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Nanoenergetic Gas-Generators: principles and applications

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Metastable Intermolecular Composites or so-called Nanoenergetic Materials have been widely touted for their potential to fulfill dreams in high density energetic materials and nanotechnology. They are likely to become the next-generation explosives, propellants and primes as they enable flexibility in energy density and power release through control of particle size, tunable stoichiometry and choice of fuel and oxidizer. Despite intense examination by scientists and engineers worldwide the temperature progress and velocity of the thermal front propagation on the nanostructured formulations, however, gas pressure evolution and rate of gas release are not well investigated and understood. This issue has seriously impeded realization of various potential emerging applications envisioned in rocket solid fuels and explosives, which require a high pressure discharge in a short period of time as well as in bio-defeat systems. This highlight describes principles and development of Nanoenergetic Gas-Generators (NGG) systems comprising high PV (pressure \times volume) values and energy densities (up to 25.7 kJ cm^{-3}) that may have several potential civil and military applications. Our recent study revealed that Al/Bi₂O₃ and Al/I₂O₅ nanocomposites can generate a transient pressure pulse more than three times larger than that during the explosion of traditional thermite reactive mixtures.

Introduction

Major progress has been made during the past two decades in developing energetic

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materials such as Metastable Intermolecular Composites (MIC) or so-called Nanoenergetic Materials (NM). These materials can rapidly release temperature and pressure waves and have extensive potential applications as propellants, explosives and primers and currently are the subject of extensive research.^{1,2} They

can have higher energy densities than conventional explosives and can generate shock wave with velocities of up to 2500 m s^{-1} .³ The composites are mainly mixtures of two nanoparticles components, one of which is defined as a fuel and the second as oxidizer. The use of nanoscale particles instead of microparticles increases the intimate contact between the fuel and oxidizer. This decreases mass transport limitations which increases the reaction rate and reactivity of the mixtures. Thermodynamic calculations of the adiabatic temperature, equilibrium composition, and reaction enthalpy help select a MIC mixture from a large number of candidate thermite mixtures. The shock wave velocity and the rate of energy release increased by up to 3 orders of magnitude when the particles size of either aluminium and/or the oxidizer was reduced to a nanosize range.

Well established nanoenergetic thermite reactions include those of mixtures of Al and metal oxides. Among numerous



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thermodynamically feasible MIC mixtures the most widely investigated are Al/Fe₂O₃, Al/MoO₃, Al/WO₃, Al/CuO and Al/Bi₂O₃ nanosystems.^{4,5} The main distinguishing features of these reactions are their significant enthalpy release and tunable rate of energy discharge, which gives rise to a wide range of combustion rates, energy release and ignition sensitivity.⁶ Recent advances in the integration of nanoenergetic components into micro-electro-mechanical systems (MEMS) imply a possible development of “nano-energetics-on-a-chip” devices, which can be have several potential applications in digital propulsion systems and aircraft corrections systems. Most previous research in this area was concerned with the development of suitable fuel/metal oxidizer nanocomposites and studying the impact of the particle size on the corresponding amplitude and velocity of the propagating temperature front and ignition features.

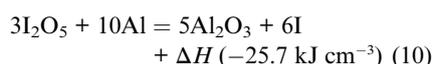
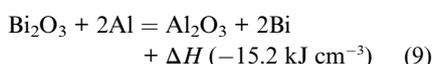
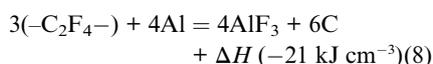
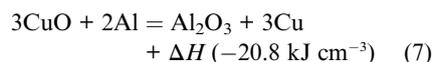
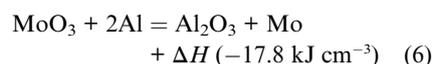
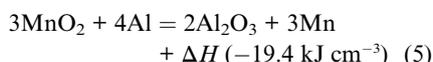
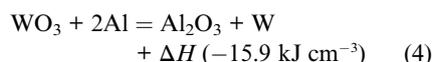
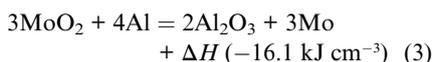
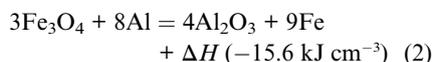
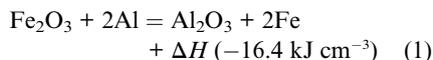
This highlight describes recent progress on the development of Nanoenergetic Gas-Generators (NGG) reactant mixtures having high PV (pressure × volume) values that may have several civil and military emerging applications. Our long term research focuses on the finding and characterization of new NGG formulations that rapidly releases a large amount of gaseous products and generates a fast moving thermal wave during the explosion. This involved a systematic study of various nanoenergetic reactants, their synthesis, fabrication and determination of the peak gas pressure evolution and rate of gas release.

Systems studied

We have recently shown that among common thermite reactions, the Al/Bi₂O₃ and Al/I₂O₅ mixture generated the highest pressure pulse.^{3,7,8} A possible explanation for the high pressure rise during the combustion of Al/Bi₂O₃ and Al/I₂O₅ nanosystems is that the reaction product (bismuth or iodine) boils at a temperature of 1560 and 184 °C, respectively, that is lower than the maximum reaction temperature ~2000 °C. This causes bismuth or iodine evaporation and increases the released gas pressure. The energy densities per volume of mono-molecular composites such as TNT—2,4,6-trinitrotoluene, RDX—1,3,5-

trinitroperhydro-1,3,5-triazine, PETN—pentaerythritol tetranitrate were 7.22 kJ cm⁻³; 10.13 kJ cm⁻³ and 10.64 kJ cm⁻³, correspondingly. A comparison of energy densities shows that the volumetric energy of thermites based materials can easily exceed the best existing molecular explosives by about a factor of two and can reach 25.7 kJ cm⁻³ for iodine based thermite.

Ten highly energetic reactant mixtures were tested as potential nanoenergetic gas generators by the following reactions:



Most of the reactions were conducted using mixtures of commercial reactants with an average particle size of ~100 nm. Typically the nanoenergetic reactions are highly exothermic and the mixtures may spontaneously detonate in some cases due to friction or electrostatic charge build up when the precursors are mixed or ground together. Thus, the stoichiometric mixtures of the reactants (metal oxides and Al particles) were mixed in a closed cylinder containing hexane and nitrogen by a rotary mixing machine. The hexane prevents electrostatic charge build up that may lead to ignition and/or explosion of the powders during the

mixing and handling. Moreover, this environment avoids the partial oxidation of the fine Al particles. Al nanoparticles are highly pyrophoric in air and these are usually coated with a 4–8 nm thick coating oxide (Al₂O₃) shell during their fabrication. The coating reduces the active Al content in a particle and decreases the ignition sensitivity of the nanoparticles. Aluminium and metal oxides powders were purchased from Sigma-Aldrich, and stored under nitrogen (99.9 vol% N₂ with 50 ppm O₂) in a glove box to prevent contamination by impurities present in the air. In most experiments we used aluminium nanoparticles with an average particle size ~100 nm. This powder is not very active in air and can be safely mixed with metal oxides in the preparation of thermite reactions mixtures. The high resolution TEM images in Fig. 1 show that most Al particles were spherical with a diameter from 50 to 150 nm and coated by a ~4 nm aluminium oxide layer. The images showing the thickness of the alumina layer combined with the data on the particle size distribution can be used to estimate either the volumetric or gravimetric fraction of active Al in the powder. The active aluminium content can also be determined from thermogravimetric analysis by estimating the degree of powder oxidation upon heating. The pure aluminium mass content of a particle, with the average diameter of 100 nm and an aluminium oxide layer of 4 nm thick, is estimated to be ~84%. We used these Al nanoparticles to investigate the pressure release during the reactions with different metal oxide precursors in systems (1–10). We used two sources of bismuth oxide reactants. The commercial bismuth trioxide powder with an average particle size of 100 nm and the second was prepared by a modified aqua combustion synthesis.⁹ The values of the peak pressure obtained during the combustion of different reactant mixtures are shown in Fig. 2. It can be seen that the values of pressure discharge are increasing from system (1) to system (10). The bismuth trioxide nanoparticles synthesized by combustion synthesis were generated more than three times large pressure than commercial Bi₂O₃ nanoparticles. The Bi₂O₃–Al and I₂O₅–Al mixtures generated the highest pressure peak of ~11 MPa.

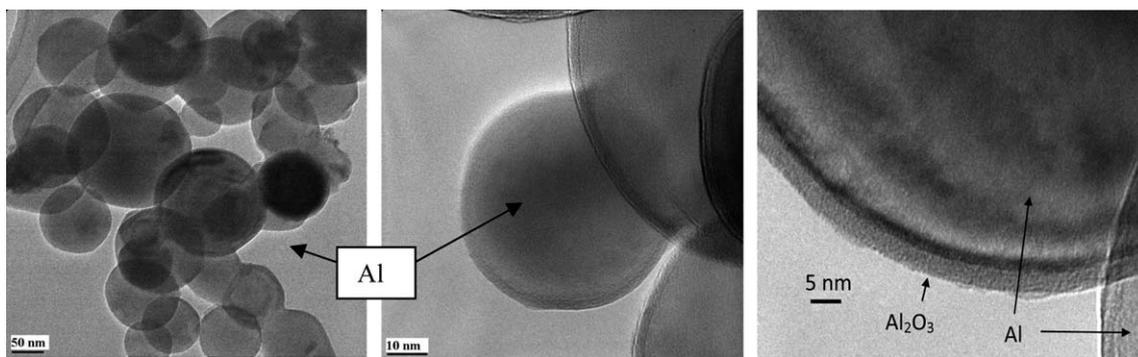
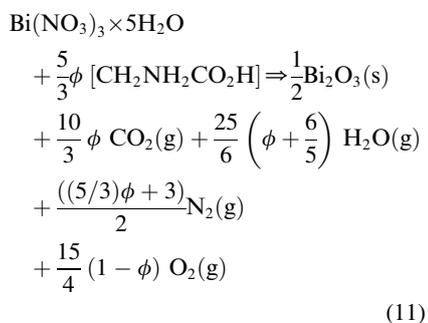


Fig. 1 TEM images and morphology of the nanoaluminium particles used in nanoenergetic gas generators.

Synthesis of bismuth trioxides

Solution combustion synthesis has attracted much attention in recent years as a prospective process to produce homogeneous, crystalline, and un-agglomerated oxide nanoparticles.¹⁰ The solution combustion synthesis can produce a homogeneous high-purity powder in a short period of time at low costs and using simple equipment. In this process a saturated aqueous solution of the desired metal salts (usually metal nitrates) and a suitable organic fuel (glycine, urea, or hydrazine) is heated till boiling temperature. The boiling mixture eventually ignites and a self-sustaining and rather fast volume combustion reaction occurs. The large amount of released gaseous products limits the particle contact and reduces the potential coarsening and agglomeration of the powder. Additional advantages are creating highly crystalline materials and the ability to tune the process to get the desired product quality. Bismuth trioxide nanoparticles were prepared by a modified solution (nitrate–glycine) combustion synthesis^{3,9} by the reactions:



$$\text{where } \phi = \frac{3}{5} \left(\frac{100}{x} - 1 \right) \frac{M_b}{M_g} \quad (12)$$

and ϕ is the fuel stoichiometric coefficient that shows if the mixture is fuel rich ($\phi > 1$) or fuel lean ($\phi < 1$). x is the bismuth nitrate pentahydrate weight percent in the mixture and M_b and M_g are the molecular weight of the bismuth nitrate and glycine, respectively. The superscripts (s) and (g) denote solid and gas phases, respectively. At $\phi \leq 1$ no atmospheric oxygen is needed to completely oxidize the fuel. High purity bismuth nitrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, was used as the oxidizer and organic compound-amino acid (glycine, $\text{CH}_2\text{NH}_2\text{CO}_2\text{H}$) was used as the fuel. The chemicals were purchased from Sigma-Aldrich and used without any purification. In conventional solution combustion synthesis both the fuel and oxidizer are dissolved in water to form a homogeneous solution. To avoid the formation of hydrated bismuth nitrate in water the procedure was modified by dissolving molten bismuth nitrate pentahydrate ($T_m = 71^\circ\text{C}$) into molten glycine ($T_m = 172^\circ\text{C}$) in a Pyrex dish.³ The concentrations of bismuth nitrate in the mixture were varied from 88.57 to 98.72 wt% that corresponded to ϕ from 0.5 to 0.05, respectively. The bismuth nitrate and glycine formed a clear homogeneous solution that was vigorously stirred for 1 h and introduced into a muffle furnace preheated up to 250°C . It is then ignited releasing a large amount of gases producing white-yellow bismuth trioxide nanoparticles. Fig. 3 shows the X-ray diffraction pattern and TEM images of the as-synthesized bismuth oxide at two ϕ values. Low angle XRD patterns of the powder synthesized with $\phi = 0.05$ (combustion temperature of 280°C) contain an “amorphous hump” indicating that some amorphous Bi_2O_3 formed. A pure crystalline bismuth trioxide

nanoparticles with a lattice parameter $a = 7.736(7) \text{ \AA}$; $c = 5.628(9) \text{ \AA}$ formed from a mixture with $\phi = 0.1$ at a combustion temperature of 370°C . The computed crystallite sizes of the bismuth oxide samples obtained at $\phi = 0.05; 0.1; 0.2; 0.3; 0.4$ and 0.5 were 18, 36.7, 45.6, 54.6, 67.8, and 95.8 nm, respectively.³ This was determined by using Scherrer equation $D = 0.9\lambda / (B \cos \theta_B)$, where D is the crystallite diameter, $\lambda = 1.54 \text{ \AA}$ the wavelength of the Cu filament in the XRD machine, B the width of a peak at half of its intensity and θ_B the angle of the same peak. Thus, the crystallite size of the bismuth trioxides was larger at elevated ϕ and consequently at higher combustion temperatures.

The nitrate/glycine combustion caused considerable gas evolution, mainly carbon dioxide, N_2 and water vapor, which caused the synthesized powders to become friable and loosely agglomerated. The average bismuth trioxide particle size was about 20 nm at the lowest ($\phi = 0.05$) concentration of glycine. Higher magnification (see Fig. 3) of these samples shows that the agglomerates contained mixed amorphous and crystalline structures with a smooth surface. Increasing the glycine concentration to $\phi = 0.1$ and 0.3 increased the average particle size from 40 to 60 nm, consistent with the particle diameter (D) of 36.7 and 54.6 nm, respectively, determined from the XRD patterns.

Pressure discharge and shock wave velocity in Bi_2O_3 –Al system

IR images of the surface temperature during the reaction of the thermite reactant mixture show that the maximum temperature was $\sim 2000^\circ\text{C}$.⁷ To initiate the combustion the reactant mixture was

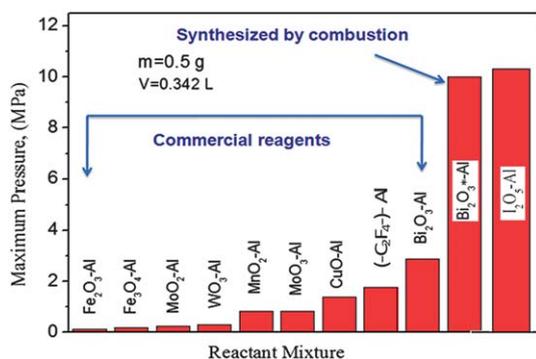


Fig. 2 The values of the peak pressure obtained during the explosion of different nanoenergetic thermite formulations. The mass of the samples was 0.5 g, and the reactor volume of 0.342 L.

locally ignited by an electrically heated micro-coil. The combustion started at the center of the sample and rapidly propagated over the surface leading to an abrupt temperature rise. The temperature front emitted many sparks (hot zones) and small particles. The estimated average rate of temperature rise was $\sim 40\,000\text{ }^{\circ}\text{C s}^{-1}$. The experiments showed that the pressure peak depended on the bismuth trioxide concentration in the mixture. The largest pressure peak of $\sim 11\text{ MPa}$ was obtained for 80% weight percentage of highly crystalline Bi₂O₃.³ We determined the pressure release during the reaction in Bi₂O₃-Al system with different fuel stoichiometric coefficients: amorphous-like nanoparticles at $\phi = 0.05$ ($\sim 20\text{ nm}$) and highly crystalline at $0.1 \leq \phi \leq 0.4$ bismuth trioxides nanoparticles with particle size in the range of 40–100 nm. The dynamic features of the pressure discharge during the detonation of mixtures of Al and the as-synthesized

Bi₂O₃ are shown in Fig. 4. The data show that the pressure release for the crystalline bismuth oxides powder with particle size $\sim 40\text{ nm}$ was higher than for either the amorphous-like powder with 20 nm or the 100 nm highly crystalline bismuth trioxide particles. One possible explanation for the high pressure rise during the detonation of these crystalline bismuth trioxide nanoparticles is that the electron/ionic conductivity of those particles are higher than that of the amorphous-like particles. The higher electron/ionic mobility may accelerate the interchange between species during the reduction of bismuth trioxide that can increase the reaction rate and generate higher pressure. The pressure release of the Bi₂O₃/Al reaction using commercial Bi₂O₃ nanoparticles (100 nm) was approximately 3 MPa.¹¹ This is about one third of the pressure peak using the nanopowders we synthesized. To estimate the total energy release (E) we used the adiabatic ideal gas relation

$E = PV/(\gamma - 1)$, where γ is the ratio of specific heat in the system, P is the pressure, and V is the reactor volume ($V = 0.342\text{ L}$). For complex polyatomic gases $\gamma = 1.2$ and for diatomic gases $\gamma = 1.4$. Based on the measured peak pressure and assuming $\gamma = 1.3$ the energy released by the Bi₂O₃/Al reaction was calculated to be $\sim 20\text{ MJ kg}^{-1}$.

The particle size of reactants, aluminium and metal oxides, has a very strong effect on detonation front velocity. The highest front velocity ($\sim 760\text{ m s}^{-1}$) for nano-thermite composite of Bi₂O₃-Al was achieved using commercial nanoparticles bismuth trioxide (Clark Manufacturing LLC) and coated by oleic acid nanoaluminium (Al-80-P Nanotechnology Co).⁵ The experimental system shown in Fig. 5 (inset) was used to determine the shock wave detonation during reaction of mixtures of 80 wt% Bi₂O₃/Al. The stainless steel reactor consists a hollow space (diameter 2 mm, depth 40 mm) in which the nanoenergetic mixture ($\sim 0.1\text{ g}$) was placed. Two holes ($= 1\text{ mm}$) with 20 mm apart from each other were made in the reactor. Two tiny photodiodes were placed into the holes. A thin electrical coil was used to ignite the combustion reaction. After ignition, the thermal front propagated while emitting high intensity light that generated transient electrical signals by the photodiodes. The signals from the photodiodes were recorded using a Data Acquisition Board connected to a PC with a time resolution of $1\text{ }\mu\text{s}$. The velocity of the propagating reaction front was determined from the time of arrival of the flame at each photodiode and the known distance between the two photo-detectors. The loose nanoenergetic mixture was uniformly placed into the reactor and ignited. Fig. 5 shows typical signals that were recorded by the two photodiodes during the reaction. The time difference between two signals was about $8\text{ }\mu\text{s}$, accordingly, the detonation front velocity was estimated $\sim 2500\text{ m s}^{-1}$.^{3,12} This value is the highest measured velocity for the nanothermite systems and was comparable to the detonation velocities for hydrocarbon-alkylene-air mixtures, metallic azides/fulminates composites and ammonium nitrate fuel oil explosives.^{13,14} The measurements of the shock wave velocity were repeated at least three times and were always reproducible. The

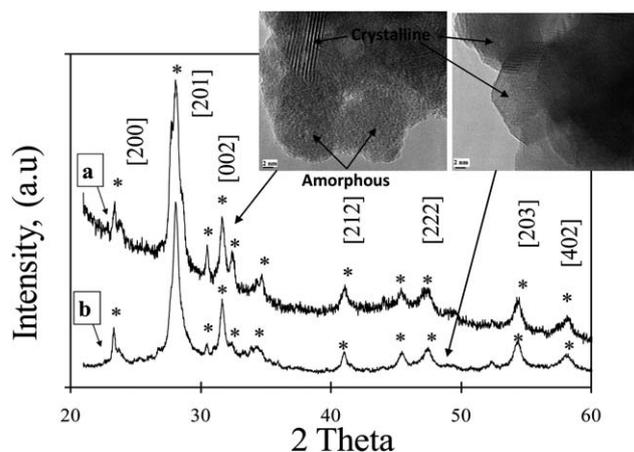


Fig. 3 XRD patterns and TEM images of Bi₂O₃ synthesized by nitrate-glycine combustion at two different temperatures and fuel/oxidant ratio, (a) $-280\text{ }^{\circ}\text{C}$ and $\phi = 0.05$ and (b) $-370\text{ }^{\circ}\text{C}$ and $\phi = 0.01$. The (*) mark indicates the major peaks of the tetragonal Bi₂O₃ phase and the scale line indicates 2 nm. Pattern (a) shows amorphous background at low scattering angle.

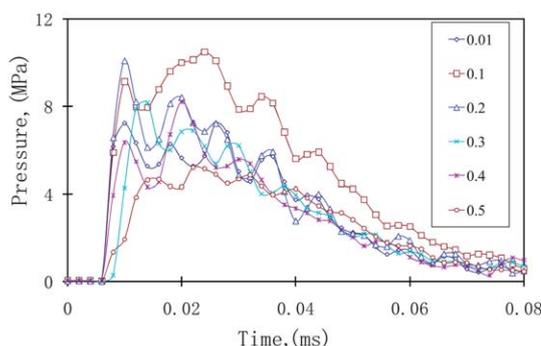


Fig. 4 Temporal pressure rise during the reaction of as-synthesized (at $\phi = 0.01$; 0.1; 0.2; 0.3; 0.4; and 0.5) Bi_2O_3 and Al nanoparticles. Experiments were carried out with 0.5 g sample mass in the vessel with volume 0.342 L.

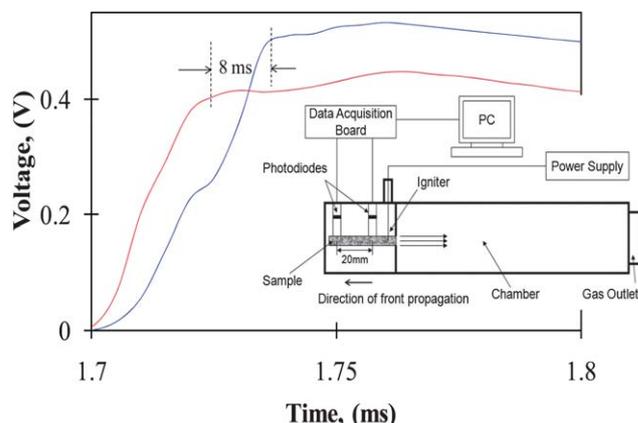


Fig. 5 The electric voltage recorded by the two photodiodes during detonation of the Al/ Bi_2O_3 nanoenergetic mixture. The time difference between two signals was about 8 μs . The inset is the schematic of experimental system for measuring thermal front velocity.

standard deviation for this experiment was $\pm 32 \text{ m s}^{-1}$.

The bismuth trioxide based nanothermite reactions generated high temperature and pressure discharge very fast (order of microsecond) with velocity of thermal front propagation $\sim 2500 \text{ m s}^{-1}$. The estimated Mach number $M = V_f/V_s \approx 7.35$ (where V_f thermal front velocity and $V_s \approx 340 \text{ m s}^{-1}$ speed of sound in the medium) revealed that the high temperature and pressure promote the hypersonic detonation mode.

Iodine pentoxide system

The enthalpy of the reaction $3\text{I}_2\text{O}_5 + 10\text{Al} = 5\text{Al}_2\text{O}_3 + 6\text{I}$ is (-25.7 kJ cm^{-3}) higher than those of the common stoichiometric thermite systems (1)–(9).¹⁵ The adiabatic temperature in this reaction, accounting for phase changes, was estimated to be 3253 K. This indicates that following

ignition this reaction can propagate in a self-sustaining manner. A recorded IR image shown in Fig. 6 (inset) demonstrates that the highest front temperature was $\sim 2000 \text{ }^\circ\text{C}$. Fig. 6 shows the

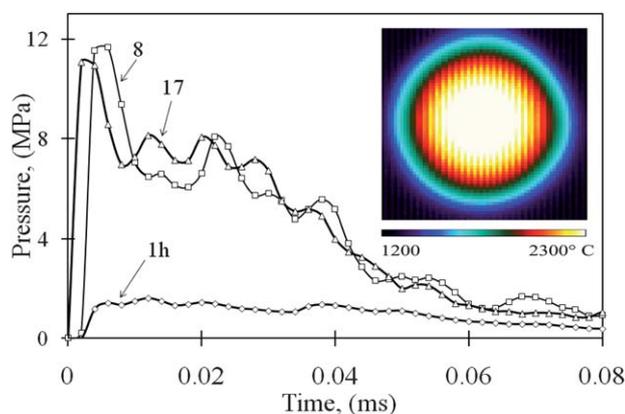


Fig. 6 Temporal pressure rise during reaction of the Al/ I_2O_5 nanoenergetic mixture at different mixing times. (inset) Typical IR thermal image during detonation.

dependence of the maximum generated pressure *versus* the mixing time of the Al/ I_2O_5 mixture of nanoparticles. The maximum peak pressure of $\sim 11 \text{ MPa}$ was generated after mixing for 8 hours. Probably, mixing for less than 8 hours is not sufficient to form a homogeneous mixture of reactants while longer mixing times generate agglomerates. In addition, during long mixing time oxidation of the active aluminium decreased its concentration in the mixture. This can decrease the pressure peak during the nanoenergetic reaction. The maximum (pressure \times volume) PV -value per gram was $\sim 7.6 \text{ kPa m}^3 \text{ g}^{-1}$.⁸ As shown in Fig. 6 the pressure (for mixing times of 8 and 17 h) in the reactor rose rapidly to its peak ($\Delta P/\Delta t \approx 2750 \text{ GPa s}^{-1}$) with a duration of about 4 μs . A possible explanation for the high pressure rise during the explosion of the Al/ I_2O_5 mixture is that the boiling temperature of one of the reaction products (iodine, $\sim 60 \text{ wt}\%$), of $184 \text{ }^\circ\text{C}$, is much lower than the maximum reaction temperature $\sim 2000 \text{ }^\circ\text{C}$. This iodine evaporation increased the pressure inside reactor. In contrast, the boiling temperatures of the metal product formed during other thermite reactions ($< 1500 \text{ }^\circ\text{C}$) are much higher than that of iodine.¹⁶

An important safety constraint on the use and storage of explosives, propellants or pyrotechnics is the value of their ignition temperature (T_{ign}) or thermal sensitivity. The differential scanning calorimetry (DSC) was used to determine the lowest temperature which caused a thermal explosion of the samples. The ignition temperatures in all these experiments were in the range of 605–620 $^\circ\text{C}$,

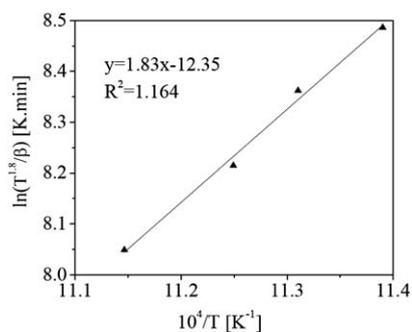


Fig. 7 Arrhenius plot for the exothermic peaks of the DSC curves for the Al/I₂O₅ nanothermite mixture at different heating rates.

which exceeds by at least 100 °C those of conventional thermite systems. This indicates that the mixture of Al/I₂O₅ can be safely stored and handled.⁸ The activation energy from the DSC data by using the isoconversion method suggested by Starink¹⁷ provides a more accurate value than the Kissinger and Ozawa methods. The Starink method determines the activation energy from the equation:

$$\ln \left\{ \frac{T^{1.8}}{\beta} \right\} = (1.0070 - 1.2 \times 10^{-5} E_a) \frac{E_a}{RT} + \text{const}$$

where E_a is the apparent activation energy (kJ mol⁻¹), β the heating rate in the thermal analysis (K min⁻¹), T the peak temperature of the exothermic curve (K), and R the universal gas constant. The activation energy is estimated from the slope of the graph of $\ln(T^{1.8}/\beta)$ vs. $10^4/T$ shown in Fig. 7. The activation energy for I₂O₅-Al was estimated to be 152 kJ mol⁻¹, this is the minimum energy required to start the chemical reaction. This number compares well with activation energy of thermite reactions reported in the literature for nanoenergetic materials.⁵ These behavioral features of the Al/I₂O₅ mixture demonstrate its potential for applications as propellants, primers and explosives composites. This composite offers both a thermal event and release of biocidal agent (atomic iodine) useful in mitigating detrimental biological materials. Interest in neutralizing biological-based weapons has posed a challenge to the use of conventional energetic materials that produce a very short-lived thermal event. Thus, iodine pentoxide based nanoenergetic gas generators could possibly be

used to neutralize spore forming bacteria and the threat of biological weapons.

Concluding remarks

Nanoenergetic gas generators based on bismuth and iodine oxides possess desirable reaction characteristics such as fast energy release, higher gas discharge and shock wave velocity among the common nano-thermite systems. A possible explanation for the high pressure rise during the combustion of Al/Bi₂O₃ and Al/I₂O₅ nanosystems is that the reaction product (bismuth or iodine) boils at a temperature of 1560 and 184 °C, respectively, that is lower than the maximum reaction temperature ~2000 °C. This causes bismuth or iodine evaporation and increases the released gaseous phase pressure.

The nitrate-glycine combustion synthesis enabled efficient production of high quality bismuth oxide nanocrystalline particles, which generate a higher pressure peak than when using commercial Bi₂O₃ particles. Increasing the crystallinity of the Bi₂O₃ led to a higher value of the pressure peak and shock waves. The maximum detonation front velocity up to 2500 m s⁻¹ was recorded for Bi₂O₃/Al. The estimation of Mach number ~7.35 revealed that the high temperature and pressure promote the hypersonic detonation mode. Because of their enhanced reactivity, the NGG systems can be used in several emerging applications including propellants, solid fuels, explosives and bio defeat treatment systems. There are several advantages, which can be accomplished by using Al/Bi₂O₃ and Al/I₂O₅ nanocomposites: (i) reduced ignition delay and reaction times; (ii) superior heat-transfer rates; (iii) tunability of novel energetic fuel/propellants with desirable physical properties; (iv) enhanced density impulse; and (v) incorporating nanoenergetic materials into the MEM and NEM systems.

Acknowledgements

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