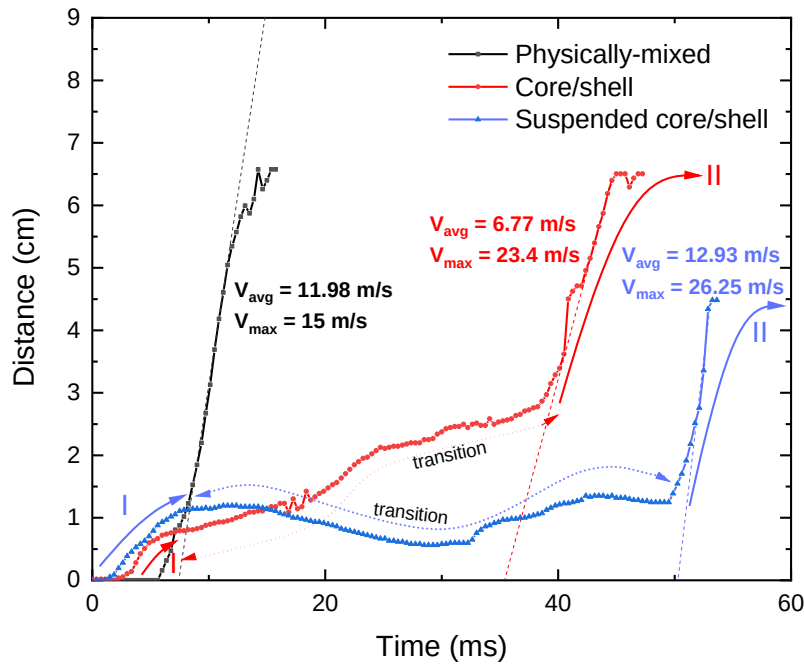


Figure 6.16: Flame propagation distance (cm) vs time (ms) for physically mixed, core-shell and suspended core-shell $\text{Al@Fe}_3\text{O}_4$ nanoparticles for $\Phi = 3.0$

During the second stage of the reaction, the condensed phase reaction between Al and Fe_3O_4 played the dominating role for the combustion propagation, while the participation of oxygen became less important. Therefore, the core-shell $\text{Al@Fe}_3\text{O}_4$ clearly outperformed the physically mixed $\text{Al}/\text{Fe}_3\text{O}_4$ during this stage, thanks to the vastly enhanced surface contact between Al and Fe_3O_4 in the core-shell sample [220, 221]. Note that the reactivity of $\text{Al}/\text{Fe}_3\text{O}_4$ nanocomposites are lower than other types of

nanothermites, which results in a slow and smooth reaction path across the different reaction stages for the physically mixed Al/Fe₃O₄. For the core-shell Al@Fe₃O₄ however, due to the significantly enhanced condensed phase reaction kinetics, the drastic dissimilarity between these two stages of reaction was clearly distinguishable.

6.3 Conclusion

This study reports the development of a facile route to fabricate functional magnetic nano-sized Al@Fe₃O₄ core-shell composites. The targeted assembly is triggered by the seed-mediated crystal-growth approach superimposed on the polyol method. The product is seen to switch from chunky to powdery upon increasing the nominal equivalence ratio between the raw materials, with $\Phi = 3.0$ as the point of inflection. In contrast to the physically mixed Al/Fe₃O₄, core-shell particles reduce the initiation temperature by 20 °C, reduce the peak temperatures by 13.8 °C and 157.2 °C, increase the specific energy release by 68% and promote the entire thermite reaction to happen before the aluminum's melting temperature (owing to the closely packed Al fuel and Fe₃O₄ oxidizer in core-shell structure). The core-shell structure lowered the apparent activation energy by 95.77 kJ/mol by eradicating the problem of phase separation which was evident in the physically mixed samples, thus leading to an enhanced and consistent energetic performance. Upon laser heating, both core-shell Al@Fe₃O₄ and physically mixed composite present a two-stage combustion (a surface combustion stage followed by a volume burning stage). However, the as-prepared core-shell nanoparticles illustrate a much shorter delay of ignition and an impressively shorter second stage of combustion signifying an increased reactivity as a consequence of increased surface contact between Al and Fe₃O₄.

Furthermore, the shell material (IONPs) imparts a magnetic character to this core-shell MIC which adds an additional degree of freedom to this composite to tune combustion behaviors. By virtue of this property, the core-shell Al@Fe₃O₄ can be delivered in any oxygen-absent and/or oxygen-deficit region by the aid of magnetic field that can further facilitate the ignition of these suspending composites and provide tremendous application potential. An interesting transition of a grow-shrink-grow flame was observed.

Chapter 7

Conclusion and future work

7.1 Summary and Research Contributions

This thesis presents a fabrication process for three innovative core-shell structured MICs and characterizes them for morphology and thermal response. The major contributions from the author towards this research are listed below:

- 1) Wang, A., Maini, S., Hickey, J. P., & Wen, J. Z. (2022). Solution synthesis of core-shell n-Al@ CuO based on electrostatic self-assembly for enhanced energetic performance. *Chemical Engineering Journal Advances*, 11, 100323. [102]
- 2) Maini, S., Wang, A., & Wen, J. Z. (2024). Characteristics of Gasless Combustion of Core–Shell Al@ NiO Microparticles with Boosted Exothermic Performance. *ACS Omega*. [140]
- 3) Maini, S., Wang, A., & Wen, J. Z. (2024) Fluctuating Flame from Suspending Ferrimagnetic Core/Shell Al@Fe₃O₄ Nanoparticles in a Magnetic Field. *Advanced Materials Interfaces*, 2400328. [179]

A summary of the major findings from above contributions are as follows:

7.1.1 Core-shell Al@CuO MIC

Ignitable micro- and nano-sized energetic particles are desirable in MEMS devices in delivering energy to a target and producing heat *in-situ*. It is challenging however to fabricate these particles due to the incomplete mixing between the fuel and oxidizer during the manufacturing process and its sensitivity to external stimuli. The core-shell structure is considered one of the most promising microstructures as it provides a standalone reactive system composed of fuel and oxidizer packed in a single assembly. A wet-chemistry synthesis route was developed to fabricate spherical core-shell Al/CuO MICs. XRD and electron microscopy results revealed how synthesis parameters control the fabrication of the final product. By changing the ammonia content during the synthesis, the structure of the final product could be “switched” between a well-mixed nanocomposite and individual nanosized core-shell spheres, likely due to electrostatic forces between Al nanoparticle and intermediate compounds of Cu and ammonia. DSC results indicated that the as-synthesized core-shell Al/CuO reduced the onset

temperature by 8 °C and peak temperatures by 20 °C compared to Al/CuO nanoparticles physically mixed by ultrasonication by the reason of increased proximity between the reacting components. The activation energy of core-shell Al/CuO was also reduced by about 20 kJ/mol compared to physically mixed products. More importantly, the core-shell nanoparticles showed a significantly reduced ignition delay and homogeneous combustion behavior, which was different from physically mixed Al/CuO. The wet-chemistry method enables bulk production of both Al/CuO nanocomposite and core-shell nanostructures for larger-scale industrial applications.

7.1.2 Core-shell Al@NiO MIC

Microstructures and thermochemical behavior of the core-shell structured $\mu\text{Al@NiO}$ energetic composites were characterized. The core-shell structure was synthesized using a wet-chemistry based one-pot synthesis and the assembly was proposed to be driven by electrostatic force between negatively charged Al and positively charged Ni-NH₃ complex. SEM images of these composites displayed nickel oxide nanoparticles adhering to the surface of Al nanoparticles irrespective of the equivalence ratio and NH₃/Ni ratio taken during synthesis. Thermal analysis suggested two simultaneous exothermic peaks coming from the thermite reaction followed by the intermetallic/alloy-formation reaction. The formation of alloy was substantiated by the melting peaks corresponding to AlNi₃, AlNi and Al₃Ni, in the DSC curves. The core-shell structure decreased the apparent activation energy of the reaction by a mere 9.24 kJ/mol; however, it increased the combustibility by manifold. The physically mixed composite was incapable of getting ignited at all upon laser ignition, while the core-shell counterpart ignited at 2.55 ms and got completely combusted within 6.5 ms accompanying a violent thud.

7.1.3 Core-shell Al@Fe₃O₄ MIC

MICs composed of core-shell fuel@oxidizer nanostructures are highly desirable due to their enhanced reactivity attributed to a short oxygen diffusion length. A ferrimagnetic MIC, being successfully engineered, allows for manipulation using an external magnetic field, which facilitates the target delivery of samples and an additional controllable combustion process. This research reported on fabrication, microstructures, thermochemical stability, and combustion properties of the core-shell structured, ferrimagnetic Al@Fe₃O₄ MICs. Serving as an oxidizer, as well as a functional ferrimagnetic component, IONPs were grown, in situ, on nano-sized Al particles. Electron microscopic images showed monodispersed IONPs decorating the surface of n-Al. XRD and XPS confirmed the

coexistence of Fe^{2+} and Fe^{3+} in fabricated IONPs. Effects of nominal equivalence ratio (Φ) on morphology and thermochemical behavior of these MICs were studied when the maximum energy release was optimized at $\Phi = 3.0$. The as-prepared core-shell MICs dominantly illustrated a solid-state reaction mechanism and exhibited a reduced activation energy which was nearly 70% of that for the physically mixed nanocomposites. Upon laser heating, the core-shell MICs were able to ignite and combust as suspensions in a magnetic field. While the ignition delay and burning rate were comparable to these powders sitting on the bottom of the tube, interesting combustion dynamics were observed for these magnetically packed powders including a grow-shrink-grow flame under the influence of an external magnetic field.

7.2 Limitations of Current Work and Insights for Future Study

This section lists the limitations of the current research and provides recommendations for future work.

- All three thermites manufactured in this research work, despite demonstrating superior energetics, displayed a few flaws from the perspective of morphology. The bulk of the powder products exhibited a core-shell structure; however, many heterogeneities were seen across samples. Till date, no research has been able to successfully get rid of this heterogeneity. In other words, separating the engineered core-shell structure from the randomly arranged nanoparticles can form an interesting topic for future research.
- From the STEM images of core-shell Al@CuO , the approximate size of CuO nanoparticles was found to be 20-30nm and from the SEM images of the NiO generated in core-shell Al@NiO samples, the size of NiO was observed to be 40-50nm. Since the intent behind a structured composite is better surface contact between reactants, it is hypothesized that reducing the size of these oxidizers below 10nm can significantly enhance the energetics of the respective nanothermite. Therefore, new studies can focus on developing the core-shell structure using different oxide-precursors. Different precursors not only result in different sized oxidizer nanoparticles, but they can also result in exciting morphologies of these oxidizer particles in terms of nanowires, hollow spheres, flowers, cubes etc.
- The fabrication process for core-shell Al@CuO and Al@NiO involved vacuum filtration and annealing of the residue from filtration and the assumption was made that there was no loss of product during these steps. However, this assumption was not validated by any additional

characterizations. The filtrate from filtration could be viewed by SEM/EDS to identify the elements removed during this step. The annealing process could be performed in TGA/DSC and the gases released during this step could be analyzed simultaneously using FTIR. This could deduce the decomposition steps for Cu-NH₃ complex and Ni-NH₃ complex. It is recommended that these tests are performed in any future research conducted on these composites.

- In the context of fabricating gasless nanothermites intended towards the application in welding and microinitiators, less-gas or no gas formation from the core-shell Al@NiO and Al@Fe₃O₄ can be substantiated by using a constant volume pressure cell or a bomb calorimeter or a pressure change detectors outside the combustion tube inside the combustion chamber. An experimental study can be done by looking at the amount of gases formed for the structured composite vs the physically mixed counterpart. Other fuel/oxidizers like Al/MnO₂ or Al/KMnO₄, known for considerable gas formation can be used as a benchmark in such research work.
- The three contributions from this research work propose a reaction mechanism for the thermite reaction. Although theoretical evidence is provided for the different steps of the proposed thermite reaction, it would be good to authenticate these reaction steps by characterizing the reaction products at various stages of the reaction.
- Since Al/CuO is the widely studied MIC, it has been built into many structures in literature like layer-by-layer, 3DOM, etc. beside the others. Research can be extended to engineering Al/NiO and Al@Fe₃O₄ pair into other structures which can provide a thorough insight into the behavior of these fuel/oxidizer pairs.
- The core-shell Al@NiO MIC was constructed using micro-Al. A core-shell MIC was fabricated using n-Al as well and it unveiled superfluous energetics on the DSC. However, the results were not replicable at that time. Further investigations are strongly encouraged into this matter.
- A simple application was set out for Al@Fe₃O₄ MIC exploiting its magnetic nature. Since magnetic substances also showcase an ability towards magnetic levitation, new research can be conducted demonstrating the combustion of core-shell Al@Fe₃O₄ MIC while being

magnetically levitated in air. This is a super fascinating topic from the perspective of practical research.

To conclude: Al@CuO publication from this research work combined with our previous publication form a comprehensive and complete study in itself. However, Al@NiO and Al@Fe₃O₄ imbibe a lot of research potential and should be further explored in future.

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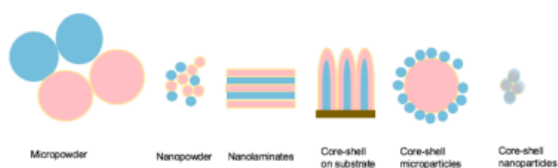
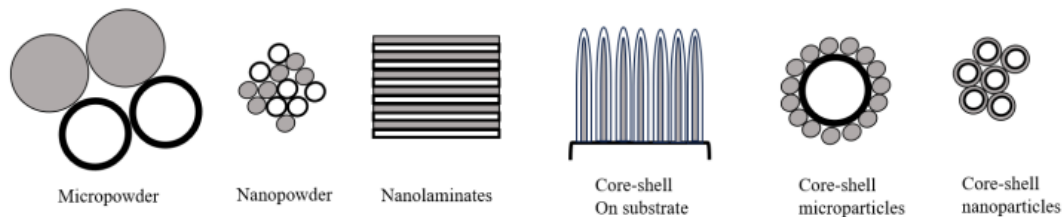


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by Deqi Wang, Guozhen Xu, Tianyu Tan, Shishuo Liu, Wei Dong, Fengsheng Li and Jie Liu * 

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