

Chemical dynamics of nano-aluminum/iodine (V) oxide

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Abstract. This proceeding describes our preliminary efforts in studying highly reactive composites containing crystalline iodine (V) oxide and nano-aluminum (nAl) with various amounts of cyclohexanone in the form of powders. In this study we report upon the application of physiochemical techniques such as thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), powdered X-ray diffraction (PXRD), and electron microscopy for chemical characterization of powder composites. In addition dynamic measurements were conducted by recording pressure trace profiles during a combustion event. These various techniques were employed to examine these energetic materials (EMs) and associate changes to the chemical dynamics of the composite with the additive.

1. Introduction

Aluminum and iodine (V) oxide reactivity was first studied by Ivanov *et al.* in 1980 who proposed a global reaction mechanism between iodine gas and various metals [1]. In this work, they observed the iodation of aluminum followed by the oxidation of aluminum iodide in a nitrogen atmosphere. In recent years binary mixtures of nano-aluminum (nAl) and iodine (V) oxides have shown very promising energetic properties. Recently, Martirosyan *et al.* reported propagation velocities upward of ~2,000 m/s for loose ball-milled powders of nano-aluminum and 10 nm I₂O₅ particles [2]. Russel and Pantoya have also reported high propagation rates (1305 ± 25 m/s) for loose powder mixtures of micron scale HIO₃ (the fully hydrated form of I₂O₅) with nano-aluminum in an argon atmosphere [3, 4]. The pressure generated when gas is evolved during combustion of this EM has also been studied by Johnson *et al.* who additionally observed the indentation of, and penetration through, aluminum pans [5].

More recently at the Air Force Research Laboratory, we performed pre-ignition reactivity studies of nAl/iodine (V) oxide composite powders utilizing electrostatic discharge (ESD) as a rapid heating method, and compared these results with that of a slow heating method (*i.e.* DSC-TGA) [6]. In this previous work it was hypothesized that during the dehydration of HI₃O₈/HIO₃ to I₂O₅ that either I₂ or HI, or both, are released. Later analysis of thermally heated alumina crucibles (under air) containing iodine (V) oxide in the form of HI₃O₈/HIO₃ always demonstrated etching and pitting at the walls of the alumina crucible.[6] Additionally, iodate salts (*i.e.* NaIO₃) were studied by DSC-TGA, and no pitting or etching of alumina crucibles was observed. Detection of HI has been observed previously by Sherwood, *et al.* while performing sublimation/decomposition studies on iodine (V) oxide utilizing



mass spectrometry [7]. Similar observations by our group have also observed the release of HI gas via mass spectrometry during sublimation/deposition studies of HI_3O_8 . Based upon the above observations we conclude that HI must be present within similar temperature regimes as that of dehydration of $\text{HI}_3\text{O}_8/\text{HIO}_3$. The formation of HI during dehydration provides the origin of the mechanism for the premature ignition of the composites well below the decomposition temperature of I_2O_5 ; a mechanism discussed below.

In some cases, energetic materials undergo a critical energy release step in the condensed phase that strongly influences the ignition and burn rate (flame propagation velocity) of the reactive composite. This event occurs well below, and is independent of, the melting/decomposition point of the oxide and is associated with a phenomenon described as a pre-ignition reaction [8]. In the preliminary work conducted by our group, we proposed a mechanism to describe the onset of pre-ignition in nAl/iodine (V) oxide composites [6]. During heating of the composites the iodine oxide component begins to dehydrate releasing HI gas. At the oxide surface of the nAl particles HI gas etches away the alumina passivation layer protecting the nAl core. Then, as I_2O_5 decomposes to I_2 and O_2 , a violent reaction occurs with the now bare aluminum such that AlI_3 and Al_2O_3 is formed in an iodination-then-oxidation step as described by the work of Ivanov *et al.* [1]. This conclusion is supported by structural phase identification of the combustion products via PXRD from nAl-iodine (V) oxide composites containing a cyclohexanone additive. The state of the alumina shell is also in question during this reaction. Alumina is known to form the chemical species Al_4C_3 after exposure to carbon monoxide at elevated temperatures under argon [9]. During thermal heating of nAl-iodine (V) oxide composites containing cyclohexanone, it is currently understood that cyclohexanone initially reacts with HI to form iodo-cyclohexanone which decomposes exothermically and generates carbon monoxide as one of many products. The scavenging of HI by cyclohexanone during dehydration of the hydrated iodine oxide prevents etching of the alumina shell, and thus, prevents early ignition of the composite mixture. For these reasons, we have identified cyclohexanone as an ideal candidate to desensitize nAl/iodine (V) oxide composite materials. Chemical dynamics and energetic performance characterizations are still required to capture the full effect of the additive.

In this proceeding we report on our preliminary efforts to study the combustion properties of nAl- HI_3O_8 powders via their pressurization rates and DSC-TGA results.

2. Experimental details

The source chemicals of tertiary butanol (Sigma-Aldrich 98%), iodine pentaoxide (Alpha Aesar 98%), and cyclohexanone (Aldrich Chemical Co. Inc., 99.8%) were used as received unless otherwise stated. Nano-aluminum was received from ARDEC containing an average particle size of 78 nm with 67 ± 3 % active aluminum with an outer alumina coating of 2.8 ± 0.4 nm. Iodine pentoxide (I_2O_5) was determined to be predominately HI_3O_8 which is a common occurrence with iodine (V) oxide as received from commercial vendors [10, 11].

Samples of HI_3O_8 powder were milled with tungsten carbide balls utilizing a LabRam mixer to reduce the particle size of the oxidizer. Afterwards the oxidizer and fuel were blended in a suspension of tertiary butanol under stirring and continuously sonicated for several hours. Cyclohexanone was then added and the suspension was allowed to stand under stirring for several hours before the suspension was poured into Velostat containers to dry under flowing nitrogen. For the bomb-calorimetry (Parr Instrument Co.) experiments, 50 mg samples were contained in either an open glass vial or a ceramic crucible with either nichrome wire or titanium wire in contact with the surface. The bomb calorimeter was closed and pressurized to 30 atm in either oxygen, argon, or a mixture of oxygen and argon. A pressure sensor is fitted to the top of the bomb calorimeter lid and is triggered with the heating of the wire. The sampling rate for the pressure transducer is fixed at 500 kHz with a variable data acquisition (DAQ) board recording at 200 kHz. Pressure trace recordings were minimally filtered by the removal of the excessive “ringing” due to transient pressure pulses deflecting from the walls of the container. Such a filtering improves the goodness of fit on the initial/instantaneous pressurization rate (k_{pi}). Powdered samples were imaged with a scanning electron microscope (SEM)

in backscattered detection mode. Composition analysis of the percent reactant by sample weight was determined by Reitveld refinement using the following crystallographic files: HI_3O_8 (04-007-4859) and Al (04-007-9709). The percent mass amount of cyclohexanone present in the samples labeled Sample 2, 3 and 4 was qualitatively determined by TGA analysis. The TGA results on Samples 2 - 4 reflect appreciable weight loss between 78 - 188 °C with a broad peak at 153 °C (bp. of cyclohexanone is 155 °C) as compared to Sample 1. The TGA measurements were conducted at a heating rate of 10 - 60°C min⁻¹ under air in a crucible featuring a pin-hole in the lid. Absolute weight loss for Samples 2 - 4 were normalized against the neat composite, labeled Sample 1 below, which was measured under the same conditions.

3. Discussion and results

3.1. Structure and composition of $n\text{Al-HI}_3\text{O}_8$

Electron microscopy images of samples 1 and 4 are presented in figure 1 below. HI_3O_8 , the lighter shaded particles, are observed to be large (<10 μm) and irregular in shape as compared to the smaller, spherically shaped, nAl aggregated particles (dull gray color). Electron microscopy images do not appear to show any significant differences structurally between Samples 1 and 4, nor Samples 2 and 3 (data not shown). However, TGA of Samples 2, 3 and 4 depicts the retention of cyclohexanone in increasing amounts as formulated, as seen in table 1. Furthermore, all samples are fuel rich with respect to stoichiometric conditions as determined by powdered XRD due to the loss of oxidizer over time. The loss of oxidizer is presumed to have occurred due to partial solvation of the oxidizer during the long mixing times (2-3 weeks).

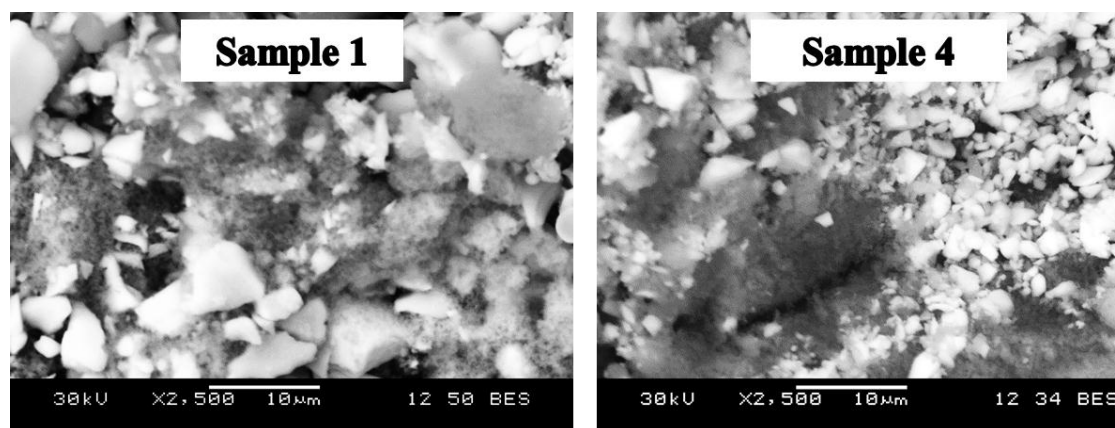


Figure 1. Electron microscopy images of $n\text{Al}/\text{HI}_3\text{O}_8$ powder a) sample 1: neat; b) Sample 4: highest additive content.

Table 1. Percent by weight of $n\text{Al}$ and HI_3O_8 per sample type as determined by PXRD; percent cyclohexanone determined via TGA analysis; and E_a values determined via DSC analysis.

Sample#/type	percent Al by wt.	percent HI_3O_8 by wt.	percent cyclohexanone by wt.	Energy of activation (kJ/mol)
1/ $n\text{Al-HI}_3\text{O}_8$	51.2	48.8	0.0	135.12 ± 4.13
2/ $n\text{Al-HI}_3\text{O}_8$	55.3	43.8	0.89	$273. \pm 71.1$
3/ $n\text{Al-HI}_3\text{O}_8$	51.3	46.3	2.41	212.91 ± 6.22
4/ $n\text{Al-HI}_3\text{O}_8$	46.6	46.2	7.23	230.32 ± 66.1

3.2. Reactivity of nanoAl-HI₃O₈

Zhang *et al.* observed ignition of Al-I powder between 200 °C to 400 °C and associated this reactivity with elevated decomposition rates of AlI₃ [12, 13]. It was also reported by our group that a change in reactivity, after the addition of an additive, was found to be ~200 °C for nAl-HI₃O₈ powder [6]. Shown in figure 2 is a DSC plot for Samples 1 thru 4. Thermal analysis of Samples 1 thru 4 depict several exothermic steps beginning as early as ~34 °C (peak) followed by another, heating rate dependent, exothermic step peaking between 181 °C to 215 °C. The activation energies for the latter step were calculated for all samples utilizing the Type B-1.92 Starink method [14, 15]. Samples containing a cyclohexanone additive have higher E_a values which are in agreement with previous work which demonstrated greater ESD thresholds with composites containing cyclohexanone, also summarized in table 1.

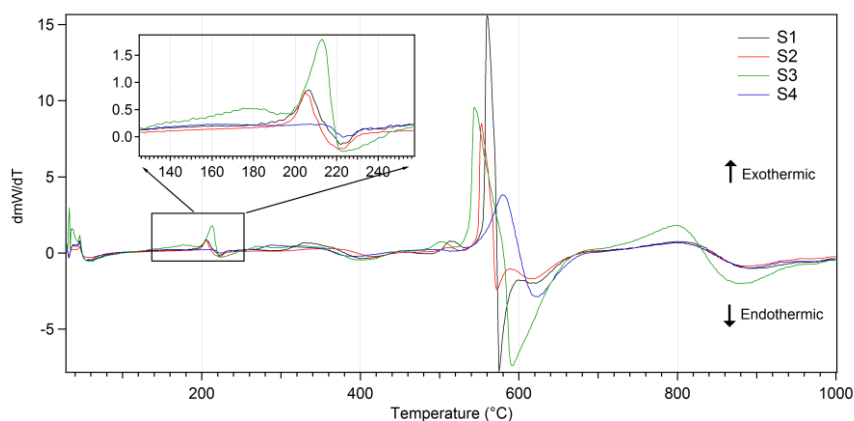


Figure 2. Derivatives of heat flow (mW) as a function of heating rate versus temperature for Samples 1(S1) thru 4(S4). Experiments conducted under air at a heating rate of 60 K/min. Inset: magnified view of area outlined in square

Furthermore, in one trial run the second step was observed to release significant pressure (specifically the first pressurization step) in which the lid of the crucible was forcibly ‘expelled’ at ~206 °C under a heating rate of 60 K min⁻¹. Post-analysis of the latter run did not reveal evidence of the oxidizer, but did demonstrate evidence where the nAl was physically expelled out of the crucible without undergoing oxidation. Presented in figure 3 are the pressurization rates recorded for Samples 1 thru 4 pressurized to 30 atm and ignited in various oxygen atmospheres; oxygen was diluted with argon and the total amount of oxygen per trial volume is reported as moles. The initial pressurization rate was obtained by fitting the slope of the pressure rise at approximately zero pressure (P_0) to a final pressure (P_f) in the pressure rise curve demonstrated in figure 3 inset; P_f is defined as the peak pressure value in the first significant oscillation for fast pressure traces or the pressure value approximately at the midpoint of the pressure rise for slow pressure traces (see figure 3 inset). Pressurization rates for Samples 2 and 4 are similar and appear to reflect a mild increase in reactivity with increasing moles of oxygen as compared to Samples 1 and 3. Samples 1 (the neat composite) and 3 reflect the highest pressurization rates of all candidates under various atmospheric conditions, as well as reflecting a stronger dependence with increasing moles of oxygen. The higher pressurization rates with increasing moles of oxygen observed for all samples is most likely due to a faster burn rate for the fuse wire igniting the material. This is a reasonable assumption because of the fact that these composites take only 0.00279 moles of oxygen to burn the nAl present in each sample based on the following reaction(s): $2\text{Al} + 3/2\text{O}_2 \rightarrow \text{Al}_2\text{O}_3$ or $2\text{Al} + 3/2\text{I}_2 \rightarrow 2\text{AlI}_3$ then $2\text{AlI}_3 + 3/2\text{O}_2 \rightarrow \text{Al}_2\text{O}_3 + 3\text{I}_2$.

Furthermore, it has been documented that the burn rates of metal wires increase in environments containing a higher oxygen concentration and pressure [16].

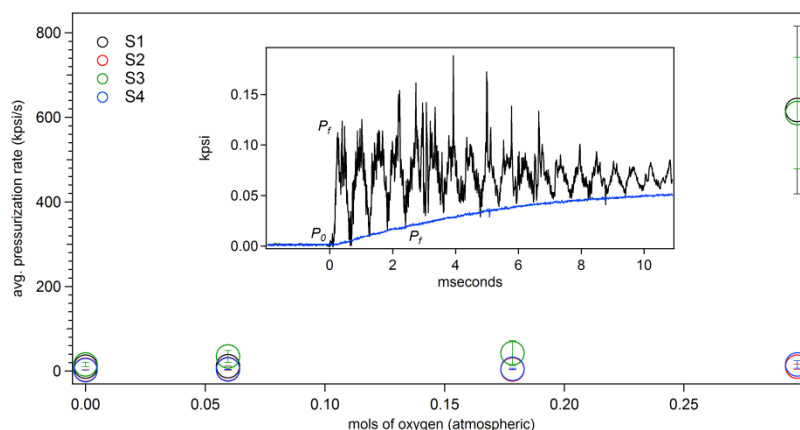


Figure 3. Plot of the average pressurization rate as a function of moles of oxygen in the bomb calorimeter. Error bars represent the variance in the experimental data. Inset: Pressure traces of Sample 1 and 4. P_0 = initial pressure; P_f = final pressure.

4. Conclusions

We have reported on our preliminary efforts to formulate nAl/HI₃O₈ and characterize both its chemical composition and morphology. We have also identified the effects the desensitizing additive cyclohexanone has upon the reactivity (pressurization rate) of this composite. The energy of activation appears to be associated with the degree of reactivity observed from a hot wire ignition method. The results of this study suggest that the additive increases the ignition threshold of the energetic composite, as observed in previous ignition studies with ESD. However it appears that reactivity levels similar to that of the neat composite are obtainable with composites containing the additive under ideal conditions (hot wire burn rate, high starting pressure, amount of additive, etc.). The critical conditions for ignition to steady state combustion of nAl/HI₃O₈ will be further explored in the form of powders and films with the goal being to optimize the reactivity and safety properties of this composite. Future studies will also probe the dependency of the reactivity on the reactant particle size, composite porosity and theoretical maximum density of formulated blends.

Acknowledgements

This research was performed while B.K.L and S.B.E. held National Research Council Research Associateship Awards. This work was supported by research grant 3002NW from the Air Force Office of Scientific Research and Program Officer Dr. Michael Berman. The authors would also like to acknowledge the support of Lucas Martinez, Rosa Saenz and Craig Bramlett.

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