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Potential Usage of Energetic Nano-sized Powders for Combustion and Rocket Propulsion

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ABSTRACT

Nano-sized energetic metals and boron particles (with dimensions less than 100 nanometers) possess desirable combustion characteristics such as high heats of combustion and fast energy release rates. Because of their capability to enhance performance, various metals have been introduced in solid propellant formulations, gel propellants, and solid fuels. There are many advantages of incorporating nano-sized materials into fuels and propellants, such as: 1) shortened ignition delay; 2) shortened burn times, resulting in more complete combustion in volume-limited propulsion systems; 3) enhanced heat-transfer rates from higher specific surface area; 4) greater flexibility in designing new energetic fuel/propellants with desirable physical properties; 5) nano-particles can act as a gelling agent to replace inert or low-energy gellants; 6) nano-sized particles can also be dispersed into high-temperature zone for direct oxidation reaction and rapid energy release, and 7) enhanced propulsive performance with increased density impulse. In view of these advantages, numerous techniques have been developed for synthesizing nano-particles of different sizes and shapes. To reduce any possible hazards associated with the handling of nano-sized particles as well as unwanted particle oxidation, various passivation procedures have been developed. Some of these coating materials could enhance the ignition and combustion behavior, others could increase the compatibility of the particles with the surrounding material. Many researchers have been actively engaged in the characterization of the ignition and combustion behavior of nano-sized particles as well as the assessment of performance enhancement of propellants and fuels containing energetic nano-particles. For example, solid fuels could contain a significant percentage of nano-sized particles to increase the mass-burning rate in hybrid rocket motors, the regression rate of solid propellants can be increased by several times when nano-sized particles are incorporated into the formulation. Specifically, hybrid motor data showed that the addition of 13% energetic aluminum powders can increase the linear regression rate of solid HTPB-based fuel by 123% in comparison to the non-aluminized HTPB fuel at a moderate gaseous oxidizer mass flow rate. Strand burner studies of two identical solid propellant formulations (one with 18% regular aluminum powder and the other with 9% aluminum replaced by Alex® powder) showed that nano-sized particles can increase the linear burning rate of solid propellants by 100%. In addition to solid fuels and propellants, spray combustion of bipropellants has been conducted using gel propellants impregnated with nano-sized boron particles as the fuel in a rocket engine. High combustion efficiencies were obtained from burning nano-sized boron particles contained in a non-toxic liquid-fuel spray. Materials characterization such as chemical analyses to determine the active aluminum content, density measurements, and imaging using an electron microscope have been performed on both neat nano-sized particles and mixtures containing the energetic materials. In general, using energetic nano-sized particles as a new design parameter, propulsion performance of future propellants and fuels can be greatly enhanced.

INTRODUCTION

In recent years much research has focused on the use of energetic nano-sized particles for many applications including in solid propellants, gelled propellants, solid fuels, and explosives. Performance increases arise from the use of nano-sized energetic particles in shortened ignition delay time, decreased burning time (generally following the d^2 burning law), enhanced heat transfer from the higher specific surface area, enhanced mechanical properties of the composite solid materials, energetic gelling agents instead of inert gellants, and higher density impulse. Nano-energetics can store a greater amount of energy then conventional energetics and have the ability to tailor the location of the release of energy to maximize effectiveness.

Excess internal energy can be stored in nano-sized particles. Excess stored energy can be created by lattice dislocation. Many of the dislocated atoms do not anneal during the irradiation process and the net result is an increase of internal energy of the nano-sized material. This increase is usually referred to as a "stored energy". Radiation damage can alter many properties of the material. In heavily irradiated material, the stored energy can be as much as 600 cal/g. If suddenly released, this energy can result in an increase of adiabatic temperature by several hundred degrees. The spontaneous release of the stored energy can be triggered off by an external heating process. Such energy release can take place, since lattice defects can relocate inside the crystal and take part in various annealing processes in which the clusters rearrange themselves into more stable forms.

Experiments have shown that only a fraction of the energy consumed by plastic deformation of metals is stored in the metal, the remaining energy was dissipated during the plastic deformation. The experimental data indicate that 1-15% of the energy can be stored, but the results may change considerably with the metal itself and its purity.

There are several methods which can be used to produce stored energy in materials. Among the most important is fast plastic deformation of solids, quenching of a metastable structure in alloys, and irradiation of solids by a neutron beam or hard γ-ray irradiation. Obviously super-fast cooling makes it possible to freeze metastable structures; mechanical deformation or irradiation produces dislocations, vacancies and other faults. Evidently the effect of "stored energy" represents thermodynamically a highly non-equilibrium state. Usually, the relaxation time is sufficiently long, sometimes expressed in years or months scale. Therefore, because of the energetically stressed medium these nano-sized materials can be extremely reactive. Experimental data indicate that the stored energy can change the reactivity of solid materials by many orders of magnitude.

Energy storage mechanisms unique to nanoparticles include the interface energy contribution and interface curvature contribution. It is useful to study energy storage mechanisms in nanoparticles. Nanoparticles have tremendous surface area. If agglomerated or sintered, they have similarly large grain boundary area. The root source of the extra energy is the bonding configuration of the atoms at the surface or grain boundary. Surface atoms, by definition, are not fully bonded on all sides, and therefore have one or more dangling bonds. Wherever there are dangling bonds, these bonds do not have to be broken first (requiring energy input) before they can participate in a chemical reaction that will subsequently release energy. Thus, the total energy produced by the reaction is greater. Specifically, the extra energy released in combustion (J/g) would be $\gamma A_s/\rho$, where γ is the surface or grain boundary energy of the powder in J/m^2 (this is, fundamentally, the extra energy associated with not having a fully bonded atomic configuration at the interface), A_s is the specific surface area in m^2/m^3, and ρ is the density of the material in g/m^3. When the particle is 10 μm in size, the atoms on the surface have negligible amount of stored energy; however, when the particle is 5 nm in size, about half the particle is comprised of "surface" atoms and therefore can react more readily with surface adsorbates.

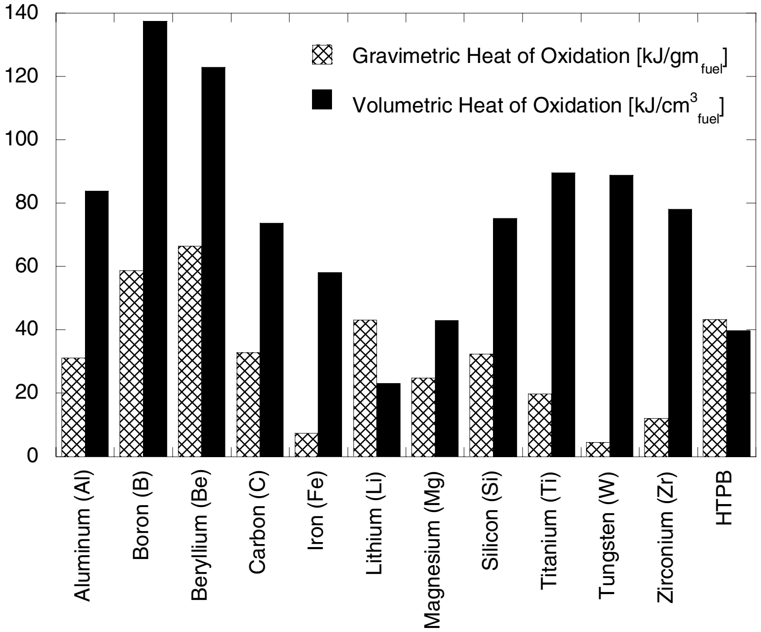
In terms of interface curvature contribution, the curved, strained state of an interface has to be supported by a pressure differential between the materials on the concave side of the interface relative to the convex side. Thus, within a balloon or soap bubble, the air pressure inside is greater than that outside. The pressure differential for a spherical object enclosed by an interface is $2\gamma/r$, where γ is the surface or grain boundary energy (depending on whether the powders are loose or sintered), and r is the radius of the sphere. Thus, for a nanoparticle, the material inside of the particle is subjected to an internal pressure (or intragranular stress) that is quite large – about 200 MPa for a particle with a 10 nm radius. This internal pressure gives rise to many interesting solid-state phenomena, such as the dramatically increased solubility of nano-crystalline particles, and the tendency for nanoparticles to exist in high-pressure crystallographic forms even though the ambient pressure is only atmospheric. The high degree of intragranular stress can also deform the material, giving rise to a stored energy term. In addition to energy storage mechanisms that rely on high surface areas, or tight particle curvatures — features unique to nanoparticles — it is possible to “load” nanoparticles with other forms of stored energy commonly used in larger particle, such as excess vacancies.

This paper addresses formulation consideration of energetic materials containing nano-sized particles, their application to various aspects of combustion, and enhancement of propulsive power. Several areas of energetic particles can be considered including: metastable intermolecular composites (MICs) as powerful igniters, sol-gels as a process for manufacturing nano-materials, nano-particles used in solid fuels/propellants, and nano-gellants. These will be discussed in detail in the following sections.

Why nanoenergetic particles are attractive for combustion enhancement

In the formulation of energetic solid propellants or solid fuels, one important factor to consider is the heats of oxidation of the fuel ingredients. Another factor is the density of the selected fuel ingredient. Hydroxyl-terminated polybutadiene (HTPB) is a common fuel binder material for solid propellants as well as for polymeric solid fuels. Figure 1 gives a comparison of the heats of oxidation of a set of energetic fuel ingredients with HTPB. It is evident that many ingredients (such as B, Al, Ti, W, etc.) have higher volumetric heats of oxidation than that of HTPB. For volume limited propulsion systems, the volumetric heat of oxidation is more important than the gravimetric heat of oxidation. Boron has the highest volumetric heat of oxidation among this group. However, due to its high melting temperature (T_{melt}= 2,348K) and ultra-high boiling temperature (T_{boil}= 4,273K), micron-sized particles have not been incorporated successfully into the existing propellants or fuels. The increased ignition delay time due to the high melting temperature of boron for micron sized particles causes complete combustion of boron particles within the combustion chamber to be very difficult. This makes boron particles not very attractive when only micron-sized particles are available. For nano-sized particles, the residence time becomes less of an issue because of the drastic reduction of ignition delay and burning times of the particles (using the d^2 burning law) making nano-sized boron particles highly attractive as energetic additives. As seen in Fig. 1, beryllium also has a very high volumetric heat of oxidation. However, beryllium has not been used in propulsion systems due to the high toxicity of beryllium oxide. Titanium demonstrates a relatively high volumetric heat of oxidization as well but due to the high cost of titanium and also the unavailability of nano-sized titanium particles, this metal has not been utilized. The high volumetric heat of oxidization of aluminum, as well as the ability to easily ignite aluminum particles has made it a main focus of nano-particle combustion research. Many commercial nano-sized aluminum particles are available (including Alex®, Technanogy, Nanotechnologies, Silberline, etc.) and many researchers have tested the effect of various nano-sized aluminums on the propulsive performance of solid propellants or solid fuels. The use of tungsten has not been considered in any great depth even though it has a high volumetric heat of oxidization as well. The melting temperature of tungsten is the highest among any metal (T_{melt}= 3,695K) and its extremely high boiling temperature (T_{boil}= 5,828K) may have deterred researchers away from studying this material as an energetic additive. Recently, nano-sized tungsten particles have been synthesized (by NanoMat, Inc.). Unlike boron, tungsten does not require extremely high temperatures in order to ignite. Oxidation of tungsten begins to occur at 700-800 K and rapid reaction could occur at temperatures above this range based upon CRC data. Nano-sized tungsten particles could have a chance to serve as energetic additives for propulsion applications. It can be seen in Fig. 1

that all the particles in this group, except lithium, have much higher density than that of HTPB. This is beneficial for volume-limited rocket propulsion systems, since the most important parameter is the density-specific impulse.



Material	Density [g/cc]
Aluminum	2.700
Boron	2.340
Beryllium	1.850
Carbon	2.267
Iron	7.870
Lithium	0.534
Magnesium	1.740
Silicon	2.330
Titanium	4.510
Tungsten	19.300
Zirconium	6.520
HTPB	0.920

Figure 1. Heats of oxidation and densities for several energetic fuels in comparison with HTPB

SEVERAL SPECIFIC FOCUSED AREAS OF RESEARCH

Although the use of nano-energetics is a relatively new field of research, many research teams have recently focused their attention in this field. The use of nano-sized energetics can decrease the sensitivity of propulsion systems (which is a high priority issue), increase specific energy release, and enhance the mechanical behavior of propellants/fuels. In the following discussion four areas are covered: metastable intermolecular composites (MICs) as powerful igniters, sol-gel methodology for producing nano-materials, nano-sized particulate additives for solid propellants and fuels, and nano-particles for gelling liquid fuels.

Metastable intermolecular composites (MICs)

In the development of MICs, the mixture Al/MoO_3 was considered to have the potential for generating higher thermal energies through thermite reactions. In general, MICs are formulations of nano-powders that exhibit thermitic behavior (they are a subclass of materials known as thermites). Thermites, traditionally an aluminum powder and metal oxide mixture, are commonly used in incendiary weaponry due to the large amounts of energy that are produced by the combustion of such material. Unlike traditional energetics whose heat release depends on intramolecular properties, thermite materials heat release is a function of intermolecular properties. Mixing of the reactants occurs at the nanometer length scale, with tens of nanometers as the typical particle sizes. Alteration of the size of the MICs results in an effect on the amount and rate of heat release allowing the optimization of heat release efficiency to the surrounding materials. This is advantageous for design of future munitions and propulsion systems. Although many capable researchers are performing research, the mechanism of propagation of the reactions is still not fully understood. Some possible applications of MICs, as outlined by Miziolek [1], include environmentally clean primers and detonators, chemical agent neutralization, improved rocket propellants, IR flares/decoys, thermal batteries, and others. The use of MIC formulations to obtain performance increase in these areas has resulted in attention in research to be placed on three formulations: Al/MoO_3, Al/Teflon, and Al/CuO.

Researchers have studied dynamic gas condensation methods for production of nano-sized aluminum powders as well as MIC formulations with precision control of particle physical characteristics. The dynamic gas condensation method can reproducibly generate small particles down to tens of nanometers with a very narrow size distribution. This is important in MIC production due to the need to tailor energy release by the use of MIC particles of desirable sizes. There still exists the need for much research into the production and characterization of these MIC materials, including the fundamental mechanisms that control the propagation of the reaction, safety characterization, etc. Initial studies of the safety characteristics (i.e. sensitivity to impact, friction, and electrostatic discharge induced ignition) show promise but further testing to fully characterize the behavior of MICs is needed. Another area of need is the production of nano-sized ingredients for MIC formulations. Work in this area is being conducted by several companies (such as Nanotechnology and Technanogy) but further improvements are still required to make MIC a practical material for applications. Several attractive features of MICs include: energy output of two times that of typical high explosives, the capability to tailor the reactive power (10 to 10^7 KW/cc), the ability to control the flame-front propagation velocities over a wide range (0.1-1500 m/s), and reaction zone temperatures on the order of 3000K. These characteristics have shown broad applications in propulsion fields.

Sol-gels as processing technique for nano-sized particles

The sol-gel process involves the reaction of chemicals to create the initial nano-particles in a solution; this solution is called the “sol”. The particles that are created are then linked in a 3-D solid structure; this is called the “gel”. There exists open pores between connected particles and these pores are usually filled with the solution. Two different types of sol-gels are typically produced from this. The first type is called a “xerogel” which is produced by evaporating the remaining solution resulting in a dense, porous solid matrix. The second type is named “aerogels”, which are produced by a supercritical extraction of the remaining fluid in the solution. By this process the surface tension is eliminated and results in a material in which the pores have not collapsed as in the xerogel method. Both the particles and the pores of aerogels are on the nano-scale and the material in general is very uniform [1].

The production of Fe_2O_3 via a sol-gel method was also developed. Fe_2O_3 was chosen due to its thermite reaction with nano-sized aluminum. This reaction is very exothermic, and therefore beneficial for application purposes. The reaction to produce Fe_2O_3 can be performed in solution that already contained the nano-sized aluminum. The resulting material can have very uniformly dispersed aluminum within the Fe_2O_3 [2]. The intimate mixing of Fe_2O_3 and Al allows for a high energy density composition that has good safety characteristics. This methodology as it is advanced may provide a simple means of producing nano-energetic materials that will greatly increase the performance of future propulsion systems as well as decrease sensitivity.

Nanoparticles as additives to solid propellants and solid fuels

The addition of nano-sized particles to high explosives and solid-propellant formulations is an ongoing investigation by many groups. Many different methods are used to create particles that will increase performance. Some methods include the coating of passivated aluminum particles in an energetic matrix (e.g., RDX), production of nano-sized nitramine particles, and the addition of pure nano-sized metallic particles to an energetic fuel binder. For example, NanoMat, Inc. manufactured nano-sized aluminum rods for consideration as energetic additives in solid propellants and solid fuels.

Figure 2 shows a TEM micrograph of nano-sized aluminum rods. Since the thermal conductivity of aluminum is very high in comparison with solid propellants, these rods increase the energy transfer in the subsurface region and alter the burning characteristics of the propellant.

Jigatch, et. al. [3] have investigated the addition of nano-sized aluminum powders in high explosives. Considered were aluminum nano-particles coated with various types of coating (unsaturated carbonic acids and organo-silicon) to prevent metal-to-metal contact of the particles. The coated particles were then passivated by a controlled rate of oxygen for safe handling. The passivated particles are then introduced into an energetic material solution (i.e. RDX) and dispersed by ultrasonic sonication. The solution is then injected through an injector. The atomization of the solution causes fast evaporation of the solution droplets. The resulting RDX-coated aluminum particles are then used for characterization of physical properties. This methodology was capable of creating nanometer scale particles of aluminum particles coated externally with RDX. Through this same methodology, pure nano-sized RDX particles can also be produced. The presence of aluminum in the composite aluminum/RDX particles was identified by electron probe analysis. Further study is required to determine the optimum solution of RDX to obtain particles with an ideal coating. From this study, it was proven that their general procedure is plausible for manufacturing nano-sized particles that exhibit desirable combustion characteristics for explosives and solid propellants.

The ability to generate nano-sized nitramine particles is desirable for solid propellants and explosives. The use of nano-sized particles causes the mechanical properties of the solid propellant to be more desirable as well as enhances the insensitive munitions characteristics. For these reasons, several studies for the effects of the addition of nano-particles, high nitrogen compounds, and insensitive ingredients on the burning rate behavior of solid propellants. Various techniques for nano-sized nitramine particle production are being developed (e.g., expansion of solutions). There are many challenges to be overcome in the near future, for example, the increase of particle production rates, the accurate control of particle size distribution, and control of the morphology of the final product. Future work will refine this type of methodology and determine an optimum method of production for mass manufacturing.

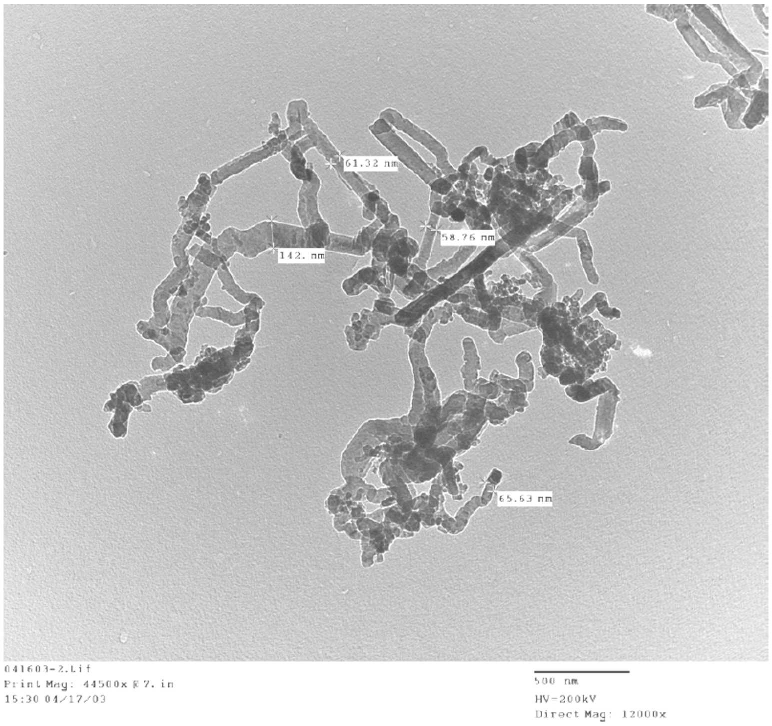


Figure 2. TEM photograph of nano-sized aluminum rods
(courtesy of Mr. C. Skena of NanoMat, Inc., North Huntingdon, PA)

The addition of nano-sized aluminum powder in a matrix of solid propellant can result in a much higher burning rate. Experiments with ultra-fine aluminum and ammonium perchlorate have indicated that the burning velocity may increase 10 to 20 times compared to the use of regular industrially available aluminum [4]. In solid propellants, mixtures with 40% conventional aluminum are not combustible. However, by using nano-sized aluminum, high burning rates can be achieved. The burning velocities with metal content near stoichiometric are as high as 18 cm/sec. Mench, Yeh, and Kuo [5] also studied the influence of nano-sized aluminum particles on the burning rate of solid propellants by replacing a portion of conventional Al with Russian made ultra-fine Al particles (called ALEX®). As depicted in Fig. 3, their results indicated significant increases in burning rates at two different initial temperatures. It is known that during the combustion process, micron-sized aluminum particles melt and agglomerate to large drops on the propellant burning surface; thus, these large agglomerates have no time to be completely oxidized in the rocket motor. There are two modes of energy loss; one due to incomplete combustion and the other due to two-phase flow losses induced by particle drag. These losses can be significantly reduced using nano-sized particles in energetic materials and therefore, the characteristics of combustion can be substantially improved.

While the use of nano-scale particles can significantly increase burn rates and minimize incomplete combustion, their very high surface area can also impede our ability to predict and control their behavior. For example, high surface areas make nanoparticles more susceptible to unwanted ignition during processing. In addition, they are more susceptible to long term environmental degradation (oxidation). To minimize these deleterious effects, the surface of the nanoparticles can be modified with a polymeric, metallic, or metal oxide layer. The passivation layer can stabilize the particles against unwanted ignition, and reduce long-term degradation, and surface contamination.

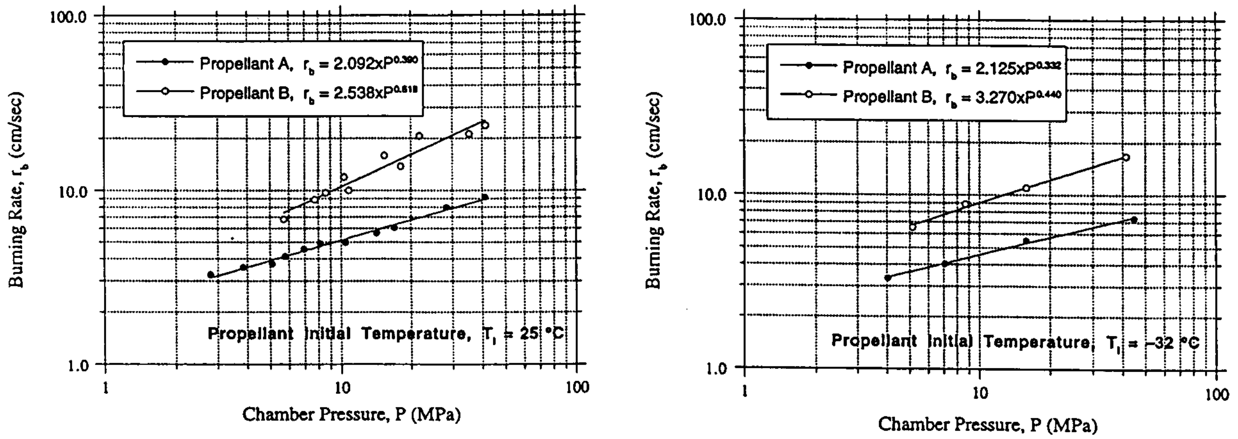


Figure 3. Comparison of burning rates of Propellant A (with 18% conventional aluminum powder) and a similar Propellant B (with 9% ALEX® aluminum powder & 9% conventional aluminum powder) at two initial temperatures (After Mench, Yeh, and Kuo [5])

A traditional hybrid rocket motor uses a solid-fuel grain to burn with a liquid oxidizer. Hybrid propulsion systems utilizing solid fuel and liquid or gel oxidizer have many advantages over conventional liquid- or solid-propellant systems including inherent safety, more environmental friendliness, and improved operability.

A problem encountered with solid-fuel formulations using HTPB-based solid fuels (traditionally used in a hybrid rocket motor) is the relatively low burning rates (and thus mass consumption rate of fuel) in comparison to solid propellants. Since the thrust produced is directly proportional to the mass flow of propellant products through the nozzle, a hybrid rocket motor requires an intricate grain design in order to produce an equivalent amount of thrust to a solid-propellant rocket motor system if the fuel-burning rate is not greatly enhanced. Recent advances in high-energy reactive materials and nano-sized particles have been used to formulate new energetic solid fuels with greatly improved regression rates, physical properties, and propulsive performances. Lab-scale hybrid rocket testing provides relatively inexpensive and rapid means to screen performance of various solid fuel formulations containing different types of nano-sized energetic particles. Low burning rates of solid fuels have shown to be enhanced by the addition of energetic metal powders. The use of nano-sized energetic powders allows the thermochemical energy to be released closer to the surface of the regressing fuel; this increases the energy feedback rate, thus increasing the regression rate of the fuel surface. Table I shows various energetic particles utilized in a family of HTPB-based solid fuels, which were tested and characterized by Risha et al. at the Pennsylvania State University (PSU) [6].

Evaluation of the energetic materials has been conducted with 3 different hybrid rocket motors at PSU including a 2-D slab motor, long-grain center-perforated (LGCP) motor, and an X-ray translucent casing (XTC) motor. Chiaverini, et al. [7] used the 2-D slab motor to study the effect of various weight percentages of Alex® aluminum nano-particles (4%, 12%, and 20%) in HTPB-based solid fuel. The addition of 20% of Alex® enhanced mass burning rates up to 70% in comparison to pure HTPB fuel formulations. Research by Risha et al. [6] evaluated the addition of energetic nano-sized particles in the LGCP hybrid rocket motor. For each additive, three fuel grains were cast with 13% by weight addition of nano-sized energetic particles. The fuel grains were then burned at three different oxidizer flow conditions in order to determine dependence of the regression rate of the fuel surface on the oxidizer mass flux (mass flow rate of oxidizer divided by the port area of the fuel grain [M/L^2-t]). The oxidizer mass flux was varied since theoretically the regression rate of a solid fuel is dependent on the oxidizer mass flux. Results were compared as a function of the average oxidizer mass flux (oxidizer mass flux averaged over the duration of the test). Figure 4 shows a comparison of the mass-burning rate for various fuel formulations in relation to pure HTPB for a selected average oxidizer mass flux of 112 kg/m^2-s.

Table I. Energetic nano-sized particles evaluated in study

Nanoparticle	Specific Surf. Area [m^2/g]	Size [nm]	Density [g/cm^3]	Supplier
Alex aluminum	13.3	100-150	2.7	Argonide Corp.
WARP-1 aluminum	27.5	70	2.7	Ceramics & Materials Processing, Inc. (CMPI)
Silberline aluminum flakes	-	thickness 50-200	2.7	Silberline Manufacturing Co. (Silberline)
Aluminum flakes w/ Viton-A coating	-	thickness 50-200	2.7	Particle: Silberline Coating: NAVAIR-CL
AVEKA aluminum in R-45 resin	75.0	30-40	2.7	Aveka, Inc.
Technanogy aluminum	44.4	46	2.7	Technanogy
Alex aluminum w/ Viton-A coating	13.3	100-150	2.7	Particle: Argonide Corp. Coating: NAVAIR-CL
Aluminum particles quenched in argon	50.0	41	2.7	NSWC-IH
Aluminum particles quenched in helium	70.0	26	2.7	NSWC-IH
Aluminum particles	20.0	80	2.7	Nanotechnology
Aluminum particles	36.0	50	2.7	Nanotechnology
Amorphous boron	31.0	<150	2.34	SB Boron Co.
Amorphous boron w/ Viton-A coating	31.0	<150	2.34	Particle: SB Boron Co. Coating: NAVAIR-CL
B_4C	13.0	120	2.6	CMPI
B_4C with catalyst coating	13.0	120	2.6	CMPI

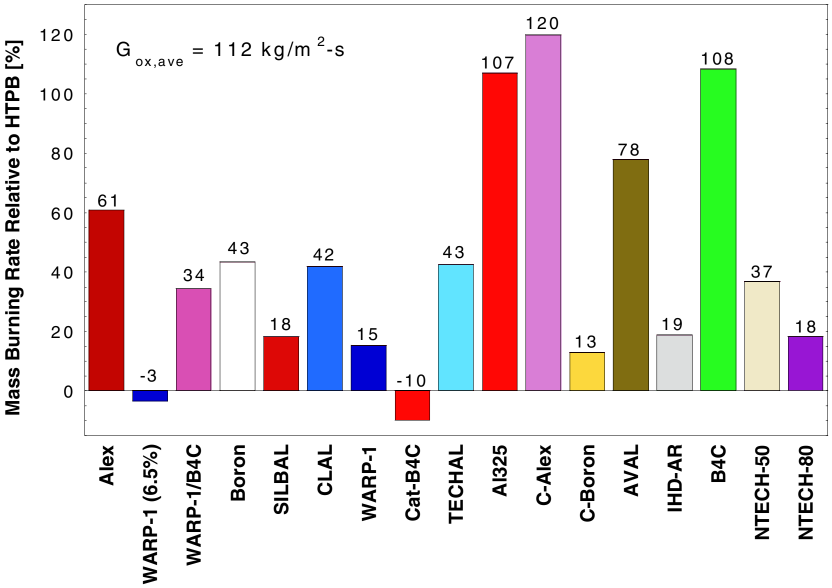


Figure 4. Comparison of percentage increase of solid-fuel mass-burning rates for various formulations in comparison to pure HTPB solid fuel

The coated Alex® (C-Alex) had the highest percentage increase in fuel mass-burning rate which was enhanced by 120% compared to pure HTPB fuel formulations. C-Alex fuel (with Viton-A coated particles) demonstrated more than a two-fold increase in mass burning rate in comparison to the fuel with uncoated Alex®. Similarly, the fuel formulations labeled SILBAL and CLAL contain the same aluminum flake particles except that the CLAL particles were coated with Viton-A flouropolymer coating. Viton-A coated aluminum flakes (CLAL) show a mass-burning rate twice as high as uncoated Al flakes (SILBAL). It is believed that the fluorine and fluorine compound produced from the dissociation of Viton-A contributes to the rapid ignition and combustion of the nano-particles. As the particles are exposed to the regressing fuel surface and dissociation of the Viton-A begins to occur, the particles were exposed to an extra energy source that can help in facilitating ignition. This coating along with other possible coatings (e.g. Mg) could help in initiating ignition for aluminum or boron particles and help to further increase solid fuel regression rates.

The test results of solid fuels containing mesh-325 micron-sized aluminum (Al-325) are also shown in Fig. 4. Even though the percentage of mass-burning rate of this fuel seems to have a substantial increase by the aluminum powder addition, the exhaust plume jet of this solid fuel exhibited numerous particle streaks indicating poor combustion efficiency. The C* efficiency of this fuel is around 81-85%, which is about 7% lower than the C-Alex containing solid fuels.

High energy propellant development

Another program concerning the use of nano-particles is working to develop a family of next generation high-energy propellants for artillery applications. These propellants are being designed to provide: 1) High impetus ($\equiv R^*T_f$) 2) low-flame temperature, 3) low vulnerability, 4) low glass transition temperature, 5) high density, and 6) good mechanical properties at extreme temperatures. The new propellants can be formulated to be environmentally friendly and to have a life cycle cost comparable to currently fielded baseline energetic propellants. For fast-core propellants, the layered propellants should consist of two similar propellants, with compatible ingredients in order to have bonding between them. The higher-energy propellant should have a regression rate several times greater than the lower-energy propellant at chamber pressures between 200-700 MPa.

Nano-sized aluminum and/or boron particles can be utilized to control the burning rate and impetus of the functionally graded propellants (FGPs). These propellants are defined as those possessing desirable spatial gradients in material composition. Due to the formulation variation in specific directions, the combustion/mechanical behavior of a given FGP is also a function of the distance perpendicular to the burning surface. Some new processing techniques of feeding nano-sized materials as propellant ingredients can be incorporated into the existing twin-screw extrusion (TSE) device [8]. It is expected that the burning rates of FGPs can be accurately tailored as a function of burning web thickness. This can be achieved by variations in propellant composition and particle size distribution. For example, by introducing different amounts and shapes of aluminum particles (e.g. nano-sized aluminum rods vs. nano-sized spherical aluminum particles), the burning rate of the propellant could vary by several hundred percent. This implies that the burning rate of the future gun propellants can be tailored to the desirable variations if properly formulated with the functionally graded ingredients.

In the development of high-energy propellants with desirable burning characteristics, nano-energetic materials for oxidizers (such as HNF and ADN) and nano-sized fuel particles (such as aluminum or boron) will likely have some important roles to achieve the design goals. It is also anticipated that other nano-sized particles can be introduced into the propellant formulation to serve as burning rate modifiers. These particles can be utilized also in new explosive formulations. The binder materials with high burn rates will also be important in the formulation of new propellants and explosives.

Aluminum flake burning and modeling

Aluminum particles have been utilized broadly in the field of rocket propellant combustion as an energetic additive and to produce condensed phase particles for damping any combustion instabilities. They can also be used as energetic fuel ingredients in explosive applications to tailor the energy release rates. A single aluminum flake ignition/combustion study was conducted by Tatum and Kuo [9]. Their fundamental investigation is to determine the ignition characteristics of aluminum flakes in the post combustion region of fuel-rich gas mixtures. The development of a comprehensive model with detailed chemical kinetics and fluid dynamics/heat transfer behaviors simulation can definitely be helpful to understand the energy release process associated with the ignition and combustion of aluminum flakes. Recovery and analysis of partially burned particles can also help the model validation with experimental evidence.

Nano-energetic particles used in gel propellants

Gelled propellants exhibit thixotropic material behavior with viscosities 5 to 10 times that of regular liquid propellants. The term “thixotropic” means that the material has a jelly-like consistency when at rest, but flow easily when a large enough shear stress is applied. Gellants create a cross-linked structure in the liquid propellants causing the increase in viscosity. Benefits to using gelled propellants include enhanced safety, increased fuel density, reduced leakage, reduced slosh of the propellant in the storage tank, and reduced boil-off of cryogenic propellants. For this reason much interest has been focused on the production of gelled propellants for next generation propulsion systems.

NASA Glenn Research Center in collaboration with many government and industry research groups has initiated research into the development of new-gelled cryogenic and non-cryogenic propellants using nano-gellants. According to Palaszewski [10], due to the large specific surface area of nano-gellants, gelled cryogenic propellants with nano-gellants require 25-50% less mass of gellant compared to traditional micron sized gellants. Metal particles can be suspended in the gelled propellants to further increase the fuel density and the performance of the propellant. In addition to the use of nano-gellants that are low energy or inert material, metal particles with sufficiently small particle sizes can be used as gelling agents. Several recent studies were conducted by various groups focusing on the use of nano-sized aluminum as a gelling agent; for example, for gelled RP-1 fuels (studied by Mordosky, et al. at PSU and Argonide Incorporated [11]) and gelled liquid hydrogen (studied by Orbital Technologies). Spray combustion tests conducted by Mordosky, et al. of gaseous oxygen atomized sprays of RP-1 gel propellants with ultra-fine aluminum particles (Alex®) were performed in a rocket engine. Alex® aluminum particles were added in by weight percentages up to 55%. The addition of aluminum particles to RP-1 gel propellants increased the heat of reaction over neat RP-1 due to the high volumetric energy release of aluminum.

The use of nano-sized particles as the gelling agents further increases the performance, density, and combustion efficiency of the propellants. Various gelled bi-propellants are currently being developed for future propulsion applications. The partitioning of the fuel-rich and oxidizer-rich components can greatly enhance the safety aspects of the propulsion system. Future work will focus on further development of methods of production of these gelled propellants, testing of next generation gelled propellants, and optimization of propellants to obtain performance goals.

CONCLUSIONS AND PROJECTED FUTURE DIRECTIONS

1) Numerous advantages of using nano-sized energetics (i.e. aluminum, boron, etc.) in solid fuels and solid and gelled propellants have been identified and partially demonstrated. New formulations of energetic materials containing nano-sized materials can have tailored burning behavior, density, and propulsive performance. Essentially the availability of nano-sized particles with different dimensions and shapes has added a new dimension to the design of energetic materials for propulsion applications.
2) Various methodologies have been developed for production of nano-sized energetic materials. Special coating techniques with desirable and compatible materials are an important area for reducing the sensitivity of nano-sized materials. These nano-sized particles can be applied to both propellants and explosives.
3) Processing of energetic materials containing nano-sized particles is another fast-developing area. Self-assembling materials and computer-controlled processing of functionally graded propellants/explosives will be essential for state-of-the-art advancements in this area.
4) Many characterization studies have been conducted to study the enhancement of combustion behavior of propellants/fuels with energetic nano-sized powders. In the future there will be even more sophisticated techniques required to fully diagnose the physicochemical processes associated with the combustion of these energetic materials, so that the detailed mechanisms of combustion enhancement by nano-energetic materials can be understood.
5) The knowledge gained from the mechanistic study will allow better design and control of the ignition/combustion processes of energetic materials to achieve the goals of new generations of propulsion systems.

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