COMPARATIVE STUDY OF EXOTHERMIC BEHAVIOR OF VARIOUS NANO-PARTICLES

Dissertation-II

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By

Eppaturi Venugopal Reddy

(11300582)

Under the guidance of

Manmeet Singh

(19321)

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SR.NO.	NAME OF STUDENT	REGISTRATION NO	BATCH	SECTION	CONTACT NUMBER
1	Venu Gopal Reddy Eppaturi	11300582	2013	M1326	07696030113

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DAA Nominee Name: Kamal Hassan	UID: 17469	Recommended (Y/N): NA

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CERTIFICATE

I hereby certify that the work being presented in the dissertation entitled "**Comparative study of exothermic behavior of various nano-particles**" in partial fulfillment of the requirement of the award of the Degree of master of technology and submitted to the Department of Mechanical Engineering of Lovely Professional University, Phagwara, is an authentic record of my own work carried out under the supervision of Manmeet Singh, Designation Department of Mechanical Engineering, Lovely Professional University. The matter embodied in this dissertation has not been submitted in part or full to any other University or Institute for the award of any degree.

Date:

Eppaturi Venugopal Reddy
11300582

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Date:

Manmeet Singh
(19321)

COD (ME)
Sudanshu Dogra
(16900)

The external viva-voce examination of the student was held on successfully ________________

Signature of Examiner

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ABSTRACT

The term nano energetic composite is used to characterize energetic materials consisting of nanoscale components. This is relatively a new field of research and will lead to several developments in explosives, pyrotechnics and propulsions. Nano composites are preferable over traditional energetic composites due to their relatively high energy densities and reactivity's. The most developed nanoenergetic materials are based on nano metals produced by different methods in several research laboratories. Another research area in this field is to study metal oxides which have wide range of applications. Compositions of both metal and metal oxides formulate a nanoenergetic composite that provides a better reactivity over micron sized composites.

The unique properties possessed by nano composites can only been known by studying intrinsic mechanisms of reactions at atomic level. For formulating better and improved nanocomposite that may be used in several untamed applications, better understanding of combustion characterization is required. This study compares three different nano composites to understand the combustion mechanism and to formulation of a composite that may decrease the ignition temperature, improve reactivity and provide higher energy densities for further applications.

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CHAPTER 1

1.1 INTRODUCTION

Combustion is defined as a process in which rapid chemical reaction occurs, producing both heat and light. In case of energetic composites, combustion occurs between fuel and an oxidizer. These reactions are called as redox reactions as both oxidation and reduction of reactants occur.

Energetic composite is a mixture of both fuel and oxidizer, when ignited they produces massive amount of energy. These energetic composites are classified broadly in to two types: homogenous composites and heterogeneous composites. Homogenous composites are formed by bonding both fuel and oxidizer together in a single molecule. When there is enough energy available to break the bond, then combustion starts rapidly and flame with high velocity will be produced because of very high reaction rate [ex: RDX]. While heterogeneous composites contains a mixture of the fuel and the oxidizer in a considerable ratios mixed separately using different approaches. These composites have relatively low reaction rates and flame velocities than homogenous composites, but produce very large energy densities.

The characterization of energetic materials is done by some standard mechano-chemical techniques used in equipments such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM). In addition of these techniques, energetic materials can also be further characterized in order with their sensitivities towards various stimulations to combust, and not to get ignited in the time of handling. Friction sensitivity, impact sensitivity and electrostatic discharge (ESD) sensitivity are very important aspects. Friction sensitivity can be measured in Newtons (N), whereas impact and ESD sensitivities are measured in Millijoules (mJ) or Joules (J). Increased sensitivities lead to increased reactivity and combustion speeds of the composite. The sensitivity classes of impact and friction for energetic composites are illustrated in **Table 1** [1]. Ignition temperature is also the most important factor for characterization of energetic material as initiation temperature determines whether the nano composite is suitable for particular applications.

Stimuli	Sensitivity (experimental data)	Sensitivity classes
Friction	>360 N	Insensitive
	80-360 N	Moderately sensitive
	10-80 N	Sensitive
	<10 N	Very sensitive
Impact	>40 J	Insensitive
	35-40 J	Moderately sensitive
	4-35 J	Sensitive
	<4 J	Very sensitive

Table 1. Sensitivity Classes for characterization of Energetic materials.

Energetic composites combustion start when there is enough energy available to initiate the fuel-oxidizer reaction, that energy is called as activation energy, term coined by Svante Arrhenius. He obtained a relationship between rate of reaction k(T) and activation energy given by **Eqn (1):**

$$k(T) = A*\exp(-Ea/RT) \qquad \textbf{Eqn (1)}$$

where R is given as the gas constant, T is absolute temperature, and A is the pre-exponential factor. The amount of activation energy for an exothermic reaction as a function of path of reaction is shown in **Figure 1** [2].

The initiation of these reactions is called as ignition. When ignition starts energy released by composite will be high enough to start the ignition of the surrounding composite which sustains the combustion reaction continuously. When energetic composite mixture consists of nano sized particles, then the mixtures are known as nanoenergetic composites. Heterogeneous energetic composite with nanoscale particle dimensions are called as Nanothermites /Superthermites. Since the composite mixtures have stability at room temperatures, they are also known as Metastable Intermolecular Composites [MIC]. These nanoscale mixtures consist of highly developed interface between reactive components, providing high reaction rates.

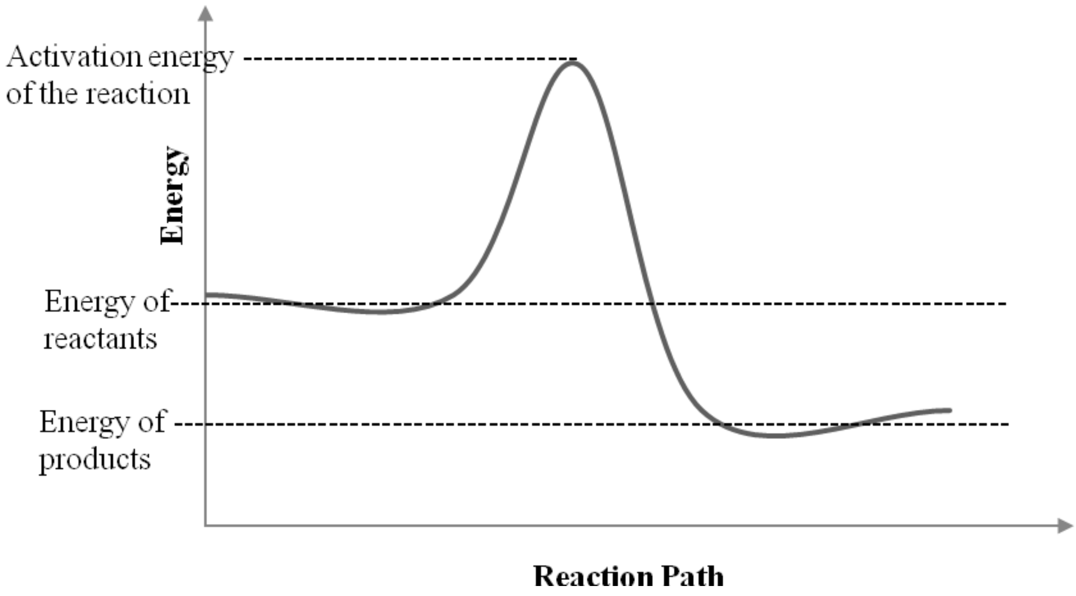

Figure 1. Activation energy for ignition of reactants in reaction path

In nanothermite reactions, commonly used fuel is nano metal particles, metal oxides are the oxidizers with primary sizes <100nm. Nanothermites with micro sized composites consists of much more homogeneous mixing between the metal and oxide, larger specific surface area results in higher evaporation and decomposition rates of oxidizers and very fast reaction rates [3] than conventional thermites. A study found that the combustion is driven convectively in nanothermites, whereas it is conductively driven in conventional thermites. Due to large characteristic length scales of diffusion in traditional micron-sized thermites, they burn at slower rates than organic energetics. But nano scale composites with reduced length scales resulting decreased diffusion lengths help to increase burn rates up to several magnitudes higher than micro scale thermites.

Aluminum [Al] is the most preferred fuel for many applications of the nanothermites because of its higher heat of combustion [~32 KJ/Kg]. In some cases Magnesium [Mg] is also preferred along with fluorine compounds when high heat of combustion is required. Since Mg nano particles are not available in the market so much, Al is preferable over Mg. But in some applications, long delay in Al ignition results in agglomeration of the molten particles and decreases the performance of energetic composite. A simple reaction between Al and metal oxide is given in **Eqn (2):**

$$M_xO_y + Al \rightarrow M + Al_2O_3 \qquad \textbf{Eqn (2)}$$

Combustion of the nanothermite composites occurs in two or more intermediate stages in which the formation of so many intermediate products and their decomposition in different gaseous media occurs [4]. A theoretical concept is explained by Boborykin et al. [5] for the formation of AlN and its further oxidation during combustion of Al and metal oxide in air. They observed AlN traces in the final products of nano composite combustion [5]. Later, role of the nitrogen in composite combustion of Al in air was proved to have no significance [6].

Nanothermite reactions are acquiring huge interest in energetic materials research because to their higher reactivity, higher energy densities and also their high adiabatic flame temperatures than traditional organic energetic materials. Unlike the organic energetic materials, nanothermite performance can easily be tuned through simple variations in fabrication methods for metal particles synthesis, metal particle sizes, passivating fuel particles, metal oxide variations, stoichiometry of the reactants, initiation methods. Tuning the performance is required for nanothermite applications including pyrotechnics, propellants, explosives, and welding. Certain applications require specific outputs from the reaction mixture, for example, nanothermites in propulsion applications require high energy density with high velocities, where as for welding applications high velocity flame propagation with low energy densities can meet the requirements.

For better understanding on combustion characterization of nanothermites, a composite made of two fuels (Al, Mg) and a metal oxide oxidizer (CuO) is studied and compared with composites of individual fuel oxidizer mixtures.

1.2 SCOPE OF THE STUDY

As nano thermites are gaining researcher's interest in the field of energetic composites because of their high reactivity and very fast combustion reaction, understanding their characterization and reaction parameters are very important. Their combustion characteristics are controlled by tuning several properties of nano particles according to requirements of their applications, so further research is required for the usage of nano thermites in several untamed applications. The expected results in these researches may provide some developments in several fields like propulsions, pyrotechnics, welding and micro energetic devices. Studying several composites and reactivity of these composites will help in formulating advanced composites with greater energy densities and reactivity. The experimental work to be carried out provides a better understanding on the combustion of nano energetic composites by comparing a composite mixture of Al/Mg in CuO with Al in CuO and Mg in CuO composites.

1.3 OBJECTIVES OF THE STUDY

- To study reactivity and combustion characterization of nano thermites of Al (Aluminum) and Mg (Magnesium) mixed with CuO (Copper oxide).
- To review effects of particle properties on the reactivity of the composite and control over combustion of nano composites.
- To study the applicable areas of nano energetic composites and to verify the combustion parameters that may meet the requirements of several untamed applications.
- To formulate a composite that may provide high reactivity and energy density.
- To provide better understanding over the combustion process of above mentioned nano thermites by comparing three different composites.

CHAPTER 2

LITERATURE REVIEW

2.1 SYNTHESIS METHODOLOGY

Methods for production of nano metal particles have been classified broadly into two methods: Chemical methods and Physical methods. Chemical methods for nano metal synthesis are: chemical pyrolysis of metal salts, electrochemical synthesis, metal salts thermal decompositions and micro emulsions. Physical methods are Electrical Explosion of Wires [EEW], microwave plasma, laser ablation, gamma radiations chemical reduction and few more procedures. Nano metal particle synthesis is carried out by two approaches: Top-Down approach and Bottom-Up approach. While Top-Down approach follows the massive metal dispersion into nano particles, Bottom-Up approach follows the particle synthesis from atoms. Among different physical methods available for production of nano metals, the most common and promising technique is Electrical Explosion of Wires [EEW] [7].

By EEW method, a metal wire is introduced with high amount of energy and the wire is transformed into nano particles at that high temperatures and pressures. The energy entered is comparable to the sublimation enthalpy of metal used and can be high enough to convert metal wires into nano particles. Nano metals produced by Electrical Explosion of Wires method contains high amount of metal content (85-95 mass %) compared with nano metal particles produced by other methods [7]. The particle size produced and active metal content present can be regulated by varying certain parameters in process. Most difficult as well as an unsolved problem for EEW process is their wide range of particle distribution where nano sized metal particles can reach up to 90% of total number of metal particles produced. But major part of the powder produced by mass consists of particles of micro size, which are only small percentage of total number of particles. A research study stated that the nano Al sample with a specific surface area S_{sp} = 12 m^2/g contains the mass fraction of micron-sized particles of 68% of total mass of the sample, however the number of micron-sized particles were less than 2% of total number of metal particles produced [8]. Another problem faced in production of nano particles by EEW method is the agglomeration of particles during their production caused by collision of liquid particles and their further storage. Active nano particles of sizes less than 30 nm are usually unstable to oxidation, clustering and sintering. Particles with such less sizes can get easily sintered even at room temperatures under an inert environment. Nano particles produced in the inert gas environment by any of available methods are generally pyrophoric in nature because of the amount of heat and rate of heat released by oxidation of particles in room temperature is sufficiently high enough to heat up the nanoparticles to ignition temperature (~400^{o}C for 100nm Al). The size distribution for particles of nano Cu-6% Ni produced by EEW is presented in **Figure 2** [7].

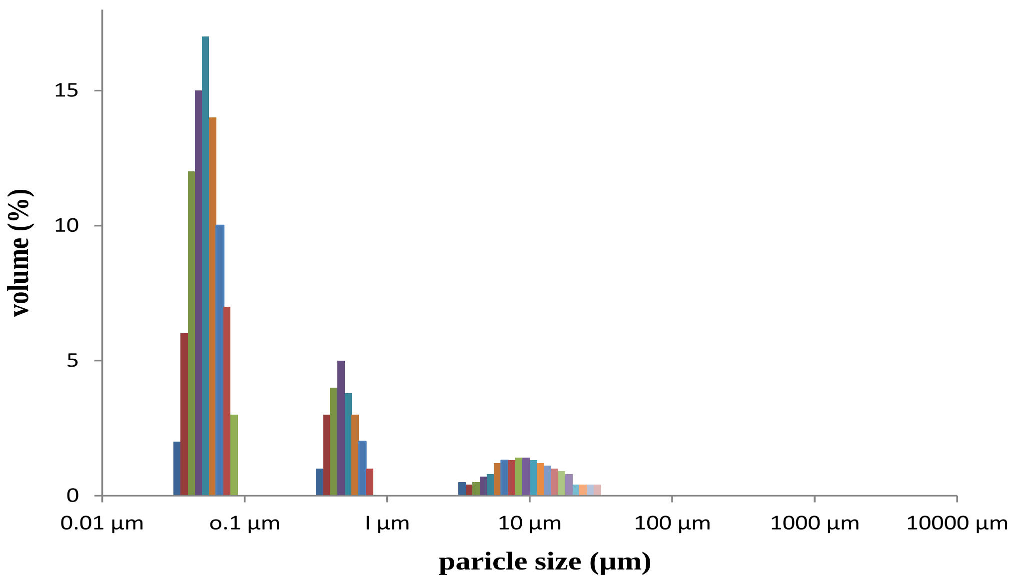

Figure 2. Size distribution of nano (Cu 6% Ni) particles produced by EEW

As some of the nano particles manufactured by different chemical methods form clusters during production and storage, physical methods are most preferable for nano metal synthesis. Among two available approaches for nano particle production, Top-Down approach mainly deals with mechanical methods and erosion of metals, Bottom-Up approach includes methods like aerosol techniques, gas phase condensation, self assembly, chemical precipitation, and structured media. Sol-gel technique is one of most commonly used and promising method for nano particle synthesis as it is the less expensive method and produced nano particles contain high uniformity and agglomeration or clustering of the particles is highly reduced compared to those of the particles synthesized from other methods.

After the production of nanometal particles, energetic nano composites are synthesized by mixing nano metal (fuel) and metal oxide (oxidizer) to form a nano thermite mixture. Several commonly used methods for formulation of nano thermites are Physical Mixing, Arrested Reactive Milling (ARM), and sol-gel methodology. From micro scale to nano, these methods provide accessibility and use of different particle sizes, and materials with different ranges of contact points in composites of fuel and oxidizer.

Physical mixing is one of the most popular and simplest methods for preparing nano thermites. Nano particles of both fuel and metal oxide are mixed in highly volatile and inert liquid (used to minimize static charge [9]). Then the sonication of the mixture is done to ensure good mixing between fuel and oxidizer and also breaks up micro scale agglomerates [10]. The volatile liquid is then evaporated and the nanothermite will be ready for applications. Physical mixing method is simple and has a vast range of applicability in many energetic systems [11]. The only major limitation of physical mixing is that the method can only be started with nano scale particles for mixing that may be available commercially or not [12].

The limitation of starting with nanoparticles will not be a necessary condition in using Arrested Reactive Milling (ARM) method. ARM technique is processed for the preparation of energetic nano composites by milling the mixture of metal fuel and metal oxide oxidizer in a ball or shaker mill. Although the process may or may not involve using nano scale particles, mixture produced by this technique posses properties similar to those nano thermites physically mixed on nano scale: fuel and oxidizer may be contained in the same particle after the preparation. The sizes of particles obtained from ARM depends on milling time and milling time of the mixture depends on initial sizes of the particle used, metal oxide in the mixture and milling media used. Due to high reactivity of the composite, after certain milling time, the milling starts ignition of the mixture when particle size is reduced below certain critical size. To reduce the static build up, hexane is usually added to the mill. The milling is stopped before the time composite gets ignited producing a useable thermite composite, so the method is termed as Arrested Reactive Milling (ARM). The composites obtained by ARM method are in the range about 1-50 µm, and contains the layers of fuel and oxidizer nanoparticles between the scale of 10-100 nm [13]. Advantages of ARM includes that the particles obtained approaches to their maximum density; fuel is hidden within the matrix reducing alumina presence on the nanoparticles which is nonreactive, advantage of starting with non-nano scale particles, and convenient control over range of intermixing and reactivity by variations of milling time [13]. The only disadvantage includes that only some nano thermite composites can be obtained from this technique as other composite are sensitive and ignites before the sufficient inter-mixing of the nanoparticles occurs.

A Nanothermite mixture prepared by sol-gel methodology takes advantage of unique mixing and structural properties of sol-gel chemistry [14]. In these composites, metal nanoparticle resides in pores of metal oxides matrix, which is determined to increase the rate of reaction compared to other methods by reducing diffusion lengths between fuel particles and oxidizer, and by increasing contact points [15]. Preparation of sol-gel nanothermite mixture involves addition of nanometal particles in a solvent to mix with a metal oxide solution just before gellation of the solution. After that the gel formed can be processed in to an energetic aero gel or xero gel. General schema of sol-gel methodology and processing of aero gels and xero gels is shown in **Figure 3** [16].

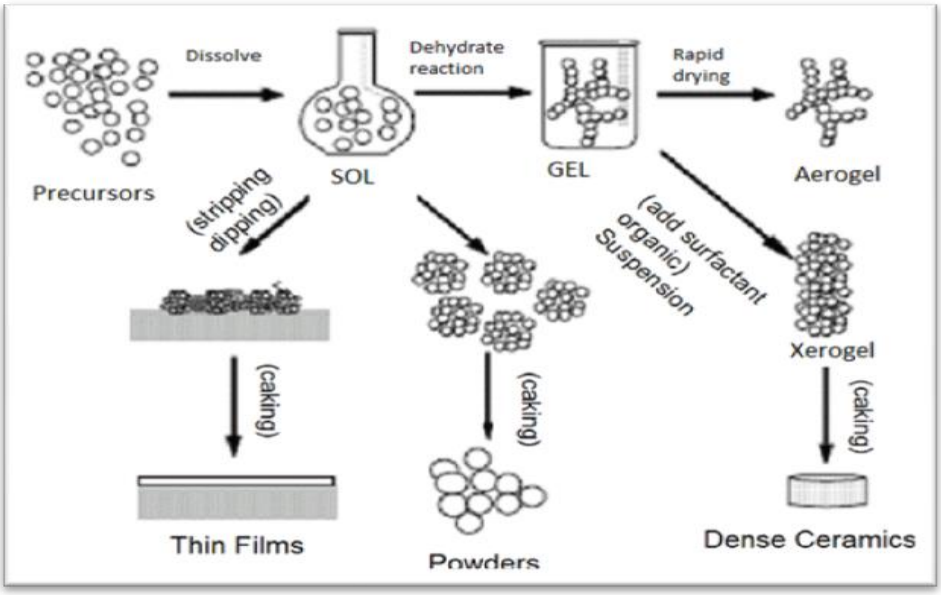

Figure 3. General schema of Sol-Gel processing

This method also allows in incorporating molecules of organic compounds in to the oxide matrix which helps in tuning of nanothermite properties by working as catalyst for gas generation [17]. A study on energetic composites impregnated with nanocarbon additives showed that addition of small amounts of carbon nano tubes CNTs increased the sensitivity towards impact ignition of the thermite due to increased friction and sheer interactions between CNTs (carbon nano tubes) and composite particles [18]. The properties of nanothermite can also be tuned by controlling interfacial contact area, pore size, and geometry of matrix through sol-gel methodology [19]. Sol-gel methodology also has the ability to produce low density xero gels or aero gels, which improves the formulation of nano energetic coatings on surface of thermite composites [15]. A xerogel is a porous matrix with very high surface area (50-500 m^2/g) and moderate density (20-75% of that of bulk), whereas aerogel is a porous matrix with moderate surface area (100-100 m^2/g) and low density (1-25% of that of bulk material). Disadvantages include oxidation of nanometal particle by water present in gel of metal oxide before solvent is removed. It can be resolved by preparing aero gels or xero gels of metal oxide matrix using sol-gel chemistry and then followed by physical mixing of metal nanoparticles [17].

A study by Planteir et al. comparing the behavior of combustion of sol-gel prepared aerogel and xerogel of oxidizers with nano metal particles and composite prepared of commercially obtained oxidizer and fuel mixed by ultrasonification. The sol-gel prepared oxidizers contain impurities that act as heat sinks and decrease the combustion velocities. Those impurities can be removed by heat treatment of aero and xero gels and a significant increase in combustion speeds were observed [20]. As xerogel has very high density compared to aerogel and composite prepared by physical mixing, it showed very less combustion velocities than both the composite mixtures [20].

Another method for formulating nano composite that took researchers interest towards its mechanism is self-assembly of binary system of particles. Method of self assembly is inspired from the recent advancements in structural developments in biological systems, molecular-assembly of binary layers in pharmaceutical and microelectronics [21]. These developments make this clear that in coming future it will be possible to synthesize any desired microscopic structure with precise location of every atom [22]. Some researchers observed that these structures are driven by entropy, which allows certain structures to form under particular conditions. Recently some studies are focusing on systems that can assemble due to forces other than entropy, like electrostatics [23]. Particles with electro-statically charged surfaces can have the ability of forming different crystal structures. But still so much research should be done on self assembly of nanocomposites. Recent energetic composites involve more than just nano particles, e.g., nano scale films and nano rods are two other structures that are being investigated.

Synthesis of nano composites in solid mixtures and liquid mixtures were commonly studied by several researchers and became applicable in several energetic applications. But all those methods for fabrication of nanothermites cannot be suitable for integration of micro electro mechanical systems (MEMS) to meet requirement of micro scale energy-demanding devices applied in microignition, micropropulsion and microactuation [24]. To make nanoenergetic materials functional in MEMS, they are prepared in the form of thin films [25] by methodologies like magnetron sputtering [26], cold spray [27], and thermal evaporation. But the above stated methods are limited to small scale application due to low deposition rates and high equipment cost, Electrophoretic Deposition (EPD) method was studied by Sullivan et al. on formation of nano thermite films. Al/CuO nanothermite film obtained from EPD resulted in significantly improved combustion and performance comparable to thermites formed by conventional methods [28]. Since, the storage stability of nano thermites is a very important property for energetic applications and conventional methods does not produce nano thermites with stability on long term storage and water resistant, a recent study proposed a process to fabricate super hydrophobic nano thermite film to improve storage stability through simple EPD method. They concluded that the film highly improved the rate of energy release, resistibility towards unconventional environments and thus increase the long-term storing capacity [29].

2.2 Effect of particle size

Energetic composites provide greater versatility in particle size over to control reactivity. Composites with micron sized metal particles were used widely in so many applications when nanotechnology was not so dominant. As nanotechnology became interesting research field in energetic materials, researchers are more concerned with energetic composites formulated by nano sized metal particles. Several researches were performed on studying the effect of material particle size in combustion of energetic materials.

As classical combustion theory states that the energetic materials undergo reactions which are diffusion controlled, decreasing the particle size of reactant significantly decreases the diffusion length and thus improves the mechanism, thereby increasing reaction velocities. Decreasing the particle size from micron scale to nano scale considerably changes the surface area to volume ratio of the composite. A large ratio results in decreased diffusion length scales between reactants and increased value in number of contact points, subsequently greater reactivity. This shows that nanoscale composites provide higher reaction velocities than micron scale, although released energy densities for both composites are nearly identical.

The technology of nanometal particle application in thermal nuclear engineering has initiated by United States (US). At the same time they were also developed in Soviet Union (Russia) for energetics during World War II. The obtained results of their work on nano energetics were published in Morokhov's book in 1977 [30]. After the publication of Gleitier's work in 1989 [31], the term nano crystalline material became well known in Western Europe. But the work on nano metal particles was started 3 decades earlier than the word nano appeared. Two Russian scientists, Kondratyuk and Tsander discovered the possibility of using powdered metal particles as additives in energetic systems in 1910 [32]. Several reviews were published in 19th century on the basic laws of combustion for micron-sized metal powders under high temperature oxidizing environments. The disadvantages of using micron-sized were observed during initial tests on metal particle propellants in 1940: agglomeration of metal particles (Al), incomplete combustion (50% of unburned metal particles), significant losses in two phase flow (15% losses for composites with 25% mass of micro Al) [33]. Later, a study by Zeldovich et al., provided an approach for reducing these losses by using ultrafine metal particles for fuels and combustion catalysts in 1970 [33].

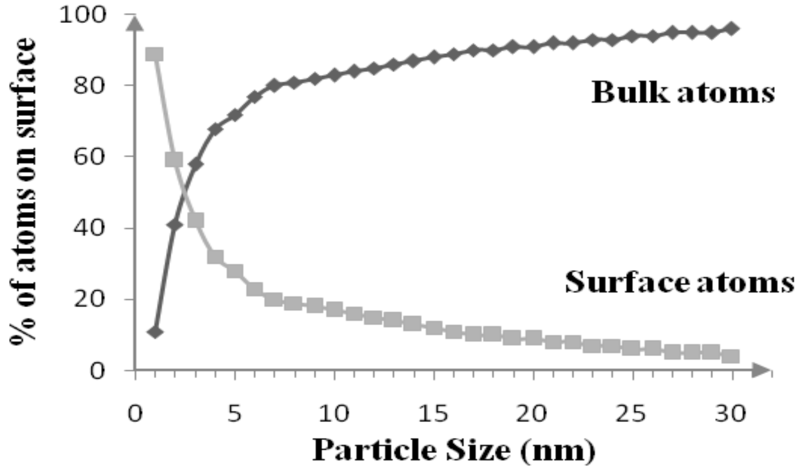

Figure 4. Surface to Bulk atoms ratio as a function of particle size

In order to understand the reasons for performance variation because of change in particle size, length scale of hydrogen atom was taken for comparison. A spherical shaped metal particle having few nanometers diameter contains only few thousands of atoms resulting higher surface atoms-bulk atoms ratio. **Figure 4** shows the how surface atoms-bulk atoms ratio changes for spherical shaped iron crystal by the effect of particle size [34]. Since the surface atoms contain low coordination between them, electrical and thermo-physical properties of these surface atoms are vastly different than bulk atoms. When the ratio becomes significant, bulk atoms tend to exhibit the properties of surface atoms. The metal particles with sizes of few nanometers show very good catalytic properties [35]. As the metal particle size gets below 30 nm, active metal content present in the powder reduces substantially (down to 30-50%). For controlling the active metal content, nano particles are stabilized using organic reagents to achieve 70-90 mass% [36]. Several studies also stated that the properties like melting point, freezing point and heat of fusion changes when the sizes of particles become less than 10 nm. Affect of particle sizes on melting point of metal and heat of fusion of the particles are shown by **Figure 5** and **Figure 6** [37]. In addition of having increased reactivity, nano sized powders exhibit super Para-magnetic behavior, super-plasticity, lowered melting temperatures, lowered sintering temperatures, higher theoretical energy densities, and higher absorption of gases and their capillary systems compared to micron sized and large sized particles [38].

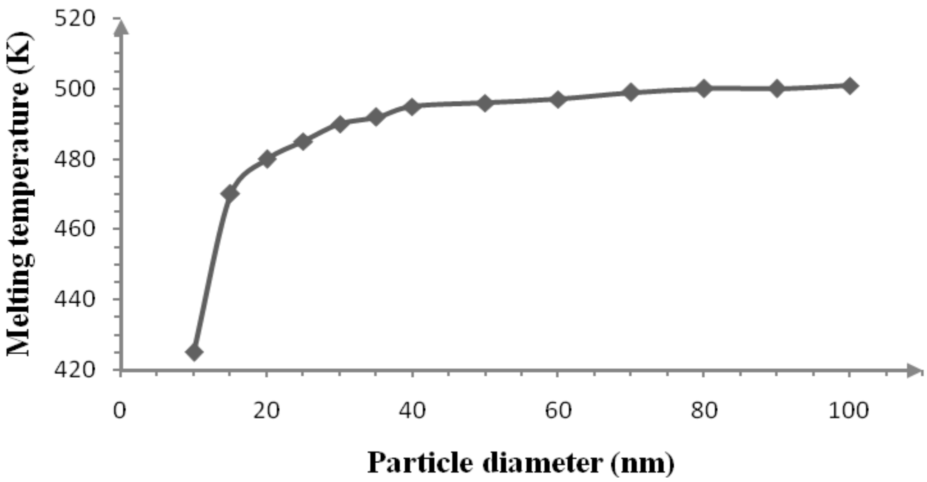

Figure 5. Effect of Particle diameter on melting point of nano particles.

In 1987, a study by Kubota and Serizawa's showed that the decrease in Mg particle size shown a significant increase in the burning rate of Mg/Teflon pellets, and a considerable increase in heat production above burning surface is observed [39]. Since

Mg is not available commercially in bulk quantities, Poehlein found that replacing Mg with Alex (nano Al produced by electrical wire explosion method) produce higher burn rates. Using nano Al helps in solving the problem of slow energy release observed in micron-sized particles, a study by Yang et al., reported [40]. When micron-sized particles were replaced with Alex particles, increase in burn rates and an increase in temperature sensitivity is observed in a study done by Mench et al., (1998) [41]. The only disadvantage of using nano metal aluminum particles is their high cost and high content of alumina present on nano Al particles and negative impact on composite processing, reported by Dokhan et al., (2002) .

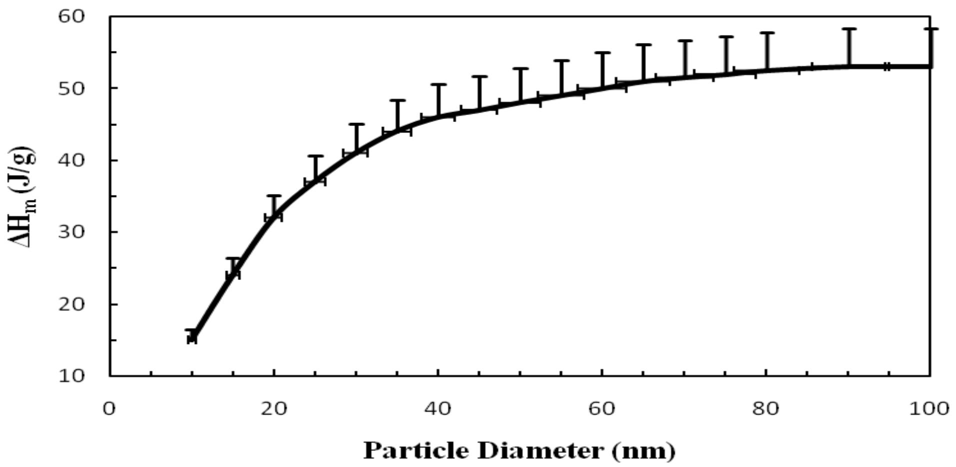

Figure 6. Heat of fusion of nano particles as a function of particle size

As the initial reactions occurring in heterogeneous energetic systems are assumed as diffusion limited solid-solid reactions, the reaction rates and combustion velocities are assumed to be increasing by reduction in particle sizes and increasing the contact points of fuel with oxidizer [42]. A study by Brown et al. [43] on comparing the combustion rates for Si/Pb_3O_4 mixture as an effect of contact points of fuel and oxidizer in a given silicon particles mixture with 5 µm Pb_3O_4. He observed that a small change in particle sizes has a significant effect on fuel-oxidizer contact points, which resulted in huge variation of combustion rates. Few results from this study are presented in **Table 2**. He also observed for Sb/KMnO4 mixture, decreasing the Sb particle size from 14 µm to 2µm showed an increase in the burn rates 28mm/s from 8 mm/s. Even though the study was not done on nano scale, it shows that particle size affects the performance of thermite mixture. Another experimental work by Shimizu et al. states that an increase in contact points of fuel and oxidizer in Fe_2O_3/W_2O_5 system shows an increase in the reaction rate of the nanocomposite [44].

Diameter of Si Particle (μm)	Contact Points (x10^8)	Combustion rates (mm/s)
2	302	257.4
4	87	100.6
5	61	71.5

Table 2. Combustion rates and Contact Points as a function of particle size in Si/Pb_3O_4

The thermite mixture sensitivity towards friction and impact is also affected by change in particle size, as particle size decreases, the sensitivities increases. Spitzer et al. [10] observed that the micron-scale thermite mixture is insensitive towards impacts and shock, whereas the nanoscale thermite mixtures are too sensitive towards both or one of the two, depending on type of metal oxide used. He observed that changing particle size from micron-scale to nanoscale in a mixture of Al/WO_3 nano composite, the thermite became very sensitive towards friction and combustion rate increased up to several times as compared to micron-scale mixture. With increased sensitivities, nano thermites are highly dangerous in handling; also have advantages towards some of practical applications like percussion primers. A study on Al/Bi_2O_3 observed that mixtures with sufficient friction sensitivity and impact sensitivity are considered for using in ammunition primers [9]. The study also states that electrostatic discharge [ESD] sensitivity of the composite is 0.125 μJ, which is easily achieved in human body, it is hazardous to handle. They also reported that the reason for increase in sensitivities is due to an increase in the ability of developing charges by high surface areas [9].

Another property that gets affected by decrease in particle size is the initiation temperature of the nanothermite mixture. An experimental research by Michelle L. Pantoya et al. showed a thermite mixture composed of 100nm MoO_3 and 40nm aluminum exhibited an ignition temperature about 458 ^oC and the same MoO_3 with 10-14 μm aluminum exhibited the ignition temperature about 955 ^oC [42]. These results indicates that for micron scale mixture, the thermite reaction starts after melting of particles and volatilization of Al and MoO_3, whereas nanothermite reaction occurs before melting of aluminum could takes place. This also indicates that reaction in micron composite is a gas

(MoO3)-liquid (Al) reaction, whereas in nanocomposite it is solid state diffusion reaction [42]. The effect on ignition temperatures as particle size changes is shown in **Figure 7**.[45]. The plotted data is obtained from several studies for various particle sizes under different conditions, so comparing should be done cautiously.

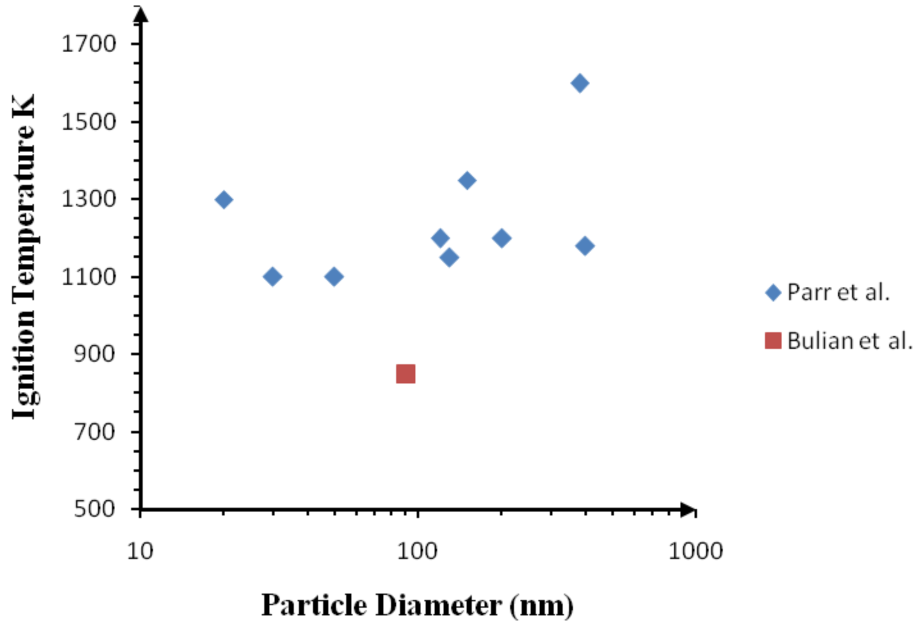

Figure 7. Ignition temperatures of Al as a function of particle diameter

Particle size also affects the burning times of the mixture. From a review paper done by [45], particle burning times affected due to change in particle diameter is obtained and presented in **Figure 8**. It is observed that as the particle size increases the burning time of the mixture also increases, whereas the particles with smaller sizes at lower ignition temperatures showed higher burning times than those at higher ignition temperatures.

Decreasing particle sizes also showed the after initiation affects. Michelle L. Pantoya along with T. Osborne studied the effects of size of nano particles on thermal degradation of composite of Al/Teflon, they concluded that the nano composites have an increased sensitivity towards ignition and exothermicity caused by pre-ignition reaction occurring in nano-Al mixture, which does not occur in case of micron composites [46]. As micron scale mixtures have low specific surface areas, influence of passivation shell is reduced, which may be the cause for pre-ignition reaction in nano composite.

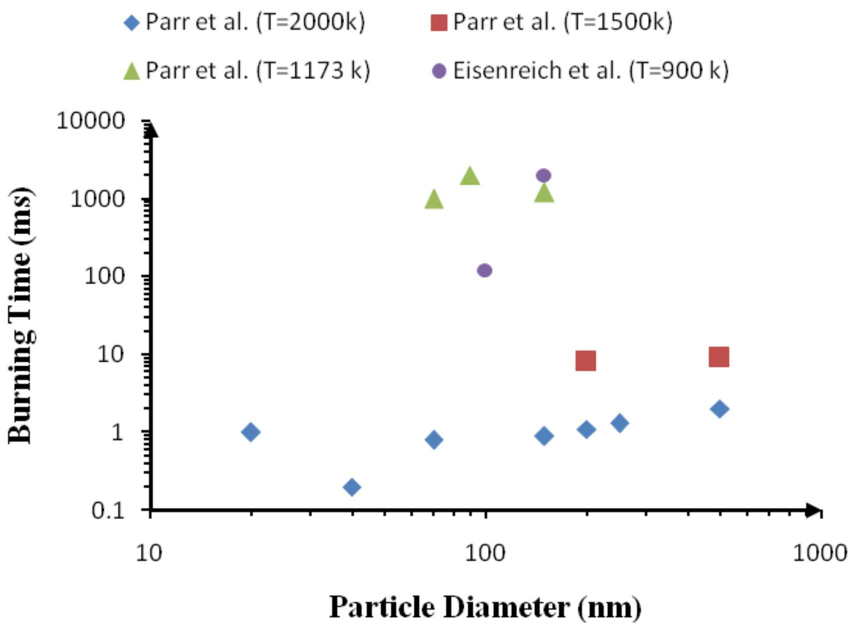

Figure 8.Burning times of nano composites as a function of Particle diameter.

All the above experimental studies show that decreasing the size of particles in an energetic composite from micron-scale to nanoscale highly improves the performance of the mixture. Some of the drawbacks of micron-scale composites can be resolved by nano composites. While the limitations of using nanocomposites are their handling hazards due to increase in sensitivities, storage problems due to agglomeration of nano particles, and unavailability of detailed understanding on the combustion reactions for several nano metal particles. Further researches are essential to get a perfect understanding on reaction characteristics of the nanocomposites affected by particle size.

2.3 Effect of passivation of nano metal particles

For thermite mixture with Aluminum nano particles as fuel, passivation of nanometal particles surface with an oxide must be considered. As Aluminum is pyrophoric in nature when comes in contact with air, oxide passivated layers are to be formed on nano-Al particles to minimize the spontaneous pyrophoric behaviour of the fuel. Aluminum oxide or alumina shell is commonly used for coating the nano Al particles. The oxide shell works as protective layer between metal and reactive gas (air) for stabilizing the metal particles. Transmission electron microscopy of Aluminum metal particles passivated with alumina shell is shown in **Figure 9**.[47].

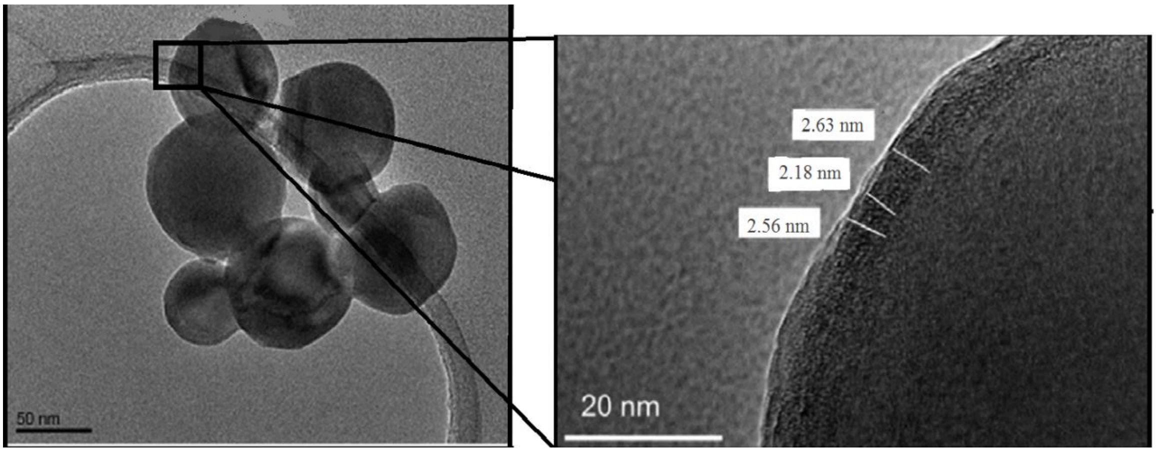

Figure 9. Transmission Electron Microscopic images of Al passivated with Al_2O_3

Although passivating the nano metal particles helps in making the particles stable and easy to use, it also affects the performance of the nanoparticles in thermite reactions. Oxide shell acts as an encapsulation for active aluminum and provides a compressive pressure that may have negative impact in the reactivity of the Al nano particles. For micron-scale Al particles, passivation layer of alumina of few nano meters is negligible compared to particle size, but for nano scale particles the passivation layer of oxide accounts for significant mass% (20-45%) of total weight of the nano particles [48]. This shows that the active aluminum content present in the nano particle is reduced (e.g., for a particle of 25 nm, 3nm oxide layer accounts for >60% of the volume of nano particle). The percentages of active Al in passivated Al nano particles are presented in **Table 3**. The data is obtained from several references stated.

A study with 49% of active aluminum in a thermite mixture with CuO showed that increased oxide layer content can decrease the thermite performance [49]. Chowdury et al., studied the mechanism of ignition in Al/CuO with fast reacting rates and observed that the ignition temperature increases above the aluminum melting point [50]. Passivation also has affects on the energy released by the composite, for a particle having 100 nm size with 3 nm oxide layer energy loss per unit volume is nearly 10%, whereas particle of 10 nm size with same oxide layer thickness, energy loss per unit volume is observed to be approximately 60% [38]. Several methods were developed for passivating nanometal particles with organic reagents other than oxides to increase the stability and active aluminum content in the nano particles [36]. Aluminum particles passivated with nitrocellulose in a thermite mixture of CuO showed a considerable decrease in ignition temperatures as compared with particles passivated with aluminum oxide layers [51].

This study is supported by another researcher who stated that passivating nanometal particles with organic compounds may provide 70-90% active metal content in nano particles [36].

Average nanoAl particle Size (nm)	Active aluminum Content (%)	Reference
30	30	[15]
45	64	[52]
50	43	[42]
50	79	[48]
79	81	[53]
80	80	[52]
80	88	[12]

Table 3. Percentage of active aluminum content for different particle sizes.

However, oxide shell doesn't participate in thermite reaction and acts more like heat absorbent. It works as a protecting layer for nano metal particles from reactivity with air. Since all the existing passivation approaches do not reach to achieve maximum active aluminum content, further research is required to develop an appropriate method for passivating nano metal particles to achieve high metal content and to improve performance of metal particles in energetic composites.

2.4 Initiation of combustion in nano composites

Initiation of combustion reaction in nano composites involve provision of certain amount of energy input, known as activation energy. Different nano composites require different activation energies for the reaction to be initiated. The initiation of these reactions is also called as ignition. After ignition, composites start to release energy due to exothermic reactions between the fuel and oxidizer. Energy released by composites is sufficient enough to ignite the surrounding composite media, thus sustaining the combustion reaction.

In simple terms, thermite reactions are initiated using various techniques, mechanical impulse, electrical heating, chemical, optical and thermal heating. Mechanical ignition includes providing physical impact on composite to initiate thermite reaction and electrical initiation includes heating of nano composites using electric energy. Thermal ignition can be processed by different experimental setups: direct contact of thermite composite with heated solid or gas igniter, radiation heat transfer from hot solid particle or gas to the composite and heat transfer from hot gas through convection. Each of the above technique provides unique combustion dynamics directly influencing the way reactants interact with each other and mechanism of reaction. This paper briefly discuss about some of the initiation methods and their effects on reaction outputs.

Impact ignition (mechanical) of nanoenergetic composites is achieved by introducing mechanical stimulus to the materials producing very high or very low heating rates. These impact initiated mechano-chemical reactions are characterized in to those reactions occurring because of solid state mechano-chemical effects which leads to shock induced reactions with heat rates ranging 10^4 K/s to 10^8 K/s. Gas guns propelling the projectiles at hypervelocity's ranging from 1-5 km/s (measured using laser beam interruption system) employs an impact that provides a heating rate of nearly 10^8 K/s, while drop weights provide an impact with heating rates as low as 10^4 K/s which are considered as low velocity impacts [54]. A simple drop weight apparatus is shown in **Figure10**.

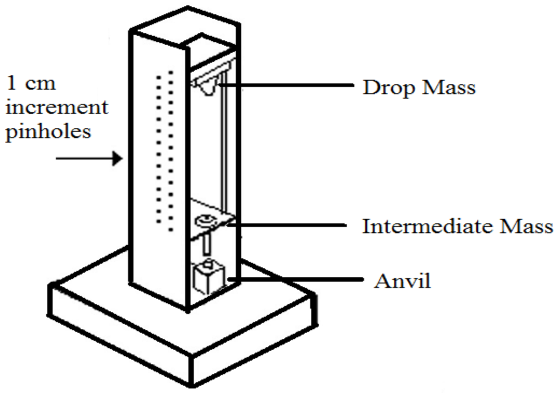

Figure 10. Drop Weight Apparatus.

Ignition by impact induced metal chemical reactions primarily depends on intrinsic mechanical and chemical properties of the nanoenergetic composite constituents, where the material deforms, fractures and undergo dispersion before ignition. An impact ignition study on micron Al mixture by Ames [54] showed that aluminum particles undergo a brittle fracture prior to ignition. They also found that some additional amount of energy is required for ignition of fractured materials which initiates the initial stages of diffusion reaction. As micron scale particles are less sensitive towards impact ignition, some additives provide additional frictional hotspots to increase the sensitivity [55]. A kinetic study of impact ignition of nanoenergetic material impregnated with additives like CNTs, nano C and graphene showed that even adding less amount of CNTs significantly increased the sensitivity while addition of nano C and graphene doesn't have any effect on sensitivity of EM [18]. Further work is needed to study how additives affect the energetic materials as the formation of hotspots on composite surface is random.

Thermal ignition of nanoenergetic composites involve thermo-chemical reaction mechanisms with heating rates ranging 10 K/s to 10^3 K/s which are slower compared to heating rates obtained by impact initiation. Thermal analysis equipments like Differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analysis (TGA) are used for thermal initiation and analysis. Ignition by radiative heat flux and conduction heat flux is more preferable over convective heat flux for thermal initiations due to several disadvantages of convection heat transfer equipments.

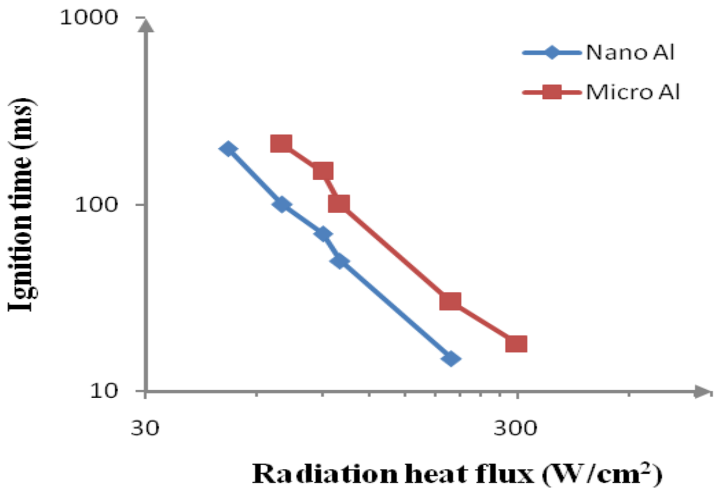

Figure 11. Ignition time as a function of radiation heat flux

Ignition by radiative heat flux can be obtained by using high power lamps which provide heating to the nanocomposite. Higher the heat input provides high rate of heating for the ignition of combustion reactions in the composite. Density of the radiative heat flux provided affects the time of ignition of the composite inversely, increasing the heat flux considerably decreases the ignition time. A study on ignition of nano aluminum by radiation heat flux provides a similar data presented in **Figure 11**.[56].

Ignition of micron aluminum and nano aluminum by conduction heat flux was studied by Vladimir which shows that the time of ignition is affected by temperature of conducting hot plate. For same temperature of the plate, ignition time is also decreased by decreasing the size of the reactant particles. The effect of ignition time of energetic composite as a function of temperature of hot plate is presented in **Figure 12** [56]. A kinetic study of thermal initiated reactions of nano thermites consisting different types of materials showed that self assembled materials exhibit great improvement in reaction properties when compared to micron-scale or nano scale thermite prepared by simple physical mixing [56].

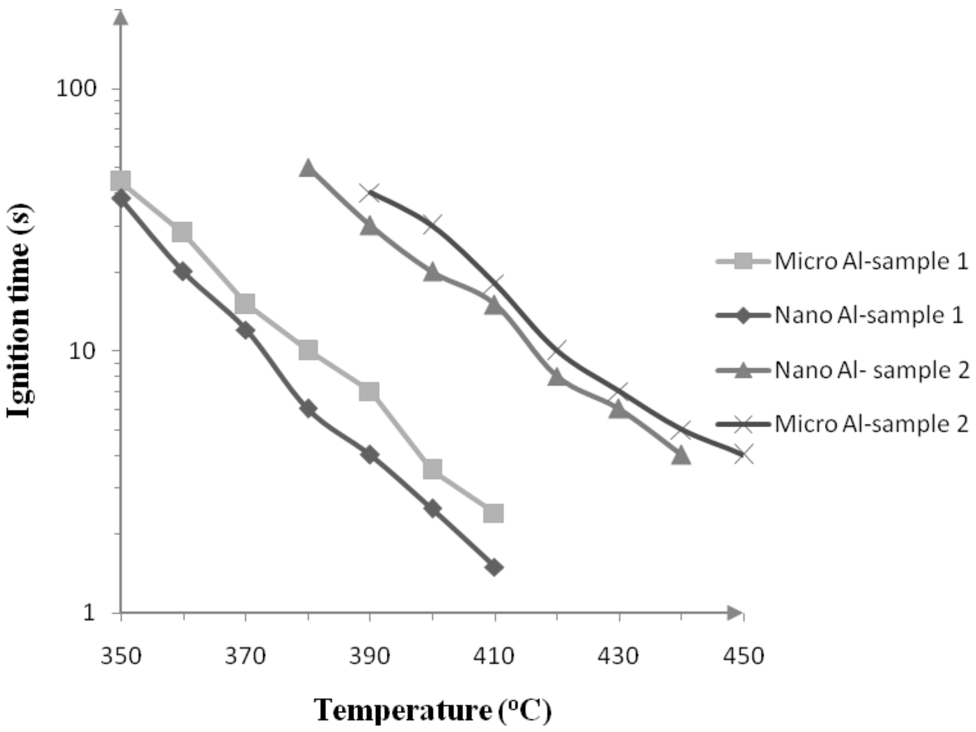

Figure 12. Ignition times as a function of hot plate temperature.

The above presented experiments conclude that the time of ignition is dependent on particle sizes, formulation of the metal nanoparticles and rate of heating of the composite. Future research studies are required to completely understand the characterization and effects of several parameters on ignition of nanoenergetic composites.

2.5 Applications

Nano energetic composites posses a large range of properties those can be considerably tuned by altering several parameters, accordingly nano composites find several applications. As nano energetic composites is relatively new to the field of range of energetic materials, many applications are proposed by several researchers and their testing in those applications has not yet performed. Several applications of nanoenergetic composites are of a direct result of their high energy densities, leading to those applications of power generations like micro scale propulsions, nano scale welding and energetic surface coatings. Other applications are a result of pyrophoric behavior of nanoenergetic composites, and those materials find applications in environmental friendly ammunition primers, electric igniters, exploding-on-contact missiles and even as primary explosives due to fast reacting thermite mixtures [57].

Micro propulsion is also referred as micro pyrotechnics or micro energetics and their applications include propulsion for small aircrafts and rapid switching. Micro propulsion involves production of thrust in micro scale (<1 mm). Traditional energetic materials like RDX or HMX used for macro scale propulsions are not considered to be used in micro scale propulsions due to significant loss of energy in combustion chambers. This is not the case for nano thermites as they contain higher energy densities and energy loses in combustion chamber will become insignificant [57].

Most common application of nano thermites is electric igniters which are used throughout the industry of nanoenergetic materials in all fields of propellants, pyrotechnics and explosives. Electric igniters have applications wherever spark ignition of materials are required. They are also known as electric matches, due to their precise timing they are used to ignite almost everything from fireworks display to igniting rockets. Electric igniters consist of a resistive bridge wire around which a flammable head is placed, when certain amount of electrical current is passed to the wire, the flammable head ignites. But only disadvantage of using these matches was that they contain toxic compounds of lead [58] which are not environmental friendly, so replacing traditional matches with nano thermites as a flammable head which are non toxic in nature showed a significant desirable application. A simple electric match is shown in **Figure 13**.

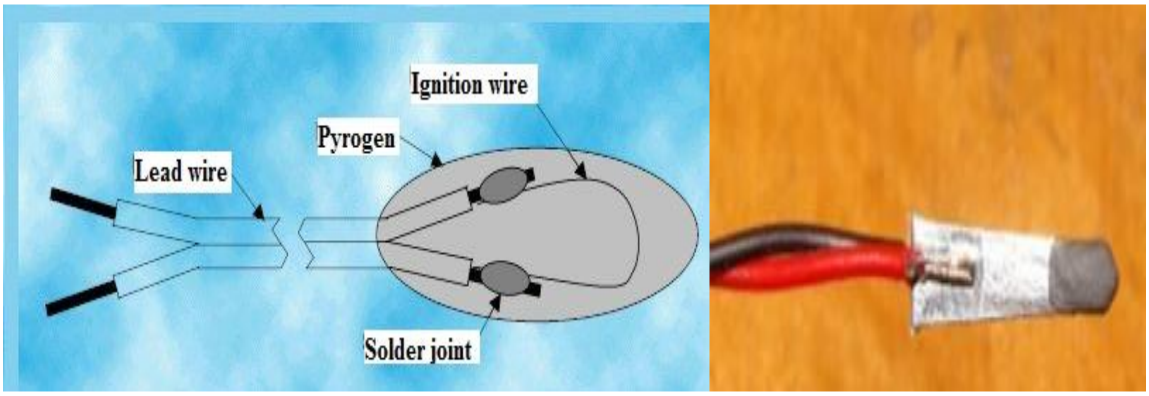

Figure 13. Electric match/igniter schematic diagram

Primers used in ammunition are traditionally made of toxic lead salts like lead azide and styphnate which are highly sensitive explosives detonate due to impact of firing pin resulting ignition of propellant in cartridge thus firing the bullet. Using such toxic primers is hazardous to both environment and to the user. Nano thermites, which are non toxic, are an effective replacement for traditional primers as their properties can be tuned accordingly to work similarly like traditional primers. Ammunition primer of a shotgun shell is shown in **Figure 14**.

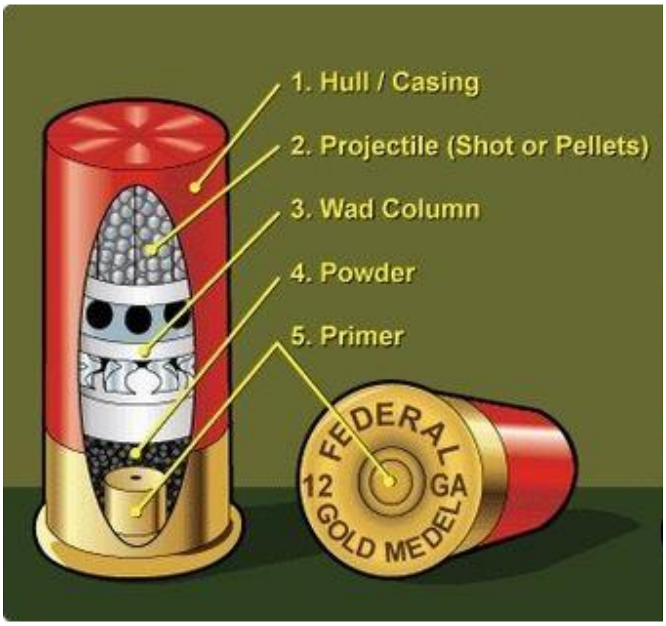

Figure 14. Shotgun shell with primer

There are several more applications of nano energetic composites which are not experimentally studied. Further research work is required to explore the areas of application of nano thermites which are effective to replace traditional explosives.

CHAPTER 3

MATERIALS AND EQUIPMENTS

This study involves in the preparation of three different nano energetic composites: Aluminum and Copper oxide (Al/CuO) composite, Magnesium and Copper oxide (Mg/CuO) composite and a composite with Aluminum, Magnesium and Copper oxide (Al/Mg/CuO) for their comparison to get a clear understanding on combustion of nano energetic materials.

MATERIALS:

1. Aluminum nanoparticles of size about 30-50 nm, 5 grams.
2. Magnesium nanoparticles of size about 30-50 nm, 5grams.
3. Copper oxide nanoparticles of size about 30-50 nm, 5 grams.
4. N-Hexane chemical solvent, laboratory grade, 500 ml.

EQUIPMENTS:

1. Ultra-Sonicator for physical mixing of nanoparticles.
2. Field Emission Scanning Electron Microscope (FESEM) for size verification.
3. Differential Scanning Calorimeter (DSC) for heat flow analysis.
4. Thermo Gravimetric Analysis (TGA) for weight loss analysis.

EXPERIMENTAL SETUP:

All nano particles are brought from nanoresearch labs of sizes 30-50 nm and used as obtained. This particular size is selected due to their availability and as 30 nm is the critical size for nano particles to exhibit completely different properties. Obtained nanoparticles are mixed into composites by physical mixing using ultrasonicator available in the university. The composites are prepared by adding metal and metal oxide nanoparticles in a hexane liquid and sonicated for about 10 min in 10s intervals. Volume of hexane selected accordingly as the volume of particles will be 5% of volume of hexane. After sonication the mixture is dried at 65oC for about 2 hours to make sure the hexane is evaporated completely. The powder obtained after drying is further crushed with glass rods to make it a fine powder. Ratios of metal and metal oxide particles are selected by following stoichiometry relations:

$$2Al + 3CuO \rightarrow Al_2O_3 + 3Cu$$

$$Mg + CuO \rightarrow MgO + Cu$$

$$2Al + Mg + 4CuO \rightarrow Al_2O_3 + MgO + 4Cu$$

Particle size of the composite will be observed in SEM (Scanning Electron Microscopy). Prepared Composites are to be tested in Differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analysis (TGA) for thermal analysis. DSC provides the heat flow through the composites which shows the exothermic activity of the composite at a provided temperature. Testing will be done at slow heating rates of 10-20 K/s to get detailed information on reactivity of the composite. TGA will show the weight loss or gain % in the composite over time providing several phases of the reaction and how reaction within the composite changes.

CHAPTER 4

RESEARCH METHODOLOGY

Initially a broad research topic has been chosen. The area of research selected is energetic materials. From energetic materials which have a wide range of applications, the combustion characteristics of nano energetic composites have been chosen. As nano technology is new to the field of energetic composites, the understanding of their behavior towards combustion is very important. Over 5 decades so many studies have already been done, but a clear understanding on the combustion of nano energetic composites has not yet been achieved. All the previous studies are performed on composites of a single metal and single or multiple metal oxide mixtures with or without additives. But no study clearly understood the nature of combustion occurring in the thermite mixtures. This study tries to contribute a small amount of understanding the process of combustion and effecting parameters by formulating a composite with two different metals in a metal oxide matrix and comparing it with individually formulated composites.

The problem statement taken initially was to formulate a nanocomposite that may produce increased reactivity and decreased ignition temperatures by mixing two different nano metals. Extensive literature review has been done on previous researches from different journals, conference proceedings and review reports. The literature survey done had been divided into sub-topics of how parameters of initial nano particles considered will affect the combustion of nanocomposite formed. Several reviews were done on each of parameters that are affecting the performance of the energetic composite.

After enough review is done, we got in to a conclusion that particle size of metal and metal oxide considered highly affects the performance of the composite. Several effecting parameters have been formulated and found a problem in using nano aluminum particles in the energetic composite. As aluminum have a long ignition delay, to improve the performance of the composite, a hypothesis is formulated as: by adding a metal which have no ignition delays in initiation of the reaction, we might ignite the composite at less temperatures and also we might be able to improve the energy density output from the composite.

As the hypothesis is made, research for designing the sample has been started. Deliberate samples have been chosen for the purpose after considering availability and cost of nano particles. Aluminum and Magnesium along with Copper oxide nanoparticles are the selected samples on which the study will be done. Samples have been selected after collection of some valuable information on the particle properties and easy availability. The information about the equipments required for the study has also been collected. The data on how to perform formulation of the composite and its experimental analysis for testing the hypothesis is also collected.

Once the materials are obtained, the sample preparation will be done on ultra sonicator available in the university. And the samples will be tested on high end equipments which are not available in house. The experiments will be conducted in SMITA research laboratories in IIT Delhi and the experimental data will be obtained. From the obtained data, hypothesis will be tested. If the hypothesis made is not true, then the selected materials or their mixing ratios will be changed and the whole process will be repeated until the results obtained satisfies the assumptions considered.

CHAPTER 5

PROPOSED WORK PLAN WITH TIME LINES

The research study conducted is divided into several sub topics. Mostly the review of previous studies are done as the subject is sophisticated and need a clear understanding on how the study is to be conducted. Review is done from the research papers collected from different journals like Combustion Science and Technology, Combust and Flame, Journal of Physics and Chemistry etc. Several theoretical concepts were also studied to get a brief knowledge on basic chemistry and combustion of energetic materials from some published books like organic chemistry of NCERT, Al based Nano Energetic Materials by Carole Rossi and Nanotechnology: Synthesis and Production by NPTEL.

Experimental work that is to be conducted takes certain planning of available time. The proposed work will be conducted according to the time line provided.

Date	Work done/ to be done	Description
August 2017	Literature Review	Literature survey is started on energetic materials.
September 2017	Problem statement	Obtained a problem statement to work on nanotechnology in energetic materials.
October 2017	Continuation of literature survey	Literature study is continued on nano energetic composites.
1 Nov 2017	Report	Started report writing as well as a review paper.
20 Nov 2017	Completed report	Completed report writing for dissertation-II
29 Nov 2017	Submission of report	Report for dissertation-II is submitted.
1 Dec 2017	Receiving hexane solvent, Nanoparticles.	Ordered quantities of nanoparticles, hexane required will be received.
3 Dec 2017	Physical Mixing	Ultra sonication of the nanoparticle

		composites will be done in a hexane solvent.
7 Dec 2017	Testing	Testing in SEM will be performed for particle size analysis.
8 Dec 2017	Testing continued	Testing in DSC and TGA will be performed for thermal analysis.
9 Dec 2017	Analysis	Analysis of the results will be performed and hypothesis checking will be done.
10 Dec 2017	Feedback	If hypothesis made is wrong, whole procedure from selection of nano particles will be repeated.
10 Dec 2017	Paper writing	If hypothesis made is true, then research paper writing will be started.

CHAPTER 6

CONCLUSIONS

The field of nano thermites is relatively new to the field of both nano technology and energetic materials, but the research done over 5 decades provide so much information about reactivity and combustion characterization of nano energetic composite. Although so many studies focused on findings several applicable areas of nano thermites, a better understanding on combustion is still needed to improve reactivity and control over combustion for improved applicability.

This study deals in improving the reactivity and decreasing ignition temperature of the nano composite by mixing two different metal particles into a metal oxide and comparing it with composites prepared by individual metals. The expected outcome of the study is to decrease ignition temperature of a metal composite by adding high reactive metal and to increase overall energy density of the composite.

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