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CHAPTER ONE

c0001 Nanoenergetic Materials: New Era in Combustion and Propulsion

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s0010 1. INTRODUCTION

p0015 The nanoworld corresponds to the place where self-arrangement of atoms leads to formation of chemical substances. The "nano" concept, which includes nanoscience and nanotechnology, was introduced in the middle of the twentieth century. Nobel Prize laureate Richard Feynman declared (in 1959) in a lecture entitled "There is plenty of room at the bottom" that no law of physics forbids the devices construction of few [**AU1**] atoms size. However, to be correct, mankind actually had deal with nanomaterials many centuries earlier. Examples are corundum mechanical tools (3000–4500 BC), the [**AU2**] Lycurgus Cup (British Museum, London, 400 BC), church windows made of molten glass with embedded gold nanoparticles (~500 AD), daguerreotype photography (1839), etc.

p0020 In recent years, new nanomaterials have been intentionally fabricated or discovered, novel nanotools have been developed and old ones industrially implemented, and novel properties of matter at the nanoscale level have been discovered. For these reasons, nanoscience and nanotechnology should not be seen as entirely new but rather as "work-in-progress science." Nanotechnology should be seen rather as an evolution, not a revolution.

p0025 The definition of nanomaterials is somewhat arbitrary and can be based on different criteria. First of all, it involves a scaling measure and usually corresponds to submicron sizes. Normally, in different fields of science and technology various subdivisions of length are used to define coarse and fine particles. Typically, 100 nm is accepted as a boundary between ultrafine and nanodiameter particles [1]. However, one may define this boundary as corresponding to sharply changing the physical properties, e.g., melting temperature. Such a boundary depends on the nature of the substance, and for aluminum (Al) it is about 15 nm, for gold (Au) about 50 nm, etc. Another approach can be based on the changes in reactive properties; for energetic materials, the nanoscale typically starts at 100 nm, at which the noticeable acceleration of ignition and

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combustion reactions is realized [2]. Thus, when discussing the issues about nanoparticles properties and their behavior, one has to consider a particular definition of nanoscale.

p0030 Nanotechnology manipulates matter for the deliberate fabrication of nanosized materials. Therefore, the definition of nanotechnology generally includes "intentionally made nanomaterials," with the nanomaterials being the objects that have at least one dimension in the nanometer scale. This conclusion has been underscored in a comment by S. Pearton [3], that nanotechnology, as any new innovation, is developing in a typical manner while passing through different periods, including pre-buzz, buzz, rave reviews, saturations, overhyped, backlash, and backlash-to-the-backlash. Such a prognostication diagram has a sine form with the first maximum at saturation point and minimum in backlash point. Various technologies have their own situation according to this "Florida law of original prognostication," and in the case of biomaterials, it seems that they are at [**AU3**] the initial peak of their potential. The situation with nanoenergetic materials has been ingeniously described recently by M. Zachariah [4]. He underlined that the interest in these materials lies in fundamental thermodynamic limitations obtained from using traditional CHNO systems. Researchers and engineers have a clear understanding that typical CHNO-based chemical systems are near the limit of stored chemical energy. Potential benefits of using nanoenergetic materials are their high volumetric energy density and the capability to produce environmentally benign products as well as controlled rate of energy release and reduced sensitivity. This made reactive nanocomposites an attractive material for wide applications, including environmentally clean primers, detonators, improved rocket propellants and explosives, thermal batteries, and many others.

p0035 In the past, there was great expectation of the probable presence of significant excess energy associated with high compressive forces in small size particles. Later it was revealed theoretically and experimentally that there is no noticeable advantage to the nanoscale that corresponds to practical applications (30–100 nm). At the same time, there was the expectation that the close proximity (a few angstroms) between the fuel and oxidizer components in energetic material would result in a strong acceleration of chemical reaction rate that could be called "nanoenergetics." These expectations have been justified, but only partly, because the experimentally observed effects were less than expected. As stated in Ref. [4], "we still do not have a good conceptual grasp of many of the initiation and propagation processes in such systems, which are significantly more heterogeneous than the molecular counterparts." Therefore, the community must pay attention to elaboration of fundamentals of the above processes in order to get answers to the question, how to make a good nanoenergetic composite?

p0040 There are some unique examples of obtaining nanoenergetic materials with an extremely fast burning rate that can be used in different applications. For example, a burn rate reaching a value of over 3000 m/s was achieved in samples of porous silicon films impregnating in nanoscale pores with sodium perchlorate [5].

p0045 It is also necessary to note that nanoenergetics, as any modern technology, gave birth to fears related to negative and dangerous consequences of its application, which were discussed in a special issue (#12, 2011) of the Proceedings of the French Academy of Sciences entitled "Nanosciences and nanotechnologies: hopes and concerns." Even if not considering different social aspects of such technology applications, it is worth mentioning that nanoparticles have to be processed with certain precautions because of their toxicity and great ability to penetrate living bodies (carbon nanotubes have been found in the brains of exposed mice), as well as of enhanced pyrophoric and energy impact sensitivity [6,7]. It is important to emphasize that until now, at least in Europe, legal texts dedicated to specific fields of objects of nanoscience and nanotechnologies do not exist. One of the reasons is that scientific knowledge about professional risks in many cases is uncertain. According to the European definition, nanoscience "concern[s] the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at larger scale."

p0050 Risk aspects have to be taken into account when establishing new legislation for nanotechnology and they have be the basis for any definition used for regulatory purposes [8]. There were some discussions in this respect related to the question whether there is a potential release of nano-objects that are the subject of investigation in nano safety research. From a regulatory point of view, the materials where the nanoscale structure does not result from discrete particles and when no risk exists if nano-objects could be released should not be considered as nanomaterials. Definitions of nanomaterials have to reflect this difference when formulating new nanotechnology legislation. Actually, regulation of nanomaterials should focus on nano-objects as concluded in the report by the European Commission Joint Research Center [9].

p0055 Nanostructured energetic materials have nanoscale structures at least in one dimension. Small critical diameter, high reaction rate, and great released heat allow those materials to fit well for explosive chips. Physical modeling and simulation in the area of nanoscale composite energetic materials is continuously under process. The situation is permanently improving, and the methods of preparation and characterization of energetic nanomaterials have become more and more sophisticated and efficient. This chapter discusses some recent developments in this area as well as possibilities for future research. The peculiarities of ignition and combustion mechanisms of individual metal particles as well as composite nanosystems and some methods of preparing the unique properties and composition are of great interest.

p0060 Several authors have stated that the exact physical mechanism for nano-Al particles ignition is currently unclear. The main reason is the lack of available commercial experimental techniques because it is difficult to design experiments to record physical changes occurring with particles of nanosizes at heating rates reaching $10^6 \div 10^8$ K/s. Additionally, while use of tiny particles increases specific surface area and reduces length scales between fuel and oxidizers, it also limits the ability of probing reactions at the scale on which they occur.

p0065 Along with the detailed research on Al-based reactive nanomaterials, essential progress has also been made in creating improved quality high explosive materials. It was recently shown that explosives' sensitivity to external stimuli decreases with decreasing crystal size. This gave a start to work on the synthesis of nanocrystals of different explosives (like RDX, HMX, Cl20, TATB) by using evaporation-assisted and sol–gel techniques.

p0070 As presented here, these materials are only introductory and illustrative in character and are not meant to be exhaustive. A large volume of information can be found in several reviews published recently [10–13]. In addition, some fresh information appears in the present volume. It must be mentioned that the usage of nanoenergetic materials has some advantages as well as drawbacks. The latter relate mostly to the problems of nanomaterials handling and preparation of the mixtures on their basis. These are briefly listed in the following sections. Prospective applications and possibilities for future research are also discussed.

s0015 2. COMBUSTION OF Al NANOPARTICLES

s0020 2.1 Heat Transfer of Nanoparticles

p0075 Recent studies of nanoaluminum particles combustion [14] revealed some peculiarities of heat transfer indicating the overestimation of heat losses from nanoparticles in surrounding gas during combustion. For nanoscale particles, the Knudsen number ($Kn = 2\lambda/d$, where λ is the mean free path of the molecules in the gas and d is the particle size) effects have to be taken into consideration when this number equals $Kn > 10$. In such conditions the noncontinuum heat transfer expressions must be used to describe heat losses from particle to ambient gas. However, it was found that formal application of these expressions gives the burning time values, which are two orders of [**AU4**] magnitude shorter than experimentally observed. This finding means that in description of heat transfer of nanoparticles it is necessary to use the energy accommodation coefficient and reasonably low sticking probability for collision of oxygen molecules in reaction with the aluminum surface. For example, in the shock tube experiments [14] with nanoaluminum particles of 80 nm size, the measured burning time was equal to 124 μs instead of 1 μs estimated by formal calculations. To fit with a theoretical estimate, the authors used the value of energy accommodation coefficient equal to 0.0035 and sticking probability equal to 0.0009. They concluded that at high ambient temperatures existing in the shock tube experiments, the nanosized metal particles experience a sort of thermal isolation from the surrounding gas. This effect has to be considered when modeling metal nanoparticle combustion.

s0025 2.2 Effect of Oxide Layer

p0080 It is well known that the presence of an oxide layer significantly reduces the amount of active metal in nanoparticles. For example, in the case of a 3 nm thick oxide layer, the content of active metal equals 99.9% for 30 μm size particles and only 51% for 30 nm size particles. That is why numerous efforts were directed in recent years toward the [**AU5**] development of methods to synthesize metal particles without a passivating oxide layer. An advanced method for protecting active metal against oxidation in air might be use of organic self-assembling monolayers, which are densely packed organic films organized on a material surface via chemisorption of a molecular amphiphile [15]. It was expected that in the case of one organic molecule thick layer "the contamination" of metal particle would be extremely small. However, in practice the content of active aluminum in the particles of 80–100 nm size passivated by perfluoroalkyl carboxylic acid ($C_{13}F_{27}COOH$) became equal to 23–25% only [16,17]. This is despite the total absence of oxide layer on the metal particle that resulted from using a wet chemistry technique with coating of metal in solution.

p0085 Another method of passivating nanometal particles has been suggested in Refs [18] and [19]. The original nano-Al particles of 50 nm size were produced by Gen–Miller flow-levitation installation [20] via metal evaporation and following condensation in a mixture of hexamethyldisilazane vapors with argon. This resulted in formation of trimethylsiloxane coating on Al nanoparticles with a small change in particle size—from 48 to 54 nm. Surprisingly, the content of active Al was found to change only to a very small extent—from 72.5% for oxide coated to 74.5% for polymer coated. This small difference in active Al content remained in both types of particles after 60 days storage (64.4% for oxide coated and 66.6% for polymer coated).

p0090 The above information demonstrates great technical difficulties in passivating the surface of metal particles without loss of the content of active metal.

s0030 2.3 Effect on the Burn Rate and Performance of Solid Propellants

p0095 One of the first applications of nanometal particles as energetic material was using them in solid propellants. It was expected that the replacement of micron-sized Al in propellant formulation would result not only in enhancement of burning rate but also in decreasing the dependency of the burning rate on pressure. Pioneering data obtained in the 1960s at the Institute of Chemical Physics (Moscow) demonstrated that the burning rate of composite propellants based on ammonium perchlorate and bitumen binder with total replacement of 13–31% of 15 μm Al by nano-Al (Gen–Miller type, 90 nm) was really increased by about 50%, but the pressure exponent in the burning law was also increased by about 10% [21]. In the following years when obtaining first the electroexploded nano-Al particles, the researchers assumed the presence of additional heat of formation contained in submicron metal particles that can be employed for enhancement of the energy content of propellant. The idea of the existence of energy excess (up to 400 cal/g) in aluminum nanoparticles was proposed in Ref. [22]. Later on, this effect was studied in detail in Ref. [23]. It was revealed in differential thermal analysis experiments that for Al (50–100 nm) nanoparticles produced by the wire electroexplosion method and aged for 0.5–1.5 years, any effect of stored energy could not be detected. The recorded weak exothermic peak at 580 °C is associated with the oxidation of the particles due to the presence of small amounts of oxygen impurities in the purge gas (argon or helium), and also with the possible effect of adsorbed air. It should be noted that the effect of stored energy should be manifested in the value of the specific impulse of the solid propellant. However, an increased amount of oxide in nanosized Al particles can reduce and mask this effect. Therefore, its detection requires specialized detailed measurements that can be performed in the future.

p0100 Another expectation related to using the ultrafine Al particles was decreasing the pressure exponent in the propellant burning law. Numerous previous attempts to realize decreasing pressure exponent in experiments with partially replaced micron-sized Al in solid propellants failed [24–26]. Those experiments established that the heat release in the condensed phase in fact becomes significantly higher in the presence of nano-Al particles, which results in increasing the burning rate. However, when replacing micron-sized Al with the oxide-coating nano-Al, the total energy content in solid propellant decreases due to enhanced content of Al_2O_3 in nanoparticles (the smaller particle size, the higher oxide fraction). This leads to decreasing the performance efficiency of solid propellant. By calculation, in the case of model propellant formulation (70% ammonium perchlorate and 15% energetic binder) containing 15% Al, the replacement of ordinary 15 μm size Al (99.5% of active metal) by 80 nm Al (82.3% of active metal) should lead to decrease in the value of specific impulse from Isp (15% Al) = 266.6 s to Isp (12.3% Al) = 260.6 s. These values are estimated for the chamber pressure 40 atm and nozzle exit pressure 1 atm.

p0105 A specific drawback of using the nanometal particles is that due to their large specific surface, the viscosity of propellant slurry at the particles contents exceeding 10% weight becomes too high and prevents application of casting technology in production of solid propellants. Studies of the rheological characteristics of HTPB-based suspensions filled with aluminum nanoparticles of Alex type (80–100 nm) have shown that the viscosity of the suspension $\eta_{\mathrm{rel,Alex}}$ is related to the volume concentration C_v of the solid additive as follows [27]:

$$\eta_{\mathrm{rel,Alex}} = \eta_{\mathrm{suspension}} / \eta_{\mathrm{HTPB}} = 1 + 5.5\, C_v - 31.4\, C_v^2 + 74.5\, C_v^3$$

p0110 This equation is valid for volume concentrations of metal nanoparticles $C_v < 50\%$.

s0035 2.4 Effect of Nanosized Particles Sintering

p0115 Some fresh results obtained experimentally and theoretically [28,29] demonstrate the fact of fast sintering of particles aggregates into bulk alumina in conditions of fast heating rate. Thus, questions are raised about "effective" particle size during ignition and combustion of ensemble of nano-Al particles. The reactive molecular dynamics calculations carried out in Ref. [30] showed that upon rapid heating of aluminum core/oxide shell particles the melted core Al atoms diffuse outward into the oxide shell, which is driven by an induced built-in electric field. It leads to the melting of oxide shell at temperatures much lower than the oxide melting point and to sintering of the particles due to action of surface tension forces. Importantly, the characteristic sintering time according to calculations is even shorter than the reaction time. This may qualitatively explain why the experiment does not give an extremely short burning time for very small Al particles.

s0040 3. COMBUSTION OF NANOTHERMITE COMPOSITIONS

p0120 Nanopowders are often used to produce so-called metastable intermolecular composites (MICs). These are mixtures of nanosized reagents that are stable under normal conditions and capable of interacting with each other with the release of large amounts of energy after activation by a triggering stimulus (thermal, mechanical, or electrical). Examples of such MICs are mixtures of nanoparticles of metals such as Al, Mg, Zr, Hf, etc., and nanoparticles of metal oxides (Fe_2O_3, MoO_3, Cr_2O_3, MnO_4, CuO, Bi_2O_3, and WO_3). It is known that in the case of classical thermites, the combustion reaction is slow due to the relatively slow diffusion process. When the reagents are in the nanoscale, the diffusion path is much shorter and the reaction rate is increased significantly as compared with the reaction rate of conventional thermites. Additives of polymer materials or binders or gas-generating agents to metal and metal oxide–based MICs are able to provide the necessary working body during combustion. An area of particular interest is the use of MICs in microscale motors. This is related to the development of microscale propulsion systems and the use of these energetic materials in micromotors and even small spacecraft. Supposedly, such mixtures could find application as the gas-generating compositions. They can combine high-energy characteristics with unprecedented stability, safety, and an opportunity to precisely control the burning rate in a wide range through the regulation of granulometric composition. In the case of nanothermites, due to fast reactions the energy losses to the combustor wall are negligible. For example, the burning rate of MoO_3–Al nanothermite, prepared by mechanical mixing of 79 nm aluminum particles and 30 × 200 nm MoO_3 flakes reaches 790 m/s in a metal tube of 0.5 mm diameter. This composition is considered a promising base for microscale rocket propellants [31]. Other possible applications of nanoscale MICs are ammunition primers and electric matches [32].

s0045 3.1 Methods of Preparing MICs

p0125 There are several advanced technologies for mixing nanoenergetic materials, such as ink-jetting, vapor deposition processes, cold spray, etc.. Three technological approaches to producing different MICs are widely used: mechanical stirring, arrested reactive mixing, and sol–gel technology. The first approach is the simplest and most common method of production of nanothermites. Nanopowders of metal oxides and a fuel are mixed in a volatile inert liquid (to reduce the static charge) and treated with ultrasound to ensure an even distribution of the components and their deagglomeration. After evaporation of the liquid, the thermite is ready to use. The technology of mechanical mixing is suitable for almost all thermite systems, and its simplicity makes it widely used. Its main drawback is the need to use nanoscale starting materials.

p0130 Arrested reactive milling is based on the use of ball mills and vibratory ball mills. The method involves co-milling of the metal oxide and aluminum. The component particles may be both nanosized and micrometer sized. In the course of milling, the particles are mixed to form nanocomposite particles in which fuel and oxidizer are contained in the same particle. The particles produced by that technology are in the size range of 1–50 nm and consist of layers of metal (e.g., Al) and oxidizer, about 10 nm thick. Particle size is a function of the milling time, but because of the high reactivity of the mixture, after some time of treatment (depending on the initial particle size, type of the components, and the milling medium) when the particles are reduced below a certain size, the ignition of the mixture may occur. The term *arrested reactive milling* implies that grinding is stopped before the moment of ignition of the mixture. Advantages of this method are: the possibility of using initial micrometer-sized particles; production of nanocomposite particles with density approaching the theoretical value; highly reduced presence of metal oxide because of the effect of encapsulation of the metal in the particle matrix; and precise control of the degree of mixing and, hence, reactivity by changing the milling time. The main disadvantage of the method is that only a few thermite mixtures can be prepared by this method as most mixtures are too sensitive and ignite before sufficient mixing is achieved.

p0135 The sol–gel method of obtaining nanostructured materials implies the processes where reactive precursors (monomers) are mixed into solution in which polymerization occurs, leading to the formation of a three-dimensional highly cross-linked solid network that results in a gel. The gel is then dried using supercritical extraction to produce samples of highly porous low-density aerogel or to produce xerogel by controlled slow evaporation. Energetic materials can be incorporated during the formation of the solution or during the gel stage of the process. The composition and size of the primary particles, the time of gel formation, surface area, and density may be tailored and controlled by methods of solution chemistry. An important area of application of the sol–gel methods is the synthesis of nanostructured metal oxides, which are used for obtaining different MICs (mainly metal/metal oxide nanothermites). These methods can be used to synthesize nanostructured oxides of various metals and metalloids: Fe, Cr, Al, Ga, In, Hf, Sn, Zr, Mo, Ti, V, Co, Ni, Cu, Y, Ta, W, Pb, B, Nb, Ge, Pr, U, Ce, Er, and Nb [33]. To obtain energetic nanocomposites containing metal oxide and metal, powdered metallic fuel needs to be introduced into the sol before the beginning of gelation, when the viscosity starts to increase rapidly. In this way, it is possible to obtain a metal oxide gel matrix with uniformly distributed Al particles. When other substances are used as the fuel, agglomeration of the particles can be prevented by ultrasonic agitation. The advantage of sol–gel methods is the broad range of materials used and relatively high productivity.

s0050 3.2 Understanding the MICs Reactive Mechanisms

p0140 Over the last three decades there has been significant growth in understanding the ignition and combustion mechanisms of nanothermites and other nanoenergetic materials. However, there is still much that is unknown about the physics and processes that control these highly exothermic reactions. The role of metal oxide oxygen release in the phenomenon of nanothermites ignition was discussed in Ref. [34]. In that work, the advanced experimental approach was used, which included simultaneous use of time-of-flight mass spectrometer, optical emission, and T-jump heating units at heating rates up to 10^5 K/s. The reactions of type $2Al + 3MO \rightarrow Al_2O_3 + 3M + \Delta Q$ were studied (MO = metal oxide). It was found that the oxygen produced by decomposition of MO particles plays an active role in the reaction. Experiments with different oxides like CuO, Fe_2O_3, and ZnO showed that the reactivity of the Al/MO pair directly depends on the capability of oxygen release from oxide particles. Therefore, higher reactivity of Al/CuO mixture can be attributed to the higher oxygen release rate as compared with the lower release rates for Fe_2O_3 and especially ZnO. Time-resolved mass spectrometry records of formation of Al suboxides (AlO and Al_2O) show that the reaction of Al oxidation does not follow thermal equilibrium calculations, indicating that the system is far from equilibrium. Supplementary records by high-speed X-ray movie (135,000 fps) confirm that the oxygen releases prior to the ignition instant, indicated by temperature measurements. Actually, ignition temperature definitely correlates to instant of oxygen release from MO. At the same time, an original observation was made with Bi_2O_3. In the system Al/Bi_2O_3 it was clearly recognized that nanothermite reaction starts before the oxygen is released from the neat Bi_2O_3. It suggests the condensed phase reaction of liquid Al with oxygen ions formed in melted Bi_2O_3 and was transported to the surface of Al particles. It is stressed that these reactions may play a more significant role than previously expected. Later on, the same authors' team published an article in a special issue of *Combustion and Flame* [35] that generalized the experimental data regarding the mechanism of condensed-phase reactions of Al with different metal oxides, which proceed simultaneously with the reactive sintering. As was mentioned in an editorial comment to this issue [36], the results suggest that condensed-phase reactions may be more prominent than previously thought. Additional evidence of the presence of developed condensed-phase reactions in ignition and combustion of nanothermite materials were presented recently in Refs [37] and [38]. The comprehensive review of state-of-the-art formulation of the reaction mechanism of nanothermites is presented in the chapter by M. Zachariah and G. C. Egan in this volume.

s0055 4. COMBUSTION OF NANOEXPLOSIVES

s0060 4.1 Carbon Nanotube Supported Explosives

p0145 Nanostructured energetic materials are a new concept composite powder, which can dramatically improve the performance of gunpowder and explosives. The combination of nanocrystals of explosives and nanoporous substrates makes the composite products possess original properties and unique parameters. Following are some examples of recently reported research results obtained in experiments with nanoexplosives.

p0150 One of the first attempts to control the combustion properties of a high explosive in the nanostate is reported in Ref. [39]. A porous chromium(III) oxide matrix was impregnated by RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine). The reactivity and sensitivity of Cr_2O_3/RDX nanocomposites were studied by impact and friction tests, differential scanning calorimetry, and time-resolved cinematography. It was found that the size of RDX nanoparticles and their distribution in the Cr_2O_3 matrix have an important influence on their reactivity, which differs significantly from those of micron-sized RDX. In particular, in the nanocomposites with the RDX contents between 6.2% and 80%, the decomposition starts before the melting point of RDX. This means that the thermal decomposition of nanometric RDX proceeds with decreased activation energy. It was also found that for an RDX content of 14.3–42.0%, the nanocomposites are less sensitive to impact than pure RDX. Note that in this case the explosive layer is not continuously distributed on the Cr_2O_3 surface, while with higher RDX content (42.0–95.0 wt%) it covers all Cr_2O_3 surface that results in increased sensitivity as compared with pure RDX. However, at highest RDX content (>95%), the same as RDX impact sensitivity has been detected. The combustion of nanocomposites with relatively low RDX content (14.3% and 25.0%) is very irregular, and it stops when cutting the laser irradiation. Self-sustained combustion after laser cut-off is realized for the RDX-rich nanocomposites (40–95%). The burning rate decreases when RDX content increases.

p0155 Observed RDX reactivity behavior correlates well with the morphology of explosive material distribution in Cr_2O_3 matrix. At low RDX contents (<10 wt%), the resulting RDX particles are separated from one another and are typically of 10 nm size. The decomposition proceeds in one step, and the composition is very insensitive to impact and friction stress. With increased RDX content (10–40 wt%), the deposited explosive particles are on the surface of the chromium oxide rods but they are still discontinuous and nanometric size. The decomposition proceeds in two exothermic stages before an RDX melting. The combustion is not self-sustaining, and there is no transition to detonation. At RDX content between 40% and about 75%, the surface of the oxide pores is totally covered with an explosive layer. The composition undergoes a self-sustained combustion, and it can detonate in a confined space. Finally, for RDX content higher than 75%, the explosive layer surrounds the Cr_2O_3 core, and the properties of composition approach those of pure RDX.

p0160 Another example of unique properties of nanostructured EMs was described recently in Ref. [40]. It was demonstrated that a self-propagating reactive wave moving faster than 2 m/s can be realized using 7 nm RDX annular shell around a multiwalled carbon nanotube (CNT). This burning rate exceeds more than 10^3 times the value for bulk RDX at atmospheric pressure. It was found that the burning rate increment depends on the structure of carbon nanotube. The effect is higher in the case of 10 walls nanotube (22 nm tube diameter) as compared with that for 9 walls nanotube (13 nm).The reaction also evolves an anisotropic pressure wave of high total impulse per mass (300 N-s/kg) and produces a concomitant electrical pulse as large as 7 kW/kg. The physical reason for unusual combustion behavior of coated CNTs is extremely high thermal conductivity of CNT, which may reach the value of 3500 W/m-K at room temperature that is more than 80 times larger than that for the best conductor Ag (430 W/m-K).

p0165 Unfortunately, there are great problems with scaling of discovered effects. Actually, with larger system size the effects become much less and special efforts have to be undertaken in order to provide practical feasibility of new phenomena. There are also some technology issues because of heterogeneities in the thickness of carbon nanotubes as well as the RDX coating, leading to irregular performance along axial position of the composites.

p0170 The continuation and further development of this direction of research was made with single-walled CNT coated with chemically bonded energetic material [41]. Using diazonium chemistry, a series of nitrophenyl-decorated CNT composites have been synthesized. The intention was to explore coated CNT, which may release energy in a controllable manner, and to investigate the effect of thermal conductivity of CNT on the rate of explosive reactions. It was established that diazonium chemistry is an efficient scheme to attach energetic molecules (Nitrobenzenes) onto CNT surface homogeneously with high density. It was found that chemically bonded composites release energy at low temperatures over physically mixed ones (T_{max} heat release = 373.6 °C against 280.3 °C) and the composites with highly conductive CNT exhibit explosive behavior at lower temperatures. In addition, it was concluded that the better performance is demonstrated when composites are made in vertically arrayed structures with "metallic" conductivity CNT.

p0175 The original attempts of using multiwalled carbon nanotubes as support for incorporating the polynitrogen, N_8, were made in Refs [42] and [43]. The N_8 possesses giant heat of formation, $H_f = +3630$ cal/g, exceeding greatly that of the best explosives (HMX $\sim +91$ cal/g). It is a known fact that pure polynitrogen systems are metastable, but advanced theoretical studies showed that when a polymeric nitrogen chain is encapsulated in a carbon nanotube, it can be stable at ambient pressure and room temperature, which makes such composites promising nanoscale energetic material. Actually, clear evidence of polynitrogen atoms present in carbon nanotubes has not yet been found. According to experimental data of Ref. [43], the content of nitrogen atoms in carbon nanotubes can vary in the range 1.7–4.0%, and nitrogen exists in the form of pyridine-like, graphite-like, oxidized nitrogen and nitrogen physisorption layer. The results of experimental studies state that it is possible to obtain nitrogen-doped carbon nanotubes with controlled concentration and structure. This will provide the development of novel nanoenergetic materials.

s0065 4.2 Porous Silicon Impregnated Composites

p0180 Porous silicon (PSi) was discovered first as a reactive material when it was tested in combustion studies being immersed in nitric acid [44]. The electrochemical etching of bulk silicon in solutions containing fluoride (e.g., HF) can be used to produce PSi. It allows adjusting the porosity from 2 to 1000 nm by selecting suitable etching parameters. Then the nanopores can be filled with a liquid oxidizer ($Ca(ClO_4)_2$, $KClO_4$, $NaClO_4$, etc.). The potentialities of PSi as fast-burning energetic material were well established in Ref. [5], when $\sim$65–95 μm thick PSi films composed of pores with diameter less than 3 nm were fabricated using a galvanic etching approach. The nanoenergetic composite was then created by impregnating the nanoscale pores with sodium perchlorate ($NaClO_4$). The combustion propagation speed was measured using specially fabricated diagnostic tools in conjunction with high-speed optical imaging up to 930,000 fps. For PSi films with specific surface area of $\sim$840 m^2/g and porosities of 65–67%, the measured burning rate reached 3050 m/s.

p0185 Even faster propagation speed up to 3660 m/s, which is at present the highest reported flame speed for available nanoenergetic systems, was recorded in specially fabricated channeled porous silicon [45]. It was found that the mechanism of enhancement of flame propagation rate in channeled porous silicon is different from the convectively controlled combustion of neat porous silicon. The aim of the study was to relate the speed of sound to events where a flame jumped ahead of the primary, visible reaction front. Supposedly, there exist acoustically aided reactions in porous silicon channel combustion and the channels more readily ignite compared to neat porous silicon. It is believed that acoustic waves traveling through the porous silicon film can carry enough energy to ignite the sensitive PSi channel structures and propagate the reaction.

p0190 Detailed study of the mechanism of propagating the reactive waves through porous silicon-sodium perchlorate composites was undertaken in Ref. [46]. The speeds of propagation were varied by changing specific surface area (SSA) of the samples. The samples with relatively low SSA (~300 m^2/g) normally exhibited baseline speeds of ~1 m/s while samples with high SSA (~700 m^2/g) exhibited fast reactive wave speed propagations of ~1000 m/s. To study the effect of microscale structures on the reactive wave propagation, specially prepared samples were used consisting of an unpatterned and a patterned section. The patterned section contained micron-sized square pillars and microchannels. The samples were ignited in the unpatterned PSi section and the reactive wave propagated into the patterned PSi. Shadowgraph records showed that upstream permeation of hot gaseous combustion products was responsible for a two order of magnitude enhancement in the reactive wave propagation speed obtained by the presence of organized microscale patterns on PSi. It was also taken into account that the oxidation of silicon atoms in the nanoporous structure results in a volume expansion, which can initiate cracks. The experiments indicated that a combination of conductive and convective burning, possibly assisted by fast crack propagation within the silicon porous silicon substrate, was responsible for the observed difference in propagation speeds and was the mechanism by which the reactive wave propagated with the speed on the order of a km/s within the porous layers.

p0195 The very specific application of energetic nanocrystalline porous silicon was demonstrated in Ref. [47]. It was shown that upon igniting the impregnated porous silicon by an electrical current passing through 100 nm thick aluminum film deposited on the unpolished side of the wafer, the ignited sample causes strong explosion, which destroys the explosive chip into small fragments. Use of such a system allows obtaining the explosion impulse, which may reach about 140 mN-s. In fact, this value is two orders of magnitude larger of impulse produced by conventional propellants [48] (about 0.1–6 mN-s for conventional propellants such as lead styphnate or ammonium perchlorate). Moreover, via stacking three porous silicon chips together, it becomes possible to get an explosion impulse of 0.25 N-s, which allows propelling a 30 g object up to 3 m high.

s0070 5. EXPERIMENTAL METHODS TO CHARACTERIZE NANOENERGETIC SYSTEMS PERFORMANCE

p0200 A wide set of advanced experimental methods and tools are used in characterization of nanoenergetic systems. These include fast video and X-ray filming, time-of-flight mass spectrometry, optical emission measurement, ion-focused tomography, etc. An important feature of listed methods is extremely high space and time resolution. Some examples of contemporary approaches are presented herein.

p0205 The exploration of structural properties of explosive materials takes using methods with the length scales spanning several orders of magnitude, from just under 10 nm to at least 10 μm. Those methods can be used for determining the sizes of nano- and microparticles as well as the sizes of pores and total porosity of the samples. In Ref. [49], a rich combination of the methods has been employed to characterize triaminotrinitrobenzene (TATB)-based explosives. It included ultra-small angle X-ray scattering, ultra-small angle neutron scattering, and X-ray computed tomography. Ultra-small angle X-ray scattering (USAXS) allows determining structural inhomogeneities from a few nanometers to a few microns scale. Ultra-small angle neutron scattering (USANS) bridges the gap between USAXS and imaging techniques, and extends the sensitivity of scattering to about 10 μm. Synchrotron-based X-ray microtomography allows imaging the low-z materials with reasonable contrast from a few microns to about 1 cm. In particular, USAXS explored the smallest voids including hot-spot voids from hundreds of nanometers to a few microns, and it was found that upon temperature cycling the number of these voids increases and size distribution shifts toward larger sizes. These derived data give important information used for better understanding of microstructural mechanisms affecting the mechanical properties of explosives and can be used as empirical input to computational models of detonation. The goal of such research is to determine the relationship between the voids and microstructure and their effect on detonation properties.

p0210 Similar information about the porosity and pores size distribution has been obtained in Ref. [50] with use of computer-aided X-ray microtomography. These data were used to correlate the laser initiation thresholds with microstructure of samples of furazanotetrazine dioxide and dinitrodiazapentane mixture, which depended on the conditions of crystallization of samples and mass ratio of components.

p0215 In Ref. [51], when studying the sensitivity of nanocomposite granules containing small RDX crystals, the method of focused ion beam (FIB) nanotomography with spatial resolution about 10 nm has been successfully employed. Using the estimates of theoretical maximum density, it was shown that most of the porosity comes from the voids with sizes less than 100 nm. It was stated that the low shock sensitivity is primarily due to the absence of large voids.

p0220 Original nanocalorimetry technique has been demonstrated in Ref. [52]. This technique allows measuring thermal effects upon heating with extremely high heating rate of the individual crystals of explosives of a few nanograms mass. Thermal sensitivity [**AU6**] of the device comprises 10 microW, the maximal heating rate reaches 1 million K/s. The device can measure the heat of phase transitions and decomposition. The preliminary tests were conducted with the single crystals of RDX, PETN, and CL-20 with mass of 7–30 ng at heating rates up to 2500 °C. The tests showed very peculiar thermal behavior of listed explosives at high heating rates, which will need to be examined in detail in the future.

s0075 6. CONCLUSION

p0225 Research in nanochemistry opened a bottom-up approach in the architecture of matter, from the atom to millimeter scale. The main idea in energetics is to enhance the surface area and intimacy between reactive components in order to increase the reaction rate and decrease the ignition delay. Existing lack of understanding of the underlying mechanisms stems from the difficulty of experimentally observing the nanoscale changes occurring in nanoenergetic materials in the very brief time scales associated with the rapid heating rates and high temperatures intrinsic to the reaction and combustion dynamics.

p0230 Obviously, the experiments in a vacuum, which prevent any significant heterogeneous gas-condensed phase reaction, can capture the interfacial condensed phase interaction of the nanoparticle systems without the convoluting effects of gas phase chemistry. The possible effects of gas phase chemistry and difficulties of interpretation of experimental data can be demonstrated in examples of measuring the displacement of the luminescent front in the plastic tubes filled with energetic material. It was shown in experiments [53] with loosely packed aluminum/copper oxide (Al/CuO) thermites in an acrylic burn tube, composed of fully and partially filled sections, that the velocity of the luminous front in unfilled regions approached 1000 m/s and was about 600 m/s in the filled region. In partially filled regions, the intermediate and product species expanded forward and completely filled the tube being that was heated to a temperature of about 3000 K. In the filled region, the temperature first increased to the value of 3200 K and then remained at 3000 K even after the front exited the end of tube. These results suggest that the luminous front may not represent the ignition of new material but rather that some reacting material part is propelled forward through the tube.

p0235 Qualitatively similar findings were obtained earlier in the burn tube experiments [54] with MoO_3/Al system. In the case of low-density samples of loosely packed nanoenergetic material, the high "burning rate" reaching 1000 m/s was experimentally recorded while for densely packed samples a moderate rate was recorded comprising ≈ 1 m/s, which was also typical of the systems with micron-sized powders. The results indicate that observed very high velocities of luminescent front propagation during combustion of nanoenergetic systems in thin channels are probably caused by the hot gas exhaustion and not by the kinetics of heterogeneous chemical reactions in nanosystems. This shows that the question about significant differences (few orders of magnitude) in the reaction kinetics of nano- and microthermite systems remains open.

p0240 Note that extremely fast burning rates exceeding 3 km/s recorded in combustion of impregnated porous silicon materials may have objective meaning, but the controlling parameters of this process are not yet known in detail. Establishing the real reaction mechanism for nanoenergetic materials takes designing special experimental conditions and techniques. Recently, for the first time clear evidence of the fact that the major part of heat release in nano-Al-based thermite reactions is contributed by a condensed phase mechanism were obtained in very detailed studies [37] when various nanothermite combinations were ignited using rapidly heated fine wire. At the same time, practically the first direct evidence of the contribution of gas-phase oxygen on the ignition and combustion of nano-Al formulations was obtained in Ref. [55]. This work tested stoichiometric mixtures of nano-Al (50 nm) as fuel and nanoparticles of periodates (KIO_4, $NaIO_4$) sized 50–300 nm. The periodate particles were prepared by atomization of aqueous solutions with subsequent solvent evaporation. Analysis of experimental data on thermal analysis and temperature-jump wire heating showed that exothermic decomposition of periodate salts contributes to the low ignition temperature of nanoenergetic formulations. It was shown that the reaction mechanism of periodate salt-based nanoenergetic formulations differs from those of metal oxide nanothermites and provides higher rates of gas release and maximum pressure in the combustion cell as compared with traditional nanothermite (Al/CuO) and Al/$KMnO_4$ mixture. It was concluded that the gas phase oxygen released in decomposition of periodate salt is critical to the ignition and combustion of periodate nanoenergetic formulations.

p0245 When dealing with nanoenergetic materials, the question arises how to obtain the advantages of nanoscale compositions without the drawbacks related to technology limitations. One of the promising options might be use of micrometer-scale particles with nanoscale features. As an example, such materials were prepared by self-assembling the energetic compounds in mesoporous substrate [56,57]. For that, HNIW (CL-20) was first dissolved in acetone and entered the mesopores of linearly ordered mesoporous material SBA-15 by capillary forces. Then, with the evaporation of acetone, HNIW was self-assembled in mesopores via host–guest hydrogen bonds. The sizes of both the nanopores and nanocrystals of HNIW were of the order of 10 nm. The maximum content of HNIW comprised about 70 wt%. The thermal properties of nanocomposites were measured by DSC analysis. Compared with pure HNIW and a physical components mixture, the decomposition peak temperature of the confined crystals decreased by 11 °C, while the total amount of heat released slightly increased. Additional experiments showed that mesoporous carbons (like FDU-15) may also play a role of potential host. When FDU-15 is used, 2,4,6-trinitrophenol (TNP) can also self-assemble in mesoporous carbon nanochannels to form nanocomposites. The weight percent of TNP in nanocomposites can reach 66%. Such nanocomposites may have great potential to be used in different applications as energetic fillings in various gas-generating propellants, in microexplosive devices, etc.

p0250 Original realization of idea of engineering the molecularly built energetic materials employing deoxyribonucleic acid (DNA), Al, and CuO has been demonstrated in Ref. [58]. The authors used the DNA "sticky properties" to graft strands of DNA onto nanoscopic beads of aluminum and of copper oxide and then mixed together the two types of nanoparticles coated with DNA strands. As a result, they obtained compact, solid material that spontaneously ignites when heated to 410 °C and releases heat up to 1.8 MJ/kg.

p0255 The above examples of creating new energetic materials with unique properties do not cover all fields of their application but clearly show the potential for utilization in various devices and installations. Due to high energy density and micro-electromechanical systems compatible fabrication methods, on-chip porous silicon compounds have considerable promise as an energetic material.

p0260 The nanoenergetic composites could also find applications as gas igniters in internal combustion engines or as fuel in aircrafts and space rockets, miniature detonators, on-site welding tools, as additives to propellants in rocket engines, etc.

p0265 There are still a number of unsolved problems in preparation and application of nanoenergetic materials. They relate, in particular, to the questions what is the role of the interface between reacting components and how to predict the reactive behavior in dependency of ignition method, and what is the relationship between nanoparticles size and the composites performance? To get answers, the results of the experimental studies have to be presented in a detailed and concise manner allowing comparison of materials prepared using different manufacturing approaches. Based on critical assessment of available information, it will be possible to construct ignition and combustion models and make reliable predictions of combustion and operational behavior.

p0270 The investigated "bottom-up" approaches must provide good tools for better understanding the structural mechanisms governing nanoenergetic materials thermal properties. Such knowledge will allow the ability to create molecularly manipulated energetic substances and formulations having well-tailored chemical and physical properties.

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ZARKO: 01

Non-Print Items

Abstract

It is a known fact that the energy densities of traditional energetic materials are limited by the enthalpies of product species formed, resulting in relatively low volumetric and gravimetric energy densities. Nanoenergetic materials became available during the last three decades and offer the promise of much higher energy densities and faster rate of energy release. The investigation of transformations in nanoenergetic materials is a very young but active field, and the expected results could lead to interesting breakthroughs in the development of microenergetic devices. The energy density in nanoenergetic devices can reach 50 MJ/kg, which is higher by the order of magnitude of that value for combustion of classical propellants. Extremely fast burning rates exceeding 3 km/s can be realized in combustion of porous silicon nanoenergetic composites. In addition, there is significant interest in miniaturization to exploit the increased efficiency and performance of microscale systems.

Keywords:
Energy density; Heat release; Measurement tools; Nanoenergetics.