Reaction kinetics study of Al-Fe₂O₃ nanoenergetics

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ABSTRACT

This thesis investigates the various important parameters such as oxidizers' morphology, size, equivalence ratio and synthetic methods which affect reactivity of Al-Fe₂O₃ nanoenergetics. Parametric studies conducted in this study are correlated with proposed reaction routes and derived reaction kinetics (Ea values) giving an overall understanding in the reactivity of nanoenergetics performance.

Morphological effects of Fe₂O₃ oxidisers were found to be of great influence in affecting nanoenergetics' reactivity which has yet been studied. Nanotubular Fe₂O₃ oxidisers + Al nanoparticles system was found to be the most reactive and the reaction route (post-thermal studies on reacted products) that facilitates this enhanced performance was proposed. A new phenomenon of nanotubular oxidizers in possible generation of "hotspots" was also observed using microscopy imaging of reacted products at respective temperature intervals. The expected higher reactivity of the nanothermites compared to micron thermites was consistent with studies made by various groups in the energetic community. In addition, new findings in the preferred reaction route taken by the nanothermite in enhancing reactivity were found. The reactivity of Al- Fe₂O₃ was found to be highly dependent on the equivalence ratio. An increase in maximum pressure output ($P_{\max}$), time to reach max pressure ($t_{\max}$) and rate of pressure released (dP/dt) were observed with increased ratio due to better thermal conductivity and energy content in fuel rich compositions, but with a delayed reaction.

Solvent mixed and surfactant assembled Fe_2O_3 nanotubes + Al nanoparticles were compared in terms of homogeneity of mixing in influencing reactivity. A new and novel assembling method was developed in this study using APTES (aminopropyltriethoxy silane) and carboxylic acid groups as molecular attracting ligands. This highly selective assembly technique was found to have higher reactivity compared to surfactant assembled system possibly due to shorter molecular linkers in reducing the overall diffusion length.

CHAPTER 1. INTRODUCTION

1.1 MOTIVATION FOR THIS WORK

In recent years, growing interest in nanostructured materials have offered attractive potential for significant performance gains compared to conventional bulk materials. Nanoenergetics are defined as reactive composite materials containing nano scale components and possess properties non-achievable by bulk energetic materials due to their higher specific surface area[1-3]. Energetic materials are generally defined as substances or mixtures with high amount of stored chemical energy that can be released for their intended application [4]. Ultrafine nanoenergetic mixtures have been reported to exhibit enhanced performance with respect to reaction rates compared to conventional grain size mixtures [5].

Some of the commonly used energetic materials such as TNT, RDX etc. are based on monomolecular compounds [6, 7]. These materials having both fuel and oxidizer in a single compound enable reaction to occur at a high release rate but with relatively low energy density. Composite energetic materials on the other hand, produce energy release density values much higher than the monomolecular ones but at a lower release rate [8]. This main drawback is governed by mass transport between the reactant components, which is inherent in composite systems resulting in slower release rate. To reduce mass transport limitations between the reactants and utilizing on the

advantage of high energy release densities, nano-scale components are used to create a superior class of energetic materials.

1.2 JUSTIFICATION FOR THE CHOICE OF MATERIALS SYSTEMS

The type of nanoenergetics examined here is a subgroup of composite energetic materials comprising of a metal fuel (e.g. aluminium) which will be closely mixed with metal oxide (e.g. iron oxide) particles. Such material is frequently known as nanothermites or metastable intermolecular composites (MIC) [9]. A thermite system usually comprises of a fuel (e.g. Al) and oxidizer (e.g. Fe_2O_3), and reaction between the two produces an extremely high amount of heat release. This will result in reaction temperature being extremely high and often used for ordinance applications. Essentially, it involves oxidation/reduction reactions that oxygen are supplied by their own for combustion resulting in self sustaining reaction and difficult to stop. One of the classical thermite system is the Fe_2O_3 /Al mixture which has been widely used for the many applications such as additives to explosives [10], airbag gas producing materials [11], hardware/IC chips destruction devices[10] and underwater welding torches etc [4]. Their adiabatic temperature can reach above 3135 K and energy density of 3.71kJ/g, making them attractive energetic materials.

1.3 SIGNIFICANCE OF THE WORK

One of the most critical challenges faced in optimization of nanothermites is the rate of energy released are insufficient to fully utilize their energetic advantage at nano-scale. The energy released in redox reactions of thermite energetic materials depends mainly on the arrangement of the oxidizer and fuel molecules. This reaction is a solid-state diffusion driven process whereby the interfacial/inter-particle contact area between the oxidizer and the fuel is an important factor. Hence, with an increase in this interfacial contact area will subsequently result in an increased rate of energy release. Majority of the research efforts made so far in energetic thermite systems usually involves inhomogenous physical mixing (using mechanical means such as milling, stirring etc.) of oxidizer and fuel, resulting an random distribution of the oxidizer and fuel with limited interfacial area of contact inhibiting the full potential of reactive thermite systems [12]. In addition, physical mixing often introduces unplanned stressed induced reactions which become an inherent dangerous process [13] thus, new synthetic methods of producing nanothermites are essentially needed for designing practical systems employing such nanoenergetics.

Knowledge in the materials properties based on size and in particular, shape of the reactant components is scarcely reported and needs to be addressed. Such effects play important roles in effective optimization of

energetic formulation and will ultimately determine the diffusion and respective reaction rates. A single synthesis process may yield nanoparticles of varying size, structure, shape and chemistry. All of these factors can greatly impact the energetic properties of such nanoenergetics. Taking into account that thermite reaction is a surface diffusion driven process, the shape and size of the reactant components will inevitably differ in its specific surface area and the way they are arranged, and ultimately influence the reaction rate. Reaction initiation mechanisms correlating to the effects of reactants' morphologies, reactant size, fuel to oxidizer ratio and modes of initiation in energetic materials are still not well understood and will be one of the main scopes of study in this thesis.

1.4 NOVELTY OF THE WORK

This PhD work presented here is focused on the synthesis and characterization of nanoenergetic thermites (primarily the Al-Fe₂O₃ system). To improve the reactivity (rate of energy released) of nanothermites, directed self assembly methods were attempted to attain ordered arrangement of fuel and oxidizer particles. By doing so, particle to particle level self assembly can be achieved whereby the fuel nanoparticles are arranged in an orderly and controlled manner around the oxidizer. The ordered composition results in increased interfacial contact area between the fuel and oxidizer, and hence attaining higher energy released at a very fast rate. In addition, the appeal of

synthesizing composite energetic materials from the bottom-up approach offers the advantages of having precise control of the morphology, particle size and composition. Besides improving reactivity of nanothermites, this study also aims to understand the different parameters (e.g. oxidizers' morphologies, reactants' size, equivalence ratio and methods of synthesis) that can affect the overall reaction kinetics of such assembled system.

1.5 OBJECTIVES AND WORK PLAN

The overall goal is to understand the reaction kinetics of Al – Fe₂O₃ nanoenergetics in promoting enhanced energetic capabilities presented in the flow diagram shown in Fig. 1.1. The project objectives are 1) to study the effects of oxidizers' morphologies and size, fuel to oxidizer ratio, and different self-assembly methods and 2) reaction kinetic studies of self-assembled nanothermites based on dynamic pressure measurements, ignition wire tests, thermal analysis (DSC), and lastly, 3) correlate the different effects in the overall reaction mechanism.

Fig. 1.1. Flow diagram illustrating the research rationale and focus of study.

1.6 BRIEF SUMMARY OF THE MAJOR NEW FINDINGS

This study uses a multi-pronged approach to investigate Al-Fe₂O₃ thermite systems with different particle sizes, morphologies and mixing methods. A summary of the major new findings are listed as follow;

- 1) Nanotubular Fe₂O₃ oxidisers (aspect ratio 3:1) have shown to improve the reactivity of Al thermite systems compared to using nanorods of the same aspect ratio and spherical particles of (APS 50nm) of the same mass. Favored reaction mechanisms by the nanotubes oxidizers compared to nanorods and nanospheres are

found. Morphology differences in nanotubes during reaction also showed evidence of “reactive hotspots” formation which contributed an important new finding.

- 2) Phase change differences during reaction between micron and nano thermites were found to be the determining factor in influencing the higher reactivity of nanothermites.
- 3) A novel assembling technique using molecular linkers to assemble Al-Fe₂O₃ thermite systems was attempted in this study. It was found that this improved assembling technique produced thermites with enhanced reactivity compared to using polymeric linkers. This highly selective assembling technique used molecular linkers which reduced the diffusion length between the oxidiser and fuel particles compared to polymeric linkers resulting in enhanced performance.

CHAPTER 2. BACKGROUND

2.1 OVERVIEW

This chapter will discuss prior and current research on reactive thermite systems. Section 2.2 provides an introduction to reactive thermite systems in particular nanothermites.. Section 2.3 describes the current research efforts including synthesis methods and current problems faced in optimizing the combustion kinetics performance of such systems. Section 2.4 describes the concept in self-assembly of binary system of particles into ordered arrays, and discusses the relevance and advantages of self-assembly to the field of energetic materials.

2.2 REACTIVE THERMITE SYSTEM

The oxidation-reduction thermite reaction was first described by Goldschmidt in 1908 [14]. These extremely exothermic reactions involve the transfer of electrons from one reactant to another, where, in essence, one reactant is oxidized, while the other is reduced. This reaction is highly reactive and produces energy in the form of heat. This energy can be of use in several applications such as reactive fill to enhance warhead projectiles and primers for conventional ammunition. In recent years, thermites have also being used in environmental protection research for the treatment of zinc

hydrometallurgical wastes [15, 16]. Interestingly, nano-sized superthermite system has even been employed in biomedical treatment of cancerous cells [17]. Such nanothermite composite leads to an accelerated rate of combustion, generating high energy shock waves comparatively to Mach numbers up to 3, literally blasting off the cancerous cells leaving nearby cells unharmed.

The scheme of a thermite reaction is shown in Eq. 2.1 involving a solid-state reduction-oxidation reaction. A summary of several thermite reactions and their associated theoretical exothermic heats of reaction are shown in Table 2.1. Note that all of these systems possess large theoretical exothermic heats of reaction.

Table 2.1 Summary of theoretical exothermic heats of reaction of selected thermite reactions [4].

Thermite mixture	$\rho_{\text{TMD}}/\text{g/cm}^3$	Adiabatic reaction temperature/ K		$\Delta H_{\text{R}}/\text{kJ/g}$
		without phase changes	with phase changes	
$\text{Fe}_2\text{O}_3 + 2\text{Al}$	4.175	4382	3135	-3.96
$3\text{Cu}_2\text{O} + 2\text{Al}$	5.280	4132	2843	-2.41
$4\text{Al} + 3\text{TiO}_2$	3.59	1955	1752	-1.53
$\text{Fe}_2\text{O}_3 + 2\text{B}$	4.661	2646	2065	-2.47
$2\text{B} + 3\text{CuO}$	5.665	4748	2843	-3.09
$5\text{Fe}_2\text{O}_3 + 6\text{Ta}$	9.185	2383	2138	-0.98

The reaction is self-sustaining upon initiation with the oxidizer acting as an oxygen source that constantly supplies oxygen to promote combustion even in the absence of surrounding oxygen supply. However, the reactant components require to be physically mixed and therefore, the mass diffusion process is the main rate determining step inhibiting energy release rate. This solid-state diffusion driven process depends mainly on the contact area

between the fuel and oxidizer with an increase in this interfacial area will result in an enhanced rate. Thus, it is expected that the arrangement of fuel and oxidizer plays an important role in the combustion kinetics of the thermite system.

Research has been recently intensified on the development of nanoenergetic composite materials. As previously mentioned, due to mass transport issues, high energy release rates are inhibited in traditional micron-scale energetic composites. It is known that optimally, the reduction in the scale of the oxidizer and fuel components will increase the number of contact points, thus achieving higher mass transport [18, 19]. The increase in specific surface area also allows for increased reaction locations and enhances the rate of heat transfer. In addition, physical properties such as melting point are altered with smaller particle sizes[20, 21]. This is particularly important in reactive materials whereby a lower melting point increases the interfacial surface tension between solid and liquid phase enhancing diffusion between molten fuel and solid oxidizers and improving reactivity[22]. In addition, the total time for complete combustion of a particle decreases significantly as the particle size decreases as stated by the D^2 law of combustion [23]. This law is based on the burning time of a spherical particle which varies linearly with the square of the particle diameter. This means that if the particle diameter is reduced by a factor of 10, there will be a 100 fold decrease in the burning time,

and this will in turn significantly increase the energy release per mass of material.

Aluminum-based thermite system is typically used since they exhibit appropriate reaction kinetics and high density. Aluminum on its own has a relatively high heat of combustion (31kJ/g) [24]. However, the reactivity of pure aluminum is such that the surface metal reacts with oxygen to form a metal oxide layer which is of no value as a fuel, and therefore reduces the efficiency. The oxide layer creates a diffusion barrier layer for oxidizers and hinders the ignition of the aluminum. Micron-sized aluminum often ignites in an oxidizing environment only after being heated up to temperatures reaching the melting point of alumina at 2300K [25]. Nano-sized aluminum however, has been reported to be reactive in even in its solid state at much lower temperature [26]. Dikici et al. previously reported the reaction mechanism for the micron-size Al which undergoes a diffusion mechanism whereby the rate of Al diffusing towards oxygen will determine the reaction rate [27]. Nano-size Al on the other hand reported by Pantoya et al. undergoes a melt dispersion mechanism whereby upon melting of the Al core, the high pressure built up causes the oxide shell to spallate and reaction is not limited by diffusion through the oxide layer. Fig. 2.1 shows the mechanisms of micron-size and nano-size Al reacting with air [28].

Fig. 2.1. (a) Micron-size Al particles react by a diffusion mechanism whereby the rate is controlled by diffusing Al and oxygen through the oxide shell; (b) Nano-size particles react by a melt-dispersion mechanism whereby the melting of the aluminum core creates significant pressure that allows spallation of the oxide shell and expose the molten Al core [28].

Besides having different reaction mechanism, it has also been demonstrated that the phase change in the alumina layer is significantly affected as the particle sizes decrease [2, 3]. The oxide layer changes to a denser $\gamma\text{-Al}_2\text{O}_3$ and exposes pure aluminium to the surface even at temperatures below the melting of alumina. This amount of surface area of pure aluminum exposed from such a phase change is reported to increase by 8000 times when particle sizes decreases from micron scale to the nanoscale [29] .

In the presence of an oxidizer, (e.g. Fe_2O_3) a thermite reaction with the exposed aluminum can produce large exothermic heat at $> 3000\text{K}$. The huge

thermal stress resulting from such reaction is sufficient to cause the alumina shell to crack or melt, and expose the fresh Al underneath for further combustion. The combustion rate can be thus be further exploited by using nano-size to improve the ignition kinetics.

2.3 SYNTHESIS OF THERMITE SYSTEMS

The traditional method of producing thermite system is by conventional mechanical mixing of powders of metal oxide and fuel. Ultrasonic mixing is one of the most commonly used methods for combining the reactants because of its relatively low cost. Large quantities can also be prepared in a short time. However, this is an inherently dangerous process due to safety issues associated with unplanned reactions if mixing is to initiate the stress-induced reaction[30, 31]. A derivative of mechanical mixing using arrested reactive milling (ARM) was extensively studied by Dreizin's group [32-34]. It mainly involves arresting/ceasing the milling process right before the spontaneous reaction of the thermite mixture in the mill to obtain a highly reactive metastable composite. ARM is a "top-down" process, whereby the composites are produced by continuous size reduction of micron-scale starting materials using a shaker mill. The high relative velocity of the grinding media will repeatedly deform and fracture powder particles and storing kinetic energy in the metal powders. It is able to raise the metals powders to an

activated state where the energy needed to overcome the energy barrier is reduced. Thus, a faster ignition and combustion kinetics can be achieved [35].

One of the problems faced using ARM is the unstructured nature (uncontrollable irregular morphology) of the milled composite that causes large variability in the combustion behavior. Morphology of the final thermite composite is also unpredictable due to the random collision process between the milling balls and the particles. Moreover, preparation of such materials requires the time of spontaneous initiation to be known as accurately as possible. Current theoretical calculation of the milling process may not be sufficient to predict initiation precisely and parametric studies are often needed to determine that [36]. This can be time consuming and costly and safety issues such as damage to the milling vial because of the highly localized temperatures and pressures caused by the reaction may need to be considered too.

Another attempt by researchers from the Lawrence Livermore National Laboratory (LLNL) used a sol-gel chemistry approach to prepare nanostructured energetic materials [12]. This method allows the fuel to reside within the pores of the solid matrix and reduces the mass transport distance between the oxidizer and fuel to increase the overall efficiency. Fig. 2.2 shows the schematic diagram of such a material produced by sol-gel synthesis. Nanometer-sized particles are first formed upon addition of chemicals in a

solution forming a “sol”. The sols are then linked to form the “gel” with the remaining solution residing within the pores.

Fig. 2.2. Schematic diagram of thermite system produced using the sol-gel method [12].

The sol-gel approach to energetic materials offers good control over the composition of the solid at the nanometer scale which is difficult to achieve by random physical mixing techniques. However, one key disadvantage of using such method is the necessary dilution of the thermite mixture with inert oxide precursors such as Al_2O_3 or SiO_2 (from dissolved AlCl_3 salt and silicon alkoxide respectively). This leads to a pyrotechnic material with reduced energy content compared to a pure iron (III) oxide-Al mixture due to the dead weight [31]. Sol-gel reactants also often have organic impurities that can make up to 10% of sample mass, which results in

reduced energy content [36]. Furthermore, the approach is still a random mixing process rather than directed assembly, and thus, the full reaction kinetics potential is not fully realized.

A modified sol-gel method that uses electrostatic forces existing between charged aerosol particles has been developed to induce interaction between the oppositely charged fuel and oxidizer particles [37]. The sol-gel precursors were atomized by an atomizer to produce aerosol- particles and subsequently charged by diffusion charging of gas ions. This electrically enhanced assembly allows the fuel and oxidizers to come together to increase the chances of contact points between the two due to opposite charges. Nevertheless, aero-sol-gel method may still possess similar inherent problem of incomplete conversion from sol-gel chemistry to form the iron oxide. This greatly reduces the total heat of reaction due to the significant amount of “dead weight” from sol-gel impurities. Recently, Yetter et al [38]. developed an electrostatic assembled Al-CuO nanocomposite microspheres using oppositely attracting ligands. Such composites are not only able to achieve close proximity between Al and CuO, it also improves the combustion overall combustion process despite having hydrocarbon ligands as diluents as compared to mixtures (comprising of thermite and ligands) prepared by sonication.

Foils of energetic Al- Fe_2O_3 , Al-CuO, and Al-Ni composites prepared by electro-depositing and thermal evaporating the reactants onto a substrate is another approach that has been considered to increase the interaction between the fuel and oxidizer [39]. Fe nanowires are first electrodeposited into porous alumina template and subsequently oxidized to Fe_2O_3 nanowires. A thin film of aluminum (~50nm) is then coated onto the nanowires by means of thermal evaporation. Similar deposition technique using physical vapor deposition (PVD) to produce Al/CuO nanowires thermite has also been developed by Petrantoni et.al. [40]. This technique makes use of electroplating Cu onto silicon substrate and subsequently thermally oxidized Cu into CuO. Aluminum is then deposited on top of the CuO nanowires producing the final nanothermite. Both methods [39, 40] allow the thickness of the deposited film to be precisely controlled allowing the diffusion distance between the reactants to be optimized in the combustion process. This allows better uniformity between reactants. However, this is at the expense of small-scale production whereby, can be time-consuming and costly, producing only small amounts of material each time. Foil-like shape of the final material also restricts further processing into formulations that require certain shape, geometry or even molding process which is less appealing to the more versatile powdered form.

Table 2.2 summaries the efforts made so far by various groups to prepare different energetic thermite systems. The advantages and possible disadvantages of the various approaches are also highlighted. These approaches mainly involve random mixing of oxidizer and fuel. Attempts to increase the interfacial contacts between the fuel and oxidizer have been done. However, many inherent problems still exist. A kinetically controlled thermite reaction requires a well-homogenized mix of the two components. The contributions of these previous work serves as an important starting point reference for this thesis in conducting a more in-depth study of adopting self assembly techniques (will be covered in details in Chapter 3) and how it could improve the reactivity of nanothermite systems from various aspects such as size, shapes and fuel to oxidizer ratio.

Table 2.2 Summary of the various groups' synthesis methods of thermite systems and their reported results.

References	Method	Types of thermite systems	Advantages	Disadvantages	Properties Studied and Results
M.L. Pantoya et. al. [30]	Ultrasonic Mixing	<ul style="list-style-type: none"> Al-MoO₃ Al-Fe₂O₃ 	<ul style="list-style-type: none"> Easy, cheap and can mix large batches of thermite powders in a short time. 	<ul style="list-style-type: none"> Dangerous process due to unplanned reactions during mixing may initiate stress-induced reaction. 	<ul style="list-style-type: none"> Varies using different sizes of Al (nano to micron) composites. Combustion velocity increased with reduced Al size from 5-50m/s. Ignition delay time reduced from 10000ms to 10ms with reduced Al size.
M.L. Pantoya et. al. [31]	Chemical Sol Gel Method	<ul style="list-style-type: none"> Al-Fe₂O₃ 	<ul style="list-style-type: none"> Enable uniformly dispersed fuel particles to residue within a nanoscale oxidizer Prevents gradients in properties of the final material due to settling. 	<ul style="list-style-type: none"> Large amount of impurities retarded wave speed. 	<ul style="list-style-type: none"> Large improvements in combustion wave velocities compared to ultrasonic mixing thermites. Significant improvements in annealed sol-gel oxidizers compared to as-synthesized ones in terms of combustion wave velocities.
E.L. Dreizin. et. al. [32-34]	Mechanical Ball milling	<ul style="list-style-type: none"> Al-Fe₂O₃ Al- 	<ul style="list-style-type: none"> Able to obtain highly metastable milled composites. Make use of arrested 	<ul style="list-style-type: none"> Unstructured nature of the milled composite may causes 	<ul style="list-style-type: none"> Activation energies of ignition were determined to be 170 ± 25 kJ/mol for the Al-Fe₂O₃ nano-composites.

		<ul style="list-style-type: none"> MoO₃ Al- CuO 	<ul style="list-style-type: none"> milling to produce the thermite prior to spontaneous reaction of the mixture. 	<ul style="list-style-type: none"> variation in the combustion behavior 	<ul style="list-style-type: none"> Ignition temperatures for Al-Fe₂O₃ and Al-MoO₃ are 1249K and 1104K at 3000K/s heating rate respectively.
R.L. Simpson et. al. [12]	Chemical Sol Gel Method	<ul style="list-style-type: none"> Al-Fe₂O₃-SiO₂ 	<ul style="list-style-type: none"> Able to obtain nanostructured thermite Fuel residues within the pores of the solid matrix reducing the mass transport distance. 	<ul style="list-style-type: none"> High % “dead weight” (up to 10wt %) from organic precursors and impurities. Random mixing process. 	<ul style="list-style-type: none"> Combustion velocity varies from 10-100 m/s with different wt% SiO₂. Combustion velocity decreases with increasing SiO₂ content.

Table 2.2 (continued)

Research Group	Method	Types of thermite systems	Advantages	Disadvantages	Properties Studied and Results
L. Menon et. al. [39]	Electro deposition and physical vapour deposition	· Al-Fe ₂ O ₃ /Al-Ni	<ul style="list-style-type: none"> · Able to obtain nanowire-array-based thin film of Al-Fe₂O₃ thermite system. · Thickness of film can be controlled to reduce the diffusion distance and optimize combustion process. 	<ul style="list-style-type: none"> · Time-consuming, expensive. · Only small samples can be produced at one time · Need a substrate which is of no value in improving combustion kinetics. 	<ul style="list-style-type: none"> · Ignition temperature was found to be from 410 °C to 700°C with different Aluminum deposition thickness · Flame temperature was also found to be independent of ignition temperature.
Petrantoni et. al. [40]		· Al- CuO			<ul style="list-style-type: none"> · 2 exotherms observed at around 515 °C and 667 °C and total energy release of this thermite is 10 kJ/cm³.
R. Zachariah et. al. [37]	Aerosol-based electrostatic self assembly	· Al-Fe ₂ O ₃	<ul style="list-style-type: none"> · Able to obtain charged aerosol particles with electrostatic interaction between the fuel and oxidizer. 	<ul style="list-style-type: none"> · Still require sol-gel chemistry as precursors and lead to large amount of dead weight. 	<ul style="list-style-type: none"> · Increasing particle charges will increase the combustion velocity. · Rate of exotherm from DSC was observed to increase by factor of 10 for charged thermite

					nanocomposites compared to uncharged ones.
R.A. Yetter et. al. [38]	Ligands based electrostatic self assembly	Al-CuO	Able to obtain electrostatically assembled reactive microspheres with improved combustion wave process compared to sonicated reference.		Effects of diluents did not decrease the overall combustion process. The increase in intimacy between the fuel and oxidizer increases the combustion wave propagation compared to sonicated reference.

2.4 BINARY NANOPARTICLES SELF ASSEMBLY

Binary nanoparticles self assembly involve the packing arrangement of two different types of nanoparticles into a superlattice. The ability to control the assembly of nanoparticles allows the synthesis of new structures with interesting properties [41-43]. This is often done by manipulating the different nanoparticles' surface by various treatments whereby they “automatically” arrange themselves to attain a thermodynamically stable binary structure. This “bottom up” approach was first motivated when researchers found organized SiO₂ nanoparticles in the opal gem which leads to its unusual optical properties [44]. These structures were first postulated to be organised by gravity and repulsive double layers and later concluded by researchers that entropy was the main driving force and requires precise conditions [45] to form such structures.

Recently, intensive work has been focused on methods that are less restrictive as entropy, making use of other forces such as electrostatics, steric and dipole forces, van der Waals attraction and biomolecular interactions using DNA hybridizations [46-51]. The fundamental knowledge lies on having the two different materials having oppositely attractive forces which bind together and not to particles of the same species. Having the ability to combine two different materials in a superlattice combines the attributes of both the materials, generating valuable properties. By doing so, a wide variety of

structures can be attained with new properties and applications. Using combinations of various nanoparticle building blocks, binary nanoparticle superlattice can be produced as shown in Fig. 2.3.

Fig.2.3 TEM images of binary assembled nanostructures formed between (a), (b) In₂O₃ nanooctahedra and Pd nanoparticles [49] (c), (d) CdTe and Au nanoparticles [50].

Self-assembly techniques to produce nanothermites could be beneficial since the relative positions of the fuel and oxidizer will determine the combustion characteristics of the energetic material. If the fuel and oxidizer are able to be specifically positioned within the material, burning characteristics could be controlled to allow tailored-made properties for specific applications. This offers great advantages such as faster rate of energy release, higher energy densities, greater safety (sensitivity to unwanted initiation) and greater stability, and This is particularly important in applications such as designing microelectromechanical systems (MEMS) which require nanothermites to specifically provide a microthrust as a source of onboard energy to generate power [52]. Most heterogeneous energetic materials are highly disordered leading to reactants separated by a longer length scale. Self assembly utilises on specific localised interactions between the components itself decreasing the distance between the two. By adopting such techniques to prepare heterogeneous energetic materials using components at nanoscale not only combines the advantages that nanoparticles can offer, but also allows a highly ordered structure to be achieved and designed to meet the required application. Further unprecedented level of control can even be attained by using different proportions of the fuel to oxidiser ratio, particle size and morphology throughout the nanoparticle constituents, making it an attractive bottom-up approach in the field of energetic materials. The following chapter will be devoted to a specific binary

self assembling technique; surfactant self assembly as well as how it was adopted as the main synthetic method used in this work.

CHAPTER 3. RESEARCH RATIONALE AND NOVELTY

3.1 BACKGROUND ON SURFACTANT SELF-ASSEMBLY

Nanostructured assembly can be achieved by utilizing properties such as electrostatic interaction, magnetic dipoles attraction, and with the use of polymers [53]. Theoretical arguments [54, 55] have previously suggested that synergistic interactions between self-organising particles and organic matrix can lead to hierarchically ordered structures. Surfactant self-assembly using polymer/copolymer allows the polymeric and particulate entities to be arranged in an organised manner without the use of external fields. This opens up a simple and general route for assembling nanoenergetics in an ordered arrangement without compromising on safety. The use of polymer to achieve self-assembly relies mainly on the availability of numerous binding sites in a polymer molecule. These binding sites provide simultaneous interaction with surrounding particulates and even if the binding strength of each site is weak; the total binding strength becomes strong when the whole polymer molecule interacts [53]. In addition, the availability of binding sites allows easy binding to nearby nanoparticles even in the event if one side of the polymer surface is being adsorbed. Poly (4-vinyl) pyridine (P4VP) is an example of one such polymer and the structure is shown in Fig. 3.1.

Fig. 3.1 Structural formulae of Poly (4-vinyl) pyridine.

As shown in Fig. 3.1, the polyvinylpyridine (PVP) structure consists of a pyridyl group with a lone pair of electrons. This serves as an important affinity group towards metal particulates with the ability to form hydrogen bonding with polar species [56]. Moreover, PVP can interact in quaternized or protonated forms with charged surfaces by electrostatic interactions forming a quasi-irreversible adsorption [56, 57]. The ability of this polymer to interact with surfaces makes it a universal modifier for immobilization of nanoparticles [56].

3.2 SURFACTANT SELF-ASSEMBLY OF Al NANOPARTICLES AROUND Fe₂O₃ OXIDIZERS

The proposed method in this project is to produce a novel combination of Fe₂O₃ nanostructures (mainly nanotubes, nanorods and nanospheres) – Al nanoparticles energetic material via surfactant self-assembly using PVP. An earlier reported work by Apperson et. al. [15] which involves PVP surfactant assembly of Al nanoparticles-CuO nanorods system serves as a starting point

reference for the development of our modified version. There are very little reports on the combustion kinetics of such self-assembled systems, and by far only the combustion wave velocities have been reported for the Al-CuO system [17]. By studying the reaction kinetics and mechanism with accordance to different thermally induced ignition measurements (slow heating using DTA/TGA and rapid heating by ignition wire tests) adds value to such self-assembled systems which will be beneficial to the energetic community in adopting this versatile and efficient method.

A schematic diagram illustrating the self-assembly of Fe_2O_3 (nanotubes/nanorods/nanospheres) – Al system is shown in Fig. 3. 2. (author's published article [58]) Fe_2O_3 nanostructures are self-assembled with Al nanoparticles to achieve maximum contact area to hasten the diffusion between the Fe_2O_3 oxidizer and Al metal fuel.

a)

b)

c)

Fig. 3.2 A schematic diagram illustrating the self-assembly of (a) Fe₂O₃ nanotubes – Al system (author's published article [58]), (b) Fe₂O₃ nanorods– Al system and (c) Fe₂O₃ nanospheres – Al system.

PVP is first adsorbed from solution onto the Fe₂O₃ oxidizers and subsequently assembled with spherical Al nanoparticles. At low PVP concentration solutions, the aromatic rings were found to adopt a parallel orientation towards the oxidizer's surface. On the other hand, high concentrations allow perpendicular orientation of the aromatic rings to take place on the surface of adsorption [56]. Both orientations were confirmed by

similar studies using surface enhanced Raman spectroscopy of PVP on silver particles [59, 60]. Fig. 3.3 shows the schematic between parallel and perpendicular orientations of PVP molecule onto for example, Fe_2O_3 nanotubes based on the concentration of solution.

Fig. 3.3 Number of available binding sites increases with increasing polymer concentration.

The adsorption from dilute solution leads to an almost flat conformation of the PVP molecule on the oxide surface leading to few sites available for binding of the Al nanoparticles. This is not recommended as it will result in weak assemblies. Adsorption from higher concentration is preferred with many free dangling bonds available to bind with the Al fuel nanoparticles. However, for concentration above 3%, the polymer adopts an even more globular conformation which results in the attachment of nanoparticles reaching saturation when the entire surface is covered with polymer molecules. Thus, it was recommended that the range of PVP concentrations should lie between 0.01% - 3% to achieve maximum binding effect [56].

3.3 Fe₂O₃ NANOTUBES AS POTENTIAL NOVEL HOLLOW OXIDIZERS

Commonly used energetic materials usually involve the mixing of spherical particles [13, 29, 31, 38, 61]. Alternative particle shapes in energetic materials have scarcely been studied or reported with limited literature available, thus will be an exciting area of research for better understanding of their reaction mechanisms. Prakash et. al. has reported the synthesis of spherical nanoporous Fe₂O₃ as potential oxidizers using aerosol technique with the ability to impregnate organic materials to generate volatile gaseous products upon combustion [62]. Researchers from Lawrence Livermore

Laboratory has also demonstrated the synthesis of porous energetic materials with the advantage of having high specific area [12]. Combination of assembled Al nanoparticles-CuO nanorods/nanowires thermite by Gangopadhyay et. al. has also showed excellent combustion wave velocities [17, 63]. It was mentioned that a cylindrical morphology is preferred as more nano-particles can be assembled as compared to spherical morphology where there may be restricted assembling of fewer small nano-particles on larger ones but comparative studies were not available [63].

The target materials include a new combination of Fe_2O_3 nanotubes + Al nanoparticles. Tubular oxidizers were selected due to their much larger surface to volume ratio as compared to rods or spherical counterparts of the same volume. This is especially advantageous in the field of energetic materials since combustion is mainly a surface-controlled process. Localized regions of higher temperature (hot spots) are clearly seen at locations of pore collapse (due to defects and existing voids) in the study of HMX crystals upon heating using continuum mixture modelling technique [64].

Fig. 3.4. Simulated temperature profiles in the HMX crystals showing localized heating associated with pore collapse [64].

Enormous energy release due to cavity collapse has been reported leading to subsequent ignition propagation [65-67]. The presence of voids was also reported to catalyse chemical reaction to occur through enhanced intermolecular collisions [68]. Based on this concept, a hollow nickel-coated aluminum mixture have been prepared and exhibited improved thermal properties in terms of lower DSC reaction peak temperature as compared to uncoated pure aluminum. (author's published work [69])

Adopting these concepts, hollow nanotube oxidizers were chosen to promote localized “hot spots” with higher temperature. Such composites have the potential to not only able to achieve maximum hot spot density due to its

ordered composition, but also rapid heat propagation upon collapse of tubular oxidizers resulting in higher rate of energy release. To our best knowledge, such attempt has not been reported. By inducing hot spot regions directly using the reactant (i.e. oxidizers/fuel particles) itself allows better efficiency of energy release throughout the whole composite as they themselves are chemically reactive as compared to void cavities which still require a vector (e.g. nanojets, shock waves [68]) to transfer that amount of energy (see Fig. 3.5). Upon ignition of the heterogeneous energetic materials, these hot-spot regions formed due to pore collapse play an important role in rapid propagation of heat, which can lead to an accelerated combustion rate.

Fig. 3.5. Simulated temperature profile around a void at a) 1km/s and b) 3km/s. A reactive hemispherical “nanojet” is formed acting as a catalyst for subsequent reaction [68].

To further evaluate the potential of adopting hollow oxidizers into nanothermites, detailed study will be conducted in comparison to conventional structures such as rods and spherical particles. Chapter 4 will describe the synthesis and characterization of Fe_2O_3 nanostructures. In Chapter 5, we will describe the synthesis and characterization of the self assembled Fe_2O_3 nanooxidizers (rods/tubes/spheres) with Al nanoparticles using a surfactant polyvinyl pyridine(PVP). Characterization techniques will also be covered in chapter 5 as well focusing on some of the unique equipments (ignition wire test and dynamic pressure test) specially designed for energetic performance study. In Chapter 6, detailed analysis on microstructural effects in particular, oxidizers' morphologies and size (nano vs micron) in affecting reactivity. Chapter 7 will discuss on the effects of stoichiometry ratio (varying fuel to oxidizer ratio) and Chapter 8 will discuss on the different synthesis methods such as solvent mixed, surfactant self assembly and APTES-assisted assembly. Finally, Chapter 9 will give a conclusion on the findings.

CHAPTER 4. SYNTHESIS AND CHARACTERIZATION OF IRON OXIDE NANOSTRUCTURES

4.1 BACKGROUND

One key goal of nanoparticle synthesis is the design of experimental methods to selectively control the composition and shape of the particles produced. Hematite ($\alpha\text{-Fe}_2\text{O}_3$), which is the most stable oxide in ambient environment, has attracted the attention of many researchers due to its excellent properties [70-72] and is one of the most commonly studied oxidizers used in thermite systems. Hematite nanoparticles can be synthesized via solvothermal [72], sol-gel [62, 73], hydrothermal method [74-76], forced hydrolysis [77], chemical precipitation [78], etc. Amongst the synthesis methods used to produce hematite nanostructures, hydrothermal method is seen as one of the most viable and possible method to scale up production [79]. This is attributed to the simplicity of the method, which incurred low cost and provides excellent morphological control. This chapter will cover the synthesis of Fe_2O_3 nanotubes via hydrothermal technique and conduct a concentration dependant study in preparation of different Fe_2O_3 nanostructures that will be used in the subsequent morphological study of nanothermites.

4.2 EXPERIMENTAL PROCEDURE

The method that was attempted for this study is a solution phase approach adopted from the work reported by Jia et al. [74]. Fe_2O_3 nanotubes were synthesized by hydrothermal treatment of a mixture of FeCl_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ solutions. In a typical experimental procedure, 4.055g of anhydrous FeCl_3 was first dissolved in 50mL of distilled water to make up a concentration of 0.5M (denoted as solution A). Similarly, 0.23g of $\text{NH}_4\text{H}_2\text{PO}_4$ was dissolved in 100mL of distilled water to make up a concentration of 0.02M (denoted as solution B). 3.20mL of solution A and 2.88mL of solution B were then extracted with a micro-pipette and distilled water was then added to a final volume of 80 mL. After stirring vigorously for 10min, the mixture was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 125 mL for hydrothermal treatment at 220°C for 48 h. The autoclave was then cooled down slowly at ambient and the precipitate was separated by repeated processes of centrifugation and washing with distilled water and acetone. The flow diagram of the Fe_2O_3 nanotube synthesis is shown in Fig. 4.1.

Fig. 4.1. Flowchart for the synthesis of Fe_2O_3 nanotubes.

The collected powders were then dried in an oven heater at 70°C for 8 hrs to remove excess solvent. The prepared powders were characterized using various techniques. A field emission scanning electron microscope (JEOL SEM JSM-6340F) and a transmission electron microscope (JEOL TEM 2010) were used to analyze the morphology of the powders. The X-ray diffraction patterns of the powders were obtained with a Bruker X-ray Diffractometer

(XRD) using a Cu target ($\lambda_{\text{Cu-K}\alpha}=1.5405\text{\AA}$). The average particle size and size distribution were measured using a particle sizer (Malvern Zetasizer).

4.3 CHARACTERIZATION OF Fe₂O₃ NANOTUBES

Characterization was done on the synthesized Fe₂O₃ nanotubes to ensure the desired microstructure and phase prior to self assembly with Al to produce the nanothermite system.

The growth control of the hematite (Fe₂O₃) crystals is greatly affected by the phosphate ions. The adsorption of phosphate ions on hematite nanocrystals has been extensively studied [80, 81]. The phosphate ions are selectively adsorbed on the planes parallel to the c axis with the exception of the (001) plane as the adsorption affinities are much lower for the (001) planes [82]. The presence of the adsorbed phosphate ions “protects” them from further reaction leading to the dissolution and growth in the [001] direction forming a tubular structure eventually. The dissolution reactions take place as follows.

Fig. 4.2. a) FESEM, b), c) and d) TEM images of the as-synthesized Fe₂O₃ nanotubes.

The SEM and TEM images of the as-synthesized nanotubes are shown in Fig. 4.2. The product consists entirely of tubular structures that are completely hollow as observed in the TEM images (Fig.4.2 (b)-(d)). The tubes are measured to be with an inner diameter of 50-55nm, outer diameters of 65-70nm and lengths of 200-300 nm. Some of the tubes were observed to be opened on one end and closed on the other. XRD analysis (Fig. 4.3) confirmed the hematite phase of the product. All the peaks can be indexed to the pure corundum structure of hematite (JCPDS: 33-0664). The average particle size was measured using the Zetasizer to be 192.4nm (Fig. 4.4) with a polydispersity value of 0.126. This relates well to having a fairly monodisperse distribution.

Fig. 4.3 XRD pattern of the hematite nanotubes.

Fig. 4.4 Size distribution by intensity graph of the hematite nanotubes.

Averages of 5 runs were done to obtain the final average particle size and distribution.

4.3.1 Concentration dependant studies- in preparation of various Fe_2O_3 nanostructures

Jia et. al. has previously briefly mentioned in his article on the concentration of phosphate ions played an important role in the formation of nanotubes [74]. For concentration of phosphate ions of lower than 0.00065M, formation of nanorods will occur and relatively large phosphate ions (> 0.001M) will form broken tubes of low aspect ratio [74]. However, studies on the formation of other hematite nanostructures using this method was not well documented thus, it is necessary to conduct a systematic study in this thesis with the objective of generating different structures for subsequent

morphological studies in nanothermite systems. The mechanism of formation of different hematite nanostructures will not be within the scope of this study.

The concentration of the phosphate ions was varied to study the ratio effects of phosphate on the formation of different hematite nanostructures. Table 4.1 summarizes the effects of $\text{Fe}^{3+}:\text{PO}_4^-$ ratio on the final morphology of the product. With increasing amount of phosphate ions, the morphology changes from nanorods $\rightarrow$ nanotubes $\rightarrow$ nanorings (Fig. 4.5). These results are consistent with what was mentioned by Jia et. al. [74]. The same general trend of decreasing PO_4^- will yield nanorods and excessive concentration will yield nanorings (destruction of nanotubes). TEM was also performed to study the hollow nature of these three main types of nanostructures, and the images are shown in Fig. 4.6.

TABLE 4.1: Summary of the iron (III) oxide nanostructures synthesized using the hydrothermal method.

Mole Ratio [Fe ³⁺ : PO ₄ ⁻]	Type of nanostructure
1:0.01	Nanorods
1: 0.02	Nanorods
1: 0.04	Nanotubes of high aspect ratio
1: 0.06	Nanotubes of low aspect ratio
1: 0.07	Nanorings + Nanoflakes
1: 0.08	Nanorings + Nanoflakes
1:0.12	Nanorings

Fig.4.5. Effect of molar ratio of Fe^{3+} to PO_4^{3-} on morphology (a) 1:0.01 ratio nanorods; (b) 1: 0.02 ratio nanorods; (c) 1: 0.04 ratio nanotubes of high aspect ratio; (d) 1: 0.06 ratio nanotubes of low aspect ratio; (e) 1: 0.07 ratio nanorings + nanoflakes; (f) 1: 0.08 ratio nanorings + nanoflakes; (g) 1:0.12 ratio nanorings.

Fig. 4.6. TEM images of the (a) nanorods (1: 0.02 ratio); (b) nanotubes (1: 0.04); (c) nanorings (1:0.12).

Based on the concentration dependant studies, the molar ratio of phosphate ions played an important role in forming the final nanostructure and further validate this facile method in generating different Fe_2O_3 nanostructures. This is crucial in the subsequent assembly with Al nanoparticles. A mole ratio of 1: 0.04 (nanotubes with high aspect ratio) and the mole ratio of 1:0.02 (nanorods) were chosen to produce the Fe_2O_3 to be subsequently used to self assemble with Al.

CHAPTER 5. SYNTHESIS AND CHARACTERIZATION OF Al-Fe₂O₃ SELF ASSEMBLED NANOTHERMITE SYSTEM

5.1 BACKGROUND

Self assembly technique has been adopted in this study to produce orderly arranged Fe₂O₃-Al nanothermites using polyvinyl pyridine [17]. This easy and efficient method allows the homogenous distribution of fuel and oxidizer particles providing high interfacial contacts as well as reducing diffusion distance for thermite reaction to occur. Section 5.1 will cover the experiment procedure for surfactant self assembly of Fe₂O₃-Al nanothermites. Section 5.2 will cover the characterization of the Fe₂O₃ nanotubes – Al nanoparticles system to assess the quality of mixing using this technique. Finally, section 5.3 will elaborate more on the characterization techniques used throughout this thesis.

5.2 EXPERIMENTAL PROCEDURE

The assembling process consists of three main steps: (1) coating of Fe₂O₃ oxidizers with P4VP, (2) mixing with Al nanoparticles (purchased from American Elements) using ultrasonication, and (3) removal of excess

surfactant by heating to obtain the final product. In the first step, 0.12g of Fe_2O_3 powders (from hydrothermal synthesized nanotubes and nanorods/ commercial purchased spherical nanoparticles from Alfa Aesar ; APS=50nm) were ultra-sonicated for 4hr in 200ml of propan-2-ol containing 0.1% (w/v) P4VP (Sigma Aldrich Mw=60kg/mol). The coated Fe_2O_3 nanopowders were subsequently separated from the solution by repeated centrifugation to ensure there was no residual polymer and dried at 65 °C for 12 hr. The second step mainly involved dispersing 0.1g of coated oxidizer nanopowders with 0.034g of Al nanoparticles (equivalence ratio of 1.0) in 1.5ml of propan-2-ol using a sonic bath for 1hr. Finally, the particles were separated by repeated process of centrifugation with propanol and dried at 60 °C for 6 hr to obtain the final material. The synthesis process is shown as a flow diagram in Fig. 5.1.

Fig. 5.1. Flowchart for the synthesis of Fe_2O_3 -Al self-assembled system.

5.3 RESULTS AND DISCUSSION

5.3.1 FTIR analysis of PVP-coated Fe₂O₃ nanotubes

The adsorption of P4VP onto the oxidizer surface is important in the whole assembling process as the polymer is the key component in providing the binding sites for both the oxidizers and fuel particles to attain an ordered assembly. To ensure the adsorption of P4VP polymer onto the oxidizer surface, FTIR analysis was done to compare the absorbance peaks of uncoated and coated Fe₂O₃ nanotubes. The results are shown in Fig. 5.2. The FTIR spectrum of the PVP-coated Fe₂O₃ nanotubes shows distinct characteristic peaks of the adsorbed polymer. The peak position and corresponding bonding mode is given in Table. 5.1.

Fig. 5.2. FTIR of PVP coated and uncoated Fe_2O_3 nanotubes.

TABLE 5.1: Characteristic peak positions of P4VP from FTIR spectrum.

Wavenumber / cm^{-1}	Peaks
2920.68	C-H stretching
1600.71	N-H Bending
1415.00	C=C ring stretching
1215.35	C-N stretching
3500.00	OH-bonds on adsorbed H_2O

Thermogravimetric analysis (TGA) in argon was done on the coated nanotubes. An initial weight drop of the coated nanotubes corresponds to the degradation of the PVP coating and confirms that there was ~10wt% of PVP coating present. The slight incremental increase in weight in the later stage is due to the constant instrumental thermal drift which is commonly seen in thermal analysis.

Fig. 5.3. TG graph showing an initial weight drop of ~10wt% corresponding to the amount of coated PVP.

5.3.2 Aging effects on Al nanoparticles

Fig. 5.4. shows an inherent oxide layer of ~4-5nm thick observed on the Al nanoparticles. A semi-quantitative controlled study was conducted to evaluate the thickness of alumina layer formed over time and the results are shown in Fig. 5.5. Al nanoparticles were suspended on a TEM Cu grid and left exposed to the ambient at 25 °C and ~ 65% RH for 60 days. A reference was made by ultrasonicing Al nanoparticles in propanol for 1hr to observe the amount of alumina formed.

Fig. 5.4. An inherent alumina thickness ~4-5nm on as –received Al nanoparticles. (*sample analyzed right after opening of as-received Al packed in sealed vacuum pack*)

Fig. 5.5. Al nanoparticles reaches a saturation thickness after 60 days.

The as-purchased Al nanopowder reached a saturation active Al content of ~65vol% upon exposure to ambient and ~63vol% upon ultrasonication in propanol for 1 hr. Active Al is defined as the portion of powder not in the form of Al_2O_3 . This study shows that the alumina layer will reach a saturation thickness upon exposure to air for more than 10 days or alternatively, suspending in propanol for 1hr. Preparation of samples in this study were done in propanol medium for an hour (both solvent mixed or assembled samples), thus it will be reasonable to assume that the Al nanoparticles have reached its saturation thickness. The amount of active Al crystalline phase with respect to iron oxide detected by the XRD was confirmed using the TOPAS analysis (see appendix) since the amorphous alumina cannot be detected using XRD.

5.3.3 X-ray diffraction pattern of self-assembled nanothermite

The phase purity of the assembled nanothermite was examined by XRD analysis. The XRD pattern (Fig. 5.6) shows no unknown crystalline phases. All the peaks correspond to the pure aluminum and haemitite phase. Rietveld analysis was done using a DIFFRACplus TOPAS software to quantify the relative amount of the phases. The calculated result of 77.42wt% Fe_2O_3 to 22.58wt% Al (Appendix A Fig. S1(a)) falls close to the initial amount of Al and Fe_2O_3 added at stoichiometric ratio of 74.6wt% Fe_2O_3 to 25.4wt% Al. The slight difference may be due to inevitable minimal loss of powder during the washing and centrifugation process.

Fig. 5.6 XRD pattern of the self-assembled Fe_2O_3 – Al nanothermite.

5.3.4 Morphological study of self-assembled nanothermite

SEI and TEM analysis were carried out on the as-synthesized self-assembled powders. The results are shown in Fig. 5.7. It is clearly seen that the spherical Al nanoparticles are assembled around the Fe_2O_3 nanotubes. Particle size distribution of the commercial bought nano Al is observed to be very broad and ranges from 20nm – 150nm. The TEM images in Fig. 5.7(b) and (c) clearly depicts that surfactant self assembly between Fe_2O_3 nanotubes and Al nanoparticles was achieved. The insert in Fig. 5.7(b) shows the TEM image of a single Al nanoparticle with a layer of alumina shell of around 5nm thick.

Fig. 5.7(a) Field emission SEI image (b), (c) and (d) TEM image of self assembled Fe_2O_3 –Al nanothermite. An insert in Fig. 5.5 (b) shows the TEM image of a single Al nanoparticle with a uniform alumina shell.

5.4 MATERIALS CHARACTERIZATION

Characterization of the powders was done using various conventional techniques. The field emission SEM (JEOL JSM-6340F) and high resolution TEM (JEOL JEM 2100F with EDX mapping) were used to image the size and morphology of the powders operating at an accelerating voltage of 15kV and 200kV, respectively. Prior to using the FESEM, the samples were coated with a layer of platinum using the SPI-ModuleTM Sputter Coater for conduction of electrons within the sample when using the FESEM. The TEM is equipped with energy dispersive X-ray spectrometer

(EDX) that allows elemental mapping to be done for qualitative compositional analysis.

The X-ray diffraction (XRD) patterns of the powders were obtained with a Bruker X-ray Diffractometer using a copper target ($\lambda_{\text{Cu-K}\alpha} = 1.5405 \text{ \AA}$). It was operated at 40kV and 30mA; with a scan speed of $2^\circ/\text{min}$.

Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA) were done in purified argon using the Mettler Toledo Simultaneous DSC-TGA to study thermal properties of the samples. Powder samples of 10 – 12 mg were contained in an alumina crucible and continuously flushed with purified argon at a rate of 70cc/min. The samples were then ramped from room temperature to 1200°C at a heating rate of $10^\circ\text{C}/\text{min}$ (unless specified). Baseline correction routine for DSC graphs is shown in the Appendix.

The following section will focus on two testing methods (ignition wire and dynamic pressure tests) which are specifically designed for energetic reaction kinetics study, and will be elaborated more in detail.

5.4.1 Ignition wire test

Ignition of the prepared powders was studied using an electrically heated wire setup shown in Fig. 5.8. This technique was adopted from Dreizin's group and has been described extensively [83, 84]. The powdered sample was coated on a graphite filament (diameter of 0.9mm) with hexane using a brush and the wire temperature was measured using an infrared pyrometer (Kleiber KG 740-LO; response time: 6 μ A) focused on an uncoated filament surface adjacent to the powder coating. The filament emissivity was set to $\varepsilon = 0.9$ which is reported to be the average emissivity for graphite filament in the temperature range of 1000 °C to 1600 °C [85]. The instantaneous ignition was detected optically using a photodiode (Thorlabs DET36A; response time: 14ns) focused on the powder coating. This method provides relatively well-controlled heating rate of ranging from 1200-8500 °C/s under ambient condition. Ignition is accompanied by a bright flash of light and the reaction temperature is obtained by measuring the blackbody emission spectrum of the igniting sample.

Fig. 5.8 a) Photo and b) schematic diagram of the ignition wire test used for ignition tests of the synthesized nanoenergetic powders.

A sudden spike in voltage will register the ignition temperature (T_{ig}) measured by the photodiode. This temperature is most commonly defined as the lowest temperature in a defined environment at which the particle would self-heat and start burning [86, 87]. However, the ignition models of different samples were observed to behave differently. Thus, a bare wire reference test was done to distinguish the point where the graph starts to deviate positively from the reference resulting in a peak/ignition hump. The ignition temperature (T_{ig}) is identified at the point whereby the voltage deviates from the baseline and attains the maximum gradient (sudden spike in voltage). The point of inflection at the slope has been taken as the T_{ig} and registered as the point of ignition attributed by the powdered sample alone. Following this rationale, the ignition delay time (t_{delay}) was introduced and defined as the time taken to

reach that point. Fig. 5.9(a) shows an example of a typical ignition test images taken at different time intervals. Fig. 5.9(b) shows the graph generated from the test and how T_{ig} and t_{delay} were derived.

a)

(b)

Fig.5.9. (a) Ignition test images taken at different time intervals and (b) graph showing an ignition wire test result.

5.4.2 Dynamic pressure measurements

Dynamic pressure measurements were used to study the rate of energy release upon combustion. Kinetic study parameters such as maximum pressure rise ($P_{\max}$) upon ignition and time delay to reach maximum pressure ($t_{\max}$) can be conducted using this test. Pressure traces are measured in a constant volume explosion vessel (Parr model no. 211B1 with volume of 342 cm³) for combustion of different charges of thermite powders as illustrated in Fig. 5.10. The powders were placed on a ceramic crucible enclosed in a pressure vessel purged with purified air. The change in pressure upon ignition was measured using a pressure transducer with a measuring sensitivity of “0.5 mV/psi” of up to a maximum pressure range of “10000 psi”. Each run was conducted with a sample size of 58.5mg. For each system, 3 runs were done, and the results were determined as an average of the 3 runs. Using this approach, the experiment can be considered as adiabatic and the pressure increase can be related to the energy produced in combustion [88].

Fig. 5.10. Schematic diagram of the dynamic pressure test conducted at constant volume combustion.

CHAPTER 6. MICROSTRUCTURAL EFFECTS IN SELF ASSEMBLED Al-Fe₂O₃ NANOENERGETICS

6.1 OVERVIEW

This chapter will discuss the influence of different microstructural effects in self assembled Al-Fe₂O₃ nanoenergetics, in particular the morphology and size of the reactants. Section 6.2 gives a short background on the influence of size and morphology of different nanostructures in affecting the final properties. Section 6.3 will focus on the effects of using different Fe₂O₃ morphologies in preparing the self assembled system and correlating it to their reaction kinetics. Finally, section 6.4 will discuss on the micron versus nano effects on the self assembled system.

6.2 BACKGROUND

In recent years, the ability to control the morphology and size of nanomaterials has been a crucial issue in nanoscience research. Fundamentally, the properties of the final product are highly dependent on the shape and size of the reactant resulting in different applications [89]. In terms of size effect, the significant difference in properties is not a result of scaling factor but due to different causes in different materials. For example, as noble metals are reduced to nanometre scale, a new very strong absorption is observed known as surface plasma absorption resulting in characteristic colour which can never

be seen in bulk. [89] One such metal would be gold particles which appear to be yellowish in bulk, become brilliant rose colour when reaches nanometers scale. Optical [90], semiconducting [91], catalytic [92] and oxidation [93] properties for nano-scale particles have been extensively studied and reviewed through the years. These studies elaborated on the fundamental effects of increase in surface to volume ratio seen in nanoparticles whereby enhanced properties were observed.

Although the size control of nanostructures has been a major topic over the past decade, it is the shape that is now a second major coordinate in the chemistry of nanostructures. Controlling the morphology and size of the reactants is of key importance for exploiting their properties in energetic applications. Thermite reaction occurs through a surface controlled diffusion process whereby shapes and sizes of the reactants play a significant role in determining the final energetic performance. However, reaction initiation mechanisms that capture the effects of reactant size and morphological effects of energetic materials are still not well understood. The following section will discuss on the effects of shapes and sizes of the reactants in affecting the reaction kinetics of superthermites.

To the best of knowledge, systematic studies on how morphology of the reactants in affecting the energetic performance of thermites are scarcely reported and not well understood. Issues of performance in terms of quality of mixing, specific surface area etc, may arise when different morphologies of

oxidizers/fuel were used [94]. Studies by Sanders et al. on the reaction propagation of nanoscale energetic composites namely Al/MoO₃, Al/WO₃, Al/CuO, and Bi₂O₃, used the same Al nanoparticles and varying the different types of oxidizers morphologies (flakes, particles, granules and rods) [95]. It was found that the propagation speed depends on the gas produced and the densities of the respective systems. However, no correlation study to the reaction propagation was made to the respective morphology and how it affects the overall performance. As mentioned earlier in Chapter 3 section 3.3, attempts by various groups adopting different particle shapes such as nanowires [17], nanorods [17], porous structure [12] has been recently reported and showed excellent performance in terms of wave velocities etc. Thus, the scope and objective of this chapter will focus on the morphological effects of Fe₂O₃ oxidizers in the reactivity of the nanothermites.

6.3 MORPHOLOGICAL EFFECTS OF Fe₂O₃ OXIDISERS

6.3.1 Comparison of reaction kinetic performance – variation in Fe₂O₃ oxidisers morphologies

As mentioned in the previous chapter, various Fe₂O₃ nanostructures can be produced by the hydrothermal technique, which allows this study to be conducted. The three morphologies of comparison for this study will be

primarily the Fe_2O_3 nanotubes (hydrothermal synthesized), nanorods (hydrothermal synthesized) and nanospheres (purchased from Alfa Aesar 99.99% purity). The dimensions, BET surface area and TEM images of these three nanostructures are shown in Fig. 6.1. The self assembled systems were prepared using the surfactant self assembly method..

The synthesized nanotubes and rods were chosen with similar aspect ratio ($L: W = 3:1$) for comparison. Due to the available purchased spherical Fe_2O_3 comes in average particle size of 50nm, it is important to note that in this study, the volume of respective individual particle varies. The volume of respective individual particle are calculated and shown in the appendix whereby calculated volume of a nanorod > volume of a nanotube > volume of a nanosphere. All samples were prepared using the same stoichiometric equivalence ratio of 1.0 (confirmed by TOPAS Rietveld analysis shown in APPENDIX Fig. S1) with the mass of Al and Fe_2O_3 used (0.1g of oxidizer nanopowders with 0.034g of Al nanoparticles) kept constant for all samples prepared. This will inevitably results in the effective number of nanospheres > no. of nanotubes > no. of nanorods present in the assembled system to make up the mass of 0.1g. The SEM and TEM images of the assembled systems are shown in Fig. 6.2. Continuous assembly of Fe_2O_3 and Al particles were clearly seen in the Fig. 6.2. EDX mapping was used to identify the distribution of Fe_2O_3 and Al nanoparticles in Fig. 6.2(d).

Fig. 6.1 Fe_2O_3 (a) nanotubes, (b) nanorods and (c) nanospheres and their respective dimensions, measured BET surface area and TEM images.

(a) Fe_2O_3 nanotubes + Al nanoparticles

(b) Fe_2O_3 nanorods + Al nanoparticles

(c) Fe_2O_3 nanospheres + Al nanoparticles

(d) EDX mapping of Al and Fe_2O_3 distribution in Al- Fe_2O_3 nanospheres system.

Fig. 6.2 Surfactant self assembled Al nanoparticles – Fe_2O_3 samples using (a) Fe_2O_3 nanotubes, (b) Fe_2O_3 nanorods, (c) Fe_2O_3 nanospheres and (d) EDX mapping of Al and Fe_2O_3 distribution in Al- Fe_2O_3 nanospheres system.

The reaction kinetics of the different systems was studied using ignition wire test and dynamic pressure measurements. DSC was conducted to understand the thermal transitions taking place during reaction.

The ignition wire test results are shown in Fig. 6.3. The instantaneous ignition was detected optically using a photodiode focused on the powder coating registering the voltage. The ignition instant was identified as the sudden deviation from the bare wire. A constant heating rate of 6666K/s was used for the test with the average reading taken for at least 3 runs. The nanotubes oxidiser system was observed to have the lowest T_{ig} at 750°C followed by the nanorods at 926°C and the nanospheres at 1042°C respectively. t_{delay} using the tubular oxidizers was also seen to be the lowest at 0.037s.

Dynamic pressure measurements during thermal-initiation of reactions using a heated wire were also performed to study the rate of energy release upon combustion on loose powdered samples. The maximum pressure rise upon ignition (P_{max}) and time delay to reach maximum pressure (t_{max}) were determined using this test. The results for the various thermite systems shown in Fig. 6.4 were found to be consistent with the results obtained from the ignition wire test. A clear trend of the higher reaction rate (dP/dt) for the Fe_2O_3 nanotubes self-assembled thermite system is visible from the

comparison of the pressure traces. It is seen that the tubular system achieved the largest $P_{\max}$ generated in the shortest time. This further supports the superior reaction kinetics achieved for the self-assembled nanotubular oxidiser-thermite.

a)

b)

Fig. 6.3 Ignition wire test a) graphs and (b) results of different Fe_2O_3 oxidiser morphologies. The error bars represent the standard deviations from multiple measurements.

Fig. 6.4 Dynamic pressure measurements of different Fe_2O_3 oxidiser morphologies

The highly exothermic thermite reactions were studied using DSC in flowing argon gas. The results are shown in Fig. 6.5. The peak reaction temperature (T_p) is used to define the temperature at which the exothermic peak occurs. T_p of the nanotubes system was the lowest at 680°C followed by the nanorods at 720°C and lastly the nanospheres at 744°C . A sharp and steep exotherm was observed for the nanotubes system compared to a more gradual and broaden exotherms for the nanorods and nanospheres. The gradient of the exotherm (dH/dT) is an indication of the rate of reaction, with the nanotubes having the best performance.

Fig. 6.5 DSC graphs of the different nano thermite systems prepared using Fe_2O_3 oxidizers of different morphologies.

6.3.2 Derivation of activation energy – variation in Fe_2O_3 oxidisers morphologies

The derivation of the activation energy (E_a) using different isoconversion processing of heat flow as a function of temperature for various heating rates from DSC have been reported for various reactive materials [96-98]. Derivation of the E_a values can be used to quantify the reaction

kinetics/reactivity of each system. Typical values of Al-Fe₂O₃ nanothermites have been reported by Fan et. al. 145kJ/mol [99], Dreizin et. al. at 170kJ/mol [100] and Maximov et. al. at 167.5kJ/mol [101]. These values differ in the materials used as well as the thermally activated methods used. Thus, it will be necessary to derive the Ea value for our specific Al-Fe₂O₃ nanothermites within our testing regime.

Fig. 6.6 shows the DSC curves of the Fe₂O₃ –Al nanothermites of different oxidizer morphologies at different heating rates. In each of the curves, the observed endothermic peak at about 580°C correspond to the melting of nano aluminum, while the exothermic peak represents the thermite reaction. The shift in peak temperatures with different heating rates allows the kinetics of reaction (activation energy) to be derived. Model-free approaches were used in determining the reaction kinetics. The derivation of activation energies is proposed by the widely used isoconversion Starink method [102] given by equation 6.5. This method has been shown to be more accurate [102] than the Kissinger [103] and Ozawa [104] isoconversion methods and thus will be used in the present study. The activation energy, which is the minimum amount of energy required for the thermite reaction to take place, can thus be derived by the Starink plot of $\ln (T_p^{1.8} / H)$ vs $1/T_p$. A series of 3 runs were conducted at each heating rate to compute the best fitted straight line graph.

$$\ln \left(\frac{T_P^s}{H} \right) = A \frac{E_a}{RT_P} + \text{constant} \quad \text{Eqn 6.1}$$

where T_P is the peak temperature of the DSC curve, H , the heating rate, A , a constant, E_a , the activation energy in kJ/mol, and R , ideal gas constant. $s = 1.8$ and $A = 1.0070 - 1.2 \times 10^{-5} E_a$ (E_a in kJ/mol)

DSC traces were measured with heating rates varying from 10 to 50 K/min. In general, the exothermic peaks shift to higher temperatures as heating rate increases, which is expected for thermally activated reactions [102, 105]. The Fe₂O₃ nanotubes-Al nanoparticles system was quantified to have the lowest average E_a value of 124 ± 3 kJ/mol compared to the nanorods (151 ± 7 kJ/mol) and nanospheres (156 ± 9 kJ/mol) mixtures. These values are comparable to the ones reported of the same order of magnitude with slightly lower values [99-101]. This may be due to differences in reactants used (Fe₂O₃ nanotubes/rods/spheres) and the degree of inherent passivating layer of as – purchased nano-aluminum [100].

Fig. 6.6 DSC curves at different heating rates with the corresponding Starink plots using (a) nanotubes; (b) nanorods and (c) nanospheres Fe_2O_3 oxidisers.

Reactions at low heating rates under static conditions (DSC thermal analysis) are relevant in terms of materials' sensitivity, especially during storage and handling. On the other hand, reactions at high heating rates provide the reaction parameters needed for combustion applications which are generally in the range of 10^2 – 10^4 K/s. The development of the custom-made ignition wire test enable the generation of much higher heating rates ranging from 1200 K/s to 8000 K/s. This non-isothermal analysis can thus be applied to derive the activation energy under such high heating rate conditions (in ambient) which will be useful in field applications.

The thermographs generated for each mixture are shown in Fig. 6.7 (a) – (c). The overall trend of the calculated activation energy was consistent with the ones derived using DSC. The nanotube mixture was calculated to have the lowest average activation energy (144 ± 4 kJ/mol) followed by nanorods mixtures (156 ± 8 kJ/mol) and nanospheres having the highest (157 ± 8 kJ/mol). The expected difference in activation energy values compared to DSC measurements was due to the ignition conditions and complexity of the reaction processes taking place during the ignition wire test. Such observation is consistent with reported works [36, 94, 106]. The DSC measurements were conducted using argon gas with an inherent lower thermal conductivity than air [107]. The smaller variation in temperature difference observed in DSC graphs can be explained due to reduced heat losses by convection, resulting in a smaller temperature difference. As a result, less “overheating” of the DSC

heating coil is needed to reach the same temperature explaining the difference in thermal properties of the atmosphere and lower relative T_p observed in argon. Both the thermal analysis and ignition wire test results were consistent where the nanotubes mixture has the highest reactivity in both ambient and inert conditions. A summary of the analysis for the three systems are presented in Table 6.1.

a)

b)

c)

Fig. 6.7 Ignition wire test graphs at different heating rates with the corresponding Starink plots using (a) nanotubes; (b) nanorods and (c) nanospheres Fe_2O_3 oxidisers.

Table 6.1. Summary of results obtained from various thermal initiated techniques.

All values are the average of three measurements taken.

Sample	Al	Fe ₂ O ₃	Method	Dynamic pressure results			Ignition wire test results			DSC thermal analysis results		
				(dP/dt) _{max} (kPa/msec)	t _{max} (sec)	P _{max} (kPa)	Ignition Temp (T _{ig}) / °C	Ignition Delay (t _{delay}) Time/sec	Activation energy/ kJ/mol	Reaction peak temp (T _p) / °C	Enthalpy/ J/g	Activation energy/ kJ/mol
A	Spherical Nano Powder (25nm)	Nanotubes (200nm; Aspect ratio = 3:1)	Self assembled	6.403	0.207	180	797	0.046	144±4	680	329.5	125±3
B	Spherical Nano Powder (25nm)	Nanorods (200nm; Aspect ratio = 3:1)	Self assembled	0.805	0.465	98	925	0.063	156±8	694	284.4	151±7
C	Spherical Nano Powder (25nm)	Nanospheres (50nm)	Self assembled	0.225	1.239	65	1042	0.082	157±8	748	223.1	156±9

6.3.3 Post thermal studies – variation in Fe_2O_3 oxidisers morphologies

Although thermite reaction has been extensively studied in recent years, the reaction mechanism is still not well understood. Post thermal analysis of the reaction products formed at different temperatures were conducted using XRD and microscopy techniques to better understand the mechanism for the enhanced reaction kinetics seen in the nanotubes oxidisers system. The reacted samples were extracted from the crucible after each DSC run at 10K/min in argon for post thermal analysis. Fig. 6.8 shows the XRD patterns of the various reaction products formed at different thermal transitions and the reaction routes taken by the respective systems. The temperatures chosen were points of inflection before/after any exo/endothermic events shown in the DSC graphs to understand more on the products formed/consumed prior and after the thermal event. Within the temperature interval of 600°C and 820 °C, the reaction route proposed was based on the phases present before and after the exothermic peak without considering the intermediate secondary reactions to reach the final product. It is noted that the the relative concentration of Al_2O_3 may be too low to be detected using XRD which is commonly seen in similar reported literature [106, 108]. Moreover, amorphous phase alumina which is commonly formed at lower temperature range cannot be detected by XRD as well. [2, 3] This assumption can be explained by the presence of an inherent

alumina layer around nano-Al which was previously confirmed by TEM shown in Fig. 5.5(b) and was not registered by the XRD showed in Fig. 5.4. The proposed general reaction route were based on the XRD of the reacted products formed and is shown as follows. The equations highlighted in blue correspond to additional reactions occurring for respective indicated systems. The Gibbs free energies of each route are presented in Table 6.2 showing all reactions were spontaneous.

Fig. 6.8 XRD patterns of the a) nanotubes; b) nanorods and c) nanospheres systems at different temperatures and the corresponding reaction routes that are proposed to have taken place. *Note the different phase changes occurring at 600 °C for the respective systems.*

Step 1: Reduction of Fe₂O₃ to Fe₃O₄ (350 °C to 600 °C)

(additional reaction occurring exclusively for nanospheres system)

Step 2: Main possible exothermic reactions between Fe₃O₄ and Al (600 °C to 820 °C)

(additional reaction due to prior incomplete reaction exclusively for nanorods and nanospheres systems)

Step 3: Formation of hercynite (FeAl₂O₄) from the melt. (concurrent reactions from 820 °C to 950 °C)

Step 4: Further crystallization of hercynite (FeAl₂O₄). (950 °C to 1200 °C)

Table 6.2 Summary of the standard thermodynamic ΔG for each reaction route[109].

Reactions	ΔG (kJ/mol)
$9\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow 6\text{Fe}_3\text{O}_4 + \text{Al}_2\text{O}_3$	-994.93
$\text{Fe}_3\text{O}_4 + 2/3\text{Al} \rightarrow 3\text{FeO} + 1/3\text{Al}_2\text{O}_3$	-266.24
$1/2\text{Fe}_3\text{O}_4 + \text{Al} \rightarrow \text{Fe} + 1/2\text{FeAl}_2\text{O}_4$	-416.93
$2\text{FeO} + \text{Al} \rightarrow 3/2 \text{Fe} + 1/2\text{FeAl}_2\text{O}_4$	-421.74
$1/2\text{FeAl}_2\text{O}_4 + 1/3\text{Al} \rightarrow 1/2 \text{Fe} + 2/3 \text{Al}_2\text{O}_3$	-129.98
$\text{FeO} + \text{Al}_2\text{O}_3 \rightarrow \text{FeAl}_2\text{O}_4$	-15.898

As the temperature increases to 600°C, the amount of Al and Fe₂O₃ was observed to decrease (shown by the decreasing peak intensities) with increasing amount of Fe₃O₄ in the initial stage. This is due to the reaction between Al and Fe₂O₃ to form Fe₃O₄ and Al₂O₃ showed in Eqn 6.2. Subsequently, the main exothermic reaction (resulting in the exotherm observed in DSC graphs) from 600°C to 820 °C took place with the

production of Fe. The XRD graph in Fig. 6.8 shows the disappearance of the Fe peaks from the temperature interval of 950°C to 1200°C. Fe evaporation due to localized heating upon the thermite reaction (able to reach temperature ~3000°C) was based on J.Meï et al. [108] whom suggested the evaporation of the Fe and oxygen due to localized temperature rise and subsequent deposition onto the surface as iron oxide layer using DTA in argon environment. Upon evaporation, Fe due to its higher thermal conductivity than other phases present may acts as a heat sink results in rapid heat removal without causing a large increase in DSC sample temperature. As temperature further increases, phases such as FeO and FeAlO₄ were observed for all the 3 mixtures. The reaction intermediates formed were similar to the work reported by Cao and Orru on stoichoimetric amount of mixed Al- Fe₂O₃ [110, 111]. Their suggested reaction mechanism includes the reduction of Fe₂O₃ to iron oxides of lower oxidation states (Fe₃O₄ and FeO) subsequently, the interaction of Fe₃O₄ and FeO with molten Al to form hercynite FeAl₂O₄ and Fe. Finally, crystallization and growth of FeAl₂O₄ from the melt. The mechanism proposed was consistent with the sequence of phases formed at different temperature intervals in our study.

It was concluded from the XRD result analysis that the 3 systems took completely different reaction routes. Key findings from this analysis showed that the nanotubes mixture favored the complete conversion of Fe₂O₃ →

Fe₃O₄ in the initial stage (at 600°C) which subsequently leads to an earlier exothermic reaction of Fe₃O₄ + Al → Fe + FeAl₂O₄. Incomplete conversion of the Fe₂O₃ → Fe₃O₄ phase (Fe₂O₃ phase was still present at 600°C as shown in Fig. 6.8 (b)) resulted in a delayed exothermic reaction for the nanorods system. For the nanospheres system, FeO phase was also found in the initial stage as shown in Fig. 6.8 (c). The formation of FeO phase in the initial stage depletes the available Fe₃O₄ needed for the subsequent exothermic reaction (Fe₃O₄ + Al → Fe + FeAl₂O₄), and hence forms a competing reaction effect. This additional reaction in the initial stage competes with the subsequent major exothermic reaction leading to the delay in T_p (peak reaction temperature).

It was also noted that distinct microstructural differences were observed from the SEM images (Fig. 6.9) of the reaction products at 820°C for the three mixtures. Self assembled Fe₂O₃ nanotubes + Al @ 820°C showed distinct fracturing/collapse of tubes upon thermite reaction which was not seen in either the nanorods or nanospheres systems. The exothermic peak was observed to occur between 600°C to 820°C, thus the collapse of these tubes occurred prior/during the reaction. Heat can be transferred more efficiently with the porous nanotubes through combination of convection (release of trapped gas within the tubes) and conduction with comparison of using solid particles which rely primarily on conduction [67]. As mentioned in the

previous section (cross ref to pg 45-46), a combination of adopting such concept on creating “hot spot” regions using the reaction components itself is the first ever to be attempted. A rapid propagation of heat upon Fe_2O_3 nanotubes collapsed may result in an accelerated rate of reaction which is proposed and illustrated in Fig.6.9 (d) (author’s published work [113]). This may be one of the explanations for the enhanced reactivity shown in nanotubular mixture. Rapid reaction propagation due to hollow oxidizer pore collapsing allows almost instantaneous reaction when the nano Al reaches its melting point. This may results in chain reactions spreading towards the whole mixture resulting in an enhanced kinetic performance shown in the ignition wire, DSC and pressure measurements.

a)

b)

c)

d)

Fig. 6.9 SEM and TEM images of reaction products at 820 °C for a) nanotubes; b) nanorods; c) nanospheres systems; d) Schematic illustration showing the rapid propagation of heat upon tubes collapsed [113].

It is important to note that the density, mass of oxidizers and fuel to oxidizer ratio used in each cases were kept constant throughout the study; the differences in the effective number of nanospheres used to make up the mass of 0.1g will be much larger than the nanorods and nanotubes due to smaller calculated volume (a magnitude smaller than nanorods and nanotubes) of each

particle. This increase in number may have affected the assembling process and reduced its overall reactivity. With comparison between nanotubes and nanorods, although there is an increase in the no. of nanotubes compared to nanorods (in terms of actual particles present) within the same mass, the effect may be less dominant compared to the fracturing of the tubes resulting in rapid heat propagation which is only solely observed in the nanotubes systems.

6.3.4 Summary – variation in Fe_2O_3 oxidisers morphologies

Morphological effects were found to be a strong influence in determining the overall reactivity of the nanothermites. Combination of Fe_2O_3 nanotubes-Al nanoparticles were found to have the highest reactivity compared to Fe_2O_3 nanorods and nanospheres systems.

Nanotubular oxidizer morphology (aspect ratio of 3:1) was found to be favored in enhancing energetic performance compared to nanorods (aspect ratio of 3:1) and nanospherical particles (APS=50nm) with the mass and equivalence ratio kept constant. In the slow heating rate regime (10K/min to 50K/min), the nanotubes favored the complete conversion of $Fe_2O_3 \rightarrow Fe_3O_4$ in the initial stage which subsequently led to an earlier exothermic reaction of $Fe_3O_4 + Al \rightarrow Fe + FeAl_2O_4$. The fracturing of the nanotubes upon thermite

reaction was also observed for the nanotubes assembled system in contrast to nanorods and nanospheres systems which may give some evidence in the differences of reaction process each system undergoes upon reaction. These may in turn form localized hot spots for rapid propagation of heat, which explain the sharp and steep exotherm observed for the nanotubes as compared to a more gradual and broadened exotherms for the nanorods and nanospheres.

In this study, it is also important to note that volume differences between respective individual particle will results in an increase in effective number of particles used in nanospheres compared to nanotubes and nanorods which may have affected the assembling process resulting in reduced reactivity.

The next section will investigate the size effects comparing micron sized to nanosized Al-Fe₂O₃ energetic composites.

6.4 SIZE EFFECTS OF Fe_2O_3 -Al NANOTHERMITES --- Nano vs

Micron

6.4.1 Comparison of reaction kinetic performance -- Nano vs Micron thermites

Recently, studies by the researchers in the energetic community have been extensively focused on nanoenergetics using nano-scale components compared to conventional micron ones [29, 94, 114]. Enhanced performance has also been reported and reasoning to why nano-scale energetic is far more superior can be summarized in three main areas. Firstly, as the particle size decreases, the number of surface atoms increases, creating larger interfacial areas beneficial in the combustion process. In composite energetic materials, the reaction kinetics is largely dependent on the mass transport rates between the components; thus an increase in effective interfacial area of the individual components will greatly enhance its energy release rate. Secondly, using nano-scale components allow the possibility of attaining a more homogenous mixed component at the nanometer scale. Since the kinetics of energetic chemical reactions depend on the distance between individual components, a better mix will result in shorter diffusive distance, decreasing the time scale (ignition delay time) needed as compared to conventional micron-sized mixtures. Finally, excess energy of the surface atoms available in nano-scale components reduced the overall activation energy required for chemical reaction to occur, and hence increases the reactivity of nanoenergetics as

compared to conventional micron-sized systems. Although extensive research work have been recently focussed on nano-scale energetic materials, the reaction route taken during nanothermite reaction and reaction kinetics compared to micron-scale thermites is are still not well-understood. Thus, this is the aim of the work described in this section.

The study of size effects between nano and micron energetic materials are carried out using three different combinations of thermite mixtures, namely sample A: surfactant self assembled Fe_2O_3 nanotubes with Al nanoparticles, sample B: solvent mixed Fe_2O_3 nanotubes with Al nanoparticles and sample C: solvent mixed micron Fe_2O_3 granules (purchased from Alfa Aesar, 325 mesh size ($\sim 44\mu\text{m}$)) with micron Al granules (purchased from Alfa Aesar, 325 mesh size ($\sim 44\mu\text{m}$)). This chapter aims to discuss the reaction kinetics as a function of size between nanothermites and micronthermites. It should be noted that both the self assembled and solvent mixed Fe_2O_3 nanotubes with Al nanoparticles will be collectively known as nanothermites and the differences in terms of reactivity between the two will only be discussed in the next chapter (methodological effects). The solvent mixed samples involves physical mixing of the Al and Fe_2O_3 components using 2-propanol as the solvent and ultrasonication mixing for about 1hr as a control reference for comparison. The mixed powders were then dried at 65°C for 6hr prior to analysis. Surfactant self assembled and solvent mixed Fe_2O_3 nanotubes

with Al nanoparticles were prepared to compare with solvent mixed micron Fe_2O_3 granules (325 mesh from Alfa Aesar) with micron Al granules (325 mesh from Alfa Aesar). All the samples were prepared with the same oxidizer to fuel ratio of 1.0. The fuel ratio composition was confirmed by TOPAS Rietveld analysis shown in APPENDIX Fig. S2.

The microscopy images of solvent mixed Fe_2O_3 nanotubes with Al nanoparticles and solvent mixed micron Fe_2O_3 granules with micron Al granules are shown in Fig. 6.10 (a) - (e). Energy dispersive x-ray images (EDX) are provided in Fig. 6.10 (d) and (e) for clear identification of the Fe_2O_3 and Al granules since both are of similar morphologies. Images of surfactant self assembled Fe_2O_3 nanotubes with Al nanoparticles were presented earlier (see Fig. 6.2(a)).

Fig. 6.10 FESEM images of (a), (b) solvent mixed Fe_2O_3 nanotubes with Al nanoparticles and (c) ,(d) solvent mixed micron Fe_2O_3 granules with micron Al granules

Ignition wire tests were conducted to compare the reactivity of the nano and micronthermites. Typical thermographs of the results are presented in Fig. 6.11 at a controlled heating rate of 6666K/s. The expected higher reactivity in terms of T_{ig} and t_{delay} of both nanothermite samples as compared to micronthermites was observed.

a)

b)

Fig. 6.11 Ignition wire test (a) graphs and (b) results of nano and micronthermites.

Fig. 6.12 shows the DSC graphs of the respective thermite mixtures. It is noted that there are 2 distinct melting peaks at 582°C and 626°C for the as-purchased nano Al. The lower melting point of nano Al has been previously reported and commonly seen in the range of 550°C to 640°C [94, 114-116] depending on the actual average particle size. The two melting peaks observed is a consequence of the bimodal particle size distribution (mixture of smaller particles of ~45nm and larger particles of 950nm) of the as-purchased nano-Al powders as shown in Fig. 6.13. This is commonly seen in bimodal distribution of aluminium nanoparticles and has been reported in similar studies [94, 117, 118]. Pure micron-sized Al (purchased from Alfa Aesar, 325mesh) DSC was also conducted for reference, and a single melting transition was observed to occur at 660 °C.

Thermite exotherm was seen to occur at a much higher temperature of ~1300°C for the micron sized sample. Since reaction is a surface controlled diffusion process, the nano Al is able to melt at a much lower temperature, resulting in reaction that can occur much earlier for both the self assembled and solvent mixed nano samples (at 766 °C for sample B and 680 °C for sample A, respectively). Exothermic reactions seen here were observed to occur only after the melting of aluminum. By using nano-sized Al with a much lower melting point of 580°C, the molten metal is able to diffuse more rapidly towards the surrounding Fe₂O₃ oxidizers in a shorter time frame or lower

temperature. Upon contact with the nano-sized Fe_2O_3 oxidizers, the reaction is further hastened due to the much higher surface area available as compared to the micron samples.

Fig. 6.12 DSC graphs of surfactant assembled and solvent mixed Fe_2O_3 nanotubes with Al nanoparticles and solvent mixed micron thermite.

Fig. 6.13 Bimodal size distribution of as-purchased nano Al measured using a Melvern nanosizer.

Dynamic pressure measurement results of the various samples are shown in Fig. 6.14. The $(dP/dt)_{\max}$, $t_{\max}$ and $P_{\max}$ values were also improved by a few factors for the nanothermites as compared to the micron one, which is consistent with the DSC results .

Fig. 6.14. Dynamic pressure measurements of surfactant assembled and solvent mixed Fe_2O_3 nanotubes with Al nanoparticles and solvent mixed micron thermite.

As the components approach nano scale dimension, the reactivity of the nanothermite systems is enhanced significantly over that of traditional micrometer-sized energetic materials. The increase of surface area in the nano-sized samples allows more fuel to be in contact with the oxidizer, therefore

reducing heat and mass diffusion effects [18]. Consequently, compared with conventional micron sized thermite materials, nano superthermites have significantly higher energy density [114, 119]. These findings have shown that the reaction kinetics of thermite composite materials can be easily improved by reducing the reactive components to nano scale.

6.4.2 Derivation of activation energy -- Nano vs Micron thermites

The reaction kinetics of nano and micronthermites were also derived using the isoconversion Starink method. DSC measurements were used to determine the activation energy as a function to size. Fig. 6.15 (a) – (d) show the DSC graphs under heating rates of 10K/min -50K/min and the corresponding Starink plots for the solvent mixed Fe_2O_3 nanotubes with Al nanoparticles and solvent mixed micron Fe_2O_3 granules with micron Al granules. Activation energy of the self assembled Fe_2O_3 nanotubes with Al nanoparticles has been presented earlier. (refer to Table 6.1)

a)

b)

c)

d)

Fig. 6.15. DSC and Starink plots of (a), (b) solvent mixed mixed Fe_2O_3 nanotubes with Al nanoparticles and (c), (d) solvent mixed micron Fe_2O_3 granules with micron Al granules.

The activation energies calculated based on DSC measurements showed both the nanothermites (self assembled; 125 ± 3 kJ/mol and solvent mixed; 158 ± 3 kJ/mol) possess a much lower activation energy than that of the micron thermite (484 ± 15 kJ/mol). The activation energy for the micron thermite is comparable to the reported value of 540 kJ/mol [120]. The activation energies for nanothermites are reduced significantly as compared to the micron thermite. It is important to note that this enhanced reactivity is primarily due to size effects rather than morphological effects (granular micron particles versus tubular and spherical nanoparticles). This is deduced based on the results presented in the previous section which showed that morphological effects will not give rise to such significant magnitude of difference in terms of improvements. Thus it is safe to assume that morphological effects in this case, will be negligible. A summary of the results by various testing techniques are presented in Table 6.3.

Table 6.3. Summary of results obtained for the various samples using different thermal initiated techniques.

All values are the average of three measurements taken.

Sample	Al	Fe ₂ O ₃	Method	Dynamic pressure results			Ignition wire test results		DSC thermal analysis results		
				(dP/dt) _{max} (kPa/msec)	t _{max} (sec)	P _{max} (kPa)	Ignition Temp (T _{ig}) / °C	Ignition Delay (t _{delay}) Time/sec	Reaction peak temp (T _p) / °C	Enthalpy/ J/g	Activation energy/ kJ/mol
A	Spherical Nano Powder (25nm)	Nanotubes (200nm; Aspect ratio = 3:1)	Self assembled	6.403	0.207	180	797	0.046	680	329.5	125±3
B	Spherical Nano Powder (25nm)	Nanotubes (200nm; Aspect ratio = 3:1)	Solvent mixed	2.500	0.338	107	967	0.054	766	63.0	158±3
C	Micron granular Powder (~44µm)	Micron granular Powder (~44µm)	Solvent mixed	0.187	0.879	48	1088	0.091	1307	6.04	484±15

6.4.3 *Post thermal studies – Nano vs Micron thermites*

Studies on nanoscale energetic materials are frequently based on their specific performance (flame propagation, combustion wave velocity, burning rates etc. [11, 121, 122] in contrast to traditional micron thermites. It has also been frequently reported that magnitudes of improvements by using nanoscale components in thermite systems have been achieved. However, to the best of our knowledge, reaction mechanism correlating between nano and micron thermites is seldom reported and not well documented. In this section, post thermal studies were conducted on both nano- and micron thermites at varying temperatures to investigate the possible reaction paths taken in each system, giving an overall better understanding in the superior reaction kinetics shown in the previous section by nanothermites.

X-ray diffraction patterns of DSC reaction products obtained in argon at constant heating rate of 10K/min are shown in Fig. 6.16. The XRD results of self-assembled Fe_2O_3 nanotubes with Al nanoparticles reaction products have been presented earlier (refer to Fig. 6.8(a)). The temperatures of interest were chosen at inflection points (before and after an endotherm/exotherm) whereby the related reaction path can be deduced. Possible minor secondary reactions that cannot be resolved by the DSC measurements (absence of any exotherms/endotherms) occurring at other temperature intervals were not considered in this case.

a)

b)

Fig. 6.16. XRD patterns of (a) solvent mixed Fe_2O_3 nanotubes with Al nanoparticles and (b) solvent mixed micron Fe_2O_3 granules with micron Al granules reaction products formed at different temperatures.

The following reaction routes are proposed based on the XRD.

Reaction route for nanothermites

(self assembled and solvent mixed Fe₂O₃ nanotubes- Al nanoparticles)

Step 1: Reduction of Fe₂O₃ to Fe₃O₄ (350 °C to 500 °C)

Step 2: Main exothermic reaction between Fe₃O₄ and Al (500 °C to 820 °C)

Step 3: Formation of hercynite (FeAl₂O₄) from the melt. (concurrent reactions from 820 °C to 950 °C)

Step 4: Further crystallization of hercynite (FeAl₂O₄). (950 °C to 1200 °C)

Note: Both the self assembled and solvent mixed nanothermites undergo the above general proposed route. Detailed differences will be discussed in the following Chapter 8 on the effects of different synthesis methods.

Reaction route for micronthermite

(solvent mixed micron Fe₂O₃ granules- Al granules)

Step 1: Reduction of Fe₂O₃ to Fe₃O₄ (500 °C to 820 °C)

Step 2: Reduction of Fe₃O₄ to FeO (820 °C to 950 °C)

Step 3: Main exothermic reaction between FeO and Al (950 °C to 1600 °C)

XRD patterns of the reacted products after DSC experiment clearly showed that the nano and micron thermites underwent somewhat different reaction paths. The expected delayed exothermic reaction seen in the DSC graph of micron thermite by XRD could be explained by the formation of Fe at temperature only after 950 °C. For the nanothermites, the formation of Fe₃O₄ was seen to play an important role prior to the main exothermic

reaction. It acted as the precursor for the subsequent exothermic reaction ($1/2\text{Fe}_3\text{O}_4 + \text{Al} \rightarrow \text{Fe} + 1/2\text{FeAl}_2\text{O}_4$) to take place. Interestingly, this was not the case for the micron thermite. Fe_3O_4 phase was formed at temperature between 500 °C to 820 °C but the formation of Fe (an indication of the main exothermic reaction occurring) was not seen immediately after this formation. Instead, Fe_3O_4 was further reduced to FeO at higher temperature and it was the reaction between FeO and Al that contributed to the exothermic reaction seen in the DSC graph.

It was previously reported in Zachariah's work [123] using time-of-flight mass-spectrometry that the reaction mechanism of nano-Al thermites was found to undergo a diffusion-governed mechanism which involves the melting of the aluminum core and subsequent diffusion of aluminum ions onto the surface of the aluminum particles which will come in contact with the surrounding oxidizers. The oxidizers behave like an oxygen storage device whereby upon decomposition, releases molecular oxygen at a very fast rate to initiate the reaction [124].

Fig. 6.17. Schematic diagram drawn with accordance to the diffusive ions mechanism proposed by Zachariah.

In our experiments, upon reaching the melting point of the nano Al, Fe_2O_3 is reduced to the more thermodynamically stable Fe_3O_4 phase [125] resulting in the subsequent exothermic reaction with the molten aluminum for the case in nanothermites. However, in the case for the micron thermite at the temperature interval of 820 °C to 950 °C, the formation of Fe_3O_4 did not react with the existing molten micron aluminum (M.P. 660 °C) which can be seen by the absence of the Fe product and exotherm in DSC. Fe_3O_4 is further reduced to the more stable FeO [125] after reaching 950 °C which subsequently react with the molten aluminum to start off the main exothermic reaction. The higher reactivity of the nanothermites may be attributed by 2 main factors namely; the faster release of oxygen molecules by the Fe_3O_4 phase nano-oxidizers which are sufficient to initiate the reaction

with the molten nano-Al, as well as the increased rate of diffusion of Al ions towards the nano Al (having a much lower melting point) surface to come in contact with the oxidizers. In the case of micron thermite, it has been reported that the reaction temperature of micron sized aluminum with air (oxidizing agent) is very close to the melting point of the alumina shell [25, 126] which can varies a large range of 1500°C to 2000 °C. This is consistent with the DSC and XRD results that showed the exothermic reaction for micron Al with Fe_2O_3 (act as oxidizing agent in this case) was only observed at 1600 °C. Furthermore, the higher melting point of micron Al will also delay the rate of Al ions towards the oxidizers for reaction to occur. It was also reported on the enhanced adsorption coefficients of nano Al compared to micron Al by Pantoya et al. [127]. Nano-scale Al particles may absorb higher radiative energy compared to micron sized Al resulting in a reduced reaction temperature and time with the oxidizer particles.

6.4.4 Summary – Nano vs Micron thermites

As the components approach nano scale dimensions, the reactivity of the nanothermite systems have shown to be enhanced significantly over that of micrometer-sized energetic materials in terms of dP/dt , P_{max} , T_{ig} , T_p .

2 contributing factors leading to nanothermites having better reaction kinetics has been proposed. The diffusion of molecules through the fuel oxide layer is the rate determining step between the Al and Fe_2O_3 particles. Nano Al having a lower melting point than micron Al becomes molten at an earlier stage resulting in build-up of thermal stress in the alumina oxide layer causing earlier crack formation. The volume change due to melting of Al was reported to induce pressures of up 0.1–4 GPa onto the oxide layer allowing cracks [28]. This effect will allow earlier diffusion of Al ions through the oxide layer cracks compared to micron size Al and subsequently react with the surrounding oxidisers. This observation is consistent with the results reported by Zachariah [123, 128]. Difference in reaction paths taken by nano and micronthermites were observed using XRD at different temperature intervals. Further reduction from Fe_3O_4 to FeO was observed for the micron thermite at higher temperature before the occurrence of the exothermic thermite reaction was observed in contrast to nanothermites.

The following chapter will cover the stoichiometry effects by varying the fuel to oxidizer ratio in affecting the reactivity of nanoenergetics.

CHAPTER 7. STOICHIOMETRY EFFECTS IN SELF ASSEMBLED Al-Fe₂O₃ NANOENERGETICS

7.1 Comparison of reaction kinetic performance – Varying fuel to oxidizers ratio

In composite energetic systems, the desired energy properties can be fine-tuned by varying the amount of fuel and oxidizer. This may in turn enable a balance between the two to maximize the performance required for their intended application. The ratio between the Al fuel and Fe₂O₃ oxidizer plays a critical role in determining the reaction kinetics of thermite systems. For example, a 10wt%Al-90wt% MoO₃ mixture will quickly extinguish upon ignition and will not self-propagate to completion due to the insufficient Al content. [127] On the other hand, a high Al content may require prolonged pre-heating resulting in a significant delayed time before ignition which may not be desired for actual applications [127]. To provide a more complete results representative of the actual composite's performance, it is necessary to conduct analysis on fuel lean/rich mixtures and will be the objective of this chapter. The fuel to oxidizer ratio was determined by performing a series of experiments varying the equivalence ratio [129] which is defined as Φ in equation 7.1 .

$$\Phi = \frac{(\text{fuel/oxidizer})_{\text{actual}}}{(\text{fuel/oxidizer})_{\text{stoichiometric}}} \quad \text{Eqn 7.1}$$

** stoichiometric ratio of 74.7wt% Fe_2O_3 : 25.3wt% Al is calculated based on the thermite reaction $\text{Fe}_2\text{O}_3 + \text{Al} \rightarrow \text{Al}_2\text{O}_3 + \text{Fe}$*

Φ of 0.4 (fuel lean), 1.0 (stoichiometric) , 1.3 (fuel rich), 1.5 (fuel rich) were chosen to compare regions of fuel lean and rich. The composition of all samples is confirmed by TOPAS Rietveld analysis on the obtained X-ray diffraction patterns shown in Appendix A, Fig. S3. The effect of stoichiometry on the reactivity of self assembled nanoscale Al- Fe_2O_3 nanotubes thermite was studied using DSC analysis, Parr dynamic measurements and ignition wire test. Figs. 7.1 – 7.4 show the DSC, dynamic pressure and ignition wire results of the various sample compositions.

Fig. 7.1 a) DSC graphs with varying equivalence ratio of surfactant self assembled Fe_2O_3 nanotubes with Al nanoparticles; b) T_p vs Φ plot and c) enthalpy vs Φ plot.

Fig. 7.2 a) Dynamic pressure measurements of surfactant self assembled Fe₂O₃ nanotubes with Al nanoparticles; with varying equivalence ratio; b) dP/dt vs Φ plot and c) P_{max} vs Φ plot

A general quasi-linear increase in reactivity with equivalence ratio was observed from both the DSC and pressure measurements. In the DSC graphs, as the ratio increases towards the fuel (Al) rich region, T_p and enthalpy of reaction increases. By having a lower Fe_2O_3 oxidizers content, the molten Al will need to diffuse greater distance to come in contact with enough molar ratio between Al and Fe_2O_3 for the reaction to occur. The reactivity (measured by T_p values) will be limited by the amount of oxidizers present in the mixtures. Once the self sustainable reaction starts, the larger amount of fuel content in fuel rich samples will thus result in more heat released.

The increase in rate of pressure released (dP/dt) with equivalence ratio seen in the dynamic pressure measurements was reported in similar work by Duraes et al. [130]. This can be explained by an increase in completeness of reaction with higher aluminum content. The increase in the thermal conductivity due to the presence of a higher amount of metallic phases in over aluminized samples (Al rich samples) may have also contributed to the increase in the pressure release rate due to enhanced heat transfer [131]. Fig. 7.3 shows the dynamic pressure graphs with the addition of nano Al and PVP coated Fe_2O_3 nanotube oxidisers for comparison. From the values shown in Table 7.1, pure nano Al is clearly seen to be the most reactive having the highest $P_{\max}$ and dP/dt values attained. The iron oxide oxidizers on the other hand, did not ignite during the test. This experiment has shown that the

amount of Al played a predominant role in determining the overall amount and rate of pressure release in thermite system with the greater reactivity of Al with air as the primary effect. With increased amount of Al, the heat and mass transfer phenomena are enhanced through the increase in thermal conductivity and the melt amount which could be the secondary effect, resulting in an overall increased reactivity [131].

Fig. 7.3. Dynamic pressure measurements with pure nano Al and PVP coated Fe₂O₃ nanotubes as control reference.

Table 7.1. Summary of results obtained from Parr dynamic pressure measurement

All values are the average of multiple measurements taken.

Sample	Dynamic pressure results	
	$(dP/dt)_{\max}$ (kPa/msec)	$P_{\max}$ (kPa)
F/O ratio 0.4	0.876	90
F/O ratio 1.0	6.403	180
F/O ratio 1.3	7.985	252
F/O ratio 1.6	15.93	297
Pure Nano Al	77.686	597
PVP coated Fe_2O_3	Did not ignite	Did not ignite

Fig. 7.4 shows the ignition wire test results as a function of equivalence ratio. There is a sharp reduction in ignition temperature and t_{delay} from equivalence ratio of 0.4 to 1.0 and being less accentuated thereafter with Φ from 1.0 to 1.5. The values seem to reach saturation with more or less similar ignition temperatures and t_{delay} . It was observed from Fig. 8.4(a) that the optical intensity (light released upon ignition) increases with equivalence ratio. This is in good agreement with the DSC and dynamic pressure results whereby the heat released, maximum pressure and light output increases with

increasing Al content. Al having a higher energy content compared to Fe_2O_3 inevitably increases the overall energy output (in terms of heat, pressure and light) of the thermite system. Kinetic parameters such as T_{ig} , t_{delay} and T_p on the other hand, approach a point of saturation the addition of excess Al content from $\Phi = 1.0$ to 1.5.

a)

Fig. 7.4. (a) Ignition wire thermographs with varying equivalence ratio of self assembled Al nanoparticles – Fe_2O_3 nanotubes. (b) T_{ig} vs Φ plot and (c) t_{delay} vs Φ plot.

7.2 Summary-- Varying fuel to oxidizers ratio

The equivalence ratio was found to be a strong function in influencing the overall performance of the nanothermites. A general quasi- linear increase with equivalence ratio was observed in both the DSC and pressure measurement graphs. (in terms of enthalpy, T_p , dP/dt and P_{max})

In DSC, T_p and enthalpy of reaction increases with Al content can be explain by having a lower Fe_2O_3 oxidizers content, the molten Al will need to diffuse greater distance to come in contact with enough molar ratio between

Al and Fe_2O_3 for the reaction to occur. The increase in rate of pressure released (dP/dt) with equivalence ratio was explained by the increased thermal conductivity due to the presence of a higher amount of metallic phases in over aluminized samples (Al rich samples). This has contributed to the increase in the pressure release rate due to enhanced heat transfer.

A sharp reduction in ignition temperature and t_{delay} from equivalence ratio of 0.4 to 1.0 and being less accentuated thereafter with Φ from 1.0 to 1.5 in the ignition wire test. The values seem to reach saturation with more or less similar ignition temperatures and t_{delay} . This may imply an optimum Tig and t_{delay} have been reached with the increase of Al content.

The following chapter will discuss on the different synthetic methods in affecting the reactivity of nanoenergetics. The 2 main comparative studies will be between (1)solvent mixed and surfactant assembled Fe_2O_3 nanotubes with Al nanoparticles and (2) APTES-assisted and surfactant assembled Fe_2O_3 nanotubes with Al nanoparticles.

CHAPTER 8. EFFECTS OF DIFFERENT SYNTHESIS METHODS IN $\text{Al-Fe}_2\text{O}_3$ NANOENERGETICS

8.1 Interfacial contact effects of Fe_2O_3 nanotubes -Al nanoparticles --- Surfactant self assembly vs solvent mixing

8.1.1 Comparison of reaction kinetics performance -- Surfactant self assembly vs solvent mixing

Different methods of synthesizing the thermite systems will lead to various interfacial contacts between the fuel and oxidizers particles.[94] Synthesis methods attempted by various research groups have been summarized in Chapter 2 (refer to Table 2.2). In this study, the surfactant self assembled system was compared with the solvent mixed system and the mechanism of how intimate contacts played an important role in improving the overall energetic performance was deduced. The experimental procedure for the preparation of surfactant self assembled Fe_2O_3 nanotubes with Al nanoparticles have been previously presented in Chapter 5. Physically solvent-mixed Al nanoparticles with Fe_2O_3 nanotubes thermite samples were also prepared using 2-propanol as the solvent and ultrasonication mixing for about 1hr as a control reference to create a randomly mixed sample for comparison. Both samples were prepared with an equivalence ratio of 1.0. The images of the as-synthesized surfactant self assembled Fe_2O_3 nanotubes

with Al nanoparticles are compared with solvent mixed mixture as shown in Fig.8.1 and Fig. 8.2. (author's published articles [58, 113])

Fig. 8.1 (a) Field emission SEI image (b), (c) and (d) TEM images of self assembled Fe_2O_3 -Al nanothermite. (author's published articles [58, 113])

Little or no
interfacial
contacts

Fig. 8.2 SEM (a) and TEM (b), (c) and (d) images of solvent mixed Fe_2O_3 nanotubes- Al nanoparticles. (authors's published articles [58, 113])

Clearly from the images in Figures 8.1 and 8.2, the quality of mixing for the two systems is different to a great extent. For the surfactant self assembled system, high interfacial contacts between the Fe_2O_3 nanotubes and Al nanoparticles were clearly seen. On the other hand, the physically solvent-mixed sample showed negligible interfacial contacts between the oxidizer and fuel particles. Distinct segregated agglomeration of respective Al and Fe_2O_3 clusters were observed throughout the sample.

Reactivity studies comparing the solvent mixed and surfactant self assembled system was done using ignition wire, DSC and Parr dynamic pressure measurements. Some of these results have been previously presented in other chapters. Since the scope of study differs in each chapter, it will be summarized here on the emphasis between the self assembled and solvent mixed samples for better comparison. Fig. 8.3 (a) – (c) shows the DSC, ignition wire and Parr dynamic results respectively. The PVP coated Fe_2O_3 nanotubes (prepared prior to assembling with Al) were used as a control reference. The small increase in pressure for PVP coated Fe_2O_3 may be due to the heat given off by the degradation of the PVP polymer or absorbed solvent content.

a)

b)

c)

Fig. 8.3 (a) DSC ; (b) ignition wire test and (c) parr dynamic pressure measurements comparing self assembled and solvent mixed Fe₂O₃ nanotubes-Al nanoparticles.

In summary, the surfactant self assembled system has improved in performance significantly in terms of T_p in DSC analysis and P_{max} , T_{delay} and dP/dt values in Parr dynamic measurements compared to solvent mixed sample. From the DSC and pressure measurements, the PVP coated nanotubes did not contribute much in terms of heat released (absence of exotherm) and pressure rise (no ignition registered). Hence, it is reasonable to assume the

effects of PVP on the overall reactivity of the self assembled system to be negligible.

Activation energies of the self assembled ($125 \pm 3 \text{ kJ/mol}$) and solvent mixed ($158 \pm 3 \text{ kJ/mol}$) samples obtained using DSC were quantified and presented previously in Table 6.1 and 6.2. The activation energy derived for the self-assembled sample was found to be reduced by more than 30 kJ/mol as compared to the solvent mixed sample. Fig. 8.4 (a) and (b) shows the derivation of activation energy for solvent mixed sample using ignition wire test under different heating rate. The values derived were consistent with those derived from DSC measurement whereby the self-assembled sample ($144 \pm 4 \text{ kJ/mol}$) had much lower average activation energy than solvent mixed sample ($158 \pm 3 \text{ kJ/mol}$) with enhanced reactivity.

a)

b)

Fig. 8.4 (a) Ignition wire test of solvent mixed Al nanoparticles with Fe_2O_3 nanotubes under different heating rates and (b) Starink plot for the derivation of activation energy.

8.1.2 Post thermal studies – Surfactant self assembly vs solvent mixing

In this section, further analysis was done to study the contributing factors and mechanism leading to such enhanced improvements. Post thermal studies were conducted at different temperatures to compare the reaction products formed in the self assembled and solvent mixed samples using XRD (Fig. 8.5). Both the samples underwent similar phase changes with a distinct difference at temperature of $\sim 600^{\circ}\text{C}$. For the assembled sample, complete conversion of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ was seen at 600°C but the solvent mixed sample showed residual Fe_2O_3 phase even at a higher temperature of 620°C . The self assembled system seemed to favor the earlier conversion towards the Fe_3O_4 which subsequently led to an earlier exothermic reaction of $\text{Fe}_3\text{O}_4 + \text{Al} \rightarrow \text{Fe} + \text{FeAl}_2\text{O}_4$. The phase changes for each temperature interval are summarized in Table 8.1.

Fig. 8.5 XRD patterns of the reacted products obtained at different temperatures for (a) surfactant self assembled and b) solvent mixed nanothermites.

Table 8.1 Summary of the phase changes at different temperatures for self assembled and solvent mixed Al nanoparticles with Fe₂O₃ nanotubes samples.

The highlighted temperature interval refers to the main differences in the 2 reaction routes.

Temperature interval	Self assembled Al nanoparticles with Fe ₂ O ₃ nanotubes	Solvent mixed Al nanoparticles with Fe ₂ O ₃ nanotubes
350 °C to 600 °C	$9\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow 6\text{Fe}_3\text{O}_4 + \text{Al}_2\text{O}_3$	$9\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow 6\text{Fe}_3\text{O}_4 + \text{Al}_2\text{O}_3$
600 °C to 820 °C	$1/2\text{Fe}_3\text{O}_4 + \text{Al} \rightarrow \text{Fe} + 1/2\text{FeAl}_2\text{O}_4$	$9\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow 6\text{Fe}_3\text{O}_4 + \text{Al}_2\text{O}_3$ (additional reaction due to previous incomplete conversion) ↓ $1/2\text{Fe}_3\text{O}_4 + \text{Al} \rightarrow \text{Fe} + 1/2\text{FeAl}_2\text{O}_4$
820 °C to 950 °C	$1/2\text{Fe}_3\text{O}_4 + \text{Al} \rightarrow \text{Fe} + 1/2\text{FeAl}_2\text{O}_4$ $\text{Fe}_3\text{O}_4 + 2/3\text{Al} \rightarrow 3\text{FeO} + 1/3\text{Al}_2\text{O}_3$	$1/2\text{Fe}_3\text{O}_4 + \text{Al} \rightarrow \text{Fe} + 1/2\text{FeAl}_2\text{O}_4$ $\text{Fe}_3\text{O}_4 + 2/3\text{Al} \rightarrow 3\text{FeO} + 1/3\text{Al}_2\text{O}_3$
950 °C to 1200 °C	$\text{FeO} + \text{Al}_2\text{O}_3 \rightarrow \text{FeAl}_2\text{O}_4$	$\text{FeO} + \text{Al}_2\text{O}_3 \rightarrow \text{FeAl}_2\text{O}_4$

Fig. 8.6 and 8.7 shows the SEM images of the reaction products formed at different temperatures and schematic illustrations showing the two

systems undergoing different reaction routes. For the assembled sample, uniform melting throughout the sample was first observed at 600°C followed by the agglomeration or fusing of the particles at 820°C. Both samples showed completely deformed fused agglomerates at 950 °C and eventually forming smooth faceted micron sized crystallites. The images shown in Fig. 8.6 and 8.7 correspond well to the reaction mechanism for thermites to a recently reported in-situ TEM heating study of Al-WO₃ nanothermite system by Zachariah [132]. It was proposed that the reaction leading to such structures were formed through a reactive sintering mechanism. The reaction took place at the interface whereby the exothermic reaction led to further fusing of the adjacent particles as heat was conducted away from the interface. Upon reaching the melting point of Al, Al was rapidly delivered to the interface via strong capillary/surface tension forces initiating the reaction with surrounding Fe₂O₃ upon contact at the interface [132]. Higher interfacial contacts in the self assembled system resulted in uniform melting of Al throughout the whole sample as seen in Fig. 8.6 (a) at 600°C. This decreased the particle-particle distance to allow the reaction to take place at a lower temperature. In comparison, segregated melting regions were observed for the randomly solvent-mixed sample. Higher temperature was needed by the molten Al to cover additional diffusion distance in order to reach sufficient amount of iron oxide in equivalence ratio before reaction could take place. This is in good agreement with the reactivity studies done on these systems whereby the self

assembled system showed significant enhancement as compared to the random solvent mixed sample.

a)

b)

Fig. 8.6 (a) SEM images and (b) schematic illustration of reaction products formed at different temperatures for self assembled Al nanoparticles with Fe_2O_3 nanotubes.

a)

b)

Fig. 8.7 (a) SEM images and (b) schematic illustration of reaction products formed at different temperatures for solvent mixed Al nanoparticles with Fe_2O_3 nanotube.

In addition, distinct fracturing of the nanotubes was also seen in the self assembled system at 820°C. However, this was not observed in the solvent mixed sample at the same temperature. It is believed that the high intimate contacts resulted in fracturing of the nanotubes due to the rapid heat propagation upon reaction in the self assembled system, and this promoted an accelerated propagation of heat throughout the whole sample. For the randomly solvent mixed sample, no fracturing of the tubes was seen. This means that the molten Al would need to cover additional distance in order to reach segregated regions of Fe_2O_3 agglomerates as seen at 820°C with globules formed only at segregated regions. The proposed mechanism is illustrated in Fig. 8.8. (author's published article[113])

Fig. 8.8 Schematic illustration showing an exaggerated perspective that demonstrates random versus ordered assembly. (author's published article[113])

8.2 Improved highly selective assembly of Fe₂O₃ nanotubes–Al nanoparticles --- APTES –assisted self assembly vs surfactant self assembly

The current surfactant self-assembled system still shows some signs of randomness in the assembly between Fe₂O₃ and Al. This may be due to the pyridyl group in the PVP molecule that binds to both Fe₂O₃ and Al particles [56]. Coupling of two Fe₂O₃ nanotubes oxidizers might restrict the binding of nearby Al nanoparticles due to steric size effect of the larger size nanotubes as shown schematically in Fig. 8.9. Hence, in order to overcome this, APTES-assisted assembled system was attempted to investigate this alternative assembling method in the overall reactivity of Al nanoparticles-Fe₂O₃ nanotubes system. The experimental details will be presented in Section 8.2.1.

Fig. 8.9 Steric hindrance of Al nanoparticles by Fe_2O_3 nanotubes using the surfactant assembly approach.

8.2.1 Experimental procedure in APTES-assisted self assembly

For the APTES- assisted self-assembled system, the whole process consists of 3 main steps as summarized in Fig. 8.10 a) coating of the Fe_2O_3 nanotubes with aminopropyltriethoxysilane (APTES from Sigma Aldrich), b) functionalization of Al nanoparticles with carboxyl ending group using oxalic acid, and finally c) assembling the Al nanoparticles with Fe_2O_3 based on electrostatic attraction between the two affinity groups. The surface functionalized Al and Fe_2O_3 particles will be uniquely attached to each other and oppositely repel the same species leading to a highly selective assembled system. The first step involving the grafting of Fe_2O_3 nanotubes with APTES was done with accordance to similar work reported by Wu et al. [133] on the

grafting of silica nanoparticles with APTES to form a 1st generation dendrimer. APTES (0.946g, 0.0043mol) and Fe₂O₃ nanotubes (0.25g, 0.00157mol) were added to a dispersion containing 74mL of toluene flowing with nitrogen for 12h at 95°C. After the reaction, the aminated Fe₂O₃ were purified with repeated cycles of centrifugation and re-dispersed in methanol and dried in an oven for 12hrs at 60°C. Functionalization of Al with oxalic acid was done by ultrasonication of Al (0.5g, 0.0185mol) with oxalic acid (0.167g, 0.00185mol) in acetone for 1hr. Subsequent centrifugation and re-dispersion in acetone was also done several times and then dried in an oven for 12hrs at 60°C. Finally, stoichiometric equivalence ratio of Al and Fe₂O₃ were ultrasonicated for 1hr in acetone and left to self assemble for 72 hrs in a test tube. The sample was prepared with the equivalence ration of 1.0. The composition was confirmed by TOPAS analysis shown in Appendix A, Fig. S4.

The surface groups of Fe₂O₃ nanotubes was characterized by Fourier-transform infrared (FTIR) spectroscopy to confirm the attachment of APTES onto the Fe₂O₃ nanotubes. The results are shown in Fig. 8.11(a). The covalent bonding of aminopropylsilane groups is by a condensation process whereby the ethanol molecule is removed and entrapping each nanoparticle [134]. The adsorption peak at 2927 cm⁻¹ is the characteristic adsorption bond of CH₂ stretching from the APTES ending group. Deformation bending of the free

amine groups was also confirmed by the adsorption peaks at 1559 and 1488 cm^{-1} [134]. Disappearance of the ethoxy, (2969 and 2886 cm^{-1}) C-O (1486 and 1444 cm^{-1}) and Si-O-C (1167, 1103, 1079 and 957 cm^{-1}) groups clearly indicated the removal of ethanol to form the new bonds Fe-Si-O at 1214 and 1150 cm^{-1} [135]. The FTIR spectrum of toluene was also provided as a control reference as it was used as the solvent during the grafting process.

FTIR analysis was also done for the functionalized Al nanoparticles and the results are shown in Fig. 8.11(b). Disappearance of the C-OH bonds was clearly seen at wavelengths ranging from 1110 cm^{-1} to 1450 cm^{-1} . The OH stretch due to the carboxylic group disappeared, which indicates that di-substitution of the oxalic carboxylic groups had occurred. This is in agreement with similar work done by Cecilia et al. [136] whereby di-substitution of oxalic acid molecules are preferred as it requires much lower binding energy for complexation process than mono-substitution. Moreover, the new Al-O-C bond formed at 1724 cm^{-1} [137] confirmed the attachment of oxalic acid molecule onto the surface of the Al nanoparticles. FTIR spectrum of physically mixed oxalic acid with Al was also provided as a control reference to confirm that all physically adhered oxalic acid was washed away during the functionalization process for the functionalized Al samples.

a)

b)

c)

Fig. 8.10 Illustration showing the (a) grafting of APTES molecule onto Fe₂O₃ nanotubes surface; (b) functionalization of Al nanoparticles with oxalic acid and (c) overall self- assembled Fe₂O₃–Al nanothermite using organosilane grafting technique.

Fig. 8.11. FTIR spectra of a) bare Fe₂O₃ nanotubes, Fe₂O₃ nanotubes grafted with APTES, APTES and toluene and b) functionalized Al with oxalic acid, physical mixed oxalic acid with Al, pure nano Al and oxalic acid.

8.2.2. Comparison of reaction kinetics performance --- APTES – assisted self assembly vs surfactant self assembly

This section will discuss on the reactivity of assembled nanothermites with the solvent mixed sample as a control reference. Microscopy images of the APTES-assisted self assembled Al nanoparticles-Fe₂O₃ nanotubes are shown in Fig. 8.13. As shown in Fig. 8.1 and 8.2, clear distinct differences are observable between random physical solvent mixed and assembled samples. Distinct separated agglomerates of the fuel and oxidizer particles are seen in the solvent mixed sample compared to the surfactant assembled one, indicating significant differences in the interfacial contact between the fuel and oxidizers. Although there are clear differences between random physical solvent mixed and surfactant assembled sample, no observable differences in terms of interfacial contacts were seen for the APTES assisted and surfactant self assembled systems. Both assembled systems showed close contacts between the fuel and oxidizer particles.

The TG graph of the APTES-assisted assembled Al-Fe₂O₃ is shown in Fig. 8.12. A weight drop of 12.5wt% was observed indicating the amount of binding agents present which is comparable to the surfactant assembled system of 11.3wt%.

Fig. 8.12. TG graph showing an initial weight drop of ~12.5 wt% corresponding to the amount of binding agents present.

Fig. 8.13 (a), (b) TEM and (c) SEM images of the APTES-assisted self assembled Fe₂O₃ nanotubes –Al nanoparticles.

Fig. 8.14 shows the DSC graphs of the samples prepared by different methods of synthesis. DSC graphs of APTES grafted Fe_2O_3 nanotubes and COO^- functionalized Al is also presented as control references. It was confirmed that the binding agents itself did not contribute much in terms of heat released (no exotherms observed) or in terms of any peak shifts. The melting point of Al for the COO^- surface functionalized nano Al is the same as pure nano Al.

It is noted that for the APTES-assisted assembled sample, the exothermic reaction peak was observed to occur even prior to the melting of the nano Al, with the exotherm convoluted with the endotherm melting of the nano Al, indicating a solid-solid phase reaction occurring in this system. As compared to the polyvinyl pyridine polymer linkage used in the surfactant assembled system, the inter-particle length would be significantly reduced in the case of the APTES-assisted assembled system adopting molecular linkage. Thus, the diffusion distance between the fuel and oxidizer particles was significantly reduced. It has been reported that an increase in 2nm of diffusion distance can increase the diffusion coefficient by an order of magnitude [138]. Using molecular interactions for assembling heterogeneous energetic materials can significantly reduce this diffusive distance required for reactions to occur at the interface as compared to the longer polymeric linkers. This may result in a much closer inter-particle distance between the fuel and oxidizers attributing to the early reaction seen in the DSC graph.

Fig. 8.14 DSC graphs showing the thermal transitions of the various samples.

The pressure measurement results for the various thermite systems are shown in Fig. 8.15. The results were consistent with that obtained from the DSC analysis. A clear trend of the higher reaction rate (dP/dt) for both self-assembled thermite systems was visible from the comparison of the pressure traces. It is seen that the APTES-assisted self-assembled thermite achieved the largest $P_{\max}$ generated in the shortest time. The rate of pressure increase (dP/dt) was also improved by more than 7.6 times as compared to the solvent mixed reference and around 3 times more than the surfactant assembled sample. The time needed to reach max pressure ($t_{\max}$) and the highest pressure reached ($P_{\max}$) were also improved significantly as compared to the surfactant assembled and solvent mixed samples.

Ignition wire tests were also conducted and the results are presented in Fig. 8.16. The lowest T_{ig} and t_{delay} are observed for the APTES-assisted nanothermite followed by the surfactant assembled and solvent mixed respectively. This further supports the superior reaction kinetics achieved for the self-assembled nano-thermite using APTES grafting technique.

Fig. 8.15 Dynamic pressure measurements of various nanothermites prepared by different methods.

(a)

Fig. 8.16 Ignition wire test (a) graphs and (b) results obtained for the various nanothermites prepared by different methods.

Due to the complexity in the convolution between the exothermic and endothermic peaks, the exact peak reaction temperature was difficult to be derived using the DSC technique. Thus, in the case of the APTES-assisted self assembled nanothermite, the ignition wire tests were used to calculate its activation energy. The activation energy derived from ignition wire test of APTES-assisted self assembled nanothermite is showed in Fig. 8.17.

a)

b)

Fig. 8.17 (a) Ignition wire test graphs and b) corresponding Starink plot of APTES-assisted nanothermite.

The activation energy derived is consistent with the results obtained from the thermal initiated experiments (DSC, arr dynamic and ignition wire). The average activation energy is taken from the T_{ave} graph and computed with the gradient using the Starink equation. 3 runs were done for each heating rate with the respective activation energies derived for each run. The mean and standard deviation are then determined from these runs. The APTES-assisted Al nanoparticles with Fe_2O_3 nanotubes have the lowest activation energy (derived from ignition wire test) of 135 ± 5 kJ/mol followed by surfactant self assembled of 145 ± 4 kJ/mol and solvent mixed nanothermite of 158 ± 3 kJ/mol. The following section will further discuss on the post thermal studies on the reacted products of APTES-assisted nanothermite to better understand the reaction path taken and possible reasons to an enhanced reactivity in this system.

8.2.3 Post thermal studies – APTES-assisted assembly vs surfactant assembly

Post thermal study on the reacted products was conducted to investigate the reaction routes taken during reaction. Fig. 8.18 shows the X-ray diffraction patterns of the reacted products at selected temperatures (prior and after the main reaction) of the APTES-assisted assembled sample. Table 8.2 summarized the reaction routes of the 2 systems highlighting the main reaction difference. The reacted products for the APTES-assisted assembled sample were retrieved and imaged using SEM, and the images are shown in Fig. 8.19. The microscopy images in Fig.8.19 did not show any observable differences in microstructure changes compared to surfactant self assembled sample. (cross-ref Fig. 8.6(a))

(b)

Fig. 8.18. X –ray diffraction patterns of a) APTES-assisted self assembled, b) surfactant self nanothermites at various temperatures. *Note the distinct differences in reaction products formed at 820 °C.*

Table 8.2 Summary of the phase changes at different temperatures for APTES-assisted and surfactant assembled Al nanoparticles with Fe₂O₃ nanotubes samples. *The highlighted temperature interval refers to the main differences in the 2 reaction routes.*

Temperature interval	APTES-assisted assembled Al nanoparticles with Fe ₂ O ₃ nanotubes	Surfactant assembled Al nanoparticles with Fe ₂ O ₃ nanotubes
350 °C to 600 °C	$9\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow 6\text{Fe}_3\text{O}_4 + \text{Al}_2\text{O}_3$	$9\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow 6\text{Fe}_3\text{O}_4 + \text{Al}_2\text{O}_3$
500 °C to 820 °C	$1/2\text{Fe}_3\text{O}_4 + \text{Al} \rightarrow \text{Fe} + 1/2\text{FeAl}_2\text{O}_4$ (complete reaction with no excess residual Fe ₃ O ₄ @ 820 °C)	$1/2\text{Fe}_3\text{O}_4 + \text{Al} \rightarrow \text{Fe} + 1/2\text{FeAl}_2\text{O}_4$ (residual Fe ₃ O ₄ present @ 820 °C)
820 °C to 950 °C	$1/2\text{Fe}_3\text{O}_4 + \text{Al} \rightarrow \text{Fe} + 1/2\text{FeAl}_2\text{O}_4$ $\text{Fe}_3\text{O}_4 + 2/3\text{Al} \rightarrow 3\text{FeO} + 1/3 \text{Al}_2\text{O}_3$	$1/2\text{Fe}_3\text{O}_4 + \text{Al} \rightarrow \text{Fe} + 1/2\text{FeAl}_2\text{O}_4$ $\text{Fe}_3\text{O}_4 + 2/3\text{Al} \rightarrow 3\text{FeO} + 1/3 \text{Al}_2\text{O}_3$
950 °C to 1200 °C	$\text{FeO} + \text{Al}_2\text{O}_3 \rightarrow \text{FeAl}_2\text{O}_4$	$\text{FeO} + \text{Al}_2\text{O}_3 \rightarrow \text{FeAl}_2\text{O}_4$

Fig. 8.19. SEM images of APTES-assisted nanothermite at various temperatures.

The APTES-assisted assembled sample was found to have a different reaction phase in particular, at 820 °C. Fe_3O_4 peak was not seen at 820 °C after the main exothermic reaction in DSC whereby on the contrary, it was still present in the case of surfactant self assembled and solvent mixed sample. This indicates that all of the Fe_3O_4 (complete reaction) was consumed during the exothermic reaction in APTES-assisted self assembled sample. This solid-solid state reaction was seen to occur prior to Al melting with a lower activation energy which is only available in the APTES-assisted sample. For the surfactant system, exothermic reaction occurred only after the melting of the Al core and subsequently diffusion of the Al towards the surrounding Fe_2O_3 oxidizers. Since the growth of product is governed by the diffusion of corresponding reactant atoms, the reaction between Fe_3O_4 and Al was seen to occur at a much lower temperature and towards completion for the APTES-assisted assembled sample. This enhanced reactivity can be explain by the shorter molecular linkers (coupled APTES and COOH molecule at $\sim 5\text{-}10 \text{ \AA}$ in length [139]) compared to using longer polymer chains (P4VP; Mw= 60kg/mol contour length of 145nm [140]) linkers between the fuel and oxidizer particles. As mentioned earlier, a mere 2nm increase in diffusion length will increase the diffusion coefficient by an order of magnitude [138]. This will greatly hasten the reaction between the fuel and oxidizers resulting in an earlier exothermic reaction in the APTES-assembled system. Ideally, rate of diffusion will be fastest with direct contacts between the fuel and oxidizer particles but it has been demonstrated that without the aid of linkers for

assembling, segregated portions of Al and Fe_2O_3 (in the case of randomly solvent mixed sample) agglomerates occurred and increased the effective diffusion distance between the two.

8.3 Summary—Effects of different synthetic methods

A comparison between surfactant self-assembled and solvent mixed Al nanoparticles with Fe_2O_3 nanotubes was done. The attempt was to create two extreme cases whereby one is randomly mixed and the other highly organized and intimately mixed. The intimately mixed surfactant assembled sample exhibits significant enhancement in energetic properties compared to the randomly mixed one. Reaction routes taken between the 2 were also showed to be different. The surfactant assembled system favored the complete conversion of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ in the initial stage which subsequently leads to an earlier exothermic reaction of $\text{Fe}_3\text{O}_4 + \text{Al} \rightarrow \text{Fe} + \text{FeAl}_2\text{O}_4$. This is mainly due to the higher interfacial contacts between the fuel and oxidizer particle hastening the diffusion process resulting in the earlier conversion of the phases which subsequently resulted in earlier exothermic reaction.

An improved assembling method using APTES via electrostatic attraction between oppositely charged ligands (APTES and oxalic acid) was

successfully attempted and compared with the surfactant assembled system. Energetic performance was seen to be enhanced with the APTES assisted improved method due to the shorter molecular linkers used compared to the polymeric surfactant assembling method.

CHAPTER 9. CONCLUSION AND RECOMMENDATIONS

9.1 CONCLUSION

In this study, self assembly methods were used to produce intimately mixed nanothermites with a novel combination of Fe_2O_3 nanotubes (oxidizers) and spherical nano Al particles (fuel). This study has detailed the study of different parameters (e.g. oxidizers' morphologies, reactants' size, equivalence ratio and methods of synthesis) in affecting the overall reaction kinetics of such assembled systems. Reaction kinetics using thermal initiation methods (DSC and ignition wire tests) were also derived and mechanistic studies on the reaction routes were also performed for the various systems.

The important findings for this study are summarized as follows:

1. Nanotubular oxidizer morphology (aspect ratio of 3:1) was found to be favored in enhancing energetic performance compared to nanorods (aspect ratio of 3:1) and nanospherical particles (APS=50nm) with the mass and equivalence ratio kept constant. T_{ig} (ignition temperature needed for reaction to occur) and t_{delay} (delay time needed for ignition to occur) was improved by at least 1 factor compared to both nanorods and nanospheres oxidizers. Rate of pressure released (dP/dt) and

maximum pressure (P_{max}) reached upon reaction was also improved by a few folds by the nanotubular oxidizers. (e.g. dP/dt increased by 28 folds and P_{max} increased by 2.8 folds compared to nanospheres)

Two contributing factors leading to nanotubular oxidizers having better reaction kinetics have also been proposed. The nanotubes favored the complete conversion of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ in the initial stage which subsequently led to an earlier exothermic reaction of $\text{Fe}_3\text{O}_4 + \text{Al} \rightarrow \text{Fe} + \text{FeAl}_2\text{O}_4$. The fracturing of the nanotubes upon thermite reaction formed localized hot spots for rapid propagation of heat resulting in a sharp and steep exotherm compared to a more gradual and broadened exotherms for the nanorods and nanospheres.

The increase in the effective number of nanospheres present may have affected the assembling process and reduced its overall reactivity. With comparison between nanotubes and nanorods, although there is an increase in the no. of nanotubes compared to nanorods (in terms of actual particles present) within the same mass, the effect may be less dominant compared to the fracturing of the tubes resulting in rapid heat propagation which is only solely observed in the nanotubes systems.

2. The energetic performance of thermite composites was found to be a strong function of the reactants' size. These findings have shown that the reaction kinetics of thermite composite materials can be easily improved by reducing the reactive components to nano scale. Nano- and micron-thermites were found to undergo different reaction routes. It was found that further decomposition of Fe_3O_4 phase to the more stable FeO phase at higher temperature was necessary in the case for micron thermite before undergoing the main exothermic thermite reaction
3. A general quasi- linear increase in P_{max} , t_{max} and dP/dt values with equivalence ratio was observed. This behaviour was attributed mainly by the increasing metal percentage which in turn increased the thermal conductivity of the overall sample. However, this increase was compromised with a delayed exothermic reaction at a higher T_p value.
4. Al with Fe_2O_3 nanothermite system prepared by self-assembly has been shown to exhibit significant improvements in reaction kinetics as compared to nano- and micro-scale thermite samples prepared by simple physical solvent-mixing. By increasing the intimacy between the fuel and oxidizer by self assembly, solid state diffusion between the

reactants is significantly enhanced. (self assembled nanothermite dP/dt and P_{max} both increased by 1.7 folds compared to physically mixed nanothermite. DSC reaction temperature was lowered by 84°C for the self assembled sample compared to physically mixed nanothermite.) A schematic reaction mechanism has also been proposed illustrating the random and ordered assembly.

5. An improved assembling method using APTES via electrostatic attraction between oppositely charged ligands was attempted to study the effects of using different synthesis methods. The APTES-assisted Fe_2O_3 nanotubes with Al nanoparticles system was observed to produce better energetic performance compared to the surfactant self assembled and solvent mixed samples. This could be explained to the shorter interaction distance between the fuel and oxidizers promoting a solid (Al)-solid (Fe_2O_3) phase reaction without undergoing prior melting of Al.

9.2 RECOMMENDATIONS

The objective of this research was to study the different parameters in affecting the overall reaction kinetics of Al-Fe₂O₃ thermite system. During the course of this work, future work has been noted to give a better understanding and the following recommendations are made.

It will be beneficial to conduct in-situ microscopy on a heating stage to capture real time images during the reaction between the 2 components (fuel and oxidizers). However, such attempt may prove to be difficult and dangerous since the reaction is highly exothermic (temperature rise up to 3000K upon reaction) and might damage the whole TEM equipment. Similar studies by Zachariah et. al. [111] investigated the in-situ reaction between Al-WO₃ nanothermite under rapid heating using a heating stage TEM and concluded the reactive sintering between the 2 components. This correlates well in our post-thermal studies whereby the samples are retrieved at respective temperature intervals to study the state after reaction. Such study is easier to manage and safety concerns are reduced.

This study can be extended to other combinations of thermite systems other than Al-Fe₂O₃ for a broader base of applications. (eg, gas generative thermites, boron fuel as a potential replacement for Al etc.) By doing so, it

has the potential to tailor combustion performance from the bottom up to achieve the desired application

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APPENDIX

a)

b)

c)

Fig.S1 shows Rietveld refinement of the XRD plots of surfactant self assembled Al nanoparticles – Fe_2O_3 (a) nanotubes, (b) nanorods and (c) nanospheres. The calculated (red) and measured (blue) XRD patterns, where the agreement identify the phase and calculate the individual components in %mass. All samples are prepared at the equivalence ratio of 1.0.

a)

b)

Fig.S2 shows Rietveld refinement of the XRD plots of a) solvent mixed Al nanoparticles – Fe_2O_3 nanotubes and (b) solvent mixed micron Al granules- micron Fe_2O_3 granules. All samples are prepared at the equivalence ratio of 1.0

a)

b)

c)

d)

Fig.S3 shows Rietveld refinement of the XRD plots of surfactant self assembled Al nanoparticles – Fe_2O_3 nanotubes in equivalence ratio of a) 0.4 b) 1.0 c) 1.3 and d) 1.5.

Fig.S4 shows Rietveld refinement of the XRD plot of APTES-assisted self assembled Al nanoparticles – Fe_2O_3 nanotubes in equivalence ratio of 1.0.

Volume and Area calculations of individual particle

$$\begin{aligned}
 \text{Volume of a nanotube} &= \pi (r_{\text{outer}}^2 - r_{\text{inner}}^2) \times h \\
 &= \pi (32.5 \times 10^{-9})^2 - (27.5 \times 10^{-9})^2 \times (200 \times 10^{-9}) \\
 &= 1.88 \times 10^{-22} \text{ m}^3
 \end{aligned}$$

$$\begin{aligned}
 \text{Surface area of nanotube} &= 2\pi(R^2 - r^2) + 2\pi h(R + r) \\
 &= 7.73 \times 10^{-14} \text{ m}^2
 \end{aligned}$$

$$\begin{aligned}
 \text{Volume of a nanorod} &= \pi r^2 \times h \\
 &= \pi (32.5 \times 10^{-9})^2 \times (200 \times 10^{-9}) \\
 &= 6.64 \times 10^{-22} \text{ m}^3
 \end{aligned}$$

$$\begin{aligned}
 \text{Surface area of nanorod} &= 2\pi(R^2) + 2\pi h(R) \\
 &= 4.75 \times 10^{-14} \text{ m}^2
 \end{aligned}$$

$$\begin{aligned}
 \text{Volume of a nanosphere} &= \frac{4}{3} \pi r^3 \\
 &= \frac{4}{3} \pi (25 \times 10^{-9})^3 \\
 &= 6.54 \times 10^{-23} \text{ m}^3
 \end{aligned}$$

$$\begin{aligned}
 \text{Surface area of a nanosphere} &= 4 \pi r^2 \\
 &= 7.85 \times 10^{-15} \text{ m}^2
 \end{aligned}$$

Morphology	Area (m ²)	Volume(m ³)
nanotube	7.73×10^{-14}	1.88×10^{-22}
nanorod	4.75×10^{-14}	6.64×10^{-22}
nanosphere	7.85×10^{-15}	6.54×10^{-23}

DSC Baseline construction routine

An example of the raw data presented for the surfactant assembled Al-Fe₂O₃ nanotubes using the Mettler Toledo Simultaneous DSC-TGA is shown below with thermal drifting causing a non linear baseline. The empty alumina crucible curve (black curve) was also presented as a baseline reference. It is clearly seen that the surfactant assembled Al-Fe₂O₃ nanotubes DSC curve comprises of 1 distinct endothermic peak and 1 exothermic peak.

Baseline correction is necessary for better comparative studies and it was done using a best polynomial fit (red curve) to the curve and subtracting the polynomial curve shown below. After subtraction, further baseline refining was done using Origin baseline correction tool.

All the values using DSC (T_p , enthalpy) has been selected based on the raw data and not the subtracted curve shown above. Thus, the baseline correction will not affect the values presented in the thesis.

PUBLICATIONS

- (1) **J.L. Cheng**, H.H. Hng, Y.W. Lee, S.W. Du, N.N. Thadhani, Kinetic study of thermal- and impact-initiated reactions in Al-Fe₂O₃ nanothermite, *Combustion and Flame*, 157 (2010) 2241-2249.
- (2) **J.L. Cheng**, H.H. Hng, H.Y. Ng, P.C. Soon, Y.W. Lee, Synthesis and characterization of self-assembled nanoenergetic Al-Fe₂O₃ thermite system, *Journal of Physics and Chemistry of Solids*, 71 (2010) 90-94.
- (3) **J.L. Cheng**, H.H. Hng, H.Y. Ng, P.C. Soon, Y.W. Lee, Improved thermal properties of Al powders coated with submicron-sized hollow nickel particles, *Journal of Materials Research*, 24 (2009) 3220-3225.
- (4) **J.L. Cheng**, H.H. Hng, H.Y. Ng, P.C. Soon, Y.W. Lee, Deposition of nickel nanoparticles onto aluminum powders using a modified polyol process, *Materials Research Bulletin*, 44 (2009) 95-99.

AWARDS

- (1) **Young Scientist award for outstanding paper** contributed at the E-MRS 2009 Symposium D - Nano-scale Energetic Materials: Fabrication, Characterization and Molecular Modeling, held in Strasbourg, France.

- (2) **Ian Ferguson Postgraduate Fellowship recipient** (2008), research attachment at Georgia Institute of Technology, USA working under Professor Naresh Thadhani.