



## Nanoscale Aluminum - Metal Oxide (Thermite) Reactions for Application in Energetic Materials

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**Abstract:** Energetic materials find use in both military and civilian applications, however many commonly used materials suffer from serious deficiencies including toxicity and high sensitivity. Nanothermites exhibit vastly differing characteristics compared to their well known micron scale relatives and through the use of various preparatory chemical techniques can be tailored to have a wide spectra of chemical and energetic properties. This may allow use as superior replacements of conventional energetic materials in various applications.

**Keywords:** nano-aluminum, materials, thermites, energetic materials

### Introduction

Research into nanothermites is a current hot topic in the field of energetic materials. Energetic materials are a class of materials containing both fuel and oxidizer in a mixture or within a single compound, and include all the broad areas of propellants, explosives and pyrotechnics. For thermite-type reactions, a metal oxide is the oxidizer, and aluminum the fuel. Thermite-type reactions (as illustrated in Equation 1) on the nanoscale have been called many names including nanothermites [1-3] metastable intermolecular composites (MICs) [1, 4, 5] or superthermites [6]. The phrase “nanothermites” comes from the particle sizes used in these energetic mixtures, in contrast to the more familiar thermite type reaction in which the particle sizes are in the order of microns. The term “metastable intermolecular composites” comes from the fact that the

mixtures of metal oxide and aluminum are stable up to their ignition temperature, at which point self-propagating high-temperature synthesis (SHS) occurs and the thermodynamic products of a metal and aluminum oxide are produced. Finally, the term “superthermite” comes from the fact that thermites composed of nano-sized materials exhibit very different combustion characteristics when compared to those mixed with micron-sized precursors. Superior combustion velocities, and explosive behavior compared to the usual observed deflagration often characterize thermites made with nanoscale precursors.



**Equation 1.** Generalized Thermite Reaction Equation.

Due to energetic materials being a very specialized area of materials chemistry, it cannot be discussed without reference to how these materials are characterized and evaluated for practicality; therefore this paper will begin with a short introduction to the specialized characterization methods used in energetic materials. It is well known that particle size has a great effect on reactivity, so this paper will then give general consequences and examples of varying energetic material properties as particle size decreases. Since this paper is limited to thermites where the fuel is aluminum powder (due to the practical uses of such mixtures) discussion will then briefly focus on special considerations that must be accounted for when working with nanoscale aluminum. This will be followed by general discussion of the various synthetic methodologies of preparing nanoscale thermites and their advantages and disadvantages. As these nanothermites do have applications and are not just chemical curiosities, discussion will then focus on areas where these materials have been proposed for use or attempted for use. Finally, this paper will close with discussion of three specific thermite reactions utilizing different metal oxide fuels. While most metal oxides have been reduced with aluminum in an exothermic thermite reaction, and many have had their reactivity studied on the nanoscale (including  $Fe_2O_3$ ,  $MnO_2$ ,  $CuO$ ,  $WO_3$ ,  $MoO_3$ , and  $Bi_2O_3$ ), discussion of all nanoscale thermite reactions performed in the literature would be too broad. Discussion will focus on iron (III) oxide, molybdenum (VI) oxide, and copper (II) oxide as they provide good examples either of differing synthetic methodologies tailoring properties, exemplary final product properties, or of a material that has a high potential for practical use.

## Energetic Materials Characterization

In addition to standard chemical techniques useful for characterizing inorganic materials such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), the energetic nature of the thermites being discussed necessitates further characterization methods. In order for any energetic material to have application, it must be sensitive enough to various stimuli to combust/explode under desired circumstances, and to not be ignited during handling. Friction, impact and electrostatic discharge (ESD) sensitivity are all important aspects. Friction sensitivity is measured in Newtons (N) by the scraping of various weights over an energetic material sandwiched between ceramic plates, impact in Joules (J) by the dropping of weights from various heights on the energetic material, and ESD in millijoules (mJ) by sending a spark of controlled energy through a sample of the energetic material. Table 1 illustrates the impact and friction sensitivity classes for energetic materials to friction and impact [7].

**Table 1.** Sensitivity Classes

Stimuli	Experimental sensitivity	Sensitivity class
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

The importance of ESD measurements is to make sure that the sensitivity of the material to static discharge is below the static potential developed by the human body (5-20 mJ). Increased sensitivities correlate with increased reactivity of the composite material, and this increased reactivity is also reflected in the speed of combustion of the energetic material. The velocity at which a nanothermite combusts is important for its potential applications, where thermites of one velocity may be suited for one application, and thermites of another velocity may be unsuitable for the same application. Combustion velocity is measured by high speed photography [1]. In this paper unless otherwise noted reported combustion velocities will be for unconfined materials (due to increased

pressure confined thermites burn faster [8]). Finally, ignition temperature is also an important aspect of nano-thermite characterization as the temperature at which one combusts is a practical aspect determining whether a thermite is suitable for a particular use (example, resistively ignited electric matches) [9]

## Particle Sizes and Reactivity

An energetic material's particle size traditionally ranges from 1-100  $\mu\text{m}$  [4]. As is known in general, smaller particles give higher reaction rates and this is no exception in energetic materials. In general, the reaction rate of a nanoscale thermite is several orders of magnitude larger than those on micron scales [4] and the much larger surface area can significantly change combustion behavior, as well as ignition behavior by increasing sensitivity [4]. The changes in properties are all associated with reduced diffusion distances and the associated surface area increases.

The initial reactions in a binary fuel-oxidizer system such as a thermite reaction are assumed to be diffusion-limited solid-solid reactions [10, 11]. As a result the rate of reaction and thereby the combustion velocity can be increased dramatically as the particle size decreases and particle contacts increase. A mathematical study done by Brown et al. [10] comparing observed combustion rates for a Si/Pb<sub>3</sub>O<sub>4</sub> pyrotechnic mixture to calculated fuel-oxidizer contact points for given silicon particle sizes mixed with 5  $\mu\text{m}$  Pb<sub>3</sub>O<sub>4</sub>. Contact points were calculated assuming the approximation that fuel and oxidizer are hard spheres. Partial results from this study are presented in Table 2, and show that a small change in particle size has a very strong effect on fuel-oxidizer contact points, and a correspondingly large effect on combustion velocity.

**Table 2.** Combustion rate as a function of contact points in Si/Pb<sub>3</sub>O<sub>4</sub> composite

Si Particle Diameter ( $\mu\text{m}$ )	Contact Points ( $\times 10^9$ )	Combustion rate (mm/s)
2	30.2	257.4
4	8.7	100.6
5	6.1	71.5

Despite this study not being on the nanoscale, it does show the dramatic effect particle size has on combustion rate where doubling particle size causes greater than halving the combustion rate. The Si/Pb<sub>3</sub>O<sub>4</sub> mixture finds use as a pyrotechnic delay mixture (slow burning mixture used for timing in pyrotechnics) as its combustion rate is easily tailored [10].

As particle sizes decrease, the sensitivity of the thermite mixture to impact and friction increases [3, 4, 12]. The micron scale thermites are usually quite insensitive to impact and shock, but thermites on the nanoscale can be quite sensitive to both or one of the two depending on the metal oxide. This is exemplified in the work of Spitzer [3] where a tungsten(VI) oxide and aluminum thermite was prepared by mixing nano and micron aluminum with nano and micron  $\text{WO}_3$ , the results of which are presented in Table 3.

**Table 3.** Sensitivities for nano vs micron Al/ $\text{WO}_3$  thermite

Al diameter (nm)	$\text{WO}_3$ diameter (nm)	Impact (J)	Friction (N)	Combustion rate (m/s)
1912	724	>49 (insensitive)	>353 (insensitive)	<0.08
51	50	42 (insensitive)	<4.9 (very sensitive)	7.3

While increased sensitivity can make nano-thermites more dangerous to handle, the increased friction or impact sensitivity is also beneficial in some practical applications such as percussion primers. However some nano-thermites have increased ESD sensitivity, which comes with no current practical applications and is a safety hazard. For example, a  $\text{Bi}_2\text{O}_3/\text{Al}$  nano-thermite has sufficient impact and friction sensitivity to be considered for use in ammunition primers [13], however it has an ESD sensitivity of  $0.125 \mu\text{J}$  (40 nm  $\text{Bi}_2\text{O}_3$ , 41 nm Al) [14]. This is a static potential easily achieved by the human body making handling hazardous, especially since the  $\text{Bi}_2\text{O}_3/\text{Al}$  thermite has a combustion velocity of over 750 m/s, so this thermite explodes rather than burns. The increased ESD sensitivity of nano vs micron composites is believed to be the result of the increased ability of high surface areas to develop charges [13].

A final property affected by the reduction in particle size from micron to nano is the ignition temperature of the thermites. For example a thermite composed of 100 nm  $\text{MoO}_3$  and 40 nm aluminum exhibits an ignition temperature of  $458 \text{ }^\circ\text{C}$  whereas the same  $\text{MoO}_3$  with 10-14  $\mu\text{m}$  Al exhibits an ignition temperature of  $955 \text{ }^\circ\text{C}$  [11]. This indicates a change in mechanism between the two as the micron composite exhibits melting and volatilization of Al and  $\text{MoO}_3$  (from DSC) before the thermite reaction occurs, whereas the nano-thermite reaction occurs before the Al melting could take place. This indicates that the reaction for the nano-composite is based on solid state diffusion, whereas for the micron composite the reaction is a gas( $\text{MoO}_3$ ) - liquid(Al) reaction [11]. This change in mechanism may apply to other thermite systems as well, however detailed DSC data for many other systems is so far unpublished.

With thermites using aluminum metal as fuel, the passivation of the metal surface with oxide must be taken into account. For micrometer sized particles of aluminum, the oxide passivation layer is negligible, but on the nano-scale this passivation layer of alumina begins to account for a significant mass portion of the nanoparticles [15]. Research is being done on passivating the aluminum surface to make for greater air stability allowing higher aluminum contents [29]. The oxide layer is not constant for all manufacturers of aluminum nanoparticles, so the researcher must use TEM to measure oxide thickness to allow calculation of active aluminum content before stoichiometric calculations are performed for the mixing of thermites. Table 4 details some of the percentages of aluminum in aluminum nanoparticles and shows just how significant and inconsistent the oxide layer can be.

**Table 4.** Active aluminum content of aluminum nanoparticles

Avg. Al Nanoparticle Size (nm)	Active aluminum content (%)	Reference
30	30	12
45	64	6
50	43	11
50	68	15
79	81	16
80	80	15, 17
80	88	18

The effect of the aluminum oxide is also known to reduce the propagation of thermite reactions as alumina is an effective absorber of thermal energy [1]. A study did by Weismiller et al. with a 49% active aluminum nanopowder in a thermite with copper oxide supports the idea that too much oxide can actually hurt thermite performance [1]. Table 5 shows his data which indicates the negative effect of a thick oxide layer on aluminum nanoparticles.

**Table 5.** CuO/Al Thermites with highly oxidized (49% Al) aluminum nanoparticles

CuO	Al	Combustion velocity (m/s)	Mass Burning Rate (g/s)
Micron	Micron	220	2700
Micron	Nano (49% Al)	200	1100
Nano	Micron	630	4850
Nano	Nano (49% Al)	900	4000

The combustion velocities shown in Table 5 show that the use of nano CuO is more of a factor towards high velocities than the Al when the Al is highly oxidized, and even slightly decreases performance when the velocity of  $\mu\text{m-CuO}/\mu\text{m-Al}$  is compared to  $\mu\text{m-CuO}/\text{nm-Al}$ . The mass burning rate shows this even more starkly, as with a given particle size of CuO, the switch from micron to heavily oxidized nano aluminum decreases the mass burning rate.

## Synthesis Methodology

In general there are three common ways of preparing nano-thermites; these include arrested reactive milling, physical mixing, and sol-gel methodology. Changing from the microscale to the nano, these methods provide accessibility and use of different particle sizes, as well as materials with different degrees of contact between oxidizer and fuel.

Arrested reactive milling (ARM) is a technique for the preparation of nano-energetic materials by milling the metal oxide and aluminum in a ball or shaker mill. While it may or may not involve particle sizes on the nanoscale, the energetic composites prepared by this method have properties more similar to those of the nano-thermites as mixing is on the nanoscale; fuel and oxidizer may be contained in the same particle after milling. The particles produced by arrested reactive milling are in the range of 1-50  $\mu\text{m}$ , and are composed of layers of aluminum and oxidizer on the scale of 10-100 nm [19]. The size of the particles obtained is a function of the milling time, however due to the reactivity of the mixture, after a certain milling time (a function of initial particle sizes, milling media used, and type of metal oxide) when the particles are reduced below a certain size, the milling causes ignition of the thermite mix. A liquid such as hexane is usually added to the mill to reduce static build up. The term arrested reactive milling comes from the fact milling is stopped before the time the mix ignites, resulting in a useable thermite mixture. Advantages of this method are that the particles produced are approaching their maximum density, aluminum is hidden within the particle matrix reducing the presence of nonreactive alumina, the ability to start with non-nanoscale precursors, and milling time offers convenient control of the degree of intermixing and thereby reactivity [20]. Disadvantages include the fact that only few thermite mixtures can be prepared by this method as many other mixtures are too sensitive and ignite before sufficient intermixing can occur.

Physical mixing is the simplest and most common method of preparation of nano-thermites. Nano-powders of metal oxide and aluminum are mixed in a volatile, inert liquid (to reduce static charge [13]) and sonicated to ensure

good fuel-oxidizer mixing and break up macroscale agglomerates [3, 6, 11]. The liquid is then evaporated off and the thermite is ready for use. Advantages of the physical mixing method is the simplicity and wide range of applicability to many thermite systems [1, 5, 21]. The only major disadvantage is the necessity of starting with nanoscale powders which may or may not be commercially available [18].

Sol-gel nanothermite preparations take advantage of the unique structural and mixing properties available from sol-gel chemistry [22]. In these nanothermite mixtures, the aluminum nanoparticles resides in the pores of the metal oxide matrix, which is widely assumed to increase thermite power compared to physical mixing by huge reduction in diffusion distances between fuel and oxidizer, and by increasing contact area [12, 23]. The synthesis of energetic sol-gel thermites involves the addition of a suspension of aluminum nanopowder in solvent to a metal oxide sol just prior to gellation, after which the gel can be processed to an energetic xero or aero gel. Through the sol-gel methodology, interfacial area, pore size, and matrix geometry can be controlled [24, 25] which results in different, tunable energetic properties. In addition, the sol-gel methodology allows the molecular incorporation of organic agents to the matrix which further tune thermite properties by acting as a gas generating agent [26]. Other than the ability to incorporate organics, advantages of the sol-gel method include ability to form low density aero or xero gels, which comes with it the ability to form energetic surface coatings [23]. Disadvantages include potential oxidation of the aluminum nanoparticles by water in the metal oxide gel before solvent can be removed. This disadvantage can be overcome by only using sol-gel chemistry to prepare aero or xero-gel oxide precursors, followed by physical mixing with aluminum, but this comes at the cost of the increased interfacial contact achievable by sol-gel chemistry [26].

## Applications

Due to the range of properties that nanothermites can be tailored to have, nanothermites find application in a correspondingly large number of applications. As research on nanothermites is a relatively new topic, many applications have only been proposed and testing in such areas has not yet been done. Many of the potential applications of nano-thermites are a direct result of their high energy densities, which are comparable to those of lithium batteries [16] leading to applications of the power-generating variety such as microscale propulsion [3, 4, 16], energetic surface coatings [23] and nano-scale welding [3]. Other

applications are a direct result of the pyrotechnic behavior of nano-thermites, and such materials may find use as gas generating agents for automobile airbags [3, 22, 26], exploding-on-contact missiles [24], environmentally friendly ammunition primers [5, 13, 18] and electric igniters [5, 9], and even potential application of the fastest thermites as primary explosives [17]. The applications of microscale propulsion, ammunition primers, and electric igniters have had more experimental work conducted with them compared with other potential applications for nano-thermites, and show very promising results.

Microscale propulsion involves the production of thrust on the microscale (<1mm). This is referred to as micropyrotechnics or microenergetics [16], and applications include rapid switching and propulsion for small spacecraft [16]. Performance energetic materials used for propulsion on the macroscale including RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) or HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) are unable to function on the microscale, as they cannot sustain combustion in such small diameters as too much energy is lost to the combustion chamber inhibiting propagation through the energetic material. Nanothermites have no such problem as they have a much higher energy density [23], so energy lost to the chamber becomes insignificant.

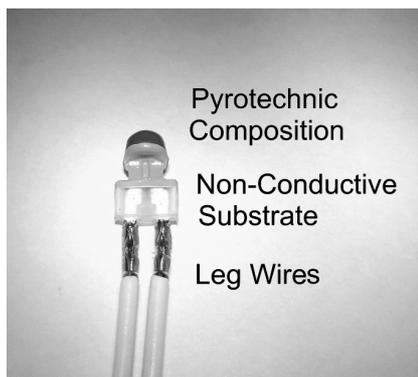
An ammunition primer is the part of a round of ammunition that is impacted by the firing pin of the firearm. Traditional primers contain lead containing compounds including lead azide and lead styphnate, as these sensitive explosives detonate from the impact of the firing pin, and the resultant flame ignites the propellant in the cartridge, firing the bullet. Figure 1 shows a shotgun shell primer. The toxicity of lead means the use of such primers is both an environmental and personal hazard to the user [28]. Nanothermites have been shown to be an effective replacement for the lead salts, as they have been tailored to have properties similar to the currently used lead azide/styphnate mixture [5, 13].

Electric igniters find throughout the energetic materials industry in all areas of propellants, explosives and pyrotechnics; they are used wherever an electric current is desired to be used to initiate an energetic material. As a result of the precise timing they afford, they can be used for igniting everything from rockets to blasting caps, to fireworks displays. Electric igniters are also known as electric matches, and they consist of a flammable head of material around a resistive bridgewire, igniting when a certain electrical current is passed through the match. Figure 2 shows a labeled electric match (not shown is the electrically resistive bridgewire beneath the pyrotechnic composition). Like primers, commonly used electric matches contain toxic lead compounds including the tetroxide, thiocyanate and nitroresorcinate [9] so finding nontoxic replacements is desirable.

Again, the use of nano-thermites has shown significant promise as non-toxic, green replacements for the lead compounds [5, 9].



**Figure 1.** Shotgun shell primer.



**Figure 2.** Electric igniter/match.

## Iron Oxide/Aluminum Thermite

On the macroscale, iron oxide/aluminum thermite finds use for the high temperature welding of iron railway rails; its slow rate of energy release and high combustion temperature makes this possible. On the nanoscale, however, iron oxide/aluminum thermite behaves very differently. In the literature, this thermite system is often synthesized by sol-gel methods [22, 24, 25] as iron oxide sol-gel chemistry is well known, however it has been made by arrested reactive milling [19] and physical mixing [26] as well.

The iron oxide thermite is a very good demonstration of the versatility of the sol-gel thermite methodology. Table 6 shows the huge effect the type of synthesis can have on the thermite properties.

**Table 6.**  $\text{Fe}_2\text{O}_3/\text{Al}$  Thermite synthesis effect on combustion velocity

Synthesis Methodology	Velocity (m/s)	Reference
Arrested Reactive Milling (max mill time before ignition)	0.5	19
Physical Mixing (80 nm Al, oxidizer size unmentioned)	9	26
Sol gel (aerogel oxide physically mixed with 80 nm Al)	80	26
Sol gel ( xerogel, 70 nm Al added before gellation)	320	23
Sol gel (aerogel, 70 nm Al added before gellation)	895	23

From these numbers, the wide range of thermite properties that become available is apparent. The ease of tuning energetic properties is also apparent from the high velocity (320 and 895 m/s) xero and aerogels prepared by Gash et al. [23] as the xero and aerogel have different sensitivities to ESD and to impact. These differences are shown in Table 7.

**Table 7.** Impact and ESD sensitivities of aero and xero gel  $\text{Fe}_2\text{O}_3/\text{Al}$  thermite [12, 23]

Type	Impact(J)	ESD (mJ)
Xerogel	36.6	>1000
Aerogel	21.9	30

The impact sensitivity of the aerogel thermite may make it suitable for use in primers, whereas all the other preparatory methods for the iron oxide thermite produce thermites unsuitable for this application. The especially sensitive nature of aerogel thermites comes from the inability of the aerogel matrix to conduct heat, a character only applicable to aerogels, due to their insulating ability [23].

A further development on the synthesis-dependent application of iron oxide thermite is that of Clapsaddle et. al. [26]. Tailoring of energetic properties was obtained by the addition of organo-silicon precursors to the sol leading to aerogel oxidizers containing any desired percentage of organic-functionalized silica. The silica functioned to reduce the combustion velocity, and the organic addition to increase gas release upon combustion. The research is still in the initial stages, but the thermites may have application in the propulsive and gas-generating fields.

## Copper Oxide/Aluminum Thermite

Copper oxide and aluminum thermite is well known for its high combustion velocity even on the micron scale. This high combustion velocity is further pronounced on the nano-scale where the thermites reach the highest combustion velocities known for a mixture of metal oxide and aluminum [17].

While in the literature  $\text{CuO}/\text{Al}$  thermites have not been prepared by reactive milling or sol-gel methods, unique to  $\text{CuO}/\text{Al}$  thermite is a new synthesis methodology by Shubhra Gangopadhyay called self-assembly [17]. In this method, the authors coated copper nanorods (20x100 nm) with a coordinating polymer (P4VP) followed by coating the coated rods with 80 nm aluminum powder. The result of this self-assembly process is the thermite with the highest

combustion velocity known of 2400 m/s. Table 8 gives the combustion velocity of the self-assembled thermite compared with physically mixed thermites.

**Table 8.** Combustion velocities of CuO/Al thermite (80 nm Al, 2.2 nm oxide layer)

Synthesis method	CuO morphology	Combustion velocity (m/s)
Physical mixing	micron	675
Physical mixing	nanorods	1650
Self assembly	nanorods	2400

Gangopadhyay et al. [17] state the reason for the increased combustion velocity is the highly improved interfacial contact between fuel and oxidizer. However the presence of an organic material binding fuel and oxidizer will increase combustion pressure which has been shown by Weismiller [1, 8] and Bulian [27] to have an increase on combustion rates. The dependence of combustion velocity on pressure has been thought of as resultant of decomposition of CuO to gaseous oxygen at 1000 °C [27] which may be the active oxidizer.

Despite the reason for the high combustion velocity being under debate, the high combustion velocity is in the range of explosive velocities, so the CuO/Al thermite may have application as a primary explosive. The more easily prepared physically mixed CuO nanothermite has been patented for use in ammunition primers [13]. Sensitivity data for CuO/Al thermite is unavailable; however it is expected to be relatively high. High impact sensitivity may be the reason there are no literature reports of preparation by arrested reactive milling.

## Molybdenum Trioxide/Aluminum Thermite

MoO<sub>3</sub>/Al has been prepared exclusively by physical mixing and arrested reactive milling [18, 20]. Due to the availability of both MoO<sub>3</sub> and aluminum nanopowders, the preparation used exclusively in practical applications [5, 9, 13, 16] of these thermites is physical mixing. With combustion velocities ranging from 150-450 m/s [6, 18] MoO<sub>3</sub>/Al thermites are perhaps some of the most widely studied nano-thermites, and extensive work has been done on their practical applications of electric igniters [5, 9], primers (patented [13]), and microscale propulsion [16].

A study done by Son et al. [16] on the feasibility of the use of a MoO<sub>3</sub>/Al nanothermite (79 nm spherical Al, 30x200 nm sheet MoO<sub>3</sub>) for microscale

propulsion and microscale pyrotechnics shows great promise for the application of these materials. It was found that confined in tubes with a diameter of 0.5 mm, MoO<sub>3</sub>/Al thermite would combust at rates as high as 790 m/s. This is an advantage over conventional energetic materials such as HMX which cannot even propagate in tubes under 1mm [16].

Naud et al. [9] have preformed extensive work on the use of MoO<sub>3</sub>/Al nanothermite for application in electric matches. Electric matches prepared from this thermite mixture have been shown to have lower friction, impact, thermal and ESD sensitivity than the currently used matches containing toxic lead compounds making them both safer and more environmentally friendly to use [9].

## Conclusion

The field of nanoscale thermite reactions is a relatively new field of research, but already it has shown that a spectrum of thermite reactivity is able to be produced with combustion velocities ranging from less than one meter per second, to the current maximum of two thousand four hundred meters per second. The thermites have been shown to have sensitivities tunable by varying particle sizes and preparation amenable to different methods. Preliminary experiments have shown these thermites to be superior replacements for current energetic materials in certain applications. There are many thermite systems incompletely characterized and with no studies yet carried out for practical application feasibility so this field can only grow.

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