Energetic Nanocomposites: Review on Metal based Nano thermites

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ABSTRACT

A brief review on metal based nanothermites is presented in this paper for better understanding on exothermic behavior of nanoenergetic composites. Nanoenergetic composites are extensively young and interesting field in energetic materials because of their high reactivity and very low ignition temperatures. Metal based thermites have a huge range of applications theoretically which are yet to be approached practically. A better understanding in their characterization is required to continue the work; this paper presents the methods and parameters affecting the performance of nanoenergetic composites. Results of various studies on affecting parameters including particle size and passivation methods are also being presented and compared to give a clear understanding to the readers. A qualitative review has been reported here from synthesis of the composites to their initiation methods which help the researchers in further approach on nanothermites.

Keywords: Nanothermites, Nano Energetic Composites, Metal Particle Combustion, Thermite Reaction

1. Introduction

A 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 produce 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 high velocity flame will be produced due to their very high reaction rate [ex: RDX]. While heterogeneous composites contain 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 equipment's such as XRD, SEM, and 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.

Energetic composites combustion starts when around is abundant energy available to initiate the fuel-oxidizer reaction, that energy is called as stimulation energy.

Author obtained a connection between rate of reaction k(T) and activation energy given by Equation (1):

$$k(T) = A * \exp(-\frac{Ea}{RT}) \quad \text{Eqn. (1)}$$

where T refers to absolute temperature,
R refers as a gas constant, and
A is the pre-exponential factor.
The amount of activation energy required for an exothermic reaction is a function of path of the reaction.

Table 1. Sensitivity Classes for characterization of Energetic materials

Stimuli	Sensitivity (experimental data)	Sensitivity classes/Responsive
Friction	Greater Than 360 N	Unresponsive
	80-360 N	Reasonably responsive
	10-80 N	Responsive
	Less than 10 N	Precise Responsive
Impact	Greater than 40 J	Unresponsive
	Is 35-40 J	Reasonably responsive
	Is 4-35 J	Responsive
	Is less than 4 J	Precise Responsive

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.

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 since of its higher heat of ignition [~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):

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

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 essential 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 even less energy densities can meet the requirements.

2. 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 Bottom-up and Top-down approaches. While Bottom-Up approach follows the particle synthesis from atoms, Top-Down approach follows the massive metal dispersion into nano particles. 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 decomposed into nano particles at high temperatures and pressures. The energy entered is comparable to the sublimation enthalpy of metal used and be able to be high sufficient to convert metal wires into nano particles. The particle size produced and active metal content present can be regulated by varying certain parameters in process.

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. Physical mixing is one of the most popular and simplest methods for preparing nano thermites. Nano particles of both fuel and metal oxide are varied 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 ARM. 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 1 [16].

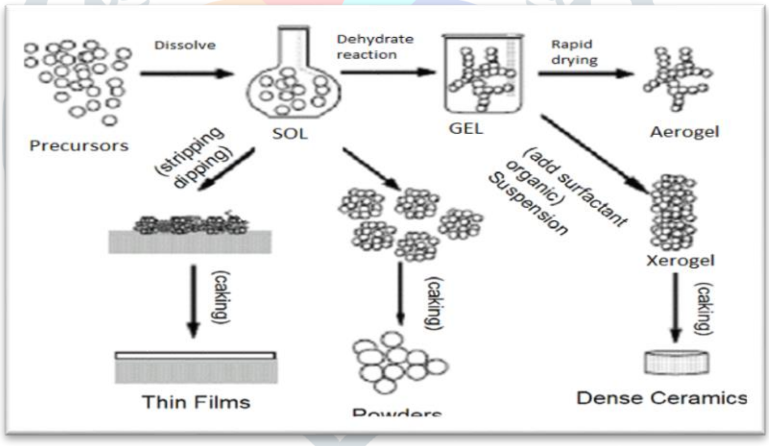

Figure 1. General schema of Sol-Gel processing

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].

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 [21]. To make nanoenergetic materials functional in MEMS, they are prepared in the form of thin films [22] by methodologies like magnetron sputtering [23], cold spray [24], 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 [25]. 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 [26].

3. EFFECTS 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.

The technology of nanometal particle application in thermal nuclear engineering has initiated by America (US). At the same time, they were also developed in Russia for energetics during World war I. The obtained results of their work on nano energetics were published in Morokhov's book in 1977 [27]. After the publication of Gleitier's work in 1989 [28], 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 [29]. 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) and significant losses in two phase flow (15% losses for composites with 25% mass of micro Al) [30]. Later, a study by Zeldovich et al. provided an approach for reducing these damages by ultrafine metal particles for fuels and combustion catalysts in 1970.

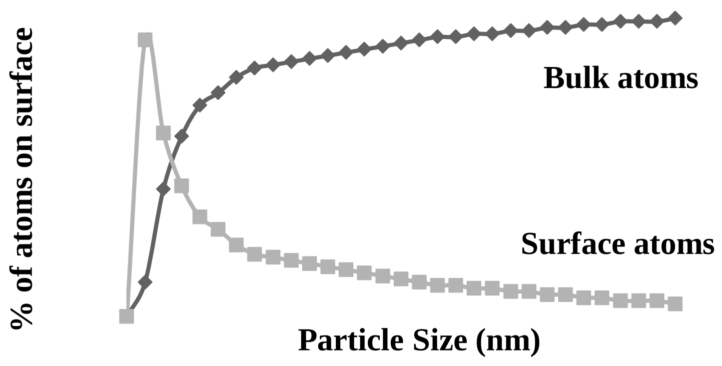

Figure 2. Surface to Bulk atoms ratio as a function of particle size

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 2 shows the how surface atoms- bulk atoms ratio changes for spherical shaped iron crystal by the effect of particle size [31]. 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 [32]. 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% [33]. 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 3 and Figure 4 [34]. 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 [35].

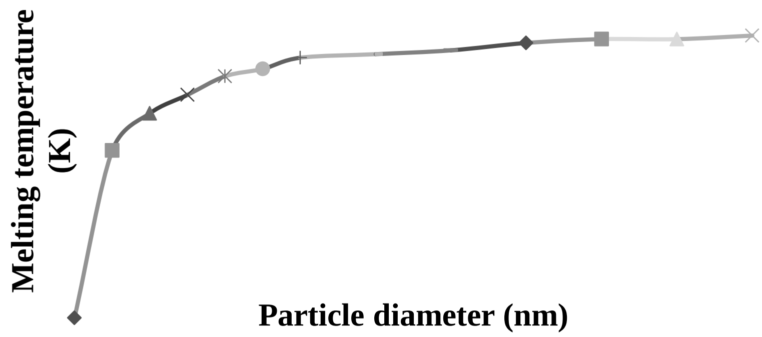

Figure 3. Effect of Particle diameter on melting point of nano particles.

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 [36]. 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 [37]. 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) [38]. 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) .

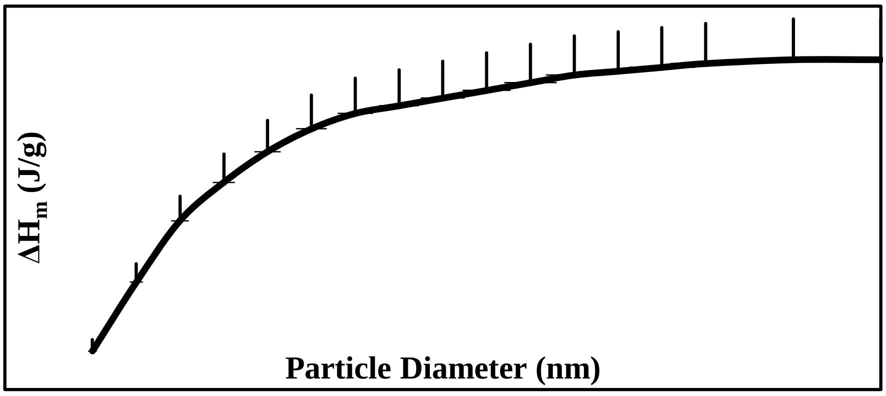

Figure 4. Heat of fusion of nano particles as a function of particle size

As the initial reactions occurring in heterogeneous energetic systems are assumed as dispersion (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 [39]. A study by Brown et al. [40] 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. Table 2 shows the small change in particle size has a important result of contact points of oxidizer and fuel interaction points. 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 [41].

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

Diameter Silicon Particle (µm)	($x10^8$) Interaction/ Contact Points	Ignition rates (mm/s)
2	302	257.4
4	87	100.6
5	61	71.5

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].

These results indicate 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 Molybdenum trioxide -liquid (Aluminum) reaction, whereas in nanocomposite it is solid state diffusion reaction [39]. The effect on ignition temperatures as particle size changes is shown in Figure 5 [42]. The plotted data is obtained from several studies for various particle sizes under different conditions, so comparing should be done cautiously.

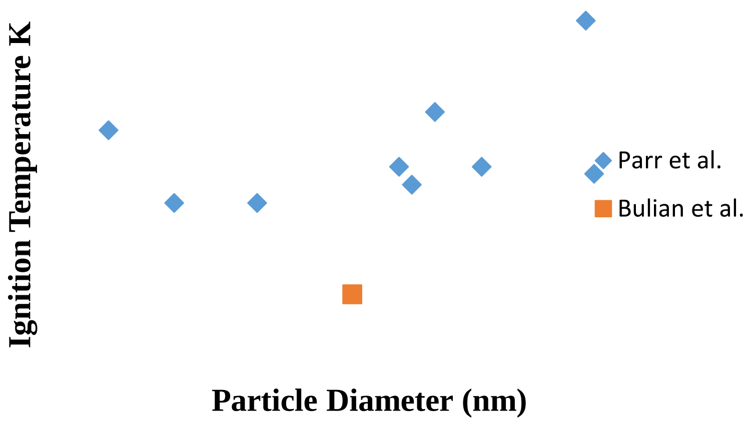

Figure 5. Ignition temperatures of Al as a function of particle diameter

Particle size also affects the burning times of the mixture. From a review paper done by [42], particle burning times affected due to change in particle diameter is obtained and presented in Figure 6. 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 [43]. 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.

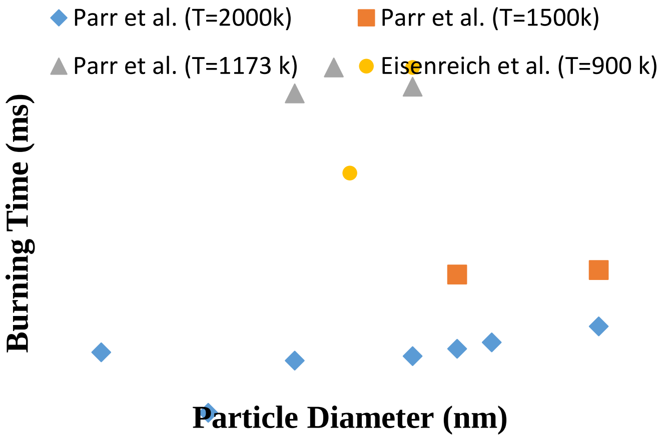

Figure 6.Burning times of nano composites as a function of Particle diameter.

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.

4. 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 behavior 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 7 [44].

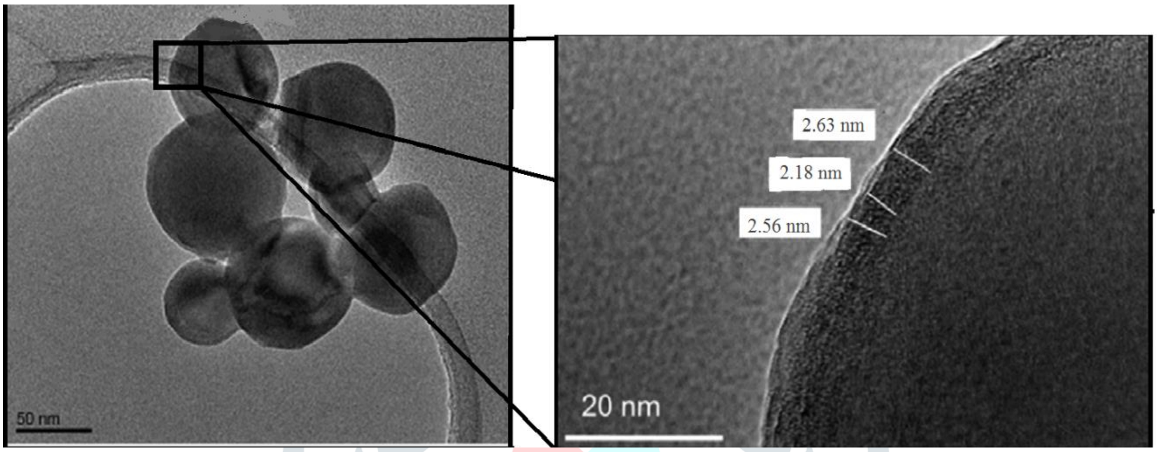

Figure 7. Transmission Electron Microscopic images of Al passivated with Al_2O_3

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 [45]. 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 [46]. 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 [47]. 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% [35]. 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 [33]. 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 [48]. 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 [33].

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

Average Nano Al particle Size (nm)	Aluminum (%)	Reference
30	30	[15]
45	64	[49]
50	43	[39]
50	79	[45]
79	81	[50]
80	80	[49]
80	88	[12]

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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.

5. 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 [51].

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 [51] 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 [52]. 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.

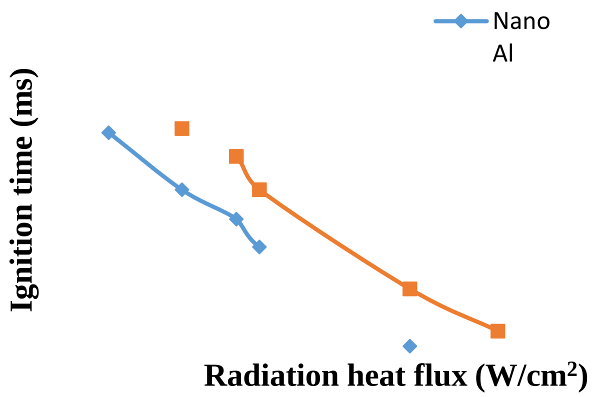

Figure 8. Ignition time as a function of radiation heat flux

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 8.[53].

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 reducing the dimension of the reactant particles. The effect of ignition time of energetic composite as a function of temperature of hot plate is presented in Figure 9 [53]. 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.

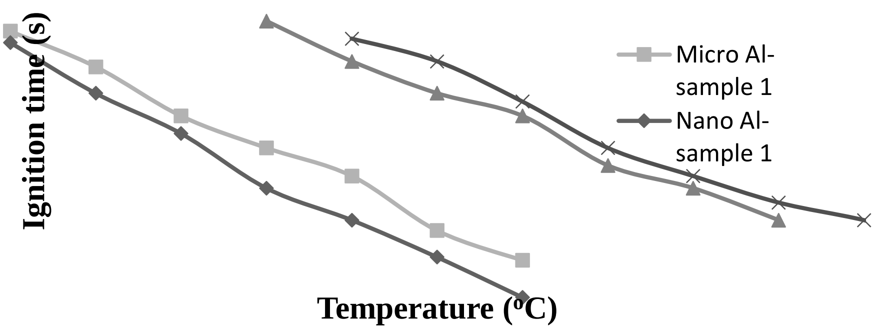

Figure 9. Ignition times as a function of hot plate temperature.

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.

6. 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 straight outcome of their high energy densities, leading to those applications of power generations like micro scale propulsions, nano scale welding and energetic surface coatings. Further uses 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 [54].

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.

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 [55] 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 11(obtained from google images).

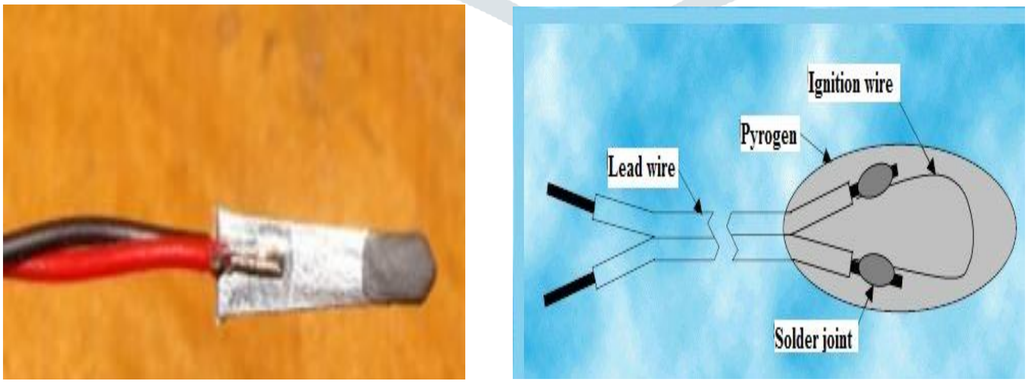

Figure 11. Electric match/igniter schematic diagram

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. 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.

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