Development of nanoenergetic materials based on Al/I_2O_5 system

K.S. Martirosyan*, L. Wang, and D. Luss

Department of Chemical and Biomolecular Engineering,
University of Houston, Houston, TX, USA, 77204
*kmartirossian@uh.edu

ABSTRACT

We studied the gas generation and thermal wave behavior during the detonation of a novel nanoenergetic mixture of iodine oxide and aluminum. The ignition of a homogeneous mixture of iodine pentoxide (78 wt. %) and aluminum nanoparticles (22 wt. %) occurs in the range of 605-620 °C. It generates a high discharge pressure (~11 MPa) and a shock wave with a velocity of ~2000 m/s. The pressure very rapidly rose to its peak during ~ 4 μs with a $\Delta P/\Delta t$ of up to 2750 GPa/s. The ignition temperature exceeded by at least 100 °C those of conventional thermite systems implying that the Al/I_2O_5 nano mixtures can be safely stored and handled. The activation energy for the nanoscale reaction of $3I_2O_5+10Al=5Al_2O_3+6I$ was estimated to be 152 kJ/mol. The maximum pressure x volume (PV-value) obtained by a 0.5 g mixture was ~3.8 $kPa.m^3$. This compares well with the highest reported value of 3.9 $kPa.m^3$ for the Bi_2O_3/Al mixture for the same sample mass.

Keywords: nanoenergetic materials, gas generation, detonation, thermite, activation energy, rapid pressure rise.

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 [3-8] and can generate shock wave with velocities of up to 2500 m/s [9-11]. 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 systems [3-11]. Recent advances in the integration of nanoenergetic components into micro-electro-mechanical systems (MEMs) suggest a possible development of "nanoenergetics-on-a-chip" devices, which will have many potential applications in digital propulsion systems.

Recently we developed Nanoenergetic Gas-Generators (NGG) [11-14] and have shown that Al/Bi_2O_3 and Al/I_2O_5 nanocomposites can release up to seven times more gas product during explosion among traditional thermite compositions.

Our 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). We describe here a novel potential MIC mixture based on Al/I_2O_5 that releases a large amount of gaseous products and generates a fast moving thermal wave during the explosion.

2 EXPERIMENTAL

2.1 Sample preparation

The enthalpy of the reaction

$$3I_2O_5 + 10Al = 5Al_2O_3 + 6I + (-\Delta H=6.22kJ/g) \qquad (1)$$

is higher than those of the following common stoichiometric thermite mixtures: Al/Fe_2O_3 (3.97 kJ/g), Al/MoO_3 (4.72 kJ/g), Al/WO_3 (2.92 kJ/g), Al/CuO (4.09 kJ/g) and Al/Bi_2O_3 (2.12 kJ/g). The adiabatic temperature this reaction accounting for phase changes was estimated to be 3253 K [15]. This indicates that following ignition this reaction can propagate in a self sustaining manner.

The aluminum and iodine pentoxide powders were purchased from Sigma-Aldrich Co and stored in a glove box under (99.9 % pure) nitrogen to prevent contamination by any air impurities. The reactants were thoroughly mixed in hexane under a nitrogen environment for up to 8 h in a rotary mixing and grinding machine. The hexane was used as a mixing agent to prevent buildup of an electrostatic charge on the particles surface that may lead to ignition and/or explosion of the powders during the mixing and handling. The mixing of the reactants in hexane under nitrogen environment prevents the partial oxidation of the Al nano particles and averts the need to reduce the active metal. In most experiments we used aluminum nanoparticles with an average particle size of ~100 nm. This powder is not very active in air and can be safely

mixed with metal oxides to prepare the thermite reactions mixtures.

2.2. Nanopowder Characterization

The composition and crystal structure of the powder was determined by X-ray diffraction using a Siemens D5000 diffractometer with Cu Kα radiation (λ=1.54056Å). The scans were taken at room temperature over a wide range of 2θ = (20-80°) at 0.05 degrees intervals. High-Resolution Transmittal electronic microscopy (HRTEM, JEOL JEM-2000 CX2) was used to determine the particles size and morphology of the Al and iodine pentoxide nanoparticles.

2.2 Pressure release and thermal front velocity

The experimental test system, shown schematically in Figure 1,a measured the peak gas pressure evolution and the pressurization rate (ΔP/Δt) during reaction (1). The detonation experiments were conducted inside a commercial stainless steel, high pressure, cylindrical reactor, 30.7 mm ID and 115 mm long (Parr, V=0.342L). A loose reactants mixture was loaded into a ceramic boat, placed in the reactor. Due to the high energetic nature of the reactions the experiments were conducted with a small sample, i.e, 0.5 g reactant mixture. The reactants mixture was ignited by an electrically heated coil, inserted into the sample. High-frequency pressure transducers (PCB Piezotronics Inc. Model S101A02) on top of the reactor measured the pressure up to 30 MPa. The thermal front propagation velocities were measured by using the experimental setup shown schematically in Figure 1,b.

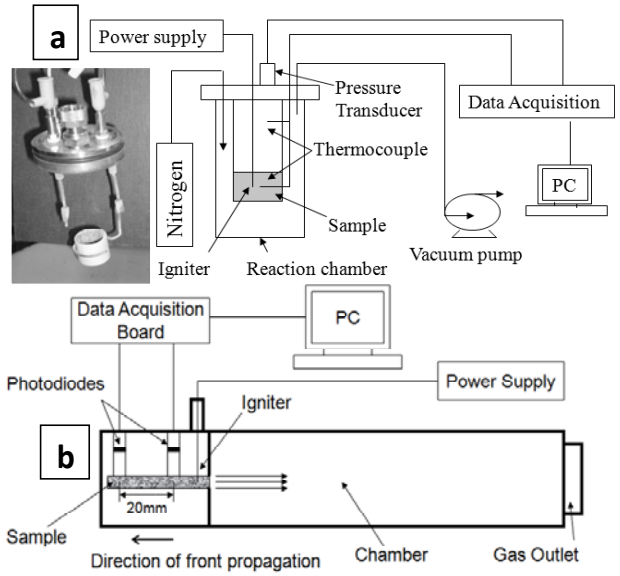

Figure 1: Schematic of experimental systems for measuring: (a) - evolution of pressure and (b) - thermal front velocity during performance of high energetic gas generators systems.

The stainless steel reactor consists a hollow space (diameter 2 mm, depth 40 mm) in which the nanoenergetic mixture (~ 0.1 g) were placed. Two tiny photodiodes were inserted into the reactor through two holes (Ø=1 mm) 20 mm apart from each other. 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. These signals were recorded using a Data Acquisition Board connected to a PC with a time resolution of 1 μs. The velocity of the propagating combustion front was determined from the time difference of the arrival of the flame at the two photodiode and the distance between the two photo-detectors.

3 RESULTS AND DISCUSSION

The TEM images of an Al/I_2O_5 mixture (Figure 2) show that most Al particles were spherical with a diameter from 50 to 180 nm and were coated by a 4 nm aluminum oxide layer. The iodine pentoxide particle size was ~10 nm. The active aluminum content was estimated to be ~84 wt % by mass.

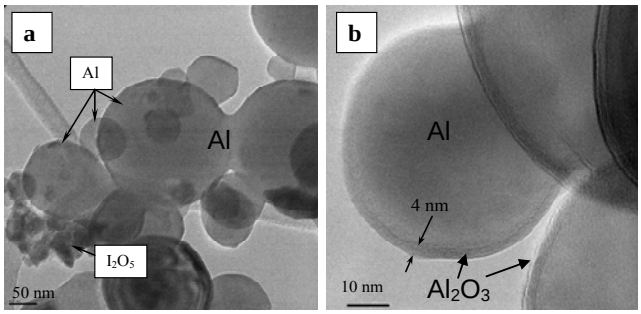

Figure 2: TEM images of (a) - mixture of iodine pentoxide and aluminum particles after 8 h mixing/grinding; and (b) - aluminum particles.

An infrared (IR) high speed camera (FLIR, SC4000) was used to view and record the sample surface radiation in an open stainless steel cylindrical reactor (38 mm ID and 12 mm long), the inside of which was insulated by alumina foam. A gold plated mirror positioned on the top of the reactor reflected the infrared radiation to the IR camera. A recorded IR image shown in Figure 3,a demonstrates that the highest front temperature was about 2000 °C.

Figure 3,b shows the dependence of the maximum generated pressure versus the mixing time of the Al/I_2O_5 mixture of nanoparticles. The maximum peak pressure of ~11 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 aluminum decreased its concentration in the mixture. This can decrease the pressure peak during the nanoenergetic reaction. The maximum

(pressure x volume) PV-value was ~3.8 kPa.m^3. This value compared well with the pressure of 3.9 kPam^3 generated by an Al/Bi_2O_3 mixture that we reported recently as the best mixture for nanoenergetic gas generators [11].

As shown in Figure 3,b the pressure (for mixing times of 8 and 17 h) in the reactor rose rapidly to its peak ($\Delta P/\Delta t$ ~2750 GPa/s) with a duration of ~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 reaction products, (iodine, ~60 wt. %) of 184 °C, is much lower than the maximum reaction temperature ~2000°C. This iodine evaporation increased the pressure inside reactor. In contrast, the boiling temperatures of the metal product formed during other thermite reactions of (<1500°C) are much higher than that of iodine.

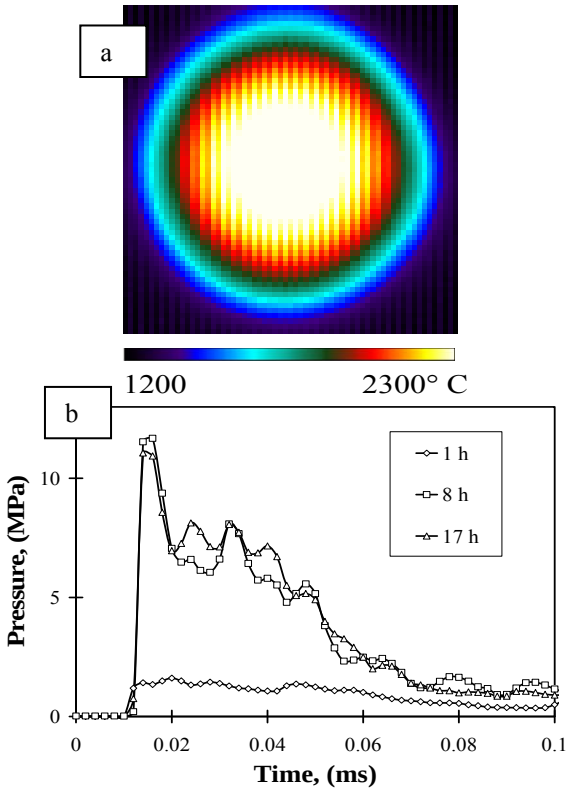

Figure 3: (a) - Typical IR thermal image and (b) - temporal pressure rise during reaction of Al/I_2O_5 nano thermite for different mixing time.

The dependence of the peak pressure on the Al particle size is shown in Figure 4. The peak pressure increased upon a decrease in the size of the aluminum particles. For example, decreasing the Al particle size from 20 μm to 100 nm increased the peak pressure from 0.4 MPa to 11 MPa. Previous reports [2, 4] have predicted and experimentally shown that use of nano Al increased the combustion temperature of thermite reactions. The higher combustion temperature increased the volume of the vaporized reaction products. This, in turn, led to a higher peak pressure. The characterization of the products by X-ray analysis verified that the combustion products consist of aluminum oxides and iodine.

Figure 5 shows typical voltage signals recorded by the two photodiodes during reaction (1). The time difference between the two signals of about 10 μs indicates that the detonation front velocity was ~2000 m/s. This supersonic velocity of the front propagation confirms that the reaction between aluminum and iodine pentoxide nanoparticles was a detonation.

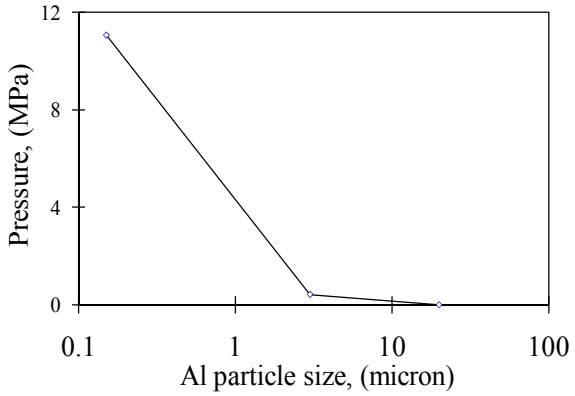

Figure 4: Dependence of the pressure peak on the Al particle size during reaction (1), mixing time 8 h.

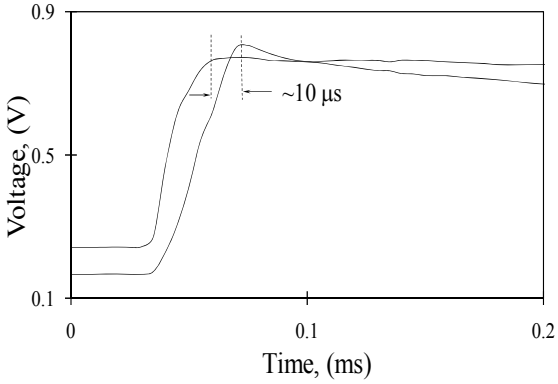

Figure 5: The electric voltage recorded by the two photodiodes during the detonation of Al/I_2O_5 nano thermite mixture (m=0.08 g and mixing time 8 h).

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. We used a differential scanning calorimetry (DSC) to determine the lowest temperature which caused a thermal explosion of the samples. Figure 6,a shows a typical temporal temperature rise during reaction (1) at various heating rates from 47 to 66 °C/min. The ignition temperatures in all these experiments were in the range of 605-620°C, which exceeds by at least 100°C those of conventional thermite systems. This indicates that the mixture of Al/I_2O_5 can be safely stored and handled.

We estimated the activation energy from the DSC data by using the isoconversion method suggested by Starink

[16], which was shown in (Ref 17) to provide a more accurate value than the Kissinger and Ozawa methods [18, 19]. The Starink method determines the activation energy from the equation:

$$\ln\left\{\frac{T^{1.8}}{\beta}\right\} = (1.0070 - 1.2\times10^{-5} E_a)\frac{E_a}{RT} + const$$

where E_a is the apparent activation energy (kJ mol^{-1}) , β the heating rate in the thermal analysis (K/min), T - the peak temperature of the exothermic curve (K), and R the universal gas constant. Ea is estimated from the slope of the graph of $\ln(T^{1.8}/\beta)$ vs. 1/T shown in Figure 6,b. The activation energy for I_2O_5-Al was estimated to be 152 kJ/mol, 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].

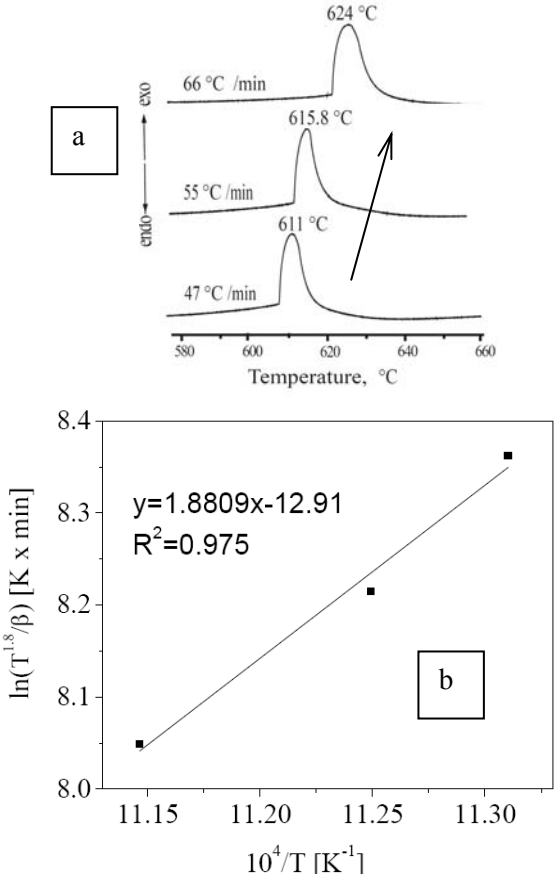

Figure 6: (a) - DSC patterns of Al/I_2O_5 nano thermite mixture at different heating rates; (b) - Arrhenius plot for the exothermic peaks of the DSC curves.

4. CONCLUSIONS

A high discharge pressure of about 11 MPa and a shock wave with a velocity of ~2000 m/s was generated during the reaction between iodine pentoxide and aluminum nanoparticles. The maximum reaction temperature ~2000º C was measured by an IR camera. The behavioral features of the Al/I_2O_5 mixture indicate potential for applications as propulsion explosives and pyrotechnic components. The activation energy of the reaction $3I_2O_5+10Al=5Al_2O_3+6I$ using nanoscale reactants is estimated to be 152 kJ/mol.

ACKNOLEDGMENTS

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