Tuning the Gas Pressure Discharge of Nanoenergetic Materials by Boron and Carbon Nanotubes Additives

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ABSTRACT

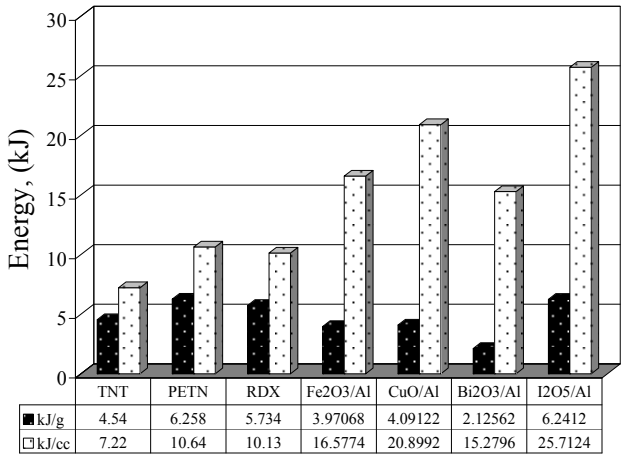
Thermite reactions are highly exothermic and may rapidly release high amount of stored chemical energy in the form of heat, light and wave. Nanothermite formulations that use aluminum or magnesium as the reducing agent and Fe_2O_3, MoO_3, WO_3 etc as the oxidizer have wide range of potential applications due to high energy density and the large energy release in a shorter time than by conventional thermites. We present here a study of the effect of addition of boron and carbon nanotubes (CNT) to the reactive mixture on the gas pressure discharge and thermal wave behavior during nanoenergetic reactions. The experiments show that addition of boron and carbon nanotube can increase gas peak pressure for some thermite nanocomposites by more than twice. The vaporization of B_2O_3, CO and CO_2 at ~2000 ºC increased the gaseous release. The behavioral features of the nanothermite-boron-CNT mixtures suggest potential for applications as propulsion, explosives and pyrotechnic components.

Keywords: nanothermite, bimuth trioxide, iodine pentoxide, nanoaluminum, boron, carbon nanotubes.

1 INTRODUCTION

Metastable Intermolecular Composites (MIC) also known as Nanoenergetic Materials (NM) have 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 [3] and can generate shock wave with velocities of up to 2500 m/s [4]. These materials 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 micro particles 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 an MIC mixture from a large number of candidate thermite mixtures. Among numerous thermodynamically feasible MIC mixtures the most widely investigated are Al/Fe_2O_3, Al/MoO_3, Al/WO_3, Al/CuO and Al/Bi_2O_3 nano mixtures [3]. The energy densities of some monomolecular composites (TNT-2,4,6-Trinitrotoluene, PETN-Pentaerythritol tetranitrate, RDX-1,3,5-Trinitroperhydro-1,3,5-triazine) and thermites stoichiometric formulations are shown in Figure 1. A comparison of energy densities shows that the volumetric energy of thermites based materials can exceed the best existing molecular explosives by about a factor of 2.

Our research goal is to identify novel multicomponent high density nanoenergetic materials for superior energy and gas release. Recently we developed several Nanoenergetic Gas-Generators (NGG) [3, 5-8] and have shown that Al/Bi_2O_3 and Al/I_2O_5 nanocomposites can release up to seven times more gas during the explosion than traditional thermite compositions. The long term research focuses on the finding and characterization of new NGG materials that rapidly release vigorous amount of gases and have high PV-values (pressure x volume).



	TNT	PETN	RDX	Fe2O3/Al	CuO/Al	Bi2O3/Al	I2O5/Al
kJ/g	4.54	6.258	5.734	3.97068	4.09122	2.12562	6.2412
kJ/cc	7.22	10.64	10.13	16.5774	20.8992	15.2796	25.7124

Figure 1: Energy densities of some monomolecular composites (TNT- 2,4,6-Trinitrotoluene, PETN-Pentaerythritol tetranitrate, RDX- 1,3,5-Trinitroperhydro-1,3,5-triazine) and thermites stoichiometric formulations.

This report focused on the tuning of the gas pressure discharge of nanoenergetic materials by *boron* and *carbon nanotube* additives. This involved a study of the peak gas evolution and rate of gas release in various nanoenergetic reactants with different concentration of boron and carbon

additives. The exothermic nature of boron and carbon combustion can be utilized for increasing energy in nanoenergetic composites for propellants and high explosives applications.

2 EXPERIMENTAL

We conducted experiments with the following reactions:

$$MoO_3+2Al=Al_2O_3+Mo \quad (1)$$

$$Bi_2O_3+2Al=Al_2O_3+2Bi \quad (2)$$

$$3I_2O_5 + 10Al = 5Al_2O_3 + 6I \quad (3)$$

In some cases, up to 10 wt. % carbon and boron nanoparticles were added to the mixtures. Addition of boron or carbon generates B_2O_3 or CO and CO_2 that may increase the pressure release.

Aluminum and metal oxides powders were purchased from Sigma-Aldrich Co. and stored under nitrogen (99.9 vol. % N_2 with 50 ppm O_2) in a glove box to prevent contamination by impurities present in the air. The bismuth oxide was prepared by a modified aqua combustion synthesis [7]. Most nanoenergetic reactions are highly exothermic. The mixtures may spontaneously detonate in some cases due to friction or electrostatic charge build up when the precursors are mixed or ground together. Stoichiometric mixtures of the reactants (metal oxides and Al particles) were mixed in a closed cylinder containing hexane and nitrogen for up to 8 hrs by a rotary mixing machine. This environment avoids the partial oxidation of the fine Al particles. The hexane prevents electrostatic charge build up that may lead to ignition and/or explosion of the powders during the mixing and handling.

The experimental system, shown schematically in Figure 2, was used to measure, the peak pressure, ignition temperature and the pressurization rate ($\Delta P/\Delta t$). The reactions were conducted inside a commercial stainless steel, high pressure, cylindrical reactor, 30.7 mm ID and 115 mm long (Parr, V=0.342L). High-frequency pressure transducers (PCB Piezotronics Inc.) on top of the reactor measured the pressure up to 14 MPa. A loose reactants mixture (0.1-0.5 g) was loaded into a ceramic boat, placed in the reactor. Due to the high energetic nature of the reactions they were conducted with a small sample, i.e, not exceeding 0.5 g reactant mixture.

The reactants mixture was ignited by an electrically heated coil, inserted into the sample. The ignition temperature was measured by an S-type (Pt-Rh) thermocouple (Ø=0.1 mm) inserted in the center of sample. The pressure transducer and thermocouple readings were recorded and processed by an Omega data acquisition board connected to a PC with a resolution of 1 µs.

An infrared (IR) camera (Merlin, Indigo Systems) viewed and recorded the sample surface radiation in an open stainless steel cylindrical reactor (38 mm ID and 12 mm long), insulated on the inside by alumina foam.. The reactant mixture was loosely placed inside an alumina ring (10 mm id and 5 mm high) on the bottom of the reactor, and ignited by an electrically heated coil. A gold plated mirror was positioned on the top of the reactor in 45 degree to reflect the infrared radiation to an IR camera which had a 256 x 256 indium antimonide detector array sensitive to 3-5 µm radiation. The recorded images determined the maximum temperature and shape of the propagating temperature front.

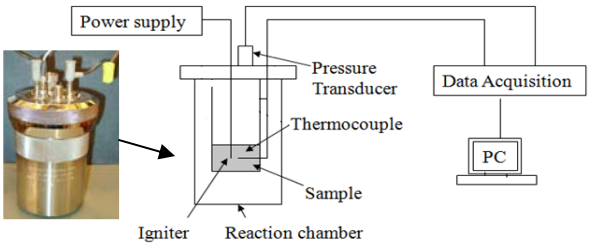


Figure 2: Schematic of the experimental system used for measuring of pressure discharge of nanoenergetic systems.

3 RESULTS AND DISCUSSION

Morphological features and microprobe analysis of loose powder fixed to a graphite disk were determined by scanning electron microscopy (SEM; JEOL JAX8600, Japan). High-Resolution Transmittal electronic microscopy (HRTEM, JEOL JEM-2000 CX2) determined the particles size and electron diffraction pattern of the Al nanoparticles and the bismuth oxide. The TEM images in Figure 3 show that most Al particles were spherical with a diameter from 50 to 150 nm and coated by a ~4 nm aluminum oxide layer. The same thickness of exterior oxide layer surrounded particles of different sizes. The pure aluminum mass content of a particle, with the average diameter of 100 nm and an aluminum oxide layer 4 nm thick, is ~84 %. We used these Al particles to investigate the pressure release during the reactions with different metal oxide precursors.

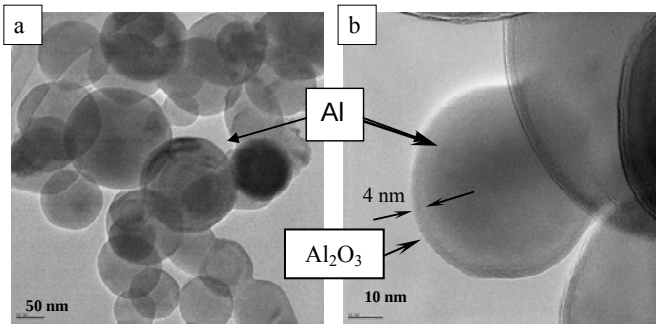


Figure 3: (a)- TEM images of commercial Al particles; (b)- high resolution TEM of an aluminum oxide layer ~ 4 nm.

3.1. Influence of carbon and CNT addidtion

Carbon nanotubes, graphite and amorphous carbon are structurally different, which is reflected in their reactivity and the resistance to oxidation. Addition of carbon

(nanoparticles of graphites) to the reactants mixtures increased the overall enthalpy and produced gases but decreased the maximum pressure by about 10-20 %. Possibly, the slow rate of graphite particle combustion reduced the maximum pressure peak. Hovewer, addition of 3 wt. % of single wall carbon nanotubes (SWCNT) increased the pressure discharge by the Bi_2O_3/Al reaction by about 30 %. The peak pressure rise during the nanothermite reactions of Bi_2O_3 - Al and Bi_2O_3 - Al - SWCNT is shown in Figure 4. The same bahaviour was observed during detonation of system (3). The pressure discharge was increased by about 35 %.

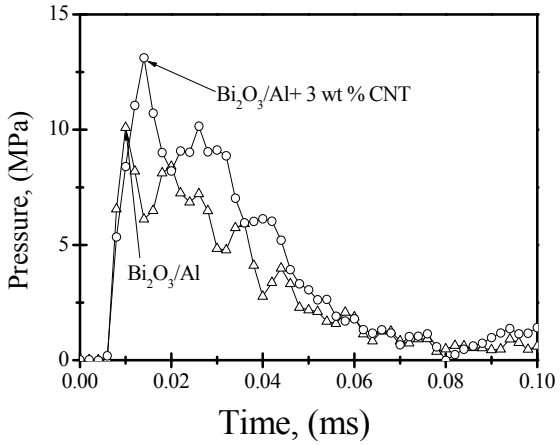


Figure 4: Peak pressure rise during the nanothermite reactions Bi_2O_3+Al with 3 wt % of carbon nanotube addition.

This result confirms that SWCNTs oxidation is more reactive than graphite. Recently, non-isothermal techniques were employed to determine the kinetic parameters for the oxidation of different carbon structures such as nanotubes, amorphous carbon and graphite [9]. The single-walled carbon nanotubes were found to be the most reactive, followed by multi-walled nanotubes, amorphous carbon and graphite. The oxidation of carbon nanotubes appears to be a single step reaction well represented by a cylindrical shrinking core model $t/\tau=1-(1-X)^{1/2}$ [10]. The consistency of this model was assessed both by comparing the activation energy extracted from TGA and DSC, and by theoretical considerations on the geometrical development of CNT oxidation. The activation energy of about 150 kJ/mol, was determined from both Kissinger method (without assumption of a model) and from isothermal experimental data. It was shown that the activation energy of MWCNT oxidation is slightly greater than the SWCNTs [11], which confirmes also the active combustion behaviur of SWCNTs. It was also shown that an increase of 5 % of oxygen content could dramatically increase the reaction rate, i.e.the heat flow rate [11].

The structure of CNTs gives unique properties, including high thermal and electrical conductivity, and a very high aspect ratio, since their diameters are nanoscale while their lengths can be micro-scale. These properties make them attractive candidates as a additives for tuning burning rate and tailoring detonation properties.

3.2. Influence of boron addidtion

Addition of boron to the thermite systems increased the maximum pressure. At low boron concentrations, its addition increased the temperature rise because -ΔH of $2B+1.5O_2 \rightarrow B_2O_3$ (~18.8 kJ/g) is much higher than that of the thermite reactions (3-5 kJ/g). The vaporization of B_2O_3 at ~2000 ºC increased the gaseous products. For example, the maximum peak pressure was generated when adding 2.53 wt. % boron to the MoO_3-Al mixture (Figure 5).

This increased the maximum pressure from 0.5 MPa to 1.3 MPa, i.e., by more than twice. Probably, at higher boron concentration the amount of oxygen in the vessel was not sufficient to oxidize all the boron. Thus, this excessive amount of boron actually decreased the –ΔH of the mixture, the maximum temperature and the peak gas pressure. Figure 6 shows temporal pressure signal during detonation of the MoO_3/Al mixture with different boron concentrations. The boron addition to the mixture changed the amplitude of the pressure dicharge but didn't change the duration time of the signal. The pulse of the pressure dicharge signal was about 0.1 ms.

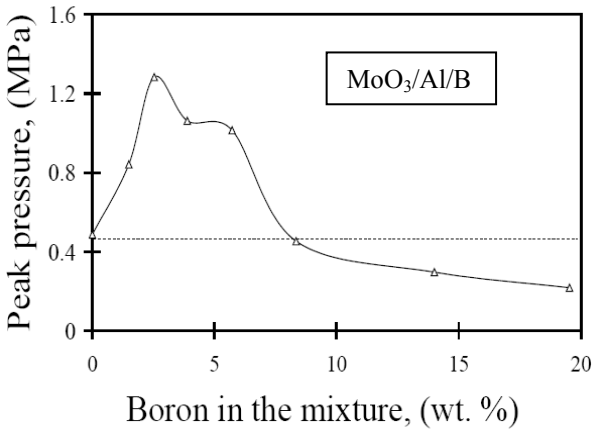


Figure 5: Dependence of peak pressure in the system on the boron wt. % in the mixture, Horizontal dashed line shows peak pressure without boron addition.

The temporal pressure increase in the reactor during the detonation of Bi_2O_3-Al–B mixtures are shown in Figure 7. In all of these reactions, the pressure in the vessel rose very rapidly to its peak value with duration of about 7.5 μs. However, the impact of boron additives to the inctreasing pessure discuarge for Bi_2O_3-Al–B was not large (about 8 %).

The combustion of boron is a complex process involving heterogeneous chemistry. There are two major limitations to extracting the desired performance of these fuels which have been encountered. One is that boron particles are coated with B_2O_3. This limits the initial vaporization of boron particles since boron trioxide is

difficult to remove either by vaporization or chemical reaction. The second problem is that the condensstion of the final combustion products to liquid boron trioxide is slow, especially if boron oxyhydrides are formed as relatively long-lived intermediate species. For maximum efficiency of the boron combustion is achieved when both the boron particles oxidation and condensation to liquid boria (at temperature higher than 450 ºC) occur during the short combustion time, typically less than 10^{-4} s.

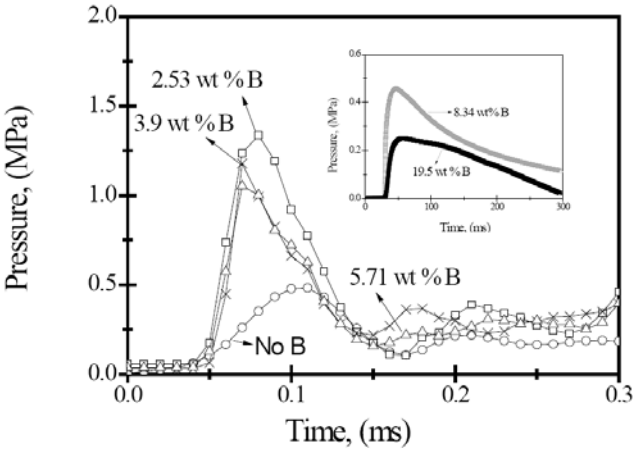


Figure 6: Temporal pressure discharge during detonation of MoO_3/Al system with different boron additives

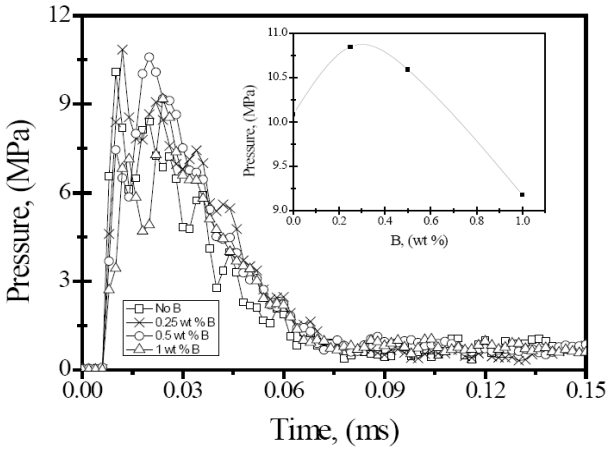


Figure 7: Peak pressure rise during the reaction Bi_2O_3+Al using as-synthesized bismuth trioxide nanoparticles. Inset: dependence of the pressure peak on boron concentration.

4 CONCLUSIONS

The reactivity of nanothermite systems can be tuned to a specific levels by addition of either carbon or boron. The SWCNT addition into nanoenergetic systems Bi_2O_3/Al and I_2O_5/Al increased the pressure discharge by up to 35 %. The incorporation of boron into different nanothermite systems also may effectively increase the specific reaction rate and the pressure release. The results reported here open up new horizons for tuning of nanoenergetic materials reactive properties. It shows how it is possible to design energetic materials according to specific requirements.

ACKNOWLEDGMENTS

The research was sponsored by the Air Force Research Laboratory under agreement number FA8650-07-2-5061. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes not withstanding any copyright notation thereon.

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