ABSTRACT

Title of Dissertation: EXPLORING THE RELATIONSHIPS BETWEEN FUEL AND OXIDIZER REACTION OF BIOCIDAL ENERGETIC MATERIALS

Tao Wu, Doctor of Philosophy, 2019

Dissertation directed by: Professor Michael R. Zachariah, Department of Chemistry and Biochemistry and Department of Chemical and Biomolecular Engineering

Energetic materials are defined as a class of material with extremely high amount of stored chemical energy that can be released when ignited, along with intensive light emission and shock generation. Developing new energetic materials with high efficiency neutralization of biological warfare agents has gained increased attention due to the increased threat of bioterrorism. The objective of this dissertation is to develop new energetic materials with biocidal capabilities and apply them in various nanothermite systems to explore the relationships between fuel and oxidizer reactions.

Aerosol techniques offer a convenient route and potentially direct route for preparation of small particles with high purity, and is a method proven to be amenable and economical to scale-up. Here I demonstrate the synthesis of various iodine oxides/iodic acids microparticles by a direct one-step aerosol method from iodic acid.
A previously misidentified phase of $\text{I}_4\text{O}_9$ hydrate is in fact a new polymorph of $\text{HIO}_3$ which crystalizes in the orthorhombic space group $P2_12_12_1$.

Various iodine oxides/iodic acids, including $\text{I}_2\text{O}_5$, $\text{HI}_3\text{O}_8$ and $\text{HIO}_3$, were employed as oxidizers in thermite systems. Their decomposition behaviors were studied using a home-made time resolved temperature-jump/time-of-flight mass spectrometer (T-Jump/TOFMS). In addition, nano-aluminum (nAl), nano-tantalum and carbon black were adopted as the fuel or additive in order to fully understand how iodine containing oxidizers react with the fuel during ignition. The ignition and reaction process of those thermites were characterized with T-Jump/TOFMS. Carbon black was found to be able to lower both initiation and iodine release temperatures compared to those of Al/iodine oxides and Ta/iodine oxides thermites.

Their combustion properties were evaluated in a constant-volume combustion cell and results show that nAl/a-$\text{HI}_3\text{O}_8$ has the highest pressurization rate and peak pressure and shortest burn time. However, an ignition delay was always present in their pressure profiles while combusting. To shorten or eliminate this ignition delay, a secondary oxidizer CuO is incorporated into Al/$\text{I}_2\text{O}_5$ system and four different Al/$\text{I}_2\text{O}_5$/CuO thermites by varying the mass ratio between two oxidizers are prepared and studied in a constant volume combustion cell. Significant enhancement is observed for all four thermites and their peak pressures and pressurization rates are much higher than that of Al/$\text{I}_2\text{O}_5$ or Al/CuO. Two other oxidizers also demonstrate similar effects as to CuO on promoting the combustion performance of Al/$\text{I}_2\text{O}_5$.

A novel oxidizer AgFeO$_2$ particles was prepared via a wet-chemistry method and evaluated as an oxidizer in aluminum-based thermite system. Its structure,
morphologies and thermal behavior were investigated using X-ray diffraction, scanning electron microscopy, TGA/DSC, and T-Jump/TOFMS. The results indicate the decomposition pathways of AgFeO₂ vary with heating rates from a two-step at low heating rate to a single step at high heating rate. Ignition of Al/AgFeO₂ at a temperature just above the oxygen release temperature and is very similar to Al/CuO. However, with a pressurization rate three times of Al/CuO, Al/AgFeO₂ yields a comparable result to Al/hollow-CuO or Al/KClO₄/CuO, with a simpler preparation method.

T-Jump/TOFMS was used to study the ignition and decomposition of boron-based thermites. The ignition behaviors of bare boron nanopowders and boron-based nanothermites at various gaseous oxygen pressure were investigated using the T-Jump method. High-heating rate transmission electron microscopy studies were performed on both B/CuO and B/Bi₂O₃ nanothermites to evaluate the ignition process. I propose a co-sintering effect between B₂O₃ and the oxidizer play an important role in the ignition process of boron-based nanothermites.
EXPLORING THE RELATIONSHIPS BETWEEN FUEL AND OXIDIZER REACTION OF BIOCIDAL ENERGETIC MATERIALS

by

Tao Wu

Dissertation submitted to the Faculty of the Graduate School of the University of Maryland, College Park, in partial fulfillment of the requirements for the degree of Doctor of Philosophy 2019

Advisory Committee:
Professor Michael R. Zachariah, Chair
Professor Efrain E. Rodriguez
Professor Bryan W. Eichhorn
Professor Dongxia Liu
Professor John Cumings, Dean’s Representative
Dedication

To
My Parents
Jinping Wang and Xiangdong Wu
And My Sister: Fei Wu
And My Niece: Jiayi Zhou.

Thank you for your unconditional love and support.

谨以此论文献给我的母亲王金平，父亲武向东，姐姐武菲和外甥女周珈熠。

感谢你们对我无条件的爱和支持。
Acknowledgements

I am grateful for all the people who helped make this dissertation possible over the past 5 years.

First and foremost, I would like to thank my advisor, Dr. Michael Zachariah for his continuous guidance, encouragement and support throughout my PhD study. I felt extremely lucky to be able to work in such an environment where everyone in the group is completely open to share and help each other in their research. I am grateful for everything Dr. Zachariah has done for me and everything I have learned from him has been very valuable and it is information that I will use throughout my life.

I would like to thank Dr. Peter Y. Zavalij for his valuable help on determining the crystal structures of materials prepared in Chapter 3-5. I learned a lot about XRD from him and am thankful for everything he has done for me.

I would also like to thank all the group members from Dr. Zachariah’s group for both contributing the work in this dissertation and making my graduate study at the University of Maryland enjoyable. Special thanks to Dr. Xizheng Wang, Scott Holdren, Dr. Jeffery DeLisio and Dr. Haiyang Wang for their invaluable suggestions and continuous support throughout my PhD studies especially the toughest first two years. Scott Holdren also helped edit Chapter 1 in my dissertation and I am very grateful for that. I would like to thank Dr. Lu Liu, Miles Rehwoldt, Dylan Kline, Dr. Yi Wang, Yong Yang, Dr. Phillip Guerieri, Dr. Wenbo Zhou, Michelangelo Romano, Dr. Luning Wang, Dr. Garth Egan, Dr. Rohit Jacob, Dr. Haihan Chen, Feiyu Xu, Wanjun Zhao, Xiuli Hu, Chenbo Ru and Xiangyu Li for their support in our collaborative work.
Thanks to Dr. Sz-Chian Liou and Dr. Wen-An Chiou of the UMD Nanocenter’s AIMLab.

Finally, I’d like to acknowledge my advisory committee for their time and advice. I’d also like to thank the Army Research Office and the Defense Threat Reduction Agency for financial support of my projects.

Tao Wu

武 涛
# Table of Contents

Dedication ........................................................................................................ ii  
Acknowledgements ........................................................................................ iii  
Table of Contents ............................................................................................ v  
List of Tables ................................................................................................... ix  
List of Figures .................................................................................................. x  
List of Abbreviations ....................................................................................... xiii  
Chapter 1: Introduction .................................................................................. 1  
  1.1 Energetic materials ............................................................................... 1  
  1.2. Nanothermites .................................................................................... 3  
  1.3. Fuels and thermite reaction mechanisms ............................................ 5  
  1.4. Biocidal energetic materials ................................................................. 15  
  1.5. Scope of the Dissertation ..................................................................... 20  
Chapter 2: Experimental Methods ................................................................ 21  
  Overview ..................................................................................................... 21  
  2.1. Temperature-jump Time-of Flight Mass Spectrometry (T-Jump TOFMS) ... 21  
  2.2. Constant volume combustion cell ......................................................... 23  
Chapter 3: Aerosol Synthesis of Phase Pure Iodine/Iodic Biocide Microparticles ... 26  
  Overview ..................................................................................................... 26  
  3.1. Introduction .......................................................................................... 27  
  3.2. Experimental Details ............................................................................ 29  
    3.2.1. Materials ....................................................................................... 29  
    3.2.2. Preparation of various iodine oxide/iodic acid particles via aerosol spray pyrolysis ................................................................. 29  
    3.2.3. In-situ heating XRD measurement ............................................... 30  
    3.2.4. Thermogravimetric/differential scanning calorimetry (TG/DSC) measurement ................................................................. 30  
  3.3. Result and discussion .......................................................................... 31  
    3.3.1. Preparation of I₂O₅ ....................................................................... 34  
    3.3.2. Preparation of δ-HIO₃ .................................................................. 35  
    3.3.3. Preparation of HI₃O₈ ................................................................... 38  
  3.4. Conclusions .......................................................................................... 40  
  3.5. Supplemental Information ................................................................... 41  
Chapter 4: Crystal structure of a new polymorph of iodic acid, δ-HIO₃ ............ 46  
  Overview ..................................................................................................... 46  
  4.1. Introduction .......................................................................................... 46  
  4.2. Experimental and structure determination ........................................... 47  
  4.3. Discussion ............................................................................................ 50  
  4.4. Conclusion ........................................................................................... 56  
  4.5. Supplemental Information ................................................................... 56  
Chapter 5: Performance of iodine oxides/iodic acids as oxidizers in thermite system 57  
  Overview ..................................................................................................... 57  
  5.1. Introduction .......................................................................................... 58
10.2.3. To deliver independent silver and iodine products from a single system for biocidal application.  ................................................................. 228
10.2.4. Florine-containing thermite system; to deliver Florine gas considering it is biocidal. ........................................................................... 230
Bibliography ......................................................................................... 232
List of Tables

Table 3.1. The chemical composition of HIO3 during in-situ heating XRD test at different temperatures in air.......................................................... 34
Table 3.2. The chemical composition of “I4O9• xH2O” during in-situ heating XRD test at different temperatures in argon environment..................................... 36
Table 3.3. Summarizing the parameters of ASP for preparing different product...... 41
Table 4.1. X-Ray diffraction patterns for δ-HIO3 and I4O9• xH2O (PDF#00-045-0872) ........................................................................................................ 49
Table 4.2. Details of the crystal structure determination of δ-HIO3. ...................... 51
Table 4.3. Atomic coordinates and isotropic displacement parameters (Å²) of δ-HIO3........................................................................................................ 51
Table 4.4. Selected interatomic distances (Å) and angles (°) δ-HIO3 in comparison to corresponding geometries of similar compounds. ........................................ 55
Table 5.1. Crystalline compositions of all the samples employed in Figure S6 determined by Rietveld refinement of the corresponding XRD pattern. ......... 69
Table 5.2. Combustion cell test data for nAl-based thermites with different oxidizers. Each sample was repeated at least three times. All the numbers have a deviation at ~25. ........................................................................................................... 78
Table 7.1. Thermodynamic equilibrium predictions of Al/I2O5, Al/CuO and Al/Ag2O thermites. ................................................................. 162
Table 8.1. Combustion performance of mixed thermites of Al/AgFeO2. ............... 188
Table 8.2. Thermodynamic equilibrium predictions of Al/CuO, Al/Ag2O and Al/Fe2O3 thermites. Data is taken from Fisher and Grubelich a [53].................... 189
Table 8.3. The XRD pattern of Al/AgFeO2 reaction product. ................................ 190
Table 8.4. Representative SEM images (A and B) of the Al/AgFeO2 reaction product collected inside the combustion cell; 2D elemental mapping (Ag, Fe, Al and O) of Figure 8B using EDS. ................................................................. 191
Table 9.1. Ignition temperatures for different fuel-based thermites..................... 206
Table 9.2. Ignition temperature of various B based nanothermites with different oxidizers. The oxygen release temperature from neat oxidizer as detected by TOFMS and the melting point of the oxidizers are also included. Heating rate ~ 5 × 10⁵ °C/s. ............................................................................................................. 210
List of Figures

**Figure 1.1.** (A) Gravimetric and volumetric energy densities of some metals and homogeneous energetic materials in pure oxygen at stoichiometric conditions.[5] (B) Maximum combustion enthalpies for some reactive metals and homogeneous energetic materials.[1].......................................................................................................................... 2

**Figure 1.2.** Volumetric and gravimetric densities of energy for some thermites and conventional high explosives.[6] ................................................................................................................................................. 3

**Figure 1.3.** Surface to bulk atom ratio for spherical iron crystals.[2] .............................................................................................................................................. 5

**Figure 1.4.** Ignition temperature of Al/oxidizer vs O2 release temperature from bare oxidizer.[20] .......................................................................................................................................................... 8

**Figure 1.5.** Maximum combustion enthalpy for the reaction of various metals with CuO. ........................................................................................................................................................................... 11

**Figure 2.1.** Schematic illustration of T-jump/TOFMS system. This figure is a modification to one in reference. ................................................................................................................................. 23

**Figure 2.2** A schematic illustration of the combustion cell. .................................................................................................................................... 24

**Figure 2.3** Pressure and optical traces obtained from the combustion cell. The sample used is Al/CuO. .............................................................................................................................................. 25

**Figure 3.1.** Aerosol spray pyrolysis to synthesize various iodine oxides/iodic acids.31

**Figure 3.2.** The TGA and DSC curves of a fully hydrated silica gel under argon environment at a heating rate of 5 °C/min. ............................................................................................................................ 32

**Figure 3.3.** TGA and DSC curves of HIO3 under air environment at a heating rate of 5 °C/min...................................................................................................................................................... 33

**Figure 3.4.** SEM image (a and b), XRD pattern (c), TGA and DSC (Ar, 5 °C/min) (d) of as-prepared I2O5...................................................................................................................................................... 35

**Figure 3.5.** XRD pattern (a), TGA/DSC (b) and SEM images (c and d) of as-prepared I4O9 • xH2O after vacuum drying treatment. ........................................................................................................................................... 38

**Figure 3.6.** XRD pattern (a), TGA/DSC (b) and SEM images (c and d) of as-prepared HI3O8............................................................................................................................................................. 40

**Figure 4.1.** The Rietveld plot of δ-HIO3 (Circles - experimental profile, solid line - calculated, their difference is shown at the bottom, vertical lines show reflection position). .................................................................................................................................................. 50

**Figure 4.2.** The structure of δ-HIO3 showing: (a) a layer in ab plane with chains H-bonded along b axis and (b) corresponding polyhedral representation. Blue dotted lines show H…O contacts and dashed black lines show I…O contacts. Red, blue and grey balls represent oxygen, iodine and hydrogen atoms, respectively.............................. 53

**Figure 4.3.** The polyhedral representation of (a) α-HIO3, (b) γ-HIO3 (both in zy plane) and (c) HI3O8 (in xz plane) structures. Blue dotted lines show H…O contacts and dashed black lines show I…O contacts. Red and grey balls represent oxygen and hydrogen atoms respectively. The pink and yellow pyramids in (c) represent I2O5 and HIO3, respectively......................................................... 54
Figure 5.1. Representative plot showing the temporal profile of oxygen and iodine upon heating a-HI$_3$O$_8$ when heated at $\approx$5$\times$10$^5$ °C/s (A); time-resolved mass spectra of a-HI$_3$O$_8$ (B) ................................................................. 67
Figure 5.2. Time-resolved mass spectra of nAl/a-HI$_3$O$_8$ (A) and nTa/a-HI$_3$O$_8$ (B) ............................. 73
Figure 5.3. Sequential snapshots of nTa/a-HI$_3$O$_8$ thermit burning on a high rate heating (5 $\times$ 10$^5$ °C/s) Pt wire under vacuum, captured by a high-speed camera. The labels in each image are the time elapsed after triggering............................................. 74
Figure 5.4. I and O$_2$ release temperature in neat iodine oxides/iodic acids, and the ignition temperature of corresponding nAl-based and nTa-based thermites under vacuum. Error bars correspond to at least two measurements. The orange dashed line stands for a perfect correlation................................................................. 75
Figure 5.5. Direct comparison between the pressure (A) and optical (B) trace of nAl/m-CuO and nAl/a-HI$_3$O$_8$.................................................................................. 79
Figure 6.1. Release temperature of I and O$_2$ from neat I$_2$O$_5$ vs. initiation temperature of corresponding Al-based, Ta-based and CB-based thermites under vacuum. Error bars represent two replicates. The diagonal dashed line would imply a perfect correlation between initiation and release temperature. ............................... 131
Figure 6.2. Release temperatures of iodine/oxygen vs. initiation temperatures of different thermites.................................................................................................................. 133
Figure 6.3. Time-resolved mass spectra of I$_2$O$_5$ (A) and CB/I$_2$O$_5$ (B) ........................................... 135
Figure 6.4. TGA results of neat I$_2$O$_5$, CB/I$_2$O$_5$, Al/I$_2$O$_5$ and CB$_{3\text{wt}}$%/Al/I$_2$O$_5$ thermites ........................................................................................................................................ 137
Figure 6.5. The relation between iodine/oxygen release temperatures and initiation temperatures of thermites employing carbon allotropes as the fuel. ........................................ 138
Figure 6.6. ATR-FTIR spectra of bare I$_2$O$_5$, CB$_{3\text{wt}}$%/I$_2$O$_5$ and CB$_{8\text{wt}}$%/I$_2$O$_5$ at room temperature showing I-O bond red-shift upon addition of CB .......................................... 139
Figure 7.1. Temporal pressure traces of Al/CuO and Al/I$_2$O$_5$ ............................................................. 157
Figure 7.2. Temporal pressure traces of different Al/I$_2$O$_5$/CuO thermites. The number listed after the series name represent the weight fraction of CuO within oxidizers in each thermite........................................................................................................... 158
Figure 7.3. Combustion cell results of Al/I$_2$O$_5$ with different amount of nano-sized CuO addition ................................................................................................................................. 162
Figure 7.4. Flame temperatures of Al/I$_2$O$_5$ with different amount of nano-sized CuO addition obtained via color camera pyrometry ......................................................................... 164
Figure 7.5. Temporal reaction temperature profiles of Al/I$_2$O$_5$ (A) and Al/I$_2$O$_5$/20% CuO (B) obtained via high speed spectrometer temperature measurement........ 165
Figure 7.6. Combustion cell results of Al/I$_2$O$_5$ thermites with addition of different secondary oxidizer ........................................................................................................... 168
Figure 8.1. XRD spectrum (A) and SEM image (B) of AgFeO$_2$ prepared via co-precipitation ........................................................................................................................................ 181
Figure 8.2. TGA result of AgFeO$_2$ in Ar at a heating rate of 10 °C/min (A); AgFeO$_2$ decomposed product after heated to 1000 °C (B) ................................................................. 181
Figure 8.3. Temperature and O$_2$ temporal profile of AgFeO$_2$ .......................................................... 182
Figure 8.4. Sequential snapshots of Al/AgFeO$_2$ burning on a high-rate heating Pt wire in T-Jump chamber (in vacuum). The labels in each image are the time elapsed after triggering. .................................................. 185
Figure 8.5. Ignition temperature vs. oxygen release temperature from the corresponding oxidizer. The diagonal dash line presents a perfect correlation.

Figure 8.6. Direct comparison between the pressure and optical trace of Al/AgFeO2 and Al/nCuO.

Figure 8.7. TEM image (A) and 2D elemental mapping (B) of the Al/AgFeO2 reaction product. Red represents Ag, blue represents Fe, yellow represents Al and green represents O.

Figure 8.8. A representative TEM image and the corresponding EDS line-scan data of the Al/AgFeO2 reaction product.

Figure 9.1. Maximum combustion enthalpy for the reaction of various metals with CuO.

Figure 9.2. SEM images of boron nanoparticles.

Figure 9.3. Ignition temperature of boron measured using the T-Jump ignition at varying O2 pressures.

Figure 9.4. Oxygen release temperature of various oxidizers vs ignition temperature of various B based nanothermites.

Figure 9.5. The ignition temperature of B-based nanothermites as a function of O2 pressure.

Figure 9.6. TEM images of B/CuO nanothermites prior to (A) and after (B) in situ heating at 4×10^5 °C/s to 800 °C/s for 10 ms. A and B are the same position.

Figure 9.7. TEM images and elemental line scan of B/Bi2O3 nanothermites prior to (A) and after (B) in situ heating at 4×10^5 °C/s to 800 °C/s for 10 ms.

Figure 10.1. The iodine release temperature (A) and the TGA results (B) of B/I2O5 composite with different weight ratio of boron.

Figure 10.2. The ignition temperatures and iodine release temperatures of B/Al/I2O5 composites with different weight ratio of boron.

Figure 10.3. The ignition temperatures and iodine release temperatures of Al/I2O5 composites with different oxides additives.

Figure 10.4. Digital image of B/Al/I2O5 suspensions after sonication treatment.

Figure 10.5. FTIR results of I2O5, boron, physical mixed B/I2O5 and sonicate mixed B/I2O5 composites.

Figure 10.6. XRD spectrum and SEM image of Ag_{1.8}Mn_{8}O_{16} prepared via wet chemistry method.

Figure 10.7. XRD spectrum of Ag_{1.8}Mn_{8}O_{16} decomposed products after heated to 1000 °C in Ar.

Figure 10.8. A snapshot of Al/I2O5/Ag2O thermite burning on a high rate heating Pt wire under vacuum capture by a high-speed camera and its corresponding high speed pyrometry frame.

Figure 10.9. The XRD result of the combustion products of Al/I2O5/Ag_{1.8}Mn_{8}O_{16} with 0.72 I2O5 in the oxidizer collected inside the pressure cell chamber.
List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASP</td>
<td>Aerosol Spray Pyrolysis</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy/Microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy/Microscope</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected Area Electron Diffraction</td>
</tr>
<tr>
<td>EDS/EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered Electrons</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>T-Jump</td>
<td>Temperature Jump</td>
</tr>
<tr>
<td>TOFMS</td>
<td>Time-of-Flight Mass Spectrometer</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>MEMS</td>
<td>Microelectromechanical Systems</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>LLNL</td>
<td>Lawrence Livermore National Laboratory</td>
</tr>
<tr>
<td>nAl</td>
<td>Nanoaluminum</td>
</tr>
<tr>
<td>nTa</td>
<td>Nanotantalum</td>
</tr>
<tr>
<td>nTi</td>
<td>Nanotitanium</td>
</tr>
<tr>
<td>nB</td>
<td>Nanoboron</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon Black</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>FGS</td>
<td>Functionalized Graphene Sheet</td>
</tr>
<tr>
<td>a-I$_2$O$_5$</td>
<td>Aerosol route synthesized I$_2$O$_5$</td>
</tr>
<tr>
<td>Al-NPs</td>
<td>Aluminum Nanoparticles</td>
</tr>
<tr>
<td>RDX</td>
<td>Cyclotrimethylenetrinitramine</td>
</tr>
<tr>
<td>TNT</td>
<td>2, 4, 6-trinitrotoluene</td>
</tr>
<tr>
<td>NC</td>
<td>Nitrocellulose</td>
</tr>
<tr>
<td>MIC</td>
<td>Metastable Intermolecular Composites</td>
</tr>
<tr>
<td>ESD</td>
<td>Electrostatic Discharge</td>
</tr>
<tr>
<td>MDM</td>
<td>Melt Dispersion Mechanism</td>
</tr>
<tr>
<td>ARM</td>
<td>Arrested Reactive Milling</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

1.1 Energetic materials

Energetic materials are defined as a class of material with an extremely high stored chemical energy that can be released when ignited, along with intensive light emission and shock generation.[1, 2] Once one part of the material ignites, the heat released from the combustion can be further conducted to adjacent regions leading to continuous propagation.

Using different categorization methodologies, energetic materials can be classified into various types. Based on their function, energetic materials comprise explosives, propellants, pyrotechnics, batteries, etc. The disadvantage with this classification method is these categories are vaguely defined that the same energetic material can be classified as either an explosive, propellant, or pyrotechnic. A typical example is gunpowder that consists of a mixture of sulfur, charcoal and potassium nitrate, which has been employed in the fields of explosives, propellants and pyrotechnics.[3, 4]

A better way to categorize energetic materials is based on their formulations; they can be divided into heterogeneous energetic composite materials where the fuel and oxidizer are in different molecules and homogeneous energetic materials where both the fuel and oxidizer exist as one molecule. Take gunpower again for example, it contains fuels (sulfur and carbon) and oxidizer (potassium nitrate) in separate formulations; thus, it is classified as a heterogeneous energetic material. However, homogeneous energetic materials have both fuel and oxidizer components within one formulation. In other words, a single molecule functionalizes as the fuel and the
Thus, homogeneous energetic materials usually can achieve a very rapid energy release due to the lack of the diffusion length between the fuel and oxidizer. Materials like dynamite, 2, 4, 6-trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), etc, have been widely studied in energetic fields and used in military applications. However, homogeneous energetic materials suffer from low energy density owing to the limitation of their physical density and extremely high sensitivity that obstructed their development in energetic studies.[5] As indicated in Figure 1.1, the energy densities of homogeneous energetic materials are significantly lower than those of heterogenous energetic composites materials. Due to these reasons, researchers have devoted their attention to heterogeneous energetic materials in recent times.

Figure 1.1. (A) Gravimetric and volumetric energy densities of some metals and homogeneous energetic materials in pure oxygen at stoichiometric conditions.[5] (B) Maximum combustion enthalpies for some reactive metals and homogeneous energetic materials.[1]

Thermite reactions refer to a redox reaction between a physically mixed metal fuel and solid metal oxides and have been substantially studied due to their high energy densities and greater stabilities. The thermite reaction was first employed in welding especially for joining rail tracks starting in 1899. This thermite welding process employs an exothermic reaction of aluminum powder and a metal oxide. Researchers
expanded to other reactive metals as a replacement of aluminum, which defines a thermite reaction in a broad sense. As shown in Figure 1.1, most metal-based energetic materials feature high energy densities that make them a potential fuel in thermite reactions. Typically, a thermite reaction undergoes as follows:

$$A + BO \rightarrow B + AO + \Delta H$$

where A represents a reactive metal, B refers to a less reactive metal, $\Delta H$ represents the heat of reaction. The overall reaction is exothermic because the metal oxide on the product side has a much lower enthalpy of formation than the metal oxide on the reactant side. As indicated in Figure 1.2, aluminum-based thermite reactions have much higher volumetric energy densities compared to those of homogeneous energetic materials (e.g. TNT, RDX).

![Graph showing energy densities of energy for some thermites and conventional high explosives](image)

**Figure 1.2.** Volumetric and gravimetric densities of energy for some thermites and conventional high explosives.[6]

### 1.2. Nanothermites

Even though thermites usually feature a high energy density, the slow rates of energy release caused by the low mass transfer rate between reactants limits their applications. To increase the mass transfer rate, one obvious method is to reduce the size of the
reactants and therefore shortening the diffusion length between fuel and oxidizer due to the increased surface to volume ratio of the nano-sized materials. The length scales of the nanoparticles are normally distributed in between 1 to 100 nanometers. By decreasing the particle size (assuming spherical particles), the ratio of surface atoms to bulk atoms increases dramatically as indicated in Figure 1.3. As a result, the energy release rate of the energetic materials is enhanced. Aumann et al first reported the benefits by employing nano-sized aluminum in thermite systems.[7] Since then, employing nanoparticles in energetic materials has drawn great attention.[1, 2, 7-11] Yetter et al reported that nano-sized aluminum-based thermites show more than $10^3$ increase in reaction rates compared to micron-sized thermites.[2] Later, researchers named those energetic materials employing nano-size fuels or oxidizers, nanothermites. By increasing the interfacial contact area between fuels and oxidizers, the performance of nanothermites is significantly improved. By employing nanostructure in thermite studies, the reactivity of the nanothermites can be tuned easily by just varying the particle sizes, morphology, composition or packing. In addition, it has been reported that the ignition temperature of aluminum-based thermite decreases when the aluminum particle sizes decreases. On the other hand, ignition with high heating rate by its nature is essentially the point where the self-heating by an exothermic reaction exceeds heat loss and a non-linear reaction event occurs; therefore, the initial heat release from thermite reaction should not be affected by oxidizers particles size.[12]
Nanothermite reactions occur over extremely short time periods (several microseconds). To be able to probe these fast reactions, ultrafast heating rate diagnostic tools are needed. By utilizing rapid heating techniques and in-situ measurements, the initiation mechanisms and reaction kinetics of nanothermites have been studied throughout this dissertation. An overview of these tools is provided in Chapter 2.

1.3. Fuels and thermite reaction mechanisms

In nanothermites, the most commonly studied metal is aluminum because of its abundance and relatively high reactivity compare with other metals (Figure 1.1). Moreover, aluminum is often coated with a layer of aluminum oxide due to its high reactivity in air and this passivated oxide layer serves as a barrier between the metal core and the outside oxygen to prevent the aluminum core from further oxidizing in air. However, once the aluminum core reaches near the melting temperature, it can diffuse through the oxide shell and interact with any available oxidizer which leads to ignition. Those unique properties inspired researchers to adopt aluminum into numerous types of explosives and rocket propellants for improving the reaction heat; however, the very existence of a passivated oxide layer outside of aluminum leads to
long ignition delays and a slow combustion rate, which limits the performance of aluminum additives. To solve those problems, considerable effort has been devoted to studying the initiation mechanism of aluminum-based nanothermites.

As reported, the initiation/reaction of aluminum-based nanothermites differ significantly upon different heating rates. At low heating rate, Trunov et al discovered that the oxide shell undergoes phase transitions when heating to above 550 °C, in which the aluminum core and oxygen can transfer through the shell and therefore enables continuous combustion/reaction.[14] The scenarios are much more complicated at high heating rates, but it is believed that the molten aluminum is essential for ignition. Rai et al and Nakamura et al reported, about the same time, a hollow alumina particle after oxidization, which was ascribed to the outward leaking of the aluminum core due to the concentration/pressure gradient across the shell.[15, 16] Later, Sullivan et al used a high heating rate microscopy measurement to examine Al/WO₃ nanothermite and reported a reactive sintering mechanism is dominating the initiation/reaction of Al/WO₃ nanothermite, in which initiation occurred at a fuel/oxidizer interface. The generated heat further melts/sinters adjacent particles as heat is conducted away from the interface and more unreacted materials transfer to the reactive sites to react until no more material is left.[17] On the other hand, Stamatis et al reported Al/MoO₃ ignited at a temperature lower than the melting point of aluminum due to an alumina phase transition at 500 °C.[18] It seems the ignition mechanism of aluminum-based nanothermites is somehow related to the metal oxides. Later, Sullivan et al reported that a reactive sintering mechanism is occurring early during the combustion of most aluminum-based nanothermites.[19]
Jian et al investigated the role of gas phase oxygen generation from different oxygen carriers in the ignition of aluminum-based nanothermites, where ignition temperature is used as the criterion for the onset of the thermite reaction.[20] In general, ignition temperature is defined as the temperature where the self-heating by the exothermic reaction exceeds heat loss and a self-sustained reaction occurs. As shown in Figure 1.4, it turns out the ignition temperature has no clear correlation with the gas phase oxygen generation. For example, the ignition temperatures of Al/CuO and Al/Fe$_2$O$_3$ nanothermites are slightly higher than the oxygen release temperature from the pure oxidizers indicating gas-phase oxygen generated from the oxygen carrier may be the key for their ignitions. However, the ignition temperature of Al/Bi$_2$O$_3$ and Al/SnO$_2$ is lower than the oxygen release temperature of the corresponding oxidizers; in other words, it can be ignited without any available gaseous oxygen, suggesting a condensed phase reaction mechanism might be dominant here. Along with the fact that the ignition of Al/Bi$_2$O$_3$ and Al/SnO$_2$ happens slightly below the melting point of aluminum implies the oxygen and molten aluminum transports in condensed phase may be driving the ignition/reaction. It is also noted that Al/WO$_3$, Al/MoO$_3$ and Al/Sb$_2$O$_3$ can be ignited even though no gaseous oxygen can be released from the corresponding oxidizers upon heating. Therefore, the gas phase oxygen is only essential for the ignition of certain aluminum-based nanothermites and a condensed-phase mechanism seems to dominate the ignition of other nanothermites. In general, the ignition mechanism of aluminum-based nanothermites can be divided into two categories: gas-condensed heterogeneous reaction and condensed-phase interfacial reaction.
For the gas-condensed heterogeneous reaction mechanism, the gaseous oxygen released from the oxidizer dominates the ignition: either by the release rate of oxygen gas from the oxidizer or the reaction kinetics between gaseous oxygen and the aluminum. Zhou et al evaluated free vs bound oxygen on ignition of bare aluminum nanoparticles by examining them in various oxygen pressures and found a critical temperature existed for the ignition of aluminum in a gaseous oxygen environment where increasing oxygen pressure cannot further decrease the ignition temperature simply because the mobility of aluminum migrating towards the surface has become the new limiting factor. Thus, the release rate of oxygen gas from the oxidizer (earlier stage) and the reaction kinetics between gaseous oxygen and the aluminum (later stage) are both important for understanding the gas-condensed heterogeneous reaction mechanism. Zhou et al also investigated the ignition of Al/Fe$_2$O$_3$, Al/Bi$_2$O$_3$ and Al/K$_2$S$_2$O$_8$ under different oxygen pressure. It is found that the ignition temperature
of Al/Fe\(_2\)O\(_3\) is higher than that of aluminum in a gaseous oxygen environment when the same oxygen pressures are applied, indicating the reaction rate between aluminum and bound oxygen from Fe\(_2\)O\(_3\) is slower than that between aluminum and free oxygen. Even though the ignition of Al/Fe\(_2\)O\(_3\) is clearly controlled by the gas-condensed heterogeneous reaction mechanism based on the result shown in Figure 1.4; the high ignition temperature and extremely low reactivity of Al/Fe\(_2\)O\(_3\) is due to the relatively low decomposition rate of Fe\(_2\)O\(_3\), which limits the amount of released gaseous oxygen that comes in contact with the aluminum. [22, 23] Sullivan et al also examined Fe\(_2\)O\(_3\) using high heating rate in-situ microscopy and discovered oxygen is being trapped and bubbles out over a time-scale three times longer than that of CuO, suggesting the insufficient decomposition is limiting the performance of Fe\(_2\)O\(_3\) as an oxidizer.[19] By increasing the oxygen pressure from vacuum to 1 atm, the ignition temperature of Al/K\(_2\)S\(_2\)O\(_8\) deceases from 755 °C to 610 °C suggesting the gaseous oxygen is important for its ignition. Under the same oxygen pressures, Al/K\(_2\)S\(_2\)O\(_8\) always shows a lower ignition temperature than that of aluminum in gaseous oxygen which implies the rapid release of oxygen from the oxidizer could significantly increase the local oxygen concentration and thus favors a lower ignition temperature.

As for the condensed phase interfacial mechanism, it is proposed the ignition/reaction is controlled by the diffusion of molten aluminum and/or the condensed phase oxygen transport. The direct contact between the fuel and oxidizer is essential for ignition in both cases.[17, 19] Zhou et al reported that the ignition temperature of Al/Bi\(_2\)O\(_3\) is not affected by the oxygen pressure and argued that the extremely high oxygen ion conductivity of Bi\(_2\)O\(_3\) greatly enhances condensed phase
transport of oxygen and therefore gaseous oxygen would not participate in the oxidization of aluminum.[21] Considering the ignition temperature is very close to the melting temperature of aluminum, it is reasonable to assume that the condensed phase oxygen transport and the diffusion of molten aluminum both affect the ignition of Al/Bi₂O₃. Since the diffusion of molten aluminum has been systematically studied previously, more efforts are needed to discover what properties make a good oxidizer in the nanothermite reaction to better understand the condensed phase interfacial ignition mechanism.

Wang et al systematically studied different Al/Bi₂O₃ systems and reported that a critical oxygen ion conductivity exists for Bi₂O₃ to oxidize aluminum while aluminum is in the molten phase and oxygen ion transport limits the condensed state of Bi₂O₃ oxidizes thermite ignition.[24] They also discovered that a larger oxygen vacancy concentration and smaller metal-oxide bond energy in the oxidizers could give a lower ignition temperature, which suggests the microscopic properties of the oxidizers might be the key to understanding the ignition mechanism of aluminum-based nanothermites. A later time at the same year, Wang et al employed systematic doped perovskites as oxidizers in aluminum-based nanothermites and discovered a linear relationship between average bond energy and electronegativity with ignition temperature.[25] For the very first time, the tuning of the nanothermite ignition can be fulfilled by simply manipulating the properties of oxidizers.

Besides aluminum, boron features the highest gravimetric and volumetric energy densities (Figure 1.1) and the highest maximum combustion enthalpy when reacting with copper oxide shown in Figure 1.5. Thus, boron theoretically could be an attractive
alternative for aluminum. Like aluminum, boron particles also have a passivated oxide shell, B₂O₃. Since B₂O₃ melts at a much lower temperature (450 °C) than the core (2100 °C), the burning scenario of boron is very different from aluminum. Upon heating, the molten B₂O₃ shell will surround the outside which prevents the outside oxygen from diffusing through. Over the last few decades, the ignition and combustion of boron particles were extensively studied both theoretically and experimentally.

Figure 1.5. Maximum combustion enthalpy for the reaction of various metals with CuO.

Prentice [26] observed a two-stage combustion process for the ignition of boron particles in air and in oxygen-argon mixtures at atmospheric pressures. The low-temperature stage involves a surface burning process followed by a high-temperature stage corresponding to gas-phase combustion. Later, Macek and Semple [27] investigated combustion of boron particles at atmospheric pressure in hot oxidizing gases of different compositions and found that boron combustion always happens in a two-stage process verifying what Prentice claimed previously. The first short stage involves the removal of the oxide layer and can be a kinetic and/or diffusion-controlled
process. The second stage involves the burnout of a bare boron particle and is controlled by gas-phase diffusion of the oxidants. The burn time of each stage is found to be inversely proportional to the oxygen molar ratio and merge as the mole fraction of oxygen decreases. Macek and Semple [28] then studied the combustion of boron particles at elevated pressures and found that the low-temperature stage was nonreproducible at pressures above ~10 atm. There are contradictory theories about the mechanisms that dominate species diffusing into the liquid boron oxide layer during the first stage of boron particles ignition. Glassman et al [29] claimed that boron oxide production during the first ignition stage results from boron diffusion across the oxide layer rather than oxygen diffusion claimed by King [30, 31]. Yeh and Kuo [32] later verifies that the diffusion of dissolved boron into molten boron oxide dominates the diffusion process. They also found the boron oxide layer of boron particles changed from a crystalline to an amorphous structure at elevated temperatures and its chemical composition was identified as a polymeric vitreous (BO)\textsubscript{n} complex through the reaction between dissolved boron and molten boron oxide. Theoretical models were also developed by Knipe [33], Mohan and Williams [34] and others to simulate the two-stage combustion of boron particles.

The influence of the initial thickness of the boron oxide layer on ignition and combustion of boron particles was studied by Ao et al [35]. They reported the oxide layer thickness has little effect on the reactivity of the oxidation of boron particles below 775 °C. With increasing boron oxide layer thickness, the combustion efficiency decreases, and the time required for complete removal of the oxide layer is longer,
while the ignition delay time significantly increases, and the oxide layer removal rate is increased.

In recent years, more efforts have been devoted to the ignition and combustion of boron-based thermite systems. As mentioned previously, thermites involve an exothermic reaction of a metal fuel and a metal oxide. Sullivan et al [36] studied the reaction of nano-B/Al/CuO metastable intermolecular composites and reported the addition of nanoboron to Al/CuO can enhance the reactivity when the boron is less than 50 mol% of the fuel, while no enhancement was observed for micro-sized boron. From both experimental and theoretical results, they speculated that the sensible heating, removal of the oxide shell and the melting of the boron are all critical for fast reaction. Liu et al[37] prepared B/CuO nano-thermite through a chemistry precipitation method. They reported an improved thermochemistry behavior of boron particles with a coating of nano-CuO and a lower onset reaction temperature. Recently, Wang et al[38] reported a clear relationship between molecular properties of the oxidizer and ignition temperature as well as combustion performance of boron-based nano-thermites in which larger oxygen vacancy concentration and smaller metal-oxygen bond energy lead to lower ignition temperatures.

In addition to aluminum and boron, tantalum,[39] titanium[40] and carbon[24, 41] have also been investigated recently for the purpose of expanding the fields of thermite reactions. Similar to aluminum, tantalum also has a passivated oxide layer. However, tantalum has a very high melting point of about 3017 °C, which rules out the influence of the melting phase transition in the scope of ignition temperature test. In other words, the tantalum core would remain immobile at least at the point of ignition, which
provides us a different scenario to understand the relationship between the fuel and oxidizer. DeLisio et al investigated the oxidation mechanism of tantalum nanoparticles at high heating rates and discovered that a rapid crystallization occurs in the oxide shell of the tantalum nanoparticles upon heating creates cracks for oxygen to diffuse through.[39] They also conducted similar studies on tantalum-based nanothermites and reported their ignition temperatures are independent of metal oxide types because the oxide shell crystallization can induce reactive sintering of metal oxides followed by the ignition of the nanothermites. Rehwoldt et al studied the reaction mechanism and ignition characteristics of titanium nanoparticles and potassium perchlorate thermites and reported the oxide layer of titanium nanoparticles consists not just amorphous TiO₂ but also crystalline TiN and titanium oxynitride.[40] The existence of the latter two compounds make the oxide layer of titanium nanoparticles reactive to some extent. This exact titanium oxide layer can catalyze oxygen release from the oxidizer and facilitate oxygen diffusion and thus lead to a much lower ignition temperature compared to aluminum-based nanothermites.[40] Carbon, as a fuel without a passivated oxide shell, provides a very valuable perspective in understanding the ignition/reaction mechanism of thermites. With a melting point as high as 3550 °C, carbon remains immobile at least at the point of ignition. The direct contact between carbon and the oxidizer rules out the difficulty for oxygen to go through the oxide layer and therefore the oxygen transport from the oxidizer to carbon surface is controlling the ignition/reaction.[24, 42] All aforementioned fuels are used in a way to aid the understanding of the ignition/reaction mechanisms of nanothermites in this dissertation.
1.4. Biocidal energetic materials

A chemical substance that can destroy or inhibit any harmful organism like spores or bacteria can be considered a biocide. The commonly used method for spore neutralization is by suspending spores in a high-temperature environment or associated with chemical influence of the halogen gas. Take gunpowder for example, doctors in ancient China used gunpowder to treat bacterial contaminations, plague and skin infection due to biocidal effect of sulfur that is part of the ingredients in gunpowder. Therefore, any energetic materials featuring biocidal functions can be categorized as a biocidal energetic material. Over the last decades, researchers have started utilizing energetic materials in biocidal applications. Developing new energetic materials with high efficiency neutralization of biological warfare agents such as potentially harmful spores and bacteria has gained increased attention due to the increased threat of bioterrorism [43-47]. Preliminary laboratory studies have suggested that an ideal neutralization process should generate not only a high temperature, but also release a long-lasting biocidal agent such as sulfur or halogen elements [48-54]. Those elements are known to be effective biocides.[53] The main limitation of conventional energetic materials is low neutralization efficiency since the thermal neutralization mechanism is dominant in this case, with the lack of effective biocidal agent release [48]. Therefore, it has been proposed that simultaneously delivering a rapid thermal pulse with a remnant biocidal agent would prolong the exposure time and improve the inactivation process [55]. To endue biocidal function in nanothermites, biocidal agents need to be incorporated. Dreizin et al. employed mechanically alloyed aluminum-iodine composites as a fuel in energetic formulations and the initiation and combustion
tests in air indicated that higher iodine concentration lowers initiation temperatures and the combustion temperatures were not substantially diminished [54]. They also found improvements in the pressurization rate and maximum pressure at constant volume with 15 wt.% and 20 wt.% of I2 [54]. Furthermore, an effective inactivation of aerosolized spores has been achieved using Al/I2 and Al/B/I2 composites with 15-20 wt.% of iodine [56]. Since the fuel in thermites is limited to its composition, the goal to incorporate biocidal agents into thermites shifts to the oxidizer side. Among all oxides, halogen-containing and silver-containing oxidizers have drawn attention because of their excellent biocidal properties.[56-60]

Among all halogens, iodine stands out owing to its strong neutralization effect. Different methods have been reported for incorporating elemental iodine into energetic materials [56, 61-63]. To incorporate halogens into energetic materials, one can either directly add halogens into the system or assemble halogens into the oxidizers.[56] Wang et al. incorporated solid iodine into Al/CuO thermite systems and found that the Al/CuO/I2 thermite reaction rate was significantly decreased with increasing the iodine content.[62] Guerreo et al also showed that mechanical incorporation of iodine into aluminum severely decreases the reaction rate of Al/metal oxide mixtures and even resulted in failed ignition of Al•I2/Fe2O3.[63]

Another approach is to use iodine-containing oxy-compounds that can release HI or I2 when used as an oxidizer.[64] Iodine-containing oxy-compounds can be broken down into two main categories: metal iodates and iodine oxides/iodic acids. The metal iodates, AgIO3,[48, 65] Bi(IO3)3,[66] Cu(IO3)2,[55] Fe(IO3)3 [55] etc., have been previously investigated. One issue with employing metal iodates in thermites is that
part of the produced I₂ vapor (all for AgIO₃) may react with the product metal particles to form corresponding metal iodides, which lowers the effective iodine content in the metal iodate-based thermite systems. Unfortunately, there are only a limited number of iodine oxides/iodic acids which are relatively stable and obtainable. These include I₂O₅, I₄O₉, HI₃O₈, HI₂O₃, H₅IO₆, etc.[67-69] Among these compounds, I₂O₅ (~76% iodine mass fraction), is the most studied in thermite systems.[10, 70-73] In these studies, aluminum particles with different sizes were chosen as the fuel due to its high reaction enthalpy, thermal conductivity and availability. With reported propagation velocities of up to ~2,000 m/s for loose ball-milled nAl and nano-scaled I₂O₅ (~10 nm), I₂O₅ shows its high potential in aluminum-based thermites as an extremely aggressive oxidizer.[73] Constant volume combustion tests also show nAl/micro-I₂O₅ outperforms traditional aluminum-based thermites such as Al/CuO and Al/Fe₂O₃.[72] A pre-ignition reaction was proposed as the ignition trigger in which ionic I₂O₅ fragments diffused into the alumina passivation shell of aluminum to create some reactive complexes exothermically.[59, 71] However, this mechanism is far from clear as Smith et al reported that a pre-ignition reaction was not found for aluminum/nano crystalline I₂O₅ reaction in contrast to nano amorphous I₂O₅.[74]

Recently, Smith et al reported that a 150% increase in flame speed was found for Al/amorphous I₄O₉ compared with Al/I₂O₅ indicating I₄O₉ has more reactive potential than I₂O₅ as an oxidizer when combined with aluminum.[75] Other iodine-containing oxy-compounds have received comparatively much less attention due to their relatively lower iodine content and availability. Nevertheless, their iodine content is still much higher than metal iodates or per-iodates on a per mass basis. This is particularly so for
HI\textsubscript{3}O\textsubscript{8}, which has an iodine content of \(\sim 75\%\) (similar to I\textsubscript{2}O\textsubscript{5} with 76 wt\% iodine). Currently, no comparative study examining how the aforementioned iodine oxides/iodic acids perform as oxidizers in thermites system is available. This gives me motive to address this issue in this dissertation.

As for silver, it has been pointed out that silver exhibits biocidal properties in the forms of metallic Ag particles and silver ions in a humid environment.[76] Since most of the products of thermite combustion tend to be primarily in the condensed phase,[44] metallic silver particles are normally the focus. As indicated by Morones et al[77] and Smetana et al[78], small particle sizes are necessary for silver particles to perform well in biocidal activities. To deliver not only a high thermal event but also a large amount of small silver particles as the active biocidal sites could be very useful for biocidal applications.

When it comes to silver-containing oxidizers, Ag\textsubscript{2}O was the obvious choice to be considered as an oxidizer in an aluminum-based thermite system. In 2010, Clark et al[79] investigated the combustion performance and biocidal abilities of both Al/I\textsubscript{2}O\textsubscript{5} and Al/Ag\textsubscript{2}O thermites using a homemade biocidal reaction chamber. They concluded Al/I\textsubscript{2}O\textsubscript{5} thermite exhibited significant spore neutralization owing to the generation of large amounts of iodine gas. Al/Ag\textsubscript{2}O, on the other hand, underperforms in various aspects due to the poor reactivity of Ag\textsubscript{2}O. In 2011, Russell et al[80] further studied the flame propagation behaviors of Al/I\textsubscript{2}O\textsubscript{5} and Al/Ag\textsubscript{2}O thermites using mechanical impact and thermal initiation. The results show that Al/Ag\textsubscript{2}O features a lower average flame propagation by about 2.5 times in thermal ignition tests but produce much more energy than Al/I\textsubscript{2}O\textsubscript{5} in impact-driven ignition tests. They also argued that the energy
release of the thermite reactions is significantly enhanced by reducing the sizes of the oxidizer particles. In the same year, Sullivan et al.[48] investigated the performance of AgIO$_3$ as an oxidizer in aluminum-based thermite because it decomposed to O$_2$ and I$_2$ gases and O and I radicals when heated at an ultra-high heating rate. Silver was not observed in the mass spectra probably because the temperature was not high enough to reach the adiabatic flame temperature and thus could not vaporize silver. However, Al/AgIO$_3$ considerably outperformed Al/CuO in pressurization rate due to many gaseous products released from AgIO$_3$; however, its high combustion performance was mitigated by the fact that the reaction products were found to form AgI instead of elemental silver and iodine, thus obstructing its usage in biocidal applications.

Sullivan et al.[44] subsequently synthesized nano-Ag$_2$O particles and investigated its reactivity as an oxidizer in biocidal energetic systems since it produces high yields of antimicrobial silver as one of the combustion products. They found that Ag$_2$O alone performs poorly in terms of pressurization rate and burn time, but its performance is significantly improved when combined with one more reactive oxidizer, such as AgIO$_3$ or CuO. The morphology of the final products was also studied and indicated that abundant active sites of silver particles were sacrificed since some silver particles were trapped within the interior of other products, which might affect its biocidal activity to some extent.

In addition to halogens and silver, sulfur has also been considered as biocides for spores. Different sulfur-containing compounds, such as sulfur dioxide[81] and sulfuryl fluoride[82] have been studied and indicates effective bactericidal properties. Various sulfur-containing salts have also been prepared and incorporated into aluminum-based
nanothermites and demonstrated superior combustion performance and release of potential biocidal active agents.[83, 84]

1.5. Scope of the Dissertation

As discussed in the previous sections, nanothermites offers great potential in various energetic applications because they offer high energy densities and high reaction rates. By employing biocidal agents within the system, they can be the potential solution to counterfeite the threat of bioterrorism. The objective of this dissertation is to develop new energetic materials with biocidal capabilities and apply them in various nanothermite systems to explore the relationships between fuel and oxidizer reactions.

The work done in this dissertation will be discussed in eleven chapters. Chapter 1 provides a detailed literature review on nanothermites and biocidal materials. The detailed information about the high-heating rate characterization tools and bulk combustion test are included in Chapter 2. Chapter 3 and 4 present studies on preparations and characterizations of various iodine oxides/iodic acids as well as the scale-up methods. Chapter 5 and 6 investigate the initiation/reaction mechanisms and bulk combustion performance of iodine-containing nanothermites. Chapter 7 focuses on shortening the ignition delay and further improving the combustion performance of Al/I₂O₅ nanothermites. A new silver-containing oxidizer and its performance in nanothermites are discussed in Chapter 8. Chapter 9 investigates the ignition and reaction mechanism of boron-based nanothermites. A summary of my works and recommendations for future work are presented in Chapter 10.
Chapter 2: Experimental Methods

Overview

As discussed in Chapter 1, a thermite ignition/reaction by its nature is essentially the point where self-heating by exothermic reaction exceeds heat loss and product formation occurs. It should be noted that the light emission of metal-based thermites aligns well with the product release profile based on our previous work.[1-3] Considering this process occurs within a few milliseconds requires characterization methods that operate on similar time-scale. For this specific purpose, Temperature-jump Time-of Flight Mass Spectrometry (T-Jump TOFMS) is employed here for studying thermite ignition mechanism since it can provide an ultra-high heating rate (>10^5 °C/s). A brief introduction about this method is included in this chapter. In addition, constant volume combustion cell technique is included here as well since bulk combustion performance is equally important for thermite characterization as to the ignition mechanism.

2.1. Temperature-jump Time-of Flight Mass Spectrometry (T-Jump TOFMS)

Throughout this dissertation, T-Jump TOFMS has been used to study the decomposition behaviors of bare oxidizers and ignition mechanisms of thermites reactions. Typically, a ~1 cm long platinum wire (76 um in width) with a thin coating of oxidizer or thermite sample is rapidly joule-heated to about 1200 °C with a 3 ms pulse at a heating rate of ~10^5 °C/s. Different current pulses varying from 2 to 20 ms
could be applied to the wire. The current and voltage signals were recorded using an oscilloscope by measuring the resistance data of the wire while heating. And the temporal temperature on the wire was calculated according to the Callendar–Van Dusen equation that correlates resistance and temperature of the wire.[4]

When studying the ignition mechanism of thermites reaction, another analytical technique is required in order to acquire the ignition point. To achieve this goal, a high-speed camera (Vision Research Phantom v12.0) was employed to record the combustion on the wire during heating. The camera is triggered at the same time as the T-jump power supply. An external pulse generator is employed here to account for synchronization of optical and wire temperature data. Ignition temperatures of thermite reactions in vacuum were measured from the correlation of optical emission from high speed imaging and temporal temperature of the wire and were further analyzed in combination with the temporal mass spectra. Each experiment was repeated 3 times.

To analyze the gas species released from the thermite reaction, a R. M. Jordan style linear time-of-flight mass spectrometry (TOFMS) is integrated with the T-jump system was employed because it can be pulsed at high rates allowing for sufficient temporal resolution between adjacent spectra. Figure 2.1 is a schematic image of this integrated system. The gas species produced from the thermite combustion are ionized by an electron gun (operating at 70 eV and 1 mA). An electronic gate is pulsed at 10 kHz, which accelerating ions into the electric field-free region of the TOFMS. Ions are detected using a microchannel plate detector and data is recorded on an oscilloscope operating in sequence mode with a 100 Ms/s sampling rate. MATLAB scripts allowed
for simultaneous data processing on the oscilloscope. The detailed information of the scripts could be found in a dissertation by Jeffery B. DeLisio.[5]

**Figure 2.1.** Schematic illustration of T-jump/TOFMS system. This figure is a modification to one in reference.

### 2.2. Constant volume combustion cell

A customized constant volume combustion cell is employed to evaluate the bulk thermite combustion performance. Figure 2.2 shows a schematic illustration of the cell. 25 mg of thermite powders was loaded inside the cell (constant volume, \( \sim 13 \text{ cm}^3 \)) and ignited by a resistively heated nichrome wire. The temporal pressure and optical emission from the thermite reaction were simultaneously measured using a piezoelectric pressure sensor and a photodetector, respectively. The pressure and optical data were collected on an oscilloscope. By plotting the data, pressurization rate, maximum pressure and burn time can be obtained and used for evaluation of the combustion performance. Pressurization rate is calculated by dividing the first peak
pressure by the corresponding time. Burn time is defined as the full width of the half maximum of the optical profile. Since 25 mg of sample are used for each run, combustion product can be collected afterwards for post-combustion characterization.

In order to collect freshly condensed combustion product, a double-side carbon tape could be placed inside the cell during combustion cell test and later removed from the cell and examined in SEM for morphology information.

Figure 2.2 A schematic illustration of the combustion cell.
Figure 2.3 Pressure and optical traces obtained from the combustion cell. The sample used is Al/CuO.
Chapter 3: Aerosol Synthesis of Phase Pure Iodine/Iodic Biocide Microparticles *

Overview

High iodine containing oxides are of interest as biocidal components in energetic application requiring fast exothermic reactions with metallic fuels. Aerosol techniques offer a convenient route and potentially direct route for preparation of small particles with high purity, and is a method proven to be amenable and economical to scale-up. Here I demonstrate the synthesis of various iodine oxides/iodic acids microparticles by a direct one-step aerosol method from iodic acid. By varying temperature and humidity, I produced near phase pure δ-HIO₃, HI₃O₈ and I₂O₅ as determined by X-ray diffraction. δ-HIO₃, a previously unknown phase, was confirmed in this work. In addition, scanning electron microscopy was employed to examine the morphology and size of those prepared iodine oxides/iodic acids particles and the results show that all particles have an irregularly spherical shape. Thermogravimetric/differential scanning calorimetry measurement results show that HIO₃ dehydrates endothermically to HI₃O₈, and then I₂O₅, and lastly I₂O₅ decompose into I₂ and O₂.

3.1. Introduction

In recent years, the interest in developing new energetic materials with biocidal capabilities [1,2] has drawn increased attention.[3-13] The motivation for this is based on evidence that conventional energetic materials, which employ a thermal neutralization mechanism are not sufficiently efficient. Laboratory studies have demonstrated that the addition of a biocidal component can significantly enhance neutralization through a synergistic mechanism.[15-20] Therefore, it has been proposed that simultaneously delivering a rapid thermal pulse with a remnant biocidal agent would prolong the exposure time and improve the inactivation process.[21] Both halogens and silver-containing energetic materials have been explored [22-24] with the halogens offering the most promise due to their excellent biocidal properties.[25] Various methods have been used for incorporating halogens into energetic materials. One approach is through directly introducing halogens into the system, and the other is by incorporating halogens into the oxidizers.[25,26] Thus, iodine-rich compounds that can release HI or I₂ are the ideal candidates for biocidal energetics.[27]

Iodine (V) oxide, as one of the iodine-containing oxides with ~76% iodine mass fraction, has been recently studied as an oxidizer with aluminum fuel.[28] In this case, various metals (primarily aluminum) are mixed with I₂O₅ to form a thermite system whose combustion properties were studied.[29-32] The first paper concerning the reactivity between aluminum and I₂O₅ was published by Ivanov et al in 1980 in which a global reaction mechanism between iodine gas and fuels was proposed [29] and confirmed in a later work.[32] I₂O₅ has received considerable interest because it is an extremely aggressive oxidizer with aluminum with reported propagation velocities up
to ~2,000 m/s for loose ball-milled nano-aluminum and nano-scaled I₂O₅ (~10 nm).[31]

In addition, constant volume combustion tests on nano-Al/micro-I₂O₅ thermite exhibits the highest pressurization rate and the shortest burn time relative to other aluminum based traditional thermites such as Al/CuO and Al/Fe₂O₃.[32]

Moreover, oxoacids of iodine, such as HIO₃ and HI₃O₈, have been investigated in the recent decades. Until now, two polymorphs of iodic acid, the stable α-HIO₃ [33,34] and metastable γ-HIO₃,[35] have been reported and well-characterized. However, more evidence is required to verify the existence of β-HIO₃.[35] The thermal behavior of HIO₃ was studied via thermogravimetric/differential scanning calorimetry (TG/DSC) and the result shows three decomposition steps upon heating in air: the dehydration of HIO₃ into HI₃O₈ at 100 °C, the dehydration of HI₃O₈ into I₂O₅ at 210 °C and the melting/decomposition of I₂O₅ at 400 °C[36]. It also reveals that I₂O₅ would be slowly converted to the initial hydrate HI₃O₈ and later to the final hydrate HIO₃ under ambient environment. Furthermore, the crystal structure of HI₃O₈ was determined to be an adduct HIO₃•I₂O₅, which are connected by hydrogen bonds.[37]

Aerosol techniques offer a convenient route and potentially direct route for preparation of nano-sized or micro-sized particles with high purity, and is a method proven to be amenable and economical to scale-up. Along with the fact that decreasing the size of oxidizer particles can improve the burn rate of thermite,[32] in this study I develop a synthesis approach to prepare various iodine oxides/iodic acids microparticles based on aerosol spray pyrolysis (ASP) using commercial iodic acid (HIO₃) as the starting material, because of its water solubility and ready
availability.[38] The decomposition behavior of iodine oxides/iodic acids was also studied using low heating rates with TG/DSC.

3.2. Experimental Details

3.2.1. Materials

Iodic acid (HIO$_3$) (99.5 wt %) purchased from Sigma-Aldrich were directly used as received. All the other chemicals were of analytical grade and used as purchased without further treatment.

3.2.2. Preparation of various iodine oxide/iodic acid particles via aerosol spray pyrolysis

Small-sized particles of oxides were obtained via aerosol spray pyrolysis (ASP). In general, 100 mL iodic acid aqueous solution (10 mg/mL) were sprayed into small droplets (~1 um in diameter) with a homemade pressure atomizer (~35 pounds per square inch (psi) pressure air) and passed through a silica-gel diffusion drier (silica-gels were regenerated at ~50 ºC or 80 ºC in order to prepare different products) to remove water and are then passed through a tube furnace for chemical conversion. The tube reactor consisted of a ~1.9 cm diameter alumina tube with a heated length of ~40 cm. The furnace temperature was set at ~230 and ~375 ºC to obtain either δ-HIO$_3$ or I$_2$O$_5$, respectively with a residence time of about 1 second.[39] For both δ-HIO$_3$ and I$_2$O$_5$, silica-gels were regenerated at 50 ºC. I find that δ-HIO$_3$ can be obtained within a large range of temperature from 210 to 250 ºC. In addition, HI$_3$O$_8$ was obtained with a tube furnace temperature ~250 ºC and silica-gels regeneration temperature ~80 ºC. The
final product was collected on a Millipore membrane filter (0.4 um pore) and characterized by scanning electron microscopy (SEM, Hitachi, SU-70 FEG-SEM) and powder X-ray diffraction (XRD, Bruker D8 Advance using Cu Kα radiation).

3.2.3. In-situ heating XRD measurement

In-situ heating XRD was performed using a Bruker C2 diffractometer with a Vantec500 2D detector with 2θ ranging from 10º to 50º (λ = 1.5418 Å, step size = 0.05º) and the sample was heated via an Anton Paar DHS 1100 graphite-dome hot stage with a heating rate of 10 ºC/min under air condition. I collected patterns at 26, 100, 200, 300, 400, and 500 ºC and also collected a final pattern at 30 ºC after the sample was cooled. At each temperature, we collected two 10-minute frames at 20 and 40º 2θ. Integrating and merging the two frames together gave us a final powder diffraction pattern from 9.5º to 50º 2θ.

3.2.4. Thermogravimetric/differential scanning calorimetry (TG/DSC) measurement

TGA and Differential Scanning Calorimetry (DSC) were conducted using a SDT Q600 (TA instruments) equipped with a TA Discovery MKS104-S0212004 Micro Vision 2 mass spectrometer. The analysis was performed under a 100 mL min⁻¹ argon flow with ~ 1.0 mg samples placed into an alumina pan and heated from room temperature up to 550 ºC at a rate of 5 ºC min⁻¹ in argon atmosphere.
3.3. Result and discussion

Iodic acid (HIO₃) is a white solid at room temperature and is often used as the starting material for preparing iodine-containing materials due to its ready availability, high solubility in water, and that with controlled dehydration yields iodine oxides.

Atomized aqueous HIO₃ droplets in air were passed through a silica-gel diffusion dryer to produce solid HIO₃ particles, which were then directly passed through the tube furnace at a desired temperature to form various iodine oxide/iodic acids (Figure 3.1). In order to determine what temperature should be run for silica gels regeneration, thermal analysis was conducted on a fully hydrated silica gel and the result is shown in Figure 3.2. The black line represents the mass change of the silica gel with increasing temperature. From this I note that silica gel reaches its fully dehydrated state after 15% weight loss (water loss). Assume a fully dehydrated silica gel has a weight of 85 mg, it could absorb 15 mg of water to reach its fully hydrated state (100 mg weight).

Figure 3.1. Aerosol spray pyrolysis to synthesize various iodine oxides/iodic acids.
For silica gel, m=85 mg regenerated at 50 and 80 °C, they could absorb 4.4 mg and 8 mg of water, respectively, to reach their fully hydrated state based on the TGA result in Figure 3.2. Since silica-gels obtained from different regeneration temperature have different water-absorbing capabilities, silica-gels regeneration temperature also play an important role in the aerosol route. In this work, regeneration temperatures of ~50 and 80 °C were used to obtain different products to change the water absorbing properties.

![Figure 3.2. The TGA and DSC curves of a fully hydrated silica gel under argon environment at a heating rate of 5 °C/min.](image_url)

Since iodic acid droplets pass through the tube furnace where the thermal event occurs, I use TGA/DSC results to determine set points for the furnace. Figure 3.3 shows the TGA and DSC curves of iodic acid under air environment with a heating rate of 5 °C/min, which indicates that there are three decomposition steps: the dehydration of HIO$_3$ to H$_3$O$_8$ at ~120 °C, dehydration of H$_3$O$_8$ to I$_2$O$_5$ at ~210 °C and the
decomposition of I$_2$O$_5$ at 380 °C. Thus, I$_2$O$_5$ and H$_3$O$_8$ could be obtained via thermal treatment at 210-380 °C and 120-210 °C, respectively. The thermal behavior of HIO$_3$ under argon was very similar to the air case and the detailed information is shown in Figure S3.1.

![TGA and DSC curves of HIO$_3$ under air environment at a heating rate of 5 °C/min.](image)

**Figure 3.3.** TGA and DSC curves of HIO$_3$ under air environment at a heating rate of 5 °C/min.

The residence time for a droplet in the aerosol reactor is about 1 second, which is obviously much shorter than that in the TGA ramp time. To obviate this effect, I ran the furnace temperature higher than what the TGA would indicate in order to speed up the kinetics. To validate the phases indicted in the TGA, in-situ hot-stage XRD was ran the HIO$_3$ powder at a heating rate of 10 °C/min from room temperature to 500 °C in air. From Table 3.1, I$_2$O$_5$ and H$_3$O$_8$ could be obtained at 300-400 °C and 200-300 °C,
respectively. The XRD patterns of HIO$_3$ at different temperatures are provided in Figure S3.2.

Table 3.1. The chemical composition of HIO$_3$ during in-situ heating XRD test at different temperatures in air.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>26</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product(s)</td>
<td>HIO$_3$</td>
<td>HIO$_3$, HI$_3$O$_8$</td>
<td>HI$_3$O$_8$</td>
<td>I$_2$O$_5$</td>
<td>I$_2$O$_5$</td>
<td>I$_2$+ O$_2$</td>
</tr>
</tbody>
</table>

3.3.1. Preparation of I$_2$O$_5$

I$_2$O$_5$ [Figure 3.4(c)] was obtained when the tube furnace was set at 350-400 $^\circ$C which is consistent with the TGA result in Figure S3.1. TGA and DSC curves of I$_2$O$_5$ [Figure 3.4(d)] show the characteristically endothermic decomposition of I$_2$O$_5$ into I$_2$ and O$_2$ at ~360 $^\circ$C which also proves the formation of I$_2$O$_5$. The small weight loss at ~210 $^\circ$C indicates that small amount of I$_2$O$_5$ product is probably rehydrated into HI$_3$O$_8$ during the collection process and preparation for TGA/DSC test. The SEM images [Figure 3.4(a)-(b)] show that I$_2$O$_5$ particles are irregularly spherical and some large aggregates are also observed in those images indicating that some sintering/coalescence between particles takes place. Crystalline compositions of I$_2$O$_5$ determined by Rietveld refinement indicate that 9% of the product rehydrates into $\delta$-HIO$_3$. 
3.3.2. Preparation of δ-HIO₃

Based on the thermal behavior of HIO₃, HI₃O₈ could be obtained when the tube furnace was set at 120-210 °C. Considering the short residence time within the whole aerosol process and the difference between theoretical and experimental temperatures for preparing I₂O₅, the furnace temperature for synthesis of HI₃O₈ was set higher at 210-250 °C.

The XRD [Figure 3.5(a)] of as-prepared iodine oxide were consistent with an XRD pattern previously identified as I₂O₅• xH₂O (PDF#45-0872), with no indication of any other iodine oxides/iodic acids. Like I₂O₅ particles, the SEM images [Figure 3.5(c) and

**Figure 3.4.** SEM image (a and b), XRD pattern (c), TGA and DSC (Ar, 5 °C/min) (d) of as-prepared I₂O₅.
3.5 (d)] shows that “I₄O₉• xH₂O” particles are irregularly spherical due to the sintering/coalescence between particles. This is also confirmed because the resulting particles are larger than expected based on the initial droplet size and concentration used and were nominally ~ 400 nm in diameter.

The proposed structure implies that xH₂O could be removed via vacuum drying. However, TGA/DSC and XRD results shown in Figure S3.3 and Figure 3.5(b) indicated surprisingly that there were no changes after vacuum drying. Moreover, the TGA and DSC results of I₄O₉• xH₂O shown in Figure S3.3 are very similar to those of HIO₃ (Figure S3.1), and this similar behavior was further confirmed with in-situ heating XRD (Table 3.2). Given that the previous report proposed the formula I₄O₉• xH₂O without any chemical composition or any crystal structure information [40] lead us to conjecture that the proposed formula may be in error.

Table 3.2. The chemical composition of “I₄O₉• xH₂O” during in-situ heating XRD test at different temperatures in argon environment.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>26</th>
<th>100</th>
<th>200</th>
<th>300-400</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product(s)</td>
<td>“I₄O₉• xH₂O”</td>
<td>“I₄O₉• xH₂O”, HIO₃</td>
<td>HIO₃</td>
<td>I₂O₅</td>
<td>I₂ + O₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Based on its powder XRD pattern, I find a distorted octahedral crystal system, space group $P_{2_1}2_12_1$ which consists of IO$_3$ ions with three I-O bonds with distances of 1.78, 1.80 and 1.92 Å, and three I-O contacts with distances of 2.51, 2.76 and 2.76 Å. This reveals that the correct assignment of the phase is actually a previously unreported phase of HIO$_3$ which I refer to as δ-HIO$_3$. The detailed crystal information is included in Chapter 4. In addition, the difference between XRD patterns (Figure S3.4) of as-prepared δ-HIO$_3$ and as-received HIO$_3$ also suggests a new phase HIO$_3$.

Thus, instead of obtaining HI$_3$O$_8$, as the TGA results would suggest I obtain δ-HIO$_3$ which indicates that the decomposition pathways of HIO$_3$ in TGA (slow heating) and ASP (fast heating) are different. This result implies that the δ-HIO$_3$ is metastable at elevated temperatures and at slow heating converts to I$_2$O$_5$. The ASP process enables a rapid thermal ramp and rapid quench to trap the material as δ-HIO$_3$ which appears to be quite stable at room temperature. In fact, I$_2$O$_5$ was obtained when the furnace temperature was raised to above 300 °C.
3.3.3. Preparation of HI$_3$O$_8$

Based on the result in Figure 3.3, I am expecting to obtain HI$_3$O$_8$ by thermal treatment of HIO$_3$ at temperature between 120 to 210 °C in air. Therefore, we annealed HIO$_3$ at different temperatures in air for one hour and it turns out that HIO$_3$ was fully dehydrated to HI$_3$O$_8$ at 150-260 °C (Figure S3.4). Surprisingly, HI$_3$O$_8$ was obtained after only two minutes annealing at ~165 °C (Figure S3.4), which indicates that the dehydration of HIO$_3$ is fast and also suggests ASP is a promising method to prepare HI$_3$O$_8$. 

*Figure 3.5. XRD pattern (a), TGA/DSC (b) and SEM images (c and d) of as-prepared I$_4$O$_9$•xH$_2$O after vacuum drying treatment.*
Previous results show that $\delta$-HIO$_3$ rather than HI$_3$O$_8$ is the product when the tube furnace was set between 210 to 250 °C with silica-gels regenerated at ~50 °C. Considering HI$_3$O$_8$ is a dehydrated product of HIO$_3$, the failure to prepare HI$_3$O$_8$ might be caused by the relatively weak dehydrating capacity of the original set-up. Again, I$_2$O$_3$ was appeared when the tube furnace was increased to 300 °C or above. This suggested that tuning the tube furnace temperature alone could not obtain HI$_3$O$_8$. From the previous discussion, I know that the silica gel regeneration temperature also affects the aerosol synthesis and might be employed to manipulate the hydrating ability of the set-up. I found that regenerating the silica gel at ~80 °C rather than ~50 °C would form HI$_3$O$_8$ as confirmed by XRD [Figure 3.6(a)] in a single step with a tube furnace temperature of ~250°C. The TGA shown in Figure 3.6(b) indicates two decomposition steps: one is the dehydration of HI$_3$O$_8$ to I$_2$O$_3$ at ~210 °C with an experimental weight loss of 1.2% (theoretical weight loss, 1.8%; impurities, ~6%); another is the decomposition of I$_2$O$_3$ at ~360 °C, both of which are endothermic as determined by DSC. Similar to $\delta$-HIO$_3$, the SEM images of HI$_3$O$_8$ in Figure 3.6(c)-(d) show that particles are irregular spheres due to sintering/coalescence between particles during preparation. Crystalline compositions of HI$_3$O$_8$ determined by Rietveld refinement indicate that 9% of the product rehydrates into $\delta$-HIO$_3$. 
3.4. Conclusions

In summary three different products, δ-HIO₃, HI₃O₈ and I₂O₅, were obtained via ASP as summarized in Table 3.3. Both temperature and humidity control in silica gel preparation were necessary to obtain all three products without post-processing, for temperatures not listed in Table 3.3, either mixtures (HIO₃/HI₃O₈/I₂O₅) or no product was collected.
Table 3.3. Summarizing the parameters of ASP for preparing different product.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica Gel Regeneration Temperature (ºC)</td>
<td>I₂O₅</td>
</tr>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Furnace Temperature (ºC)</td>
<td>350-400</td>
</tr>
</tbody>
</table>

This study demonstrates a facile and environmentally friendly aerosol spray pyrolysis method to prepare various iodine oxides/iodic acids using a single precursor HIO₃. By tuning the furnace temperature and the humidity I was able in a single step to produce near phase pure δ-HIO₃, HI₃O₈ and I₂O₅ as determined by XRD. TGA and DSC results show that HIO₃ dehydrates to HI₃O₈, and then I₂O₅, and lastly I₂O₅ decompose endothermically into I₂ and O₂.

3.5. Supplemental Information

![TGA and DSC curves of HIO₃ in Ar](image)

Figure S3.1. TGA and DSC curves of HIO₃ under argon environment at a heating rate of 5 ºC/min.
Figure S3.2. The XRD patterns of HIO$_3$ at different temperatures.
Figure S3.3. TGA/DSC (A) and XRD (B) of as-prepared I₄O₉•xH₂O before vacuum drying treatment and XRD (C) of as-prepared I₄O₉•xH₂O and as-received HIO₃.
Figure S3.4. XRD patterns of the product by annealing of HIO$_3$ at 139 °C (A), 150 (B), 180 (C) and 260 °C (D) for one hour, respectively. XRD patterns of the product by annealing of HIO$_3$ at 150 (E) and 180 (F) for two minutes, respectively.
Table S3.1. Listed hkl values for each phase in each XRD pattern.

<table>
<thead>
<tr>
<th>2θ (º)</th>
<th>hkl values</th>
<th>2θ (º)</th>
<th>hkl values</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.29</td>
<td>-111</td>
<td>22.72</td>
<td>112</td>
</tr>
<tr>
<td>1.87</td>
<td>-102</td>
<td>23.14</td>
<td>020</td>
</tr>
<tr>
<td>22.9</td>
<td>002</td>
<td>23.58</td>
<td>200</td>
</tr>
<tr>
<td>24.4</td>
<td>210</td>
<td>26.27</td>
<td>103</td>
</tr>
<tr>
<td>24.71</td>
<td>-211</td>
<td>27.16</td>
<td>-121</td>
</tr>
<tr>
<td>26.67</td>
<td>102</td>
<td>28.03</td>
<td>022</td>
</tr>
<tr>
<td>28.13</td>
<td>-112</td>
<td>35.26</td>
<td>123</td>
</tr>
<tr>
<td>28.77</td>
<td>-302</td>
<td>36.88</td>
<td>-222</td>
</tr>
<tr>
<td>28.96</td>
<td>012</td>
<td>43.71</td>
<td>321</td>
</tr>
<tr>
<td>29.06</td>
<td>211</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29.94</td>
<td>-212</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33.86</td>
<td>-312</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33.99</td>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.02</td>
<td>-402</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37.04</td>
<td>212</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37.3</td>
<td>021</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38.5</td>
<td>410</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter 4: Crystal structure of a new polymorph of iodic acid, δ-HIO₃. *

**Overview**

A new polymorph of iodic acid, δ-HIO₃, synthesized via aerosol spray pyrolysis was characterized with powder X-Ray diffraction and its crystal structure was solved. I find that a previously misidentified phase of I₄O₉ hydrate is in fact a new polymorph of HIO₃ which crystalizes in the orthorhombic space group \( P2_12_12_1 \).

**4.1. Introduction**

As one of the iodates (MIO₃, where M = H⁺, NH⁴⁺, alkali ions, etc), HIO₃ has been of interest due to its potential application as an optically non-linear material. [1-3] The crystal structure of \( \alpha \)-phase of iodic acid was first reported in 1941 and crystalizes in the orthorhombic space group \( D_2^4-P2_12_12_1 \).[4] The structure is held together by hydrogen bonds and relatively weak intermolecular iodine oxygen bonds. More recently, neutron powder diffraction at various temperatures were able to more precisely determine the position of hydrogen atoms in the crystal structure.[1] Decreased inter-molecular distances and O-I-O angles of \( \alpha \)-HIO₃ were observed with decreasing temperature. In 2005, a new metastable, centrosymmetric polymorph of iodic acid, \( \gamma \)-HIO₃, was obtained via reaction

---

* The results presented in this chapter have been published in the following journal article: Wu, T.; Zavalij, P.Y.; Zachariah, M.R., Crystal structure of a new polymorph of iodic acid, δ-HIO₃, from powder diffraction. Powder Diffraction 2017 32(4) 261-264.
between H$_5$IO$_6$ and Cr(ClO$_4$)$_3$ in aqueous solution, which crystalizes in the orthorhombic space group $Pbca$. This phase is stabilized by hydrogen-bonded (HIO$_3$)$_2$ dimers.[5]

Thermal decomposition of iodic acid in air can lead to I$_2$O$_5$ or HI$_3$O$_8$ depending on temperature.[6] Gas phase aerosol techniques offer a convenient route and potentially direct route for preparation of small particles with high purity, and is a method proven to be amenable and economical to scale-up.[7-10] In Chapter 3, I found a new polymorph of iodic acid could be obtained with silica-gels regenerated at ~50 °C and the furnace temperature at ~210 °C.[11] Here, its crystal structure is reported for the first time.

4.2. Experimental and structure determination

Iodic acid ($\alpha$-HIO$_3$) (99.5 wt %) purchased from Sigma-Aldrich was directly used as received. All the other chemicals were of analytical grade and used as purchased without further treatment.

Small-sized particles of $\delta$-HIO$_3$ were obtained via aerosol spray pyrolysis (ASP). In general, 100 mL iodic acid solution (10 mg/mL) were sprayed into small droplets (~1 um in diameter) with a homemade pressure atomizer (~35 psi pressure air) and pass through a silica-gel diffusion drier (silica-gels were regenerated at ~50 °C) to remove most of the water, and are then passed through a tube furnace for chemical conversion. The tube reactor consisted of a ~ 1.9 cm diameter alumina tube with a heated length of ~40 cm. The furnace temperature was set at ~ 210 °C to obtain $\delta$–HIO$_3$ with a residence time of about 1 second. I
find that $\delta$-HIO$_3$ can be obtained within a large range of temperature from 180 to 250 °C. The final product was collected on a Millipore membrane filter (0.4 um pore) and characterized by powder X-ray diffraction (XRD, Bruker D8 Advance using Cu Kα radiation).

The as-prepared samples were characterized by powder X-ray diffraction. Diffraction pattern was measured using Cu Kα radiation in Bragg-Brentano geometry on Bruker D8 Advance powder diffractometer equipped with incident beam Soller slits, Ni β-filter and LynxEye position sensitive detector. Data were collected from 14° to 130° 2θ with a step size of 0.01578° and counting time of 1 sec per step (total exposure time of 180 sec per step).

The powder pattern was indexed in the orthorhombic crystal system and reflection conditions pointed to a $P2_12_12_1$ space group symmetry. This phase matched a previously reported for I$_4$O$_9$• xH$_2$O (PDF#00-045-0872) (Table 4.1). In this case “I$_4$O$_9$• xH$_2$O” was designated to refer to a crystal hydrate product of amorphous I$_4$O$_9$ according to the paper that published its XRD result.[12] However, the I$_4$O$_9$• xH$_2$O reference provides only composition and powder pattern and motivated our consideration of determining rigorously the crystal structure.

The crystal structure was solved from the integrated intensities obtained from a LeBail full pattern decomposition by a charge flipping method using an XT program from ShelX software.[13] The crystal structure (Figure 4.1) was refined by Rietveld method using the Topas software.[14] The refinement revealed a presence of preferred orientation with a March-Dollase parameter of 0.75(1).
Hydrogen atom was positioned from geometric considerations at the longest I-O bond along the shortest oxygen-oxygen contact line as it was observed in other structures of iodic acid. It was refined as riding on the attached O atom. Here I would like to acknowledge the help from Dr. Peter Zavalij on solving, refining and analyzing the crystal structure.

**Table 4.1.** X-Ray diffraction patterns for δ-HIO$_3$ and I$_4$O$_9$•xH$_2$O (PDF#00-045-0872).

<table>
<thead>
<tr>
<th>$2\theta_{\text{calc (°)}}$</th>
<th>$d_{\text{calc (Å)}}$</th>
<th>$I_{\text{obs}}$</th>
<th>$d_{\text{obs (Å)}}$</th>
<th>$I_{\text{obs}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.494</td>
<td>5.37</td>
<td>7</td>
<td>4.19</td>
<td>m</td>
</tr>
<tr>
<td>21.022</td>
<td>4.222</td>
<td>100</td>
<td>3.75</td>
<td>s</td>
</tr>
<tr>
<td>23.534</td>
<td>3.777</td>
<td>66</td>
<td>3.59</td>
<td>vw</td>
</tr>
<tr>
<td>24.642</td>
<td>3.61</td>
<td>11</td>
<td>3.46</td>
<td>m</td>
</tr>
<tr>
<td>25.585</td>
<td>3.479</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.818</td>
<td>3.448</td>
<td>13</td>
<td>3.36</td>
<td>m</td>
</tr>
<tr>
<td>28.982</td>
<td>3.078</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.760</td>
<td>2.815</td>
<td>49</td>
<td>2.81</td>
<td>s</td>
</tr>
<tr>
<td>33.344</td>
<td>2.685</td>
<td>18</td>
<td>2.68</td>
<td>m</td>
</tr>
<tr>
<td>34.337</td>
<td>2.609</td>
<td>7</td>
<td>2.61</td>
<td>w</td>
</tr>
<tr>
<td>37.667</td>
<td>2.386</td>
<td>3</td>
<td>2.39</td>
<td>vw</td>
</tr>
<tr>
<td>39.039</td>
<td>2.305</td>
<td>4</td>
<td>2.31</td>
<td>vw</td>
</tr>
<tr>
<td>40.293</td>
<td>2.236</td>
<td>3</td>
<td>2.24</td>
<td>vw</td>
</tr>
<tr>
<td>42.797</td>
<td>2.111</td>
<td>4</td>
<td>2.12</td>
<td>vw</td>
</tr>
<tr>
<td>43.886</td>
<td>2.061</td>
<td>11</td>
<td>2.055</td>
<td>m</td>
</tr>
<tr>
<td>44.826</td>
<td>2.02</td>
<td>11</td>
<td>2.015</td>
<td>m</td>
</tr>
<tr>
<td>45.672</td>
<td>1.985</td>
<td>5</td>
<td>1.98</td>
<td>m</td>
</tr>
<tr>
<td>47.538</td>
<td>1.911</td>
<td>7</td>
<td>1.905</td>
<td>m</td>
</tr>
<tr>
<td>48.143</td>
<td>1.889</td>
<td>6</td>
<td>1.882</td>
<td>m</td>
</tr>
<tr>
<td>49.144</td>
<td>1.852</td>
<td>12</td>
<td>1.847</td>
<td>m</td>
</tr>
<tr>
<td>49.414</td>
<td>1.843</td>
<td>13</td>
<td>1.837</td>
<td>m</td>
</tr>
<tr>
<td>50.527</td>
<td>1.805</td>
<td>6</td>
<td>1.803</td>
<td>m</td>
</tr>
<tr>
<td>52.570</td>
<td>1.739</td>
<td>4</td>
<td>1.737</td>
<td>w</td>
</tr>
<tr>
<td>53.079</td>
<td>1.724</td>
<td>7</td>
<td>1.72</td>
<td>m</td>
</tr>
<tr>
<td>54.760</td>
<td>1.675</td>
<td>7</td>
<td>1.672</td>
<td>m</td>
</tr>
</tbody>
</table>

(i) $d_{\text{calc}}$ – $d$-spacing calculated from lattice parameters obtained from Rietveld refinement.

(ii) Normalized observed integrated intensities as obtained from the Rietveld refinement.

(iii) Observed intensity denoted as m = medium, s = strong, vw = very weak, w = weak (Wikjord et al., 1980).
4.3. Discussion

This crystal structure determination shows that the actual chemical composition of I$_4$O$_9$•xH$_2$O is HIO$_3$ which could also be written as I$_4$O$_{10}$•2H$_2$O. This new polymorphic modification of iodic acid is further referred as δ-HIO$_3$ (CCDC#1526763).

Details of the crystal structure determination are shown in Table 4.2. The atomic parameters are listed in Table 4.3. Selected interatomic distances and
bond angles of δ-HIO₃, α-HIO₃,[1] γ-HIO₃ [5] and HI₃O₈ [15] are shown in Table IV.

**Table 4.2.** Details of the crystal structure determination of δ-HIO₃.

<table>
<thead>
<tr>
<th>Formula</th>
<th>HIO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constants, Å</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>8.44504(13)</td>
</tr>
<tr>
<td>b</td>
<td>6.95785(13)</td>
</tr>
<tr>
<td>c</td>
<td>4.49753(10)</td>
</tr>
<tr>
<td>Cell volume, Å³</td>
<td>264.272(9)</td>
</tr>
<tr>
<td>Density</td>
<td>4.421</td>
</tr>
<tr>
<td>Formula weight</td>
<td>175.91</td>
</tr>
<tr>
<td>Number of formula units</td>
<td>4</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Orthorhombic, P2₁2₁2₁</td>
</tr>
<tr>
<td>Temperature of measurement</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>Bruker D8 Advance</td>
</tr>
<tr>
<td>Radiation, wavelength</td>
<td>CuKα radiation, 1.5418 Å</td>
</tr>
<tr>
<td>Absorption coefficient, cm⁻¹</td>
<td>93.256</td>
</tr>
<tr>
<td>F000, electrons</td>
<td>312</td>
</tr>
<tr>
<td>Number of reflections</td>
<td>284</td>
</tr>
<tr>
<td>R values, %</td>
<td></td>
</tr>
<tr>
<td>Rₑxp</td>
<td>3.09</td>
</tr>
<tr>
<td>R(wp)</td>
<td>6.56</td>
</tr>
<tr>
<td>R(p)</td>
<td>5.10</td>
</tr>
<tr>
<td>R(Bragg)</td>
<td>1.22</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>2.122</td>
</tr>
</tbody>
</table>

**Table 4.3.** Atomic coordinates and isotropic displacement parameters (Å²) of δ-HIO₃.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Biso</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1</td>
<td>4a</td>
<td>0.27820(7)</td>
<td>0.23062(12)</td>
<td>0.0264(2)</td>
<td>0.79(5)</td>
</tr>
<tr>
<td>O1</td>
<td>4a</td>
<td>0.3414(16)</td>
<td>0.4389(14)</td>
<td>0.274(3)</td>
<td>0.62(13)</td>
</tr>
<tr>
<td>O2</td>
<td>4a</td>
<td>0.3542(15)</td>
<td>0.0372(16)</td>
<td>0.255(3)</td>
<td>0.62(13)</td>
</tr>
<tr>
<td>O3</td>
<td>4a</td>
<td>0.0873(7)</td>
<td>0.254(2)</td>
<td>0.1678(16)</td>
<td>0.62(13)</td>
</tr>
<tr>
<td>H1</td>
<td>4a</td>
<td>0.440511</td>
<td>0.444325</td>
<td>0.282977</td>
<td>0.92(19)</td>
</tr>
</tbody>
</table>

Delta-HIO₃ crystalizes in the orthorhombic space group P2₁2₁2₁. Figure 4.2(a-b) show the crystal structure of δ-HIO₃ with each iodine atom 3-coordinated with oxygen atoms (I1-O1 = 1.904, I1-O2 = 1.811, I1-O3 = 1.741), and all four atoms
form trigonal pyramid with iodine atoms in the apex and 3 oxygen atoms in the base. One of the I-O contacts of 2.49 Å between molecules make spiral chain along the z direction (Figure 4.2(a)), and two more long I-O contacts of ~2.76 Å bind the chains in x and y directions into a three-dimensional framework (Figure 4.2(b)). O1-H1...O2 hydrogen bond links HIO₃ molecules into a zig-zag chain along the y direction, which make it unique as compared with other two polymorphs of HIO₃. Two neighboring molecules are in a mirror position along with xy plane. Three I-O bonds and three I…O contacts together make a distorted octahedra.
Figure 4.2. The structure of $\delta$-HIO$_3$ showing: (a) a layer in ab plane with chains H-bonded along b axis and (b) corresponding polyhedral representation. Blue dotted lines show H…O contacts and dashed black lines show I…O contacts. Red, blue and grey balls represent oxygen, iodine and hydrogen atoms, respectively.
All 3 iodic acid structures α, γ, and δ differ by packing of the HIO₃ molecules and therefore by arrangement of their hydrogen bonds. In α-HIO₃, similarly δ-HIO₃ structure, hydrogen bonds link molecules into a zig-zag chains (Fig. 4.3(a)). However in γ-HIO₃ hydrogen bonds form (HIO₃)₂ pair as shown in Fig. 3(b). Figure 4.3(c) shows that HI₃O₈ molecule is an adduct of both HIO₃ and I₂O₅ moieties that are connected by a hydrogen bond.[15] Interestingly, the hydrogen bond in δ-HIO₃ structure is similar in length to γ-HIO₃ molecule and both are slightly shorter than that of α-HIO₃ and HI₃O₈ structures.

**Figure 4.3.** The polyhedral representation of (a) α-HIO₃, (b) γ-HIO₃ (both in zy plane) and (c) HI₃O₈ (in xz plane) structures. Blue dotted lines show H…O contacts and dashed black lines show I…O contacts. Red and grey balls represent oxygen and hydrogen atoms respectively. The pink and yellow pyramids in (c) represent I₂O₅ and HIO₃, respectively.
Each IO\textsubscript{3} pyramid forms 3 I…O intermolecular contacts in 2.5 to 3.1 Å range (Table 4.4) which along with 3 I-O bonds form a distorted octahedra. Each I…O contact is positioned across I-O bond so that O-I…O angle deviates from linear for not more than 17°. This is true for all HIO\textsubscript{3} structures as well as HIO\textsubscript{3} and I\textsubscript{2}O\textsubscript{5} molecules in HI\textsubscript{3}O\textsubscript{8} structure. There is also correlation, at least qualitatively, between length of I-O bonds and opposite I…O contact distances: the shorter bond corresponds to longer contact and vice versa.

**Table 4.4.** Selected interatomic distances (Å) and angles (°) δ-HIO\textsubscript{3} in comparison to corresponding geometries of similar compounds.

<table>
<thead>
<tr>
<th>Atom labels</th>
<th>Distances, Å</th>
<th>Valence angles, °</th>
<th>Contacts, Å</th>
<th>Contact angles, °</th>
<th>H bond length, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ-HIO\textsubscript{3} (this work)</td>
<td>α-HIO\textsubscript{3}</td>
<td>γ-HIO\textsubscript{3}</td>
<td>HI\textsubscript{3}O\textsubscript{8} (HIO\textsubscript{3}·I\textsubscript{2}O\textsubscript{5})</td>
<td></td>
</tr>
<tr>
<td>I1-O1</td>
<td>1.904(12)</td>
<td>1.896(2)</td>
<td>1.873(2)</td>
<td>1.880(3)</td>
<td></td>
</tr>
<tr>
<td>I1-O2</td>
<td>1.811(12)</td>
<td>1.812(2)</td>
<td>1.791(2)</td>
<td>1.792(2)</td>
<td></td>
</tr>
<tr>
<td>I1-O3</td>
<td>1.741(6)</td>
<td>1.783(1)</td>
<td>1.804(2)</td>
<td>1.790(3)</td>
<td></td>
</tr>
<tr>
<td>O1-I-O2</td>
<td>97.7(5)</td>
<td>97.63(7)</td>
<td>100.1(1)</td>
<td>93.73(12)</td>
<td></td>
</tr>
<tr>
<td>O1-I-O3</td>
<td>88.6(6)</td>
<td>93.86(6)</td>
<td>96.4(1)</td>
<td>95.07(12)</td>
<td></td>
</tr>
<tr>
<td>O2-I-O3</td>
<td>101.0(6)</td>
<td>100.92(7)</td>
<td>101.3(1)</td>
<td>99.16(13)</td>
<td></td>
</tr>
<tr>
<td>I1…O2\textsuperscript{i}</td>
<td>2.493(12)</td>
<td>2.504(2)</td>
<td>2.694(2)</td>
<td>2.545(2)</td>
<td></td>
</tr>
<tr>
<td>I1…O1\textsuperscript{ii}</td>
<td>2.757(11)</td>
<td>2.760(2)</td>
<td>2.689(2)</td>
<td>2.593(3)</td>
<td></td>
</tr>
<tr>
<td>I1…O3\textsuperscript{iii}</td>
<td>2.754(6)</td>
<td>2.889(1)</td>
<td>2.753(2)</td>
<td>3.123(3)</td>
<td></td>
</tr>
<tr>
<td>O1-I…O2\textsuperscript{i}</td>
<td>168.9(5)</td>
<td>174.47(7)</td>
<td>174.26(8)</td>
<td>176.39(11)</td>
<td></td>
</tr>
<tr>
<td>O2-I…O1\textsuperscript{ii}</td>
<td>169.6(5)</td>
<td>170.92(7)</td>
<td>168.17(9)</td>
<td>163.16(9)</td>
<td></td>
</tr>
<tr>
<td>O3-I…O3\textsuperscript{iii}</td>
<td>171.8(5)</td>
<td>163.28(7)</td>
<td>168.17(9)</td>
<td>163.16(9)</td>
<td></td>
</tr>
<tr>
<td>O1-H1…O2\textsuperscript{iv}</td>
<td>2.663(18)</td>
<td>2.718(2)</td>
<td>2.665(3)</td>
<td>2.744(4)</td>
<td></td>
</tr>
</tbody>
</table>

(i) $1/2$-x,-y,-1/2+z; (ii) $1/2$-x,1-y,1/2+z; (iii) 1/2+x,1/2-y,-z; (iv) 1-x,1/2+y,1/2-z
4.4. Conclusion

A new polymorph of iodic acid, δ-HIO₃, which crystallizes in the orthorhombic space group $P2_12_12_1$, was obtained via a reproducible aerosol spray pyrolysis method using iodic acid solution as the precursor. *Ab initio* crystal structure determination of δ-phase reveals that previously known $I_4O_9.\alpha H_2O$ phase is actually HIO₃.

4.5. Supplemental Information

Since the CIF file of δ-HIO₃ and the corresponding data for Figure 4.1 are too large to be included in this thesis, for those who are interested in these data could find them online with the link provided below.

https://www.cambridge.org/core/journals/powder-diffraction/article/crystal-structure-of-a-new-polymorph-of-iodic-acid-hio3-from-powder-diffraction/7E9176F241D23CB1246A9F905FC00930#fndtn-supplementary-materials
Chapter 5: Performance of iodine oxides/iodic acids as oxidizers in thermite system

**Overview**

Iodine oxides are of interest as biocidal components in energetic application such as thermites due to their high energy release and biocidal agent delivery. In this study, various iodine oxides/iodic acids, including I$_2$O$_5$, HI$_3$O$_8$ and HIO$_3$, were employed as oxidizers in thermite systems. Their decomposition behaviors were studied using a home-made time resolved temperature-jump/time-of-flight mass spectrometer (T-Jump/TOFMS), which identified a single step decomposition for all oxides at high heating rates (~10$^5$ K/s). In addition, both nano-aluminum (nAl, ~80 nm) and nano-tantalum (nTa, <50 nm) were adopted as the fuel in order to fully understand how iodine containing oxidizers react with the fuel during ignition. The ignition and reaction process of nAl-based and nTa-based thermites were characterized with T-Jump/TOFMS, and their combustion properties were evaluated in a constant-volume combustion cell and compared to a traditional thermite system (nAl/CuO). The ignition temperatures of nAl-based thermites using these oxidizers were all very close to the melting point of aluminum (~660 °C), which suggests that the mobility of the aluminum core dominates the ignition/reaction and the gaseous oxygen released from the decomposition of the oxidizer does not participate in the ignition until the molten aluminum is available. Unlike nAl-based thermites, the ignition temperatures of nTa-

* The results presented in this chapter have been published in the following journal article: Wu, T.; Wang, X.; Zavalij, P.Y.; DeLisio, J.B.; Zachariah, M.R., Performance of iodine oxides/iodic acids as oxidizers in thermite systems. Combustion and Flame 2018 191 335-342.
based thermites are lower than the oxygen release temperatures from the corresponding bare oxidizers. All nTa-based thermites ignited prior to the release of gas phase oxygen. In this case, a condensed phase reaction mechanism is proposed to dominate the ignition process. Moreover, combustion cell tests results show that nAl/a-HI₃O₈ has the highest pressurization rate and peak pressure and shortest burn time, and since it also has an iodine content of ~75% as high as I₂O₅ on a per mass basis, this material may be a very promising candidate in biocidal application.

5.1 Introduction

High efficiency neutralization of biological warfare agents has become a major research focus within the United States, in addition to many other countries, due to the increased threat of bioterrorism [1-7]. Preliminary laboratory studies have suggested that an ideal neutralization process should contain not only a high thermal but also long-lasting biocidal agent release [8-14]. The main problem with conventional energetic materials is low neutralization efficiency since a thermal neutralization mechanism is dominant in this case [8]. Therefore, it has been proposed that simultaneously delivering a rapid thermal pulse with a remnant biocidal agent would prolong the exposure time and improve the inactivation process [15]. Halogens-based energetic materials show the most promise because of their excellent biocidal properties [16] when compared to silver-containing energetic materials [17-19]. To incorporate halogens in energetic materials, one can either directly add halogens into the system or assemble halogens into the oxidizers [16, 20]. Wang et al. incorporated iodine molecules into Al/CuO thermite systems and found that the Al/CuO/I₂ thermite reaction
rate was significantly decreased with increasing the iodine content [21]. Guerreo et al also showed that mechanical incorporation of iodine into aluminum severely decreases the reaction rate of Al/metal oxides mixtures and even resulted in failed ignition of Al•I₂/Fe₂O₃ [22]. In addition, Dreizin et al employed mechanically alloyed aluminum-iodine composites as a replacement of aluminum as a fuel additive in energetic formulations and the ignition and combustion tests of those fuels in air indicated that higher iodine concentration lowers ignition temperatures but did not affect the combustion temperatures substantially [14]. They also found improvements in terms of pressurization rate and maximum pressure at constant volume with 15 wt.% and 20 wt.% of I₂ [14]. Furthermore, an effective inactivation of aerosolized spores was achieved using Al/I₂ and Al/B/I₂ composites with 15-20 wt.% of iodine [16].

Another approach is to use iodine-containing oxy-compounds that can release HI or I₂ when used as an oxidizer [23]. Iodine-containing oxy-compounds can be broken down into two main categories: metal iodates and iodine oxides/iodic acids. The metal iodates, AgIO₃ [8, 24], Bi(IO₃)₃ [25], Cu(IO₃)₂ [15], Fe(IO₃)₃ [15] etc., have been previously investigated. One issue with employing metal iodates in thermites is that part of the produced I₂ vapor (all for AgIO₃) may react with the product metal particles to form corresponding metal iodides, which lowers the effective iodine content in the metal iodate-based thermite systems. Unfortunately, there are only a limited number of iodine oxides/iodic acids which are relatively stable and obtainable. These include I₂O₅, I₄O₉, HI₅O₈, HIO₃, H₅IO₆, etc [26-28]. Among these compounds, I₂O₅ (~76% iodine mass fraction), is the most studied in thermite systems [29-33]. In these studies, aluminum particles with different sizes were chosen as the fuel due to its high reaction
enthalpy, thermal conductivity and availability. With reported propagation velocities of up to \(~2,000\) m/s for loose ball-milled nAl and nano-scaled I₂O₅ (~10 nm) [32], I₂O₅ shows its high potential in aluminum-based thermites as an extremely aggressive oxidizer. Constant volume combustion tests also show nAl/micro-I₂O₅ outperforms traditional aluminum-based thermites such as Al/CuO and Al/Fe₂O₃ [33]. A pre-ignition reaction was proposed as the ignition trigger in which ionic I₂O₅ fragments diffused into the alumina passivation shell of aluminum and to create some reactive complexes exothermically [31,34]. However, this mechanism is far from clear as Smith et al reported that a pre-ignition reaction was not found for aluminum/nano crystalline I₂O₅ reaction in contrast to nano amorphous I₂O₅ case [35].

Recently, Smith et al reported that a minimum of 150% increase in flame speed was found for Al/amorphous I₄O₉ compared with Al/I₂O₅ indicating I₄O₉ has more reactive potential than I₂O₅ as an oxidizer when combined with aluminum [36]. Other iodine-containing oxy-compounds have received comparatively much less attention due to their relatively lower iodine content and availability. Nevertheless, their iodine content is still much higher than metal iodates or per-iodates on a per mass basis. This is particularly so for HI₃O₈, which has an iodine content of \(~75\)% and very close to the 76% for I₂O₅. Currently no comparative study examining how the aforementioned iodine oxides/iodic acids perform as oxidizers in thermites system is available. Moreover, we have recently reported that iodine oxides/iodic acids with different particles’ sizes can be prepared via either aerosol spray pyrolysis (ASP) or thermal treatment [37,38], making a variety of these materials readily available.
Most of the focus on reactive studies of oxidizers has focused on Aluminum as the fuel. Aluminum has a passivating alumina shell that stabilized the material at ambient conditions. However once the aluminum core reaches near the melting temperature, it can diffuse through the oxide shell and interact with any available oxidizer leading to ignition [39]. To explore the fuel melting aspect of ignition, we also explore in the paper tantalum as a fuel because it has a melting point of ~3000 °C, and thus would not be melted at the point of ignition.

In this paper, I examine the performance of various iodine oxides/iodic acids (I₂O₅, HI₃O₈ and HIO₃) as oxidizers in nAl-based and nTa-based thermites system. Iodine-containing oxides/acids were prepared via an ASP method following procedures in our previous work [37]. Time-resolved temperature-jump time-of-flight mass spectrometer (T-Jump/TOFMS) was used to study the ignition and decomposition of nAl-based and nTa-based thermites. A high-speed camera simultaneously captured optical emission from the ignition/reaction of the thermites allowing for the ignition time, and corresponding ignition temperature. In addition, constant volume combustion cell tests were performed on aluminum-based thermites.

5.2. Experimental Details

5.2.1. Materials

The aluminum nanopowders (nAl) (Alex, ~80 nm) were purchased from Novacentrix. The active Al was 81 % by mass, determined by TGA. Nano-tantalum powders (nTa, <50 nm) were purchased from Global Advanced Metals, with 70% of the mass. Iodic acid (c-HIO₃) (99.5 wt %), Iodine Pantoxide (c-I₂O₅), CuO
nanoparticles (\(n\)-CuO, <50 nm) and micro-sized CuO powders (\(m\)-CuO) purchased from Sigma-Aldrich were directly used as received (“\(e\)” represents commercial product; “\(n\)” and “\(m\)” represents nano-scaled and micro-scaled sizes, respectively). All other chemicals were of analytical grade and were used as purchased without further treatment.

5.2.2. Preparation of iodine oxides/iodic acids particles

Small-sized (<1 \(\mu\)m) particles of oxides includes \(\delta\)-HIO\(_3\), \(a\)-HI\(_3\)O\(_8\) and \(a\)-I\(_2\)O\(_5\) were synthesized via aerosol spray pyrolysis (ASP). Here, “\(a\)” represents ASP and “\(\delta\)” refers to HIO\(_3\) with a delta phase. Detailed information on the ASP synthesis method has been previously described [37]. Briefly, 100 mL iodic acid solution (10 mg/mL) were aerosolized (~1 um in diameter) with a homemade pressure atomizer (~35 psi pressure air) and passed through a silica-gel diffusion drier to remove water. The dry particles are then passed through a tube furnace for chemical conversion. The furnace temperature was set at ~230 and ~375 °C to obtain either \(\delta\)-HIO\(_3\) or \(a\)-I\(_2\)O\(_5\), respectively with a residence time of about 1 second. For both \(\delta\)-HIO\(_3\) and \(a\)-I\(_2\)O\(_5\), silica-gels were regenerated at 50 °C. I find that \(\delta\)-HIO\(_3\) can be obtained within a large range of temperature from 210 to 250 °C. In addition, \(a\)-HI\(_3\)O\(_8\) was obtained with a tube furnace temperature ~250 °C with a silica-gel regeneration temperature of ~80 °C. The final product was collected on a Millipore membrane filter (0.4 um pore). HI\(_3\)O\(_8\) was also prepared via thermal treatment of commercial HIO\(_3\) at ~180 °C and labeled as \(t\)-HI\(_3\)O\(_8\). The final product was characterized by scanning electron microscopy (SEM, Hitachi, SU-70 FEG-SEM) and powder X-ray diffraction (XRD, Bruker D8 Advance using Cu K\(\alpha\) radiation).
5.2.3. Preparation of thermites

Physically mixed stoichiometric mixtures of Al and Ta with \( \delta \)-HIO\(_3\), c-HIO\(_3\), a-HI\(_3\)O\(_8\), t-HI\(_3\)O\(_8\), a-I\(_2\)O\(_5\), c-I\(_2\)O\(_5\), and CuO were based on the following equations. The mixtures were sonicated in dry hexane for 30 minutes and left uncapped at room temperature in a low-pressure desiccator to evaporate the solvent. All of the samples employed in this work were stored in a sealed desiccator for future use. Below we list the stoichiometric relations used to prepare the mixture ratios and the associated enthalpy of reactions.

\[
\begin{align*}
4\text{Al} + 2\text{HIO}_3 & \rightarrow \text{I}_2 + 2\text{Al}_2\text{O}_3 + \text{H}_2, \Delta H_{\text{theoretical}} = -2413 \text{ KJ/mol} \\
32\text{Al} + 6\text{H}_3\text{O}_8 & \rightarrow 9\text{I}_2 + 16\text{Al}_2\text{O}_3 + 3\text{H}_2, \Delta H_{\text{theoretical}} = -20721 \text{ KJ/mol} \\
10\text{Al} + 3\text{I}_2\text{O}_5 & \rightarrow 3\text{I}_2 + 5\text{Al}_2\text{O}_3, \Delta H_{\text{theoretical}} = -6740 \text{ KJ/mol} \\
2\text{Al} + 3\text{CuO} & \rightarrow 3\text{Cu} + \text{Al}_2\text{O}_3, \Delta H_{\text{theoretical}} = -1109 \text{ KJ/mol} \\
12\text{Ta} + 10\text{HIO}_3 & \rightarrow 5\text{I}_2 + 6\text{Ta}_2\text{O}_5 + 5\text{H}_2, \Delta H_{\text{theoretical}} = -9059 \text{ KJ/mol} \\
32\text{Ta} + 10\text{H}_3\text{O}_8 & \rightarrow 15\text{I}_2 + 16\text{Ta}_2\text{O}_5 + 5\text{H}_2, \Delta H_{\text{theoretical}} = -26515 \text{ KJ/mol} \\
2\text{Ta} + \text{I}_2\text{O}_5 & \rightarrow \text{I}_2 + \text{Ta}_2\text{O}_5, \Delta H_{\text{theoretical}} = -1745 \text{ KJ/mol}
\end{align*}
\]

5.2.4. X-Ray Diffraction (XRD) measurement and Rietveld refinement

The as-prepared samples were characterized by powder X-ray diffraction. Diffraction pattern was measured using Cu K\(\alpha\) radiation in Bragg-Brentano geometry on Bruker D8 Advance powder diffractometer equipped with incident beam Soller slits, Ni \(\beta\)-filter and LynxEye position sensitive detector. Data were collected from 10\(^{\circ}\) to 90\(^{\circ}\) 2\(\theta\) with a step size of 0.01578\(^{\circ}\) and counting time of 1 sec per step (total exposure time of 180 sec per step). The crystal structures were refined by Rietveld method using
the Topas software [38]. Here I would like to acknowledge the help from Dr. Peter Zavalij on refining and determining the crystal information of different thermites.

5.2.5. T-Jump/TOFMS measurement and high-speed imaging

The decomposition of each oxide listed above was investigated using T-Jump/TOFMS [8]. Typically, a ~1 cm long platinum wire (76 um in width) with a thin coating of oxidizer sample was rapidly joule-heated to about 1200 °C by a 3 ms pulse at a heating rate of ~10^5 °C/s. The current and voltage signals were recorded, and the temporal temperature of the wire was determined using the Callendar–Van Dusen equation [40]. Spectra were collected at 0.1 ms intervals. The detailed experimental set-up has been previously described [8, 40].

In order to experimentally determine the ignition temperature for each thermite, a high-speed camera (Vision Research Phantom v12.0) was used to record the optical emission from combustion on the wire during heating. Ignition temperatures of thermite reactions in vacuum were measured from the correlation of optical emission from high speed imaging and temporal temperature of the wire and were further analyzed in combination with the temporal mass spectra. Each experiment was repeated 3 times.

5.2.6. Combustion Cell Test

Combustion properties of themites were evaluated in a constant-volume combustion cell, with simultaneous pressure and optical emission measurements. In this study, 25 mg of thermite powders was loaded inside the cell (constant volume, ~13 cm^3) and ignited by a resistively heated nichrome wire. The temporal pressure and optical
emission from the thermite reaction were measured using a piezoelectric pressure sensor and a photodetector, respectively. More detailed information on the combustion cell test can be found in our previous publications [8, 40]. Each experiment was repeated at least 3 times.

5.3. Results and Discussion

Various iodine oxides/iodic acids were prepared via ASP using a previously described synthesis method [37]. All of the as-prepared iodine-containing oxides including \(a\)-I\(_2\)O\(_5\), \(\delta\)-HIO\(_3\) and \(a\)-HI\(_3\)O\(_8\) have an average particle size of about 1 \(\mu\)m with a relatively wide size distribution [37]. SEM images, XRD patterns and TGA/DSC results are presented in Chapter 3 and 4 [37, 38]. Commercial I\(_2\)O\(_5\) and HIO\(_3\) (labeled as \(c\)-I\(_2\)O\(_5\) and \(c\)-HIO\(_3\)) and \(t\)-HI\(_3\)O\(_8\) prepared via thermal treatment of \(c\)-HIO\(_3\) were employed as comparisons. The average particle size of \(c\)-I\(_2\)O\(_5\) and \(c\)-HIO\(_3\) are \(\sim\)30 \(\mu\)m and \(t\)-HI\(_3\)O\(_8\) particles have an average size \(\sim\)4 \(\mu\)m (Figure S5.1). To verify the actual compositions of \(c\)-I\(_2\)O\(_5\), \(c\)-HIO\(_3\) and \(t\)-HI\(_3\)O\(_8\), XRD and TGA results shown in Figure S5.2 and Figure S5.3 indicate that \(c\)-HIO\(_3\) is pure HIO\(_3\), \(c\)-I\(_2\)O\(_5\) has mostly hydrated (\(\sim\)80\%) to HI\(_3\)O\(_8\) and \(t\)-HI\(_3\)O\(_8\) is pure HI\(_3\)O\(_8\). As control experiments, nano-sized (<50 nm) and micro-sized (<5 \(\mu\)m) CuO were also included in this work.

T-Jump/TOFMS (3 ms, heating rate \(\sim\)5\(\times\)10\(^5\) \(^\circ\)C/s) was employed to study the initial events of bare oxides or thermites under rapid heating rates, enabling us to probe the reaction process on a time scale close to that of a combustion event. Figure 5.1A, shows the temporal evolution of elemental iodine and O\(_2\) from \(a\)-HI\(_3\)O\(_8\) during rapid heating. Iodine and O\(_2\) are released at approximately the same temperature (\(\sim\)475 \(^\circ\)C) indicating that it could be a good candidate for a molecular iodine-releasing oxidizer. The single
peak in the species vs. time plots of both Iodine and O₂ suggests that a one-step decomposition of a-HI₃O₈.

To further explore its decomposition, time-resolved mass spectra from rapid heating of a-HI₃O₈ at 0.8-1.5 ms are shown in Figure 5.1B. For mass spectra taken at t<1.1 ms (before the decomposition of the oxidizer), H₂O⁺ (m/z 18), OH⁺ (m/z 17) and N₂⁺ (m/z 28) are attributed to the background. Above the decomposition temperature (>1.2 ms), O₂⁺ and I⁺ are detected in addition to IO⁺, IO₂⁺, I₂⁺, and I₂O⁺. The appearance of these species implies that the high heating rate decomposition pathway does not go directly to the thermodynamic end product of molecular iodine and oxygen under the conditions of this experimental setup. The temporal profile of those oxygen-containing species is shown in Figure S5.4 in which O₂⁺ has the highest signal intensity. All other iodine oxides/iodic acids have similar time-resolved mass spectra as depicted in Figure S5.5.
Figure 5.1. Representative plot showing the temporal profile of oxygen and iodine upon heating a-HI$_3$O$_8$ when heated at ~5×10$^5$ °C/s (A); time-resolved mass spectra of a-HI$_3$O$_8$ (B).
To evaluate the performance of the iodine oxides/iodic acids as oxidizers in thermite systems, physical mixtures with nAl were made with 30 minutes sonication of nAl and iodine oxides/iodic acids in dry hexane. To indicate whether the mixing process has any influence on iodine oxides/iodic acids, XRD and TGA were performed and results of iodine oxides/iodic acids before and after mixing shown in Figure S5.6 and Figure S5.7. To be more specific about the exact compositions of each sample in Figure S5.6, Rietveld refinement was run for all the XRD patterns and the results are shown in Table 5.1. Almost for all the samples except for c-I_2O_5, a small portion of the original compounds either changed to another phase or dehydrated. As the most hygroscopic one among those samples, a-I_2O_5 made the most changes (~25% dehydrate into δ-HIO_3). Due to the sensitivities of those iodine-containing compounds to water, those minor changes could be resulted from preparation, characterization and/or handling. In addition, the TGA results shown in Figure S5.7 show no discernable effect of the thermite preparation process on the hydration state of the iodine oxides/iodic acids. As an example, the SEM images of a-HI_3O_8 and Al/a-HI_3O_8 shown in Figure S5.8 further indicate that the mixing procedure does not influence the particle size or morphologies of the iodine oxides/iodic acids.
Table 5.1. Crystalline compositions of all the samples employed in Figure S6 determined by Rietveld refinement of the corresponding XRD pattern.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystalline Phases</th>
<th>Samples</th>
<th>Crystalline Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-HI₃O₈</td>
<td>91% HI₃O₈</td>
<td>Al/a-HI₃O₈</td>
<td>89% HI₃O₈</td>
</tr>
<tr>
<td></td>
<td>9% δ-HIO₃</td>
<td></td>
<td>11% δ-HIO₃</td>
</tr>
<tr>
<td>t-HI₃O₈</td>
<td>100% HI₃O₈</td>
<td>Al/t-HI₃O₈</td>
<td>87% HI₃O₈</td>
</tr>
<tr>
<td>δ-HIO₃</td>
<td>100% δ-HIO₃</td>
<td>Al/δ-HIO₃</td>
<td>88% δ-HIO₃</td>
</tr>
<tr>
<td>c-HIO₃</td>
<td>89% α-HIO₃</td>
<td>Al/c-HIO₃</td>
<td>75% α-HIO₃</td>
</tr>
<tr>
<td></td>
<td>11% HI₃O₈</td>
<td></td>
<td>25% HI₃O₈</td>
</tr>
<tr>
<td>a-I₂O₅</td>
<td>91% I₂O₅</td>
<td>Al/a-I₂O₅</td>
<td>68% I₂O₅</td>
</tr>
<tr>
<td></td>
<td>9% δ-HIO₃</td>
<td></td>
<td>32% δ-HIO₃</td>
</tr>
<tr>
<td>c-I₂O₅</td>
<td>100% HI₃O₈</td>
<td>Al/c-I₂O₅</td>
<td>100% HI₃O₈</td>
</tr>
</tbody>
</table>

a: detailed results of Rietveld refinement are included in electronic supporting information as an appendix.
b: aluminum signal was found in all Al-based samples and its composition ratio is excluded here for comparison purpose.
c: PDF# 01-075-3387 HI₃O₈ [27]
d: XRD information of δ-HIO₃ could be found in [38]
e: PDF #01-079-1633 HIO₃ [41]
f: PDF #01-082-2225 I₂O₅ [42]

Figure S5.9 shows some selected temporal snapshots of the Al/a-HI₃O₈ thermite reaction under vacuum of the T-jump/TOFMS chamber. Optical emission from reaction was first observed at 1.65 ms, corresponding to a wire temperature of ~664 ºC, indicating ignition of nAl/a-HI₃O₈ thermite. Overall, the optical emission of nAl/a-HI₃O₈ is not very strong [39] which suggests lower heat generation from the nAl-based thermite [43]. These snapshots also provide an alternative method to roughly determine burn time, calculated to be ~1.2 ms, and will be discussed more in the combustion test results.

From the T-jump TOFMS results, I found that the bare a-HI₃O₈ releases oxygen at ~475 ºC when heated at ~5×10⁵ ºC/s. Under the same heating condition, the nAl/a-HI₃O₈ thermite showed oxygen appearance at ~575 ºC and thus 100 ºC higher than the
oxygen release temperature of the bare oxidizer (Figure 5.2A). This result is quite different from the most of Al/metal oxides thermites where oxygen release from the metal oxide is not influenced by the presence of aluminum fuel [44]. One exception I know of is Al/Bi$_2$O$_3$, which releases oxygen at a temperature that is 700 °C lower than that of the bare Bi$_2$O$_3$ [45]. This effect is the opposite of nAl/a-HI$_3$O$_8$. In this case, the interaction between the iodine ions of a-HI$_3$O$_8$ and the alumina shell of the fuel might form stable alumino-oxy-halides that delay the decomposition of the oxide [31, 46].

Even though the oxygen release temperature from nAl/a-HI$_3$O$_8$ thermite increased in comparison to the neat oxide, it is still lower than its ignition temperature (~664 °C). In fact, it is sufficient close to aluminum melting point to reasonable argue that aluminum mobility into aluminum oxide is the initiation process. Clearly gaseous oxygen release from a-HI$_3$O$_8$ at ~575 °C did not initiate ignition. [47]. In fact, Al/Bi$_2$O$_3$, Al/SnO$_2$, Al/AgIO$_3$, Al/CuO and Al/KClO$_4$ also ignited in vacuum at about the melting temperature of aluminum no matter what the oxygen release temperature is [44]. In addition, the ignition temperature of nAl/a-HI$_3$O$_8$ thermite in Ar environment with a 1 atm pressure was also obtained and it was decreased ~30 °C compared with that in vacuum. Considering the experimental uncertainty of ±50 °C, it is reasonable to say that the ignition temperatures of nAl/a-HI$_3$O$_8$ in vacuum and 1 atm Ar are roughly the same, which again implies the importance of the melting phase transition of aluminum fuel.

If I consider Al/Co$_3$O$_4$, which has an ignition temperature of ~1095 °C, and is higher than its oxygen release temperature and the melting point of aluminum [44]. In this case, the generated gas phase oxygen also has no correlation with its ignition. However,
the nAl/a-HI3O8 ignited right after the aluminum melted. My group members have previously investigated the ignition of nAl in an oxygen environment and found that the ignition temperature decreased with increasing O2 pressure and dropped below the melting point of bulk aluminum at >7.4 atm [47]. Why then does nAl/a-HI3O8 thermite ignite at the melting point of aluminum? Obviously, the partial pressure of O2 during the ignition of nAl/a-HI3O8 thermite under vacuum is much lower than 7.4 atm. It has been shown in prior work that the oxygen concentration in solid oxidizers (7×10^4 mol/m^3) is much higher than that in gas (100 mol/ m^3 for 18 atm O2 gas) [47]. Thus, in vacuum, the oxygen pressure around the fuel is likely very high. This is also supported by the combustion cell tests where a high pressurization rate is observed after ignition. Moreover, the local gas phase oxygen released from the oxidizer has a much higher temperature than the free O2 in the pressurized ignition temperature tests described above. Both factors suggest that the gas phase oxygen from the oxidizer might also play a role in the ignition of thermites.

Time-resolved mass spectra taken at 0.1 ms intervals from a nAl/a-HI3O8 thermite reaction is shown in Figure 5.2A. As I expected, O2⁺, I⁺ and I2⁺ peaks were first observed at a time of about 1.3 ms (~536 °C), which is prior to ignition, and earlier than IO⁺ and IO₂⁺ species appeared. At the ignition temperature, IO⁺ and IO₂⁺ concentration also diminished, which implies that those intermediate iodine sub-oxide species also took part in the aluminum combustion [33].

Reactions between solids are by their nature limited by the movement of component reactive species or fragments. To further investigate the role of these oxidizers in the thermite reaction, a fuel was chosen that unlike aluminum would be immobile at least
at the point of ignition. Aluminum was replaced with tantalum as a means to potentially
tweeze out the relationship between iodine and oxygen release with ignition. Similar to
aluminum, tantalum also has a native oxide shell (Ta$_2$O$_5$). However, tantalum has a
very high melting point of about 3017 ºC, which rules out the influence of the melting
phase transition in the scope of ignition temperature test, which reaches a maximum
wire temperature of ~1200 ºC. Sequential snapshots of the nTa/a-HI$_3$O$_8$ thermite
reaction during rapid heating under vacuum were captured using a high speed camera
and are shown in Figure 5.3. In contrast to nAl/a-HI$_3$O$_8$, the nTa/a-HI$_3$O$_8$ reaction is
surprisingly much more vigorous with strong light emission. The images in Figure 5.3
also show that multiple ignition points appeared after ignition and propagate toward
each other to ignite the whole thermite. The burn time of nTa/a-HI$_3$O$_8$ is roughly 1.7
ms, which is longer than that of nAl/a-HI$_3$O$_8$. In addition, time-resolved mass spectra
of the nTa/a-HI$_3$O$_8$ thermite reaction (Figure 5.2B) shows that its oxygen and iodine
release temperatures are ~450 ºC, which is very close to those of neat a-HI$_3$O$_8$ (~475
ºC). However, nTa/a-HI$_3$O$_8$ thermite ignited at ~400 ºC (0.96 ms) prior to the oxygen
release from the bare oxidizer (~475 ºC) and Figure 5.2B also shows neither oxygen
gas nor elemental iodine are detected before the ignition, which suggests a condensed
phase reaction mechanism was dominant. While, considering that T-jump/TOFMS has
a temperature measurement uncertainty of about ±50 ºC [44], it would be also possible
that a very small amount of the oxidizer starts decomposing around the ignition
temperature that ignites the thermite. As to the condensed phase mechanism, it has been
found that cracks on in the oxide shell are formed when tantalum is rapidly heated to
above 500 °C due to the amorphous to crystalline phase change of the oxide shell [48]. However, the ignition of nTa/a-HI₃O₈ occurs ~100 °C earlier than this phase change.

Figure 5.2. Time-resolved mass spectra of nAl/a-HI₃O₈ (A) and nTa/a-HI₃O₈ (B).
**Figure 5.3.** Sequential snapshots of nTa/a-HI$_3$O$_8$ thermit burning on a high rate heating ($5 \times 10^5$ °C/s) Pt wire under vacuum, captured by a high-speed camera. The labels in each image are the time elapsed after triggering.

The performance of all the iodine oxides/iodic acids ($\delta$-HIO$_3$, $c$-HIO$_3$, $a$-HI$_3$O$_8$, $t$-HI$_3$O$_8$, $a$-I$_2$O$_5$ and $c$-I$_2$O$_5$) as an oxidizer using nAl or nTa as the fuel are summarized in the following figures. Figure 5.4 shows the relationship between iodine and O$_2$ release temperature in neat iodine oxides/iodic acids, and the ignition temperature of nAl-based and nTa-based thermites. For all iodine oxides/iodic acids, I find that oxygen and iodine occur at the same temperature which suggests iodine oxides/iodic acids directly decomposed into iodine and oxygen at high heating rate.
Figure 5.4. I and O$_2$ release temperature in neat iodine oxides/iodic acids, and the ignition temperature of corresponding nAl-based and nTa-based thermites under vacuum. Error bars correspond to at least two measurements. The orange dashed line stands for a perfect correlation.

All oxidizers when reacting with aluminum ignited about their oxygen release temperature. Moreover, they all ignited around the same temperature under vacuum, and at approximately the melting point of aluminum 660 ºC. Those results indicate that the ignition of nAl-based thermites is dominated by the melting of aluminum. Aluminum could then react with oxygen released from the oxidizer, but more likely since this experiment is conducted in vacuum, reacts heterogeneous with the oxidizer, once aluminum becomes mobile.

In contrast to aluminum, when tantalum was employed as the fuel, all nTa-based thermites ignited at temperatures lower than the oxygen release temperatures relative
to their corresponding neat oxidizers. Clearly, in this case a condensed phase reaction mechanism is dominant [44]. DeLisio et al have previously found that the Ta₂Os has a preferred orientation during crystalline oxide growth and this crystallization upon rapid heating result in cracking of the oxide shell that may enhance oxygen diffusion [48]. Since this is below the melting point of tantalum the oxygen from the decomposition of iodine oxides/iodic acids diffuse through the Ta₂Os cracked or weakened shell to the tantalum core. Moreover, even though a-HI₃O₈ and a-I₂O₅ has a significantly smaller particle size than c-HI₃O₈ or c-I₂O₅, their ignition temperatures are essentially within the measurement uncertainty which implies that particle size of the oxidizer is relatively unimportant and that the reaction of tantalum and gaseous O₂ contributed to the ignition, in agreement with the ignition of nAl/potassium oxysalts energetic composites [49].

To investigate the combustion performance of iodine oxides/iodic acids as oxidizers in nAl-based thermites at 1atm, constant volume combustion cell tests were performed on each thermite and the results are summarized in Table 5.2. Nano-sized copper oxide outperforms micro-sized copper oxide due to the huge difference between their particle sizes [50]. Given the fact that all iodine oxides/iodic acids include in this work have average particles size larger than 1 µm (~1 µm for δ-HIO₃, a-HI₃O₈ and a-I₂O₅; ~4 µm for t-HI₃O₈; ~30 µm for c-HIO₃ and c-I₂O₅), micro-sized copper oxide was chosen to be the control experiment.

Table 5.2 shows that those iodine oxides/iodic acids prepared via ASP outperform the corresponding commercial samples, with a shorter burn time and higher maximum pressure and pressurization rate. In addition, t-HI₃O₈ has better performance than c-
I₂O₅, but since they are both really HI₃O₈ the difference in performance can probably be attributed to the smaller particle size of t-HI₃O₈. Similar to the nano-sized and micro-sized CuO, particle size plays a very important role in combustion. In our previous work, we attributed the pressurization to the oxygen release from the oxidizer particles [43]. For nAl/micro-oxidizer thermites, the decomposition of the oxidizer is the rate-limiting step that results in the delay of the pressure rise [33, 43]. Thus, the particle size of the oxidizer is crucial for a thermite to perform well in combustion cell test because smaller particle size guarantees shorter diffusion length and higher specific surface area and therefore faster heat transfer and shorter the delay time for pressure rise [51]. In other words, the decomposition reaction of commercial iodine oxides/iodic acids that have larger particles size is the rate-limiting step during nAl-based thermites combustion, which results in slower thermite reaction rate and thus relatively poor performance in terms of pressurization rate [50]. Given the fact the only difference between commercial and aerosol synthesized iodine oxides/iodic acids is the particle size, it is reasonable to conclude that the higher pressurization rates and maximum pressures are resulted from the faster heat transfer owing to the higher contact area with employing smaller sized oxidizer particles. However, ignition with high heating rate by its nature is essentially the point where the self-heating by exothermic reaction exceeds heat loss and a non-linear reaction event occurs. In this case, the initial heat release from thermite reaction was not affected by oxidizers particles size and thus the ignition temperature is independent on particles size, which is consistent with our previous reports [51,52].
In addition, the fact that \( t\text{-HI}_3\text{O}_8 \) outperforms \( c\text{-HIO}_3 \) and \( a\text{-HI}_3\text{O}_8 \) outperforms \( \delta\text{-HIO}_3 \) imply that \( \text{HI}_3\text{O}_8 \) is a better oxidizer. In fact, the pressurization rate and maximum pressure of the \( \text{nAl}/a\text{-HI}_3\text{O}_8 \) thermite reaction are \( \sim 450 \text{ Kpa/ms and } \sim 384 \text{ Kpa} \), which is significantly above the other oxidizers evaluated, and indicate that the \( a\text{-HI}_3\text{O}_8 \) is the best gas generator in this study. The \( \text{nAl}/a\text{-HI}_3\text{O}_8 \) thermite reaction shows the highest peak optical emission and the shortest burn time, demonstrating it outperforms others in heat generation rate. Figure 5.5 shows the direct comparison between the pressure and optical trace of \( \text{nAl}/m\text{-CuO} \) and \( \text{nAl}/a\text{-HI}_3\text{O}_8 \). Based on the combustion behavior, \( a\text{-HI}_3\text{O}_8 \) seems to warrant further attention for biocidal applications since it features both high-pressure generation and energy release and has almost the same iodine content as \( \text{I}_2\text{O}_5 \) on a per mass basis (\( \text{I}_2\text{O}_5: \sim 76\% \); \( \text{HIO}_3: \sim 72\% \); \( \text{HI}_3\text{O}_8: \sim 75\% \)). In a prior work it has been reported [53] that \( \text{I}_2\text{O}_5 \) showed increased reactivity with a polar solvent treatment. Since \( \text{I}_2\text{O}_5 \) likely hydrated to form \( \text{HI}_3\text{O}_8 \) and \( \text{HIO}_3 \) in the polar solvent, it is reasonable to conclude that the results were showing that \( \text{I}_2\text{O}_5 \) hydrates outperform \( \text{I}_2\text{O}_5 \) in a flame speed test. This is consistent with my results.

**Table 5.2.** Combustion cell test data for \( \text{nAl} \)-based thermites with different oxidizers. Each sample was repeated at least three times. All the numbers have a deviation at \( \sim 25 \).

<table>
<thead>
<tr>
<th>Oxidizers (( \text{nAl} ), stoichiometric)</th>
<th>Peak Pressure (Kpa)</th>
<th>Pressurization rate (Kpa/ms)</th>
<th>Burn time (ms)</th>
<th>Peak optical emission (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n\text{-CuO} )</td>
<td>405</td>
<td>5653</td>
<td>0.31</td>
<td>2.24</td>
</tr>
<tr>
<td>( m\text{-CuO} )</td>
<td>162</td>
<td>157</td>
<td>1.60</td>
<td>2.70</td>
</tr>
<tr>
<td>( \delta\text{-HIO}_3 )</td>
<td>281</td>
<td>166</td>
<td>1.39</td>
<td>6.09</td>
</tr>
<tr>
<td>( c\text{-HIO}_3 )</td>
<td>104</td>
<td>6</td>
<td>12.7</td>
<td>0.41</td>
</tr>
<tr>
<td>( a\text{-I}_2\text{O}_5 )</td>
<td>293</td>
<td>207</td>
<td>1.29</td>
<td>7.52</td>
</tr>
<tr>
<td>( c\text{-I}_2\text{O}_5 )</td>
<td>156</td>
<td>31</td>
<td>2.49</td>
<td>2.88</td>
</tr>
<tr>
<td>( a\text{-HI}_3\text{O}_8 )</td>
<td>384</td>
<td>450</td>
<td>0.96</td>
<td>11.7</td>
</tr>
<tr>
<td>( t\text{-HI}_3\text{O}_8 )</td>
<td>214</td>
<td>175</td>
<td>1.25</td>
<td>7.79</td>
</tr>
</tbody>
</table>
Figure 5.5. Direct comparison between the pressure (A) and optical (B) trace of nAl/m-CuO and nAl/a-H\textsubscript{2}O\textsubscript{8}.
5.4. Conclusions

In this study, various iodine oxides/iodic acids, including $a$-I$_2$O$_5$, $a$-HI$_3$O$_8$ and $\delta$-HIO$_3$, were prepared based on the aerosol route published previously, and were employed as the oxidizer in thermite systems. Their decomposition behavior was studied using T-Jump/TOFMS, which identified a single decomposition step for all oxides at high heating rates compared with the multi-steps process at low heating rate. The ignition temperatures of nAl-based thermites are all ~650 ºC which is at the melting point of aluminum (~660 ºC). This suggests that the mobility of the aluminum core is dominating the ignition/reaction while the gaseous oxygen released from the decomposition of the oxidizer does not participate in the ignition until the molten aluminum was available. Unlike nAl-based thermites, the ignition temperatures of nTa-based thermites are lower than the oxygen release temperatures from the corresponding bare oxidizers. In this case, a condensed phase reaction mechanism is proposed to dominate the ignition process. Combustion tests show that nAl/$a$-HI$_3$O$_8$ has the highest pressurization rate and peak pressure and shortest burn time, and since it also has an iodine content of ~75% which is as high as I$_2$O$_5$ on a per mass basis, this material may be a very promising candidate in biocidal application.
5.5. Supplemental Information

Figure S5.1. The SEM images of c-I$_2$O$_5$, c-HIO$_3$ and t-HI$_3$O$_8$. 

![SEM images of c-I$_2$O$_5$, c-HIO$_3$ and t-HI$_3$O$_8$.]
Figure S5.2. The XRD patterns of c-I$_2$O$_5$, c-HIO$_3$ and t-HI$_3$O$_8$. 

As-received HIO$_3$

PDF#06-0183 HIO$_3$

As-prepared t-HI$_3$O$_8$

@180 °C

PDF#21-1126 HI$_3$O$_8$
**Figure S5.3.** The TGA curves of c-I$_2$O$_5$, c-HIO$_3$ and t-HI$_2$O$_8$.

**Figure S5.4.** Representative plot showing the temporal profiles of oxygen and IO$^+_x$ upon heating a-HI$_3$O$_8$ when heated at $\sim 5 \times 10^5$ °C/s.
Figure S5.5. Time-resolved T-Jump mass spectra obtained at a heating rate of \(~5 \times 10^5 \, ^\circ\text{C/s}\).
Figure S5.6. The XRD patterns of a-HIO₅ vs Al/a-HIO₅, t-HIO₅ vs Al/t-HIO₅, δ-HIO₃ vs Al/δ-HIO₃, c-HIO₃ vs Al/c-HIO₃, a-I₂O₅ vs Al/a-I₂O₅, and c-I₂O₅ vs Al/c-I₂O₅.
Figure S5.7. TGA results of a-H$_2$O$_3$ vs Al/a-H$_2$O$_3$, t-H$_2$O$_3$ vs Al/t-H$_2$O$_3$, δ-HIO$_3$ vs Al/δ-HIO$_3$, c-HIO$_3$ vs Al/c-HIO$_3$, a-I$_2$O$_5$ vs Al/a-I$_2$O$_5$ and c-I$_2$O$_5$ vs Al/c-I$_2$O$_5$. 
Figure S5.8. SEM images of a-HI₃O₈ and Al/a-HI₃O₈.

Figure S5.9. Sequential snapshots of nAl/a-HI₃O₈ thermite burning on high heating rate wire under vacuum captures by a high-speed camera. The labels in each image are time elapses after triggering.

5.6. Appendix: detailed results of Rietveld refinement

5.6.1. a-HI₃O₈.raw”

R-Values
\[ R_{exp} : 5.25 \quad R_{wp} : 9.25 \quad R_p : 6.85 \quad \text{GOF} : 1.76 \]
\[ R_{exp}^\prime : 10.86 \quad R_{wp}^\prime : 19.14 \quad R_p^\prime : 18.91 \quad \text{DW} : 0.77 \]

Quantitative Analysis - Rietveld

89
Phase 1 : delta-HIO₃  9.1(3) %
Phase 2 : HI₅O₈  90.9(3) %

Specimen displacement  -0.348(9)

Structure 1
Phase name  delta-HIO₃
R-Bragg  2.513
Spacegroup  P212121
Scale  0.0000172(5)
Cell Mass  703.642
Cell Volume (Å³)  264.47(6)
Wt% - Rietveld  9.1(3)
Double-Voigt|Approach
   Cry size Lorentzian  250(30)
   k: 1 LVol-IB (nm)  158(18)
   k: 0.89 LVol-FWHM (nm)  220(20)
Crystal Linear Absorption Coeff. (1/cm)  929.55(19)
Crystal Density (g/cm³)  4.4180(9)
Preferred Orientation (Dir 1 : 1 0 0)  0.77(5)
   (Dir 2 : 0 0 1)  1.4(6)
   Fraction of Dir 1  0.8(3)
Lattice parameters
   a (Å)  8.4486(6)
   b (Å)  6.9582(9)
   c (Å)  4.4988(7)

Site  Np  x  y  z  Atom  Occ  Beq
I1  4  0.27820  0.23062  0.02640  I  1  1.5
O1  4  0.34140  0.43890  0.27400  O  1  2
O2  4  0.35420  0.03720  0.25500  O  1  2
O3  4  0.08730  0.25400  0.16780  O  1  2
H1  4  0.44051  0.44433  0.28298  H  1  2

Structure 2
Phase name  HI₅O₈
R-Bragg  4.346
Spacegroup  P121/n1
Scale  0.00002355(14)
Cell Mass  2038.866
Cell Volume (Å³)  666.96(4)
Wt% - Rietveld  90.9(3)
Double-Voigt|Approach
   Cry size Lorentzian  277(7)
   k: 1 LVol-IB (nm)  177(5)
k: 0.89 LVol-FWHM (nm) 247(7)
Crystal Linear Absorption Coeff. (1/cm) 1103.95(6)
Crystal Density (g/cm^3) 5.0762(3)
Preferred Orientation (Dir 1 : 1 0 0) 0.883(5)
          (Dir 2 : 0 1 0) 1.49(10)
Fraction of Dir 1 0.82(3)
Lattice parameters
          a (Å) 7.5752(2)
b (Å) 7.7169(3)
c (Å) 11.4095(4)
          beta (°) 90.166(2)

<table>
<thead>
<tr>
<th>Site</th>
<th>Np</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom</th>
<th>Occ</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1</td>
<td>4</td>
<td>0.24144</td>
<td>0.22767</td>
<td>0.09527</td>
<td>I</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>I2</td>
<td>4</td>
<td>0.33769</td>
<td>0.73614</td>
<td>0.10361</td>
<td>I</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>I3</td>
<td>4</td>
<td>0.75579</td>
<td>0.04724</td>
<td>0.19159</td>
<td>I</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td>0.45720</td>
<td>0.30100</td>
<td>0.05390</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td>0.12980</td>
<td>0.43130</td>
<td>0.08700</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O3</td>
<td>4</td>
<td>0.17110</td>
<td>0.82240</td>
<td>0.00800</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O4</td>
<td>4</td>
<td>0.44080</td>
<td>0.94070</td>
<td>0.13590</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O5</td>
<td>4</td>
<td>0.18330</td>
<td>0.74510</td>
<td>0.24070</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O6</td>
<td>4</td>
<td>0.78370</td>
<td>0.45460</td>
<td>0.15790</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O7</td>
<td>4</td>
<td>0.80280</td>
<td>0.84230</td>
<td>0.12420</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O8</td>
<td>4</td>
<td>0.97740</td>
<td>0.11430</td>
<td>0.22530</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>H1</td>
<td>4</td>
<td>0.87310</td>
<td>0.46530</td>
<td>0.12130</td>
<td>H</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

[Graph of data showing the percentage of HI3O8 and NaIO3]
5.6.2. Al/a-HI$_3$O$_8$.raw

R-Values
Rexp : 4.24   Rwp : 5.31   Rp : 3.93   GOF : 1.25
Rexp' : 18.76  Rwp' : 23.51  Rp' : 27.89  DW : 1.47

Quantitative Analysis - Rietveld
Phase 1 : delta-HIO3  8.3(4) %
Phase 2 : HI3O8       67.1(6) %
Phase 3 : Al          24.6(6) %

Instrument
Specimen displacement 0.142(8)

Structure 1
Phase name                delta-HIO3
R-Bragg                   1.678
Spacegroup                P212121
Scale                     0.0000135(7)
Cell Mass                 703.642
Cell Volume (Å$^3$)        264.01(9)
Wt% - Rietveld            8.3(4)
Double-Voigt Approach
Cry size Lorentzian       270(50)
k: 1 LVol-IB (nm)         170(30)
k: 0.89 LVol-FWHM (nm)    240(50)
Crystal Linear Absorption Coeff. (1/cm) 931.2(3)
Crystal Density (g/cm$^3$) 4.4258(15)
Preferred Orientation (Dir 1 : 1 0 0) 0.782(13)
Lattice parameters
a (Å)                     8.4460(8)
b (Å)                      6.9551(16)
c (Å)                      4.4942(9)

Site  Np    x      y      z      Atom Occ  Beq
I1    4  0.27820  0.23062  0.02640  I   1     2
O1    4  0.34140  0.43890  0.27400  O   1     2
O2    4  0.35420  0.03720  0.25500  O   1     2
O3    4  0.08730  0.25400  0.16780  O   1     2
H1    4  0.44051  0.44433  0.28298  H   1     2

Structure 2
Phase name                HI3O8
R-Bragg                   2.248
Spacegroup                                P121/n1
Scale                                       0.00001497(14)
Cell Mass                                 2038.866
Cell Volume (Å^3)                         665.86(4)
Wt% - Rietveld                              67.1(6)
Double-Voigt|Approach
     Cry size Lorentzian                      361(19)
     k: 1 LVol-IB (nm)                        230(12)
     k: 0.89 LVol-FWHM (nm)                   321(17)
Crystal Linear Absorption Coeff. (1/cm)   1105.77(6)
Crystal Density (g/cm^3)                  5.0846(3)
Preferred Orientation (Dir 1 : 1 0 0)   0.908(7)
                                           (Dir 2 : 0 1 0) 1.4(2)
Fraction of Dir 1                           0.86(6)
Lattice parameters
     a (Å)                                  7.5733(2)
     b (Å)                                  7.7109(3)
     c (Å)                                  11.4025(4)
     beta (°)                               90.174(3)

<table>
<thead>
<tr>
<th>Site</th>
<th>Np</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom</th>
<th>Occ</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1</td>
<td>4</td>
<td>0.24144</td>
<td>0.22767</td>
<td>0.09527</td>
<td>I</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>I2</td>
<td>4</td>
<td>0.33769</td>
<td>0.73614</td>
<td>0.10361</td>
<td>I</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>I3</td>
<td>4</td>
<td>0.75579</td>
<td>0.04724</td>
<td>0.19159</td>
<td>I</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td>0.45720</td>
<td>0.30100</td>
<td>0.05390</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td>0.12980</td>
<td>0.43130</td>
<td>0.08700</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O3</td>
<td>4</td>
<td>0.17110</td>
<td>0.82240</td>
<td>0.00800</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O4</td>
<td>4</td>
<td>0.44080</td>
<td>0.94070</td>
<td>0.13590</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O5</td>
<td>4</td>
<td>0.18330</td>
<td>0.74510</td>
<td>0.24070</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O6</td>
<td>4</td>
<td>0.78370</td>
<td>0.45460</td>
<td>0.15790</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O7</td>
<td>4</td>
<td>0.80280</td>
<td>0.84230</td>
<td>0.12420</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O8</td>
<td>4</td>
<td>0.97740</td>
<td>0.11430</td>
<td>0.22530</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>H1</td>
<td>4</td>
<td>0.87310</td>
<td>0.46530</td>
<td>0.12130</td>
<td>H</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Structure 3
Phase name                                Al
R-Bragg                                     1.236
Spacegroup                                Fm3m
Scale                                       0.00104(3)
Cell Mass                                 107.926
Cell Volume (Å^3)                         66.371(9)
Wt% - Rietveld                              24.6(6)
Double-Voigt|Approach
     Cry size Lorentzian                      141(15)
     k: 1 LVol-IB (nm)                        90(10)
k: 0.89 LVol-FWHM (nm) 126(13)
Crystal Linear Absorption Coeff. (1/cm) 133.607(17)
Crystal Density (g/cm^3) 2.7002(4)
Lattice parameters
a (Å) 4.04879(18)

Site Np  x     y     z  Atom Occ  Beq
Al  4  0.00000  0.00000  0.00000 Al  1  1

HI3O8
67.09 %
delta-HIO3 8.27 %
Al 24.64 %
5.6.3. Al/t-HI$_3$O$_8$.raw

R-Values
Rexp : 4.05  Rwp : 5.08  Rp : 3.72  GOF : 1.26
Rexp' : 20.51  Rwp' : 25.76  Rp' : 31.37  DW : 1.35

Quantitative Analysis - Rietveld
Phase 1 : delta-HIO$_3$  9.668 %
Phase 2 : HI$_3$O$_8$  63.612 %
Phase 3 : Al  26.720 %

Instrument
Specimen displacement  0.06926433

Structure 1
Phase name  delta-HIO$_3$
R-Bragg  2.188
Spacegroup  P212121
Scale  1.45283e-005
Cell Mass  703.642
Cell Volume (Å$^3$)  264.17053
Wt% - Rietveld  9.668
Double-Voigt|Approach
Cry size Lorentzian  347.0
k: 1 LVol-IB (nm)  220.903
k: 0.89 LVol-FWHM (nm)  308.825
Crystal Linear Absorption Coeff. (1/cm)  930.609
Crystal Density (g/cm$^3$)  4.423
Preferred Orientation (Dir 1 : 1 0 0)  0.7375984
Lattice parameters
a (Å)  8.4463753
b (Å)  6.9616589
c (Å)  4.4926362

Site Np  x  y  z  Atom Occ  Beq
I1  4  0.27820  0.23062  0.02640  I  1   2
O1  4  0.34140  0.43890  0.27400  O  1   2
O2  4  0.35420  0.03720  0.25500  O  1   2
O3  4  0.08730  0.25400  0.16780  O  1   2
H1  4  0.44051  0.44433  0.28298  H  1   2

Structure 2
Phase name  HI$_3$O$_8$
R-Bragg  2.703
Spacegroup                                P121/n1
Scale                                       1.30854e-005
Cell Mass                                 2038.866
Cell Volume (Å^3)                         665.98220
Wt% - Rietveld                            63.612
Double-Voigt|Approach
   Cry size Lorentzian                    331.3
   k: 1 LVol-IB (nm)                   210.894
   k: 0.89 LVol-FWHM (nm)             294.831
Crystal Linear Absorption Coeff. (1/cm)  1105.576
Crystal Density (g/cm^3)                  5.084
Preferred Orientation (Dir 1 : 1 0 0)    0.8393051
   (Dir 2 : 0 1 0)                      1.136459
   Fraction of Dir 1                    0.632521
Lattice parameters
   a (Å)                                7.5731885
   b (Å)                                7.7118932
   c (Å)                                11.4031509
   beta (°)                             90.17477

Site  Np    x           y           z         Atom Occ       Beq
I1     4   0.24144    0.22767     0.09527     I    1         1
I2     4   0.33769    0.73614     0.10361     I    1         1
I3     4   0.75579    0.04724     0.19159     I    1         1
O1     4   0.45720    0.30100     0.05390     O    1         1.5
O2     4   0.12980    0.43130     0.08700     O    1         1.5
O3     4   0.17110    0.82240     0.00800     O    1         1.5
O4     4   0.44080    0.94070     0.13590     O    1         1.5
O5     4   0.18330    0.74510     0.24070     O    1         1.5
O6     4   0.78370    0.45460     0.15790     O    1         1.5
O7     4   0.80280    0.84230     0.12420     O    1         1.5
O8     4   0.97740    0.11430     0.22530     O    1         1.5
H1     4   0.87310    0.46530     0.12130     H    1         2

Structure 3
   Phase name                                Al
   R-Bragg                                     1.391
   Spacegroup                                 Fm3m
   Scale                                      1.04188e-003
   Cell Mass                                  107.926
   Cell Volume (Å^3)                         66.37367
   Wt% - Rietveld                            26.720
Double-Voigt|Approach
   Cry size Lorentzian                       117.4
   k: 1 LVol-IB (nm)                        74.737

96
k: 0.89  LVol-FWHM (nm)  104.483  
Crystal Linear Absorption Coeff. (1/cm)  133.601  
Crystal Density (g/cm^3)  2.700  
Lattice parameters  
a (Å)  4.0488524  

<table>
<thead>
<tr>
<th>Site</th>
<th>Np</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom Occ</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>4</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>Al</td>
<td>1</td>
</tr>
</tbody>
</table>

![Graphical representation of data]
5.6.4. t-HI₃O₈.raw

R-Values
Rexp : 5.86  Rwp : 9.87  Rp : 7.41  GOF : 1.68
Rexp' : 11.45  Rwp' : 19.26  Rp' : 18.24  DW : 0.77

Quantitative Analysis - Rietveld
Phase 1 : HI₃O₈  100.000 %

Instrument
Zero error  0.2452(18)
Specimen displacement  -0.159(15)

Structure 1
Phase name : HI₃O₈
R-Bragg : 5.449
Spacegroup : P121/n1
Scale : 0.0000420(4)
Cell Mass : 2038.866
Cell Volume (Å³) : 667.70(2)
Wt% - Rietveld : 100.000

Double-Voigt|Approach
Cry size Lorentzian : 187(3)
k: 1  LVol-IB (nm) : 118.9(17)
k: 0.89  LVol-FWHM (nm) : 166(2)
Crystal Linear Absorption Coeff. (1/cm) : 1102.74(4)
Crystal Density (g/cm³) : 5.07059(17)
Preferred Orientation (Dir 1 : 1 0 0) : 0.915(3)
            (Dir 2 : 0 1 0) : 1.66(14)
Fraction of Dir 1 : 0.915(16)

Lattice parameters
a (Å) : 7.57861(14)
b (Å) : 7.71950(15)
c (Å) : 11.4131(2)
beta (°) : 90.1621(14)

Site  Np  x     y     z  Atom Occ  Beq
I1  4  0.2414  0.2276  0.0953  I  1  1
I2  4  0.3376  0.7361  0.1036  I  1  1
I3  4  0.7557  0.0472  0.1916  I  1  1
O1  4  0.4572  0.3010  0.0539  O  1  1.5
O2  4  0.1298  0.4313  0.0870  O  1  1.5
O3  4  0.1711  0.8224  0.0080  O  1  1.5
O4  4  0.4408  0.9407  0.1359  O  1  1.5
O5  4  0.1833  0.7451  0.2407  O  1  1.5
5.6.5. \( a-I_2O_5 \) raw

R-Values
Rexp : 7.80  Rwp : 8.43  Rp : 6.45  GOF : 1.08
Rexp' : 20.61  Rwp' : 22.28  Rp' : 22.43  DW : 1.73

Quantitative Analysis - Rietveld
Phase 1 : delta-HIO3  8.6(4) %
Phase 2 : I2O5  91.4(4) %

Instrument
Zero error  -0.013(3)

Structure 1
Phase name  delta-HIO3
R-Bragg  1.902
Spacegroup  P212121
Scale  0.0000075(4)
Cell Mass  703.642
Cell Volume (Å³)  264.35(13)
Wt% - Rietveld  8.6(4)
Double-Voigt|Approach
Cry size Lorentzian  93(11)
k: 1  LVol-IB (nm)  59(7)
k: 0.89  LVol-FWHM (nm)  82(10)
Crystal Linear Absorption Coeff. (1/cm)  930.0(4)
Crystal Density (g/cm³)  4.420(2)
Preferred Orientation (Dir 1 : 1 0 0)  0.9(5)
(Dir 2 : 0 0 1)  1.1(11)
Fraction of Dir 1  1(5)
Lattice parameters
a (Å)  8.4490(19)
b (Å)  6.956(2)
c (Å)  4.4976(12)

<table>
<thead>
<tr>
<th>Site</th>
<th>Np</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom Occ</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1</td>
<td>4</td>
<td>0.27820</td>
<td>0.23062</td>
<td>0.02640</td>
<td>I</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td>0.34140</td>
<td>0.43890</td>
<td>0.27400</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td>0.35420</td>
<td>0.03720</td>
<td>0.25500</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>O3</td>
<td>4</td>
<td>0.08730</td>
<td>0.25400</td>
<td>0.16780</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>H1</td>
<td>4</td>
<td>0.44051</td>
<td>0.44433</td>
<td>0.28298</td>
<td>H</td>
<td>1</td>
</tr>
</tbody>
</table>

Structure 2
Phase name  I2O5
<table>
<thead>
<tr>
<th>Site</th>
<th>Np</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom Occ</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1</td>
<td>4</td>
<td>0.12780</td>
<td>0.11700</td>
<td>0.21700</td>
<td>I</td>
<td>1</td>
</tr>
<tr>
<td>I2</td>
<td>4</td>
<td>0.37370</td>
<td>0.68300</td>
<td>0.15900</td>
<td>I</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td>0.01270</td>
<td>0.84700</td>
<td>0.15200</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td>0.19130</td>
<td>0.03500</td>
<td>0.43900</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>O3</td>
<td>4</td>
<td>0.49440</td>
<td>0.84900</td>
<td>0.33200</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>O4</td>
<td>4</td>
<td>0.30570</td>
<td>0.50000</td>
<td>0.29700</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>O5</td>
<td>4</td>
<td>0.24920</td>
<td>0.96900</td>
<td>0.11200</td>
<td>O</td>
<td>1</td>
</tr>
</tbody>
</table>
Quantitative Analysis - Rietveld

Phase 1 : delta-HIO$_3$ 24.5(4) %
Phase 2 : I$_2$O$_5$ 52.3(5) %
Phase 3 : Al 23.1(4) %

Instrument

Zero error 0.004(3)
Specimen displacement -0.04(3)

Structure 1

Phase name delta-HIO$_3$
R-Bragg 1.674
Spacegroup P212121
Scale 0.0000622(10)
Cell Mass 703.642
Cell Volume ($\AA^3$) 264.08(2)
Wt% - Rietveld 24.5(4)

Double-Voigt\|Approach

Cry size Lorentzian 141(5)
k: 1 LVol-IB (nm) 90(3)
k: 0.89 LVol-FWHM (nm) 126(4)
Crystal Linear Absorption Coeff. (1/cm) 930.93(9)
Crystal Density (g/cm$^3$) 4.4245(4)
Preferred Orientation (Dir 1 : 1 0 0) 1.1(18)
(Dir 2 : 0 0 1) 1.04(12)
Fraction of Dir 1 0(3)

Lattice parameters

a (Å) 8.4467(4)
b (Å) 6.9556(4)
c (Å) 4.4948(2)

Site | Np | x  | y  | z  | Atom Occ | Beq |
--- | --- | --- | --- | --- | -------- | --- |
I1  | 4  | 0.27820 | 0.23062 | 0.02640 | I | 1 | 2 |
O1  | 4  | 0.34140 | 0.43890 | 0.27400 | O | 1 | 2 |
O2  | 4  | 0.35420 | 0.03720 | 0.25500 | O | 1 | 2 |
O3  | 4  | 0.08730 | 0.25400 | 0.16780 | O | 1 | 2 |
H1  | 4  | 0.44051 | 0.44433 | 0.28298 | H | 1 | 2 |
Structure 2

Phase name I$_2$O$_5$
R-Bragg 1.588
Spacegroup P121/c1
Scale 0.0000426(6)
Cell Mass 1335.224
Cell Volume (Å$^3$) 433.70(3)
Wt% - Rietveld 52.3(5)

Double-Voigt|Approach
Cry size Lorentzian 122(2)
k: 1 LVol-IB (nm) 77.5(15)
k: 0.89 LVol-FWHM (nm) 108(2)

Crystal Linear Absorption Coeff. (1/cm) 1130.86(8)
Crystal Density (g/cm$^3$) 5.1123(4)
Preferred Orientation (Dir 1: 0 0 1) 0.992(3)

Lattice parameters
a (Å) 11.0324(5)
b (Å) 5.0608(2)
c (Å) 8.1313(3)
beta (°) 107.194(3)

<table>
<thead>
<tr>
<th>Site</th>
<th>Np</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom Occ</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1</td>
<td>4</td>
<td>0.12780</td>
<td>0.11700</td>
<td>0.21700</td>
<td>I</td>
<td>1</td>
</tr>
<tr>
<td>I2</td>
<td>4</td>
<td>0.37370</td>
<td>0.68300</td>
<td>0.15900</td>
<td>I</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td>0.01270</td>
<td>0.84700</td>
<td>0.15200</td>
<td>O</td>
<td>1.5</td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td>0.19130</td>
<td>0.03500</td>
<td>0.43900</td>
<td>O</td>
<td>1.5</td>
</tr>
<tr>
<td>O3</td>
<td>4</td>
<td>0.49440</td>
<td>0.84900</td>
<td>0.33200</td>
<td>O</td>
<td>1.5</td>
</tr>
<tr>
<td>O4</td>
<td>4</td>
<td>0.30570</td>
<td>0.50000</td>
<td>0.29700</td>
<td>O</td>
<td>1.5</td>
</tr>
<tr>
<td>O5</td>
<td>4</td>
<td>0.24920</td>
<td>0.96900</td>
<td>0.11200</td>
<td>O</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Structure 3

Phase name Al
R-Bragg 0.975
Spacegroup Fm3m
Scale 0.00152(3)
Cell Mass 107.926
Cell Volume (Å$^3$) 66.371(6)
Wt% - Rietveld 23.1(4)

Double-Voigt|Approach
Cry size Lorentzian 118(6)
k: 1 LVol-IB (nm) 75(4)
k: 0.89 LVol-FWHM (nm) 105(5)

Crystal Linear Absorption Coeff. (1/cm) 133.607(13)
Crystal Density (g/cm$^3$) 2.7002(3)

Lattice parameters
Site Np x y z Atom Occ Beq
Al 4 0.00000 0.00000 0.00000 Al 1 1
5.6.7. \textit{Al/c-I}_2\textit{O}_5.raw"

R-Values
Rexp : 5.21  Rwp : 7.71  Rp : 5.60  GOF : 1.48
Rexp' : 20.58 Rwp' : 30.44 Rp' : 34.94  DW : 1.38

Quantitative Analysis - Rietveld
Phase 1 : H13O8  48.6(7) %
Phase 2 : Al  51.4(7) %

Instrument
Specimen displacement  0.046(6)

Structure 1
Phase name  H13O8
R-Bragg  3.089
Spacegroup  P121/n1
Scale  0.0000103(2)
Cell Mass  2038.866
Cell Volume (Å^3)  667.69737
Wt% - Rietveld  48.6(7)
Double-Voigt|Approach
Cry size Lorentzian  330(20)
k: 1  LVol-IB (nm)  212(15)
k: 0.89  LVol-FWHM (nm)  300(20)
Crystal Linear Absorption Coeff. (1/cm)  1102.736
Crystal Density (g/cm^3)  5.071
Preferred Orientation (Dir 1 : 1 0 0)  0.996(7)
(Dir 2 : 0 1 0)  0(3)
Fraction of Dir 1  1.000(19)
Lattice parameters
a (Å)  7.5786077
b (Å)  7.7194972
c (Å)  11.4130826
beta (°)  90.16208

\begin{tabular}{|c|c|c|c|c|c|c|}
\hline Site & Np & x & y & z & Atom Occ & Beq \\
\hline I1 & 4 & 0.24144 & 0.22767 & 0.09527 & I & 1 & 1 \\
I2 & 4 & 0.33769 & 0.73614 & 0.10361 & I & 1 & 1 \\
I3 & 4 & 0.75579 & 0.04724 & 0.19159 & I & 1 & 1 \\
O1 & 4 & 0.45720 & 0.30100 & 0.05390 & O & 1 & 1.5 \\
O2 & 4 & 0.12980 & 0.43130 & 0.08700 & O & 1 & 1.5 \\
O3 & 4 & 0.17110 & 0.82240 & 0.00800 & O & 1 & 1.5 \\
O4 & 4 & 0.44080 & 0.94070 & 0.13590 & O & 1 & 1.5 \\
O5 & 4 & 0.18330 & 0.74510 & 0.24070 & O & 1 & 1.5 \\
\hline
\end{tabular}
<table>
<thead>
<tr>
<th>Site</th>
<th>Np</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom Occ</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>O6</td>
<td>4</td>
<td>0.78370</td>
<td>0.45460</td>
<td>0.15790</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>O7</td>
<td>4</td>
<td>0.80280</td>
<td>0.84230</td>
<td>0.12420</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>O8</td>
<td>4</td>
<td>0.97740</td>
<td>0.11430</td>
<td>0.22530</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>H1</td>
<td>4</td>
<td>0.87310</td>
<td>0.46530</td>
<td>0.12130</td>
<td>H</td>
<td>1</td>
</tr>
</tbody>
</table>

Structure 2
- Phase name: Al
- R-Bragg: 0.726
- Spacegroup: Fm3m
- Scale: 0.00206(4)
- Cell Mass: 107.926
- Cell Volume (Å³): 66.506(7)
- Wt% - Rietveld: 51.4(7)

Double-Voigt[Approach]
- Cry size Lorentzian: 116(7)
- k: 1 LVol-IB (nm): 74(4)
- k: 0.89 LVol-FWHM (nm): 104(6)

Crystal Linear Absorption Coeff. (1/cm): 133.335(13)
Crystal Density (g/cm³): 2.6947(3)

Lattice parameters:
- a (Å): 4.05154(13)

Site  | Np | x    | y    | z    | Atom Occ | Beq |
Al    | 4  | 0.00000 | 0.00000 | 0.00000 | Al | 1 | 1
5.6.8. c-I$_2$O$_5$.raw"

R-Values
R$_{exp}$ : 5.61  R$_{wp}$ : 7.22  R$_{p}$ : 5.46  GOF : 1.29
R$_{exp}'$ : 16.16  R$_{wp}'$ : 20.80  R$_{p}'$ : 23.59  DW : 1.30

Quantitative Analysis - Rietveld
Phase 1 : HI$_3$O$_8$  100.000 %

Instrument
Zero error  0.0663(17)
Specimen displacement  -0.138(15)

Structure 1
Phase name  HI$_3$O$_8$
R-Bragg  3.249
Spacegroup  P121/n1
Scale  0.0000237(2)
Cell Mass  2038.866
Cell Volume ($\text{Å}^3$)  665.65(2)
Wt% - Rietveld  100.000

Double-Voigt Approach
Cry size Lorentzian  910(80)
k: 1  LVol-IB (nm)  580(50)
k: 0.89  LVol-FWHM (nm)  810(80)

Crystal Linear Absorption Coeff. (1/cm)  1106.13(3)
Crystal Density (g/cm$^3$)  5.08619(15)
Preferred Orientation (Dir 1 : 0 0 1)  1.0(5)
(Dir 2 : 1 0 0)  1.0(4)
Fraction of Dir 1  1(30)

Lattice parameters
a (Å)  7.57251(13)
b (Å)  7.70991(13)
c (Å)  11.4014(2)
$\beta$ (°)  90.1792(13)

Site  Np  x  y  z  Atom Occ  Beq
I1  4  0.24144  0.22767  0.09527  I  1  1
I2  4  0.33769  0.73614  0.10361  I  1  1
I3  4  0.75579  0.04724  0.19159  I  1  1
O1  4  0.45720  0.30100  0.05390  O  1  1.5
O2  4  0.12980  0.43130  0.08700  O  1  1.5
O3  4  0.17110  0.82240  0.00800  O  1  1.5
O4  4  0.44080  0.94070  0.13590  O  1  1.5
O5  4  0.18330  0.74510  0.24070  O 1  1.5
O6  4  0.78370  0.45460  0.15790  O 1  1.5
O7  4  0.80280  0.84230  0.12420  O 1  1.5
O8  4  0.97740  0.11430  0.22530  O 1  1.5
H1  4  0.87310  0.46530  0.12130  H 1  2
5.6.9. Al/delta-HIO₃.raw"
Spacegroup                                P212121
Scale                                       0.000118(3)
Cell Mass                                 703.642
Cell Volume (Å^3)                          263.83(2)
Wt% - Rietveld                            68.9(8)
Double-Voigt|Approach
   Cry size Lorentzian                    870(150)  
   k:  1  LVol-IB (nm)                    550(100)  
   k:  0.89  LVol-FWHM (nm)               780(130)  
Crystal Linear Absorption Coeff. (1/cm)    931.83(8)
Crystal Density (g/cm^3)                    4.4288(4)
Preferred Orientation (Dir 1 : 1 0 0)      0.56(2)  
   (Dir 2 : 0 0 1)                        0.977(8)  
Fraction of Dir 1                          0.19(2)
Lattice parameters
   a (Å)                                  8.4447(3)  
   b (Å)                                  6.9575(3)  
   c (Å)                                  4.4903(3)  

Site  | Np | x            | y            | z            | Atom Occ | Beq
---   |----|--------------|--------------|--------------|----------|---
I1    | 4  | 0.27820      | 0.23062      | 0.02640      | I         | 1  | 2
O1    | 4  | 0.34140      | 0.43890      | 0.27400      | O         | 1  | 2
O2    | 4  | 0.35420      | 0.03720      | 0.25500      | O         | 1  | 2
O3    | 4  | 0.08730      | 0.25400      | 0.16780      | O         | 1  | 2
H1    | 4  | 0.44051      | 0.44433      | 0.28298      | H         | 1  | 2

Structure 3
Phase name                                Al
R-Bragg                                    1.023
Spacegroup                                Fm3m
Scale                                      0.00095(4)
Cell Mass                                 107.926
Cell Volume (Å^3)                         66.364(14)
Wt% - Rietveld                            21.5(7)
Double-Voigt|Approach
   Cry size Lorentzian                    121(16)  
   k:  1  LVol-IB (nm)                    77(10)   
   k:  0.89  LVol-FWHM (nm)               107(15)  
Crystal Linear Absorption Coeff. (1/cm)    133.62(3)
Crystal Density (g/cm^3)                   2.7005(6)
Lattice parameters
   a (Å)                                  4.0486(3)  

Site  | Np | x            | y            | z            | Atom Occ | Beq
---   |----|--------------|--------------|--------------|----------|---
Al    | 4  | 0.00000      | 0.00000      | 0.00000      | Al       | 1  | 1

112
### 5.6.10. *delta-HIO$_3$.raw*

**R-Values**

Rexp : 5.50  Rwp : 6.78  Rp : 5.08  GOF : 1.23

Rexp' : 9.45  Rwp' : 11.64  Rp' : 10.60  DW : 1.33

**Quantitative Analysis - Rietveld**

Phase 1 : delta-HIO$_3$  100.000 %

**Instrument**

<table>
<thead>
<tr>
<th>Zero error</th>
<th>0.0688(12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen displacement</td>
<td>-0.149(13)</td>
</tr>
</tbody>
</table>

**Structure 1**

<table>
<thead>
<tr>
<th>Phase name</th>
<th>delta-HIO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-Bragg</td>
<td>1.133</td>
</tr>
<tr>
<td>Spacegroup</td>
<td>P212121</td>
</tr>
<tr>
<td>Scale</td>
<td>0.000406(2)</td>
</tr>
<tr>
<td>Cell Mass</td>
<td>703.642</td>
</tr>
<tr>
<td>Cell Volume (Å$^3$)</td>
<td>264.161(10)</td>
</tr>
<tr>
<td>Wt% - Rietveld</td>
<td>100.000</td>
</tr>
<tr>
<td>Double-Voigt</td>
<td>Approach</td>
</tr>
<tr>
<td>Cry size Lorentzian</td>
<td>280(6)</td>
</tr>
<tr>
<td>k: 1 LVol-IB (nm)</td>
<td>178(4)</td>
</tr>
<tr>
<td>k: 0.89 LVol-FWHM (nm)</td>
<td>249(6)</td>
</tr>
<tr>
<td>Crystal Linear Absorption Coeff. (1/cm)</td>
<td>930.64(4)</td>
</tr>
<tr>
<td>Crystal Density (g/cm$^3$)</td>
<td>4.42316(17)</td>
</tr>
<tr>
<td>Preferred Orientation (Dir 1: 1 0 0)</td>
<td>0.639(10)</td>
</tr>
<tr>
<td>(Dir 2: 0 0 1)</td>
<td>0.987(3)</td>
</tr>
<tr>
<td>Fraction of Dir 1</td>
<td>0.197(11)</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>8.44609(13)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>6.95622(15)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>4.49614(12)</td>
</tr>
</tbody>
</table>

**Site**

<table>
<thead>
<tr>
<th>Site</th>
<th>Np</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom Occ</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1</td>
<td>4</td>
<td>0.27820</td>
<td>0.23062</td>
<td>0.02640</td>
<td>I</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td>0.34140</td>
<td>0.43890</td>
<td>0.27400</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td>0.35420</td>
<td>0.03720</td>
<td>0.25500</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>O3</td>
<td>4</td>
<td>0.08730</td>
<td>0.25400</td>
<td>0.16780</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>H1</td>
<td>4</td>
<td>0.44051</td>
<td>0.44433</td>
<td>0.28298</td>
<td>H</td>
<td>1</td>
</tr>
</tbody>
</table>
5.6.11. Al/c-HIO₃.raw

R-Values
R_{exp} : 4.29  R_{wp} : 7.16  R_{p} : 4.91  GOF : 1.67
R_{exp}^\prime : 24.08  R_{wp}^\prime : 40.21  R_{p}^\prime : 49.56  DW : 1.10

Quantitative Analysis - Rietveld
Phase 1 : alpha-HIO₃  30(3) %
Phase 2 : HI₃O₈  10(3) %
Phase 3 : AL  61(3) %

Instrument
Zero error  -0.027(4)
Specimen displacement  -0.06(3)

Structure 1
Phase name  alpha-HIO₃
R-Bragg  5.266
Spacegroup  P212121
Scale  0.000080(9)
Cell Mass  703.642
Cell Volume (Å³)  251.49(3)
Wt\% - Rietveld  30(3)

Double-Voigt\|Approach
Cry size Lorentzian  1500(1100)
k: 1  LVol-IB (nm)  1000(700)
k: 0.89  LVol-FWHM (nm)  1400(1000)

Strain
Strain G  0.00(3)
e0  0.00000(7)

Crystal Linear Absorption Coeff. (1/cm)  977.54(11)
Crystal Density (g/cm³)  4.6461(5)

Preferred Orientation (Dir 1 : 1 0 0)  0.52(5)
(Dir 2 : 0 1 0)  0.21(12)
Fraction of Dir 1  0.98(8)

Preferred Orientation Spherical Harmonics
Order  8
y00  1
y20  0.72(18)
y22p  -0.2(2)
y40  -0.7(2)
y42p  0.10(9)
y44p  -0.1(2)
y60  0.31(17)
y62p  -0.03(8)


y64p    0.07(8)
y66p    -0.16(14)
y80     0.72(13)
y82p    -0.06(10)
y84p    -0.08(7)
y86p    -0.46(8)
y88p    -0.00(7)

Lattice parameters
a (Å)      5.5359(3)
b (Å)      5.8743(4)
c (Å)      7.7334(5)


<table>
<thead>
<tr>
<th>Site</th>
<th>Np</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom Occ</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1</td>
<td>4</td>
<td>0.20395</td>
<td>-0.08538</td>
<td>0.15737</td>
<td>I</td>
<td>1.13</td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td>-0.06832</td>
<td>0.02425</td>
<td>0.25690</td>
<td>O</td>
<td>1.56</td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td>0.33409</td>
<td>0.19685</td>
<td>0.08399</td>
<td>O</td>
<td>1.79</td>
</tr>
<tr>
<td>O3</td>
<td>4</td>
<td>0.09469</td>
<td>-0.15837</td>
<td>-0.05215</td>
<td>O</td>
<td>1.73</td>
</tr>
<tr>
<td>H1</td>
<td>4</td>
<td>0.23752</td>
<td>0.32350</td>
<td>0.13452</td>
<td>H</td>
<td>3.07</td>
</tr>
</tbody>
</table>

Structure 2

Phase name          HfO$_8$
R-Bragg             3.469
Spacegroup          P121/n1
Scale                0.0000035(12)
Cell Mass            2038.866
Cell Volume (Å$^3$)  663.9(2)
Wt% - Rietveld       10(3)

Double-Voigt Approach
Cry size Lorentzian  330(100)
k: 1 LVol-IB (nm)    210(70)
k: 0.89 LVol-FWHM (nm) 290(90)
Crystal Linear Absorption Coeff. (1/cm) 1109.1(3)
Crystal Density (g/cm$^3$) 5.1000(15)
Preferred Orientation (Dir 1 : 0 1 0) 0.26(19)
(Dir 2 : 1 0 0) 0.74(10)
Fraction of Dir 1 0.22(8)
Preferred Orientation Spherical Harmonics
Order    4
y00      1
y20      2.0(10)
y22m     0.4(9)
y22p     0.2(2)
y40      -2.8(9)
y42m     -2.4(9)
y42p     0.24(15)
Lattice parameters

<table>
<thead>
<tr>
<th>Site</th>
<th>Np</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom Occ</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1</td>
<td>4</td>
<td>0.24144</td>
<td>0.22767</td>
<td>0.09527</td>
<td>I</td>
<td>1</td>
</tr>
<tr>
<td>I2</td>
<td>4</td>
<td>0.33769</td>
<td>0.73614</td>
<td>0.10361</td>
<td>I</td>
<td>1</td>
</tr>
<tr>
<td>I3</td>
<td>4</td>
<td>0.75579</td>
<td>0.04724</td>
<td>0.19159</td>
<td>I</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td>0.45720</td>
<td>0.30100</td>
<td>0.05390</td>
<td>O</td>
<td>1.5</td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td>0.12980</td>
<td>0.43130</td>
<td>0.08700</td>
<td>O</td>
<td>1.5</td>
</tr>
<tr>
<td>O3</td>
<td>4</td>
<td>0.17110</td>
<td>0.82240</td>
<td>0.00800</td>
<td>O</td>
<td>1.5</td>
</tr>
<tr>
<td>O4</td>
<td>4</td>
<td>0.44080</td>
<td>0.94070</td>
<td>0.13590</td>
<td>O</td>
<td>1.5</td>
</tr>
<tr>
<td>O5</td>
<td>4</td>
<td>0.18330</td>
<td>0.74510</td>
<td>0.24070</td>
<td>O</td>
<td>1.5</td>
</tr>
<tr>
<td>O6</td>
<td>4</td>
<td>0.78370</td>
<td>0.45460</td>
<td>0.15790</td>
<td>O</td>
<td>1.5</td>
</tr>
<tr>
<td>O7</td>
<td>4</td>
<td>0.80280</td>
<td>0.84230</td>
<td>0.12420</td>
<td>O</td>
<td>1.5</td>
</tr>
<tr>
<td>O8</td>
<td>4</td>
<td>0.97740</td>
<td>0.11430</td>
<td>0.22530</td>
<td>O</td>
<td>1.5</td>
</tr>
<tr>
<td>H1</td>
<td>4</td>
<td>0.87310</td>
<td>0.46530</td>
<td>0.12130</td>
<td>H</td>
<td>2</td>
</tr>
</tbody>
</table>

Structure 3

Phase name AL
R-Bragg 5.378
Spacegroup Fm3m
Scale 0.00403(10)
Cell Mass 107.926
Cell Volume (Å^3) 66.380(10)
Wt% - Rietveld 61(3)
Double-Voigt|Approach
Cry size Lorentzian 107(5)
k: 1 LVol-IB (nm) 68(3)
k: 0.89 LVol-FWHM (nm) 95(4)
Crystal Linear Absorption Coeff. (1/cm) 133.588(19)
Crystal Density (g/cm^3) 2.6999(4)

Lattice parameters

<table>
<thead>
<tr>
<th>Site</th>
<th>Np</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom Occ</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>4</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>Al</td>
<td>1</td>
</tr>
</tbody>
</table>

118
5.6.12. c-HIO₃.raw"

R-Values
Rexp : 5.31  Rwp : 11.82  Rp : 8.72  GOF : 2.23
Rexp' : 9.95  Rwp' : 22.16  Rp' : 20.75  DW : 0.53

Quantitative Analysis - Rietveld
Phase 1 : alpha-HIO₃  88.7(3) %
Phase 2 : HI₃O₈  11.3(3) %

Instrument
Zero error  0.2291(12)
Specimen displacement  -0.062(10)

Structure 1
Phase name  alpha-HIO₃
R-Bragg  8.740
Spacegroup  P212121
Scale  0.000284(3)
Cell Mass  703.642
Cell Volume (Å³)  252.308(8)
Wt% - Rietveld  88.7(3)
Double-Voigt Approach
Cry size Lorentzian  411(14)
k: 1 LVol-IB (nm)  262(9)
k: 0.89 LVol-FWHM (nm)  366(12)
Crystal Linear Absorption Coeff. (1/cm)  974.36(3)
Crystal Density (g/cm³)  4.63096(14)
Preferred Orientation (Dir 1 : 1 0 0)  0.86(3)
(Dir 2 : 0 1 0)  1.13(4)
Fraction of Dir 1  0.55(12)
Lattice parameters
a (Å)  5.54287(9)
b (Å)  5.88041(11)
c (Å)  7.74085(14)

<table>
<thead>
<tr>
<th>Site</th>
<th>Np</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Atom Occ</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1</td>
<td>4</td>
<td>0.20395</td>
<td>-0.08538</td>
<td>0.15737</td>
<td>I</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td>-0.06832</td>
<td>0.02425</td>
<td>0.25690</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td>0.33409</td>
<td>0.19685</td>
<td>0.08399</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>O3</td>
<td>4</td>
<td>0.09469</td>
<td>-0.15837</td>
<td>-0.05215</td>
<td>O</td>
<td>1</td>
</tr>
<tr>
<td>H1</td>
<td>4</td>
<td>0.23752</td>
<td>0.32350</td>
<td>0.13452</td>
<td>H</td>
<td>1</td>
</tr>
</tbody>
</table>

Structure 2
Phase name: \( \text{HI}_3\text{O}_8 \)

- \( R - \text{Bragg} \): 3.993
- Spacegroup: \( P121/n1 \)
- Scale: 0.00000469(15)
- Cell Mass: 2038.866
- Cell Volume (Å\(^3\)): 667.60(11)
- Wt\% - Rietveld: 11.3(3)

### Double-Voigt\|Approach

- Cry size Lorentzian: 270(30)
- \( k: 1 \) LWol-IB (nm): 170(20)
- \( k: 0.89 \) LWol-FWHM (nm): 240(30)

### Crystal Linear Absorption Coeff. (l/cm)

- 1102.90(18)

### Crystal Density (g/cm\(^3\))

- 5.0714(8)

### Preferred Orientation (Dir 1: 1 0 0)

- 0.62(16)

### Fraction of Dir 1

- 0.11(11)

### Lattice parameters

- \( a \) (Å): 7.5792(5)
- \( b \) (Å): 7.7186(8)
- \( c \) (Å): 11.4118(13)
- \( \beta \) (°): 90.181(10)

### Site

<table>
<thead>
<tr>
<th>Np</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>Atom</th>
<th>Occ</th>
<th>Beq</th>
</tr>
</thead>
<tbody>
<tr>
<td>I1</td>
<td>4 0.24144</td>
<td>0.22767</td>
<td>0.09527</td>
<td>I</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>I2</td>
<td>4 0.33769</td>
<td>0.73614</td>
<td>0.10361</td>
<td>I</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>I3</td>
<td>4 0.75579</td>
<td>0.04724</td>
<td>0.19159</td>
<td>I</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>O1</td>
<td>4 0.45720</td>
<td>0.30100</td>
<td>0.05390</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O2</td>
<td>4 0.12980</td>
<td>0.43130</td>
<td>0.08700</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O3</td>
<td>4 0.17110</td>
<td>0.82240</td>
<td>0.00800</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O4</td>
<td>4 0.44080</td>
<td>0.94070</td>
<td>0.13590</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O5</td>
<td>4 0.18330</td>
<td>0.74510</td>
<td>0.24070</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O6</td>
<td>4 0.78370</td>
<td>0.45460</td>
<td>0.15790</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O7</td>
<td>4 0.80280</td>
<td>0.84230</td>
<td>0.12420</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>O8</td>
<td>4 0.97740</td>
<td>0.11430</td>
<td>0.22530</td>
<td>O</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>H1</td>
<td>4 0.87310</td>
<td>0.46530</td>
<td>0.12130</td>
<td>H</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

### Peaks Phase 1

#### Phase name

- Peaks Phase: 0

<table>
<thead>
<tr>
<th>Type</th>
<th>Position</th>
<th>( z )</th>
<th>( I )</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP</td>
<td>21.608(3)</td>
<td>3.15(13)</td>
<td>174(12)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k: 1 ) LWol-IB(nm) 111(8)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( k: 0.89 ) LWol-FWHM(nm) 155(11)</td>
<td></td>
</tr>
<tr>
<td>FP</td>
<td>26.6321(17)</td>
<td>8.6(2)</td>
<td>174(12)</td>
</tr>
<tr>
<td>k</td>
<td>LVol-IB(nm)</td>
<td>LVol-FWHM(nm)</td>
<td>Cry size Lor</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td>---------------</td>
<td>--------------</td>
</tr>
<tr>
<td>1.000</td>
<td>111(8)</td>
<td>155(11)</td>
<td>174(12)</td>
</tr>
<tr>
<td>0.890</td>
<td>155(11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Graph of spectral data](#)
Chapter 6: Carbon addition lowers initiation and iodine release temperatures from iodine oxide-based biocidal energetic materials*

Overview

Iodine oxides are of significant interest as strong oxidizers in energetic formulation that also operate as iodine release agents for neutralization of spores using strong thermal pulses. In this Chapter incorporation of carbon black (CB) as the main fuel or additive into iodine oxides-based energetic materials are shown to lower both initiation and iodine release temperatures compared to those of Al/iodine oxides and Ta/iodine oxides thermites. Those lowering effects were triggered by a condensed phase CB-iodine oxides reaction explored by high heating rate time-resolved temperature-jump time-of-flight mass spectrometry and low heating rate thermogravimetric analysis/differential scanning calorimetry results. I observe that other carbon allotropes, such as carbon nanotubes and functionalized graphene sheets, also feature the similar effect as CB. Fourier transform infrared spectroscopy analysis shows that the presence of CB lowered the bond energy of iodine oxide on the surface to trigger the CB-iodine oxide initiation at a relatively lower temperature.

* The results presented in this chapter have been published in the following journal article: Wu, T.; Wang, X.; DeLisio, J.B.; Holdren, S.; Zachariah, M.R., Carbon addition lowers initiation and iodine release temperatures from iodine oxide-based biocidal energetic materials. Carbon 2018 130 410-415.
6.1. Introduction

Developing new energetic materials with high efficiency neutralization of biological warfare agents has gained increased attention due to the increased threat of bioterrorism [1-5]. Preliminary laboratory studies have suggested that an ideal neutralization process should generate not only a high temperature, but also release a long-lasting biocidal agent [6-12]. The main limitation of conventional energetic materials is low neutralization efficiency since the thermal neutralization mechanism is dominant in this case, with the lack of effective biocidal agent release [6]. Therefore, it has been proposed that simultaneously delivering a rapid thermal pulse with a remnant biocidal agent would prolong the exposure time and improve the inactivation process [13].

Halogen-containing energetic materials have shown the most promise because of their excellent biocidal properties [14], compared to other biological energetic materials [15-17]. Among all halogens, iodine stands out owing to its strong neutralization effect. Different methods have been reported for incorporating elemental iodine into energetic materials [14, 18-20]. For instance, Dreizin et al. employed mechanically alloyed aluminum-iodine composites as a fuel in energetic formulations and the initiation and combustion tests in air indicated that higher iodine concentration lowers initiation temperatures and the combustion temperatures were not substantially diminished [12]. They also found improvements in terms of pressurization rate and maximum pressure at constant volume with 15 wt.% and 20 wt.% of I₂ [12]. Furthermore, an effective inactivation of aerosolized spores has been achieved using Al/I₂ and Al/B/I₂ composites with 15-20 wt.% of iodine [14]. Another efficient method
is to use iodine-containing compounds as an oxidizer, particularly iodine oxides/iodic acids.

Among all the iodine oxides/iodic acids (I$_2$O$_5$, I$_4$O$_9$, H$_2$IO$_8$, HIO$_3$, H$_5$IO$_6$, etc [21-23]), I$_2$O$_5$ is the most studied in thermite systems [24-28] due to its relatively high iodine content (~76% iodine mass fraction). In these studies, aluminum particles with different sizes were chosen as the fuel due to its high reaction enthalpy, thermal conductivity and availability. With reported propagation velocities of up to ~2,000 m/s for loose ball-milled nano-aluminum and nano-scaled I$_2$O$_5$ (~10 nm) [27], I$_2$O$_5$ shows its high potential in aluminum-based thermites as an extremely aggressive oxidizer. Constant volume combustion tests also show nano-Al/micro-I$_2$O$_5$ outperforms traditional aluminum-based thermites such as Al/CuO and Al/Fe$_2$O$_3$ [28].

Aluminum has a passivating alumina shell that stabilizes the material at ambient conditions. However, once the aluminum core is heated near the melting temperature, obtaining sufficient mobility, it can diffuse through the oxide shell and interact with any available oxidizer ultimately leading to initiation [29]. However, iodine oxide releases O$_2$ at a relatively low temperature (~450 °C) which is well below the Al melting point, where reaction is most advantaged [30]. To explore the fuel melting aspect of initiation, I have also used tantalum as a fuel since it has a much higher melting point (~3000 °C) than Al (660 °C), and thus would not melt at the point of initiation. However, the immobile tantalum core will not react with iodine oxide until some cracks appeared in the Ta$_2$O$_5$ shell upon heating (higher than 500 °C) due to the amorphous to crystalline phase change of the oxide shell [31]. Those cracks serve as a low resistance pathway for the oxygen to react with the tantalum core [31].
In this work, I employed carbon as a fuel to better interpret the initiation process of iodine oxide-based energetic materials since it has a high melting point (3550 °C) and no passivating shell. Therefore, there will be direct contact between the fuel and oxidizer enabling further understanding of the initiation process. Time-resolved temperature-jump time-of-flight mass spectrometry was used to study the initial events of bare oxidizers or carbon/iodine oxides thermites under rapid heating rates, enabling me to probe the reaction process on a time scale close to that of a combustion event. Slow heating rate thermogravimetric analysis and differential scanning calorimetry in an argon environment was also employed to further probe the reaction mechanism. Both methods indicate that carbon black (CB) and other carbon allotropes, such as functionalized graphene sheets and carbon nanotubes, can lower the iodine release temperature from iodine oxides such as I$_2$O$_5$, HIO$_3$ and HI$_3$O$_8$, via a condensed phase reaction mechanism. More importantly, I also found that CB as an additive with only 3 wt% can also significantly lower the initiation and iodine release temperatures for both Al/iodine oxides and Ta/iodine oxides thermites, indicating the potential use of CB in biocidal applications. In addition, Fourier transform infrared spectroscopy analysis was employed to examine the structural changes, specifically how the vibrations of I$_2$O$_5$ are affected by the addition of carbon black. The result implies that the presence of CB lowered the bond energy of iodine oxide on the surface and therefore triggered this condensed phase reaction.
6.2. Experimental Details

6.2.1 Materials

The aluminum nanopowders (Al) (Alex, ~80 nm) were purchased from Novacentrix. The active Al was 81% by mass, determined by thermogravimetric analysis. Nanotantalum powders (<50 nm, Ta) were purchased from Global Advanced Metals. Nanosized carbon black (~50 nm, CB) was obtained from Cabot Corporation. Multi-wall carbon nanotubes and iodine pentoxide (I$_2$O$_5$) purchased from Sigma-Aldrich were directly used as received. Functionalized graphene sheets (FGS) with C:O molar ratio of 15 and 60 were obtained from Aksay et.al [32] and labeled as FGS$_{15}$ and FGS$_{60}$, respectively. All the other chemicals were of analytical grade and used as purchased without further treatment. HIO$_3$ was prepared via thermal treatment of commercial HIO$_3$ at $\sim$180 °C for 30 minutes.

6.2.2 Preparation of thermites

Aluminum, tantalum or CB was stoichiometrically mixed with I$_2$O$_5$, HIO$_3$ and HIO$_5$ based on the following equations, respectively, in hexane followed by 30 minutes of sonication.

\[
\begin{align*}
3C + 2HIO_3 & \rightarrow 3I_2 + H_2 + 3CO_2 \\
8C + 2HI_3O_8 & \rightarrow 3I_2 + H_2 + 8CO_2 \\
5C + 2I_2O_5 & \rightarrow 2I_2 + 5CO_2 \\
4Al + 2HIO_3 & \rightarrow I_2 + 2Al_2O_3 + H_2 \\
32Al + 6HI_3O_8 & \rightarrow 9I_2 + 16Al_2O_3 + 3H_2 \\
10Al + 3I_2O_5 & \rightarrow 3I_2 + 5Al_2O_3
\end{align*}
\]
After room temperature evaporation of the solvent in a desiccator, the solid thermite powders were used. To show the morphology of the thermites, as an example, the SEM images of CB/Ta/HI₃O₈ along with Ta/HI₃O₈ and HI₃O₈ are shown in Figure S6.1. The fact that fuel (CB, Ta) nanoparticles were well distributed on the surface of HI₃O₈ indicates a good mixing of fuel and oxidizer.

6.2.3. T-Jump/TOFMS measurement and high-speed imaging

The decomposition of oxide particles was investigated using a T-Jump/TOFMS [6]. Typically, a ~1 cm long platinum wire (76 um in width) with a thin layer coating of oxidizer sample was rapidly joule-heated to about 1200 °C by a 3 ms pulse at a heating rate of $5 \times 10^5$ °C/s. The current and voltage signals were recorded, and the temporal temperature of the wire was measured according to the Callendar–Van Dusen equation [29]. However, the sample temperature can be different than the wire temperature, and we are only able to directly measure the wire temperature by this method. To address this concern, we have previously developed a heat transfer model to estimate the true sample temperature during the heating event [33, 34]. The major conclusion from this quantitative model is that the characteristic heating time of nanoparticles on the wire is sufficiently fast, that even though we are using a high heating rate, the nanoparticles on the wire are expected to be essentially at the wire temperature (± 5 °C). Therefore, initiation/ignition temperatures of the materials in contact with the wire is equal to the wire temperature within any experimental and practical effect. Adding a material with a higher thermal conductivity such as carbon would only improve the situation. The temperature of the wire corresponding to the initial release of O₂ or iodine was regarded
as the O\textsubscript{2} or iodine release temperature. Mass spectra were measured every 0.1 ms. The detailed experimental set-up is given in our previous papers [6, 29].

To identify the point of initiation, a high-speed camera (Vision Research Phantom v12.0) was employed to record the combustion on the wire during heating. Initiation temperatures of thermite reactions in vacuum were measured from the correlation of optical emission from high speed imaging and temporal temperature of the wire and were further analyzed in combination with the temporal mass spectra. Each measurement was repeated 3 times.

6.2.4. Thermogravimetric analysis/differential scanning calorimetry

(TGA/DSC) measurement

Thermogravimetric analysis and Differential Scanning Calorimetry were conducted using an SDT Q600 (TA instruments). The measurement was performed under a 100 mL min\textsuperscript{-1} argon flow with ~ 1.0 mg samples placed into an alumina pan and heated from room temperature up to 550 °C (or higher temperature) at a rate of 5 °C/min.

6.2.5. Fourier Transform Infrared Spectroscopy (FTIR) analysis

Attenuated total reflection (ATR) FTIR spectra of I\textsubscript{2}O\textsubscript{5} samples with and without CB were collected using a Nicolet iS-50R spectrometer equipped with a room temperature deuterated triglycine sulfate (DTGS) detector FTIR spectroscopy. A Thermo Scientific Smart iTX accessory was installed to collect the ATR spectra shown here at 4 cm\textsuperscript{-1} resolution and averaged over 25 scans.
6.3. Results and Discussion

To investigate the performance of iodine oxides/iodic acids as oxidizers in thermite systems, I have previously employed Al and Ta as fuels in Chapter 5. However, both aluminum and tantalum have an oxide shell, which to some extent restricted our understanding on how those thermites react during initiation [35], and thus motivated the use of carbon. Commercial iodine pentoxide was first examined because it is the most extensively studied and can be obtained easily [36].

T-Jump/TOFMS was employed to study the initial events of bare oxidizers or thermites under rapid heating [37]. I plot in Figure 6.1 both the iodine and oxygen release temperatures vs. the reaction initiation temperature. Different initiation temperatures were obtained for thermites with different fuels including Al, Ta and CB. I have previously argued that the initiation of Al-based and Ta-based thermites is dominated by the melting of aluminum and the phase change of the Ta₂O₅ shell, respectively [35]. As to CB, the initiation temperature of CB/I₂O₅ is ~330 °C (determined from release of CO₂ product since there is virtually no optical signature of initiation), and more than 100 °C lower than the iodine release temperature from the neat I₂O₅, which implies a condensed phase reaction mechanism may be dominant here.

Ignition by its nature is essentially the point where self-heating by exothermic reaction exceeds heat loss and product formation occurs. It should be noted that the light emission of metal based thermites aligns well with the product release profile based on our previous work [29]. One major conclusion from this paper is that the product formation determined by mass spectrometry correlates well with the temperature at which light emission begins. Therefore, ignition/initiation in these
experiments is defined at the point of CO₂ production for C-based thermites (Figure S6.2) and the light emission of Al/Ta-based thermites.

![Graph showing release temperature of I and O₂ from neat I₂O₅ vs. initiation temperature of corresponding Al-based, Ta-based and CB-based thermites under vacuum. Error bars represent two replicates. The diagonal dashed line would imply a perfect correlation between initiation and release temperature.]

Figure 6.1. Release temperature of I and O₂ from neat I₂O₅ vs. initiation temperature of corresponding Al-based, Ta-based and CB-based thermites under vacuum. Error bars represent two replicates. The diagonal dashed line would imply a perfect correlation between initiation and release temperature.

To understand the relationship between iodine release and initiation, I plotted iodine release temperatures vs initiation temperatures in Figure 6.2. The dotted red line represents the iodine/O₂ release temperatures (~450 °C) from neat I₂O₅ obtained through a high heating method. Note that, the y-axis in Figure 6.2 is the iodine/O₂ release temperature of the fuel/I₂O₅ mixture; however, the y-axis in Figure 6.1 is the iodine/O₂ release temperature of the neat I₂O₅. Since CB/I₂O₅ ignition was initiated at
a very low temperature, 3 wt% CB was introduced into both Al/I₂O₅ and Ta/I₂O₅ systems to investigate the effect of CB as an additive.

Results in Figure 6.2 shows that the initiation temperature is correlated with the iodine release temperature for all cases except for Al/I₂O₅ in which its initiation was controlled by the mobilization of the aluminum core. When aluminum is employed as the fuel, iodine release is actually delayed to a significantly higher temperature compared with neat I₂O₅ (550 vs. 450 °C). This delay might be caused by the interaction between the alumina shell and I₂O₅, which to some extent stabilizes I₂O₅ and therefore delays its decomposition. Similar effects of halogen interactions have been reported in previous studies [26, 38].

Figure 6.2 also shows that addition of just 3 wt% CB into Al/I₂O₅ system, not only lowers the iodine release temperature but also the initiation temperature. The incorporated CB offsets the influence of aluminum on the iodine release from I₂O₅ and makes it behave like that of the bare oxidizer. As to why initiation seems not limited by the melting point of Al: the condensed phase reaction of CB/I₂O₅ is initiated first and presumably the energy generated kicks the temperature above the point of making the Al core mobile. Thus, addition of CB lowers the initiation temperature of an aluminum-based thermite.

As a comparison, CB₃wt%/I₂O₅ (non-stoichiometric) shows a lower initiation and iodine release temperatures than CB₃wt%/Al/I₂O₅, which indicates the presence of aluminum inhibits the condensed phase reaction of CB/I₂O₅ and therefore delays the iodine release from I₂O₅. On the other hand, with only 3wt% addition of CB, the iodine release temperature of I₂O₅ was brought lower by about 50 °C compared to the neat
I$_2$O$_5$, which indicates that the condensed phase CB/I$_2$O$_5$ reaction occurred before the I$_2$O$_5$ decomposition. Furthermore, the addition of 3 wt% CB into Ta/I$_2$O$_5$ system also bring both iodine release and initiation to lower temperatures, indicating the general effect of CB additive on different fuel/I$_2$O$_5$ systems. In addition, time resolved images of CB$_{3\text{wt\%}}$/Al/I$_2$O$_5$ and CB$_{3\text{wt\%}}$/Ta/I$_2$O$_5$ thermite reactions during rapid heating under vacuum were captured using a high-speed camera and are shown in Figure S6.3. In contrast to CB$_{3\text{wt\%}}$/Al/I$_2$O$_5$, the CB$_{3\text{wt\%}}$/Ta/I$_2$O$_5$ reaction is much more vigorous with strong light emission.

In fact, similar results (Figure S6.4) were also obtained for HI$_3$O$_8$-based or HIO$_3$-based thermites indicating the general effect of CB on iodine oxides/iodic acids.

![Figure 6.2](image-url)

**Figure 6.2.** Release temperatures of iodine/oxygen vs. initiation temperatures of different thermites.
I now turn to mechanistic effects, which I limit to the CB/I\textsubscript{2}O\textsubscript{5} reaction mechanism since the other oxidizers showed similar behavior.

To explore the CB/I\textsubscript{2}O\textsubscript{5} reaction further, time-resolved T-Jump mass spectra of I\textsubscript{2}O\textsubscript{5} and CB/I\textsubscript{2}O\textsubscript{5} were obtained and shown in Figure 6.3. For neat I\textsubscript{2}O\textsubscript{5}, above the decomposition temperature (>1.1 ms, 470°C), O\textsubscript{2}\textsuperscript{+} and I\textsuperscript{+} are detected in addition to IO\textsuperscript{+}, IO\textsubscript{2}\textsuperscript{+}, I\textsubscript{2}\textsuperscript{+}, and I\textsubscript{2}O\textsuperscript{+}, which is consistent with our previous result of HI\textsubscript{3}O\textsubscript{8}. Since IO\textsuperscript{+} and IO\textsubscript{2}\textsuperscript{+} were reported previously as the primary species of iodic acid, we conclude that the commercial I\textsubscript{2}O\textsubscript{5} is partially hydrated to form HI\textsubscript{3}O\textsubscript{8}. In fact, the XRD and TGA/DSC results (Figure S6.5) of commercial I\textsubscript{2}O\textsubscript{5} also prove it is ~80% hydrated to HI\textsubscript{3}O\textsubscript{8} [35, 36]. For CB/I\textsubscript{2}O\textsubscript{5}, both the disappearance of the O\textsubscript{2}\textsuperscript{+} peak and the appearance of a CO\textsubscript{2}\textsuperscript{+} peak prove CB reacted with I\textsubscript{2}O\textsubscript{5}. The time-resolved mass spectra of bare CB (Figure S6.6) clearly eliminates the possibility that the CO\textsubscript{2}\textsuperscript{+} peak is from CB. The new CO\textsuperscript{+} peak is either a fragment of CO\textsubscript{2} or a product of incomplete reaction of CB/I\textsubscript{2}O\textsubscript{5} energetic composite. Considering both facts that the reaction is extremely fast (less than several milliseconds) and the formed O\textsubscript{2} could rapidly escape the reaction interface at very low pressure, the partially incomplete reaction between the fuel and oxidizer is not a surprise.

Figure 6.3 also shows that CB/I\textsubscript{2}O\textsubscript{5} released iodine at ~360 °C, which occurred slightly later than its initiation temperature (~340 °C), indicating a condensed phase reaction mechanism was involved here. More importantly, the onset release temperature of iodine from CB/I\textsubscript{2}O\textsubscript{5} is about 100 °C lower than that of neat I\textsubscript{2}O\textsubscript{5}, which is probably due to that the condensed phase reaction of CB extracts oxygen from I\textsubscript{2}O\textsubscript{5}, and thus promoting a quicker release of iodine.
Figure 6.3. Time-resolved mass spectra of I$_2$O$_5$ (A) and CB/I$_2$O$_5$ (B).

Slow heating rate TGA in argon is shown in Figure 6.4. Neat I$_2$O$_5$ shows one minor weight loss at around 210 °C that corresponds to the dehydration of HI$_3$O$_8$ and another major weight loss at around 370 °C that results from the decomposition of I$_2$O$_5$. The DSC curve of I$_2$O$_5$ shows that both steps are endothermic (black curve in Figure S6.7).

When CB was mixed with I$_2$O$_5$ (red curve in Figure 6.4) the onset decomposition temperature is 140 °C lower than that of neat I$_2$O$_5$. In addition, the DSC (red curve in Figure S6.7) shows an exotherm around 250 °C presumably from reaction between CB and I$_2$O$_5$. Even with only 3wt% of CB, the TGA curve of I$_2$O$_5$ follows the same kinetics as CB/I$_2$O$_5$ at temperatures below 250 °C. However, as temperature increases (250<T<300 °C), the reaction effectively stops until it reaches the neat I$_2$O$_5$ condition resuming decomposition at a rate the same as neat I$_2$O$_5$. In fact, the actual weight loss of CB$_{3\text{wt}}$/I$_2$O$_5$ at 300 °C, ~35%, is very close the theoretical weight loss ~37% based on the reaction of 3 wt% CB and I$_2$O$_5$ (accounted for the 80% hydration HI$_3$O$_8$ specie).

The unchanged TGA result of Al/I$_2$O$_5$ compared with that of I$_2$O$_5$ indicates that aluminum does not pose any significant influence on the decomposition of I$_2$O$_5$ at low
heating rates, which is quite different from the T-jump/TOFMS experiment in which the presence of aluminum delays the iodine release of I₂O₅. Moreover, for CB₃wt%/Al/I₂O₅, the decomposition started at a temperature very close to that of CB/I₂O₅, thus aluminum does not influence the CB/I₂O₅ reaction at a low heating rate and again differs from the T-jump/TOFMS experiment.

The TGA curve (Figure S6.8A) of Ta/I₂O₅ starts decreasing at a lower temperature than that of bare I₂O₅, which suggests Ta/I₂O₅ reaction was probably initiated prior to I₂O₅ decomposition at low heating rate and thus causing the weight loss. The TGA/DSC of Ta in O₂ at a heating rate of 20 °C/min (Figure S6.9) shows oxidation is a one step process beginning at ~300 °C and finishing at ~500 °C, indicating that gaseous O₂ can diffuse through the Ta₂O₅. Thus, the Ta/I₂O₅ reaction was probably initiated by the interaction between the Ta core and the oxidizer I₂O₅ following a condensed phase reaction mechanism. The 3 wt% addition CB into Ta/I₂O₅ system, decreases the onset decomposition temperature, but the kinetics were found to be faster (Figure S6.8A) and a small exotherm was observed (Figure S6.8B).
Additional carbon allotropes including CNT and FGS were evaluated by stoichiometrically mixing with I$_2$O$_5$. Figure 6.5 shows the relation between iodine release temperatures and initiation temperature of those energetic composites employing carbon allotropes as the fuel from T-Jump mass spectrometry. The horizontal dotted red line represents the oxygen and iodine release temperatures of neat I$_2$O$_5$, and the dotted blue line would refer to the perfect correlation between iodine release and the onset reaction temperature. For all samples, the initiation temperatures are either lower to or the same as the corresponding iodine release temperatures and the iodine release temperature is lower than bare I$_2$O$_5$. All four stoichiometric thermites employing FGS$_{15}$, FGS$_{60}$, CNT or CB as the fuel initiated almost at the same temperature ~310 °C, implying that the different properties among those carbon materials [39-42] appear to have no significant effect on initiation. We also note that
above a threshold level of carbon the ignition temperature is not affected. So, 3% and 8% of CB addition have essentially the same ignition temperature. Additionally, the low heating rate TGA/DSC results (Figure S6.10) show similar onset decomposition temperatures and exothermic peaks as to CB/I\(_2\)O\(_5\), which are in consistent with the initiation results.

![Graph showing the relation between iodine/oxygen release temperatures and initiation temperatures of thermites employing carbon allotropes as the fuel.](image)

**Figure 6.5.** The relation between iodine/oxygen release temperatures and initiation temperatures of thermites employing carbon allotropes as the fuel.

Since I conclude that surface reaction is clearly playing a significant role, FTIR attenuated total reflection (ATR, surface) and transmission measurements (KBr pellet) were both employed to deduce any structure changes just prior to reaction [43]. FTIR-ATR spectra of bare I\(_2\)O\(_5\), CB\(_{3\text{wt\%}}\)/I\(_2\)O\(_5\) and stoichiometric CB/I\(_2\)O\(_5\) at room temperature and 200 °C, is shown in Figure 6.7. The spectra show a steady red-shift (too lower wavenumbers) with increasing CB content. For clarity, the stoichiometric CB/I\(_2\)O\(_5\) is labeled as CB\(_{8\text{wt\%}}\)/I\(_2\)O\(_5\). The redshifts indicate weaker iodine-oxygen bonds due to the
presence of CB. In addition, no new peak is detected with CB-added samples which suggests no new carbon-iodine or carbon-oxide bonds are formed between CB and iodine oxide. Transmission FTIR-KBr pellet spectra (Figure S6.11) show no discernable changes in the spectra. Keeping in mind that the ATR is a surface sensitive technique while the KBr pellet method is a bulk technique I can conclude that the surface of I$_2$O$_5$ particles even under room temperature conditions is affected by CB in a manner to enable a lower decomposition temperature.

Figure 6. ATR-FTIR spectra of bare I$_2$O$_5$, CB$_{3\text{wt\%}}$/I$_2$O$_5$ and CB$_{8\text{wt\%}}$/I$_2$O$_5$ at room temperature showing I-O bond red-shift upon addition of CB

6.4. Conclusions

In this paper, I employed carbon (CB, CNT and FGS) as both a fuel and as an additive to aluminum and tantalum fuels to study the influence of a fuel without nascent oxide shell on initiation of iodine oxide-based thermites. I found that the initiation
temperature of CB/I₂O₅ is much lower than the initiation temperature of Al/I₂O₅ and Ta/I₂O₅. When CB is used as an additive to other fuels I observe a decrease in the overall initiation temperature and a lowering of the iodine release temperature to below that of the nascent oxidizer. Other carbon allotropes showed similar results. FTIR analysis indicated at CB lowered the iodine-oxygen bond energy of I₂O₅ on the surface and thus triggered this condensed phase reaction. These results indicate that CB can be employed as an additive to any metal fuel as a means to lower both the initiation and iodine release temperature.

6.5. Supplementary Information

Figure S6.1. SEM images of (a) HI₃O₈, (b) Ta/HI₃O₈, (c) CB/HI₃O₈ and (d) CB/Ta/HI₃O₈.
**Figure S6.2.** Representative plot showing the temporal release of CO$_2$ from CB$_{3\text{wt\%}}$/I$_2$O$_5$ when heated at ~$5 \times 10^5$ °C/s.

**Figure S6.3.** Sequential snapshots of (A) CB$_{3\text{wt\%}}$/Al/I$_2$O$_5$ and (B) CB$_{3\text{wt\%}}$/Ta/I$_2$O$_5$ thermites burning on a high rate heating ($5 \times 10^5$ °C/s) Pt wire under vacuum, captured by a high-speed camera. The labels in each image are the time elapsed after triggering.
Figure S6.4. The relation between iodine/oxygen release and ignition temperatures of HIO₃-based (A) and HI₂O₇-based thermites (B).
Figure S6.5. XRD and TGA/DSC results of commercial I$_2$O$_5$. 
Figure S6.6. Time-resolved mass spectra of CB.

Figure S6.7. DSC results of neat I$_2$O$_5$ and I$_2$O$_5$–based thermites.
Figure S6.8. TGA (A) and DSC (B) results of neat $\text{I}_2\text{O}_5$, CB/$\text{I}_2\text{O}_5$, Ta/$\text{I}_2\text{O}_5$ and CB$_{3\text{wt\%}}$/Ta/$\text{I}_2\text{O}_5$ thermites.
Figure S6.9. TGA/DSC of Ta under 100 mL/min of O₂ at a heating rate of 20 °C/min.
Figure S6.10. TGA/DSC results of thermites employing carbon allotropes as the fuel.
**Figure S6.11.** FTIR-KBr pellet spectra of bare $I_2O_5$, $CB_{3\, \text{wt}\%}/I_2O_5$ and $CB_{8\, \text{wt}\%}/I_2O_5$ at room temperature.

**Figure S6.12.** TGA and DSC results of CB in Ar or air.
Chapter 7: Enhancement to the combustion of Al/I$_2$O$_5$ thermites by addition of a secondary oxidizer

Overview

Developing new iodine-containing energetic materials is attracting growing interest due to its high energy release and potential high efficiency neutralization functions. One interesting phenomenon was found for all iodine-containing energetic materials: an ignition delay was always present in their pressure profiles while combusting. Considering the fact that some Al/iodine oxides have similar performance as to Al/CuO in term of peak pressure, an instant ignition for Al/iodine oxides might boost their combustion performance further. Here, this particularly unsolved question is going to be thoroughly investigated in this chapter. To shorten or eliminate this ignition delay, a secondary oxidizer CuO is incorporated into Al/I$_2$O$_5$ system and four different Al/I$_2$O$_5$/CuO thermites by varying the mass ratio between two oxidizers are prepared and studied in a constant volume combustion cell. Significant enhancement is observed for all four thermites and their peak pressures and pressurization rates are much higher than that of Al/I$_2$O$_5$ or Al/CuO. The disappearance of the ignition delay in their pressure profiles and the shortened burn time imply CuO addition indeed does work on accelerating the ignition of Al/I$_2$O$_5$ thermite and the overall reaction. To further understand the mechanism behind this improvement, the flame temperatures of the thermites while reacting are obtained via two different methods: color camera

* I would like to thank my collaborators for this study, Dylan J. Kline, Dr. Haiyang Wang, Miles C. Rehwoldt, and Dr. Michael R. Zachariah for all their hard work and input that made this chapter possible.
pyrometry and optical spectrometer measurement. The results confirm the flame temperature of Al/I2O5/CuO thermites are comparable to Al/I2O5, indicating the CuO addition doesn’t sacrifice the high flame temperature of Al/I2O5 system. In fact, the high flame temperature potentially promotes the decomposition of oxidizers and therefore improving the combustion performance of Al/I2O5 system. Furthermore, to expand the types of the secondary oxidizer, a weaker oxidizer Ag2O and stronger oxidizer AgFeO2 compared to CuO is also incorporated into Al/I2O5 thermite and demonstrate similar effects on promoting the combustion performance of Al/I2O5. And a synergetic effect is proposed here to explain the significant enhancement on the combustion performance of Al/I2O5 by introducing a secondary oxidizer.

7.1. Introduction

Biological warfare agents with high efficiency neutralization functions has gained increased attention due to the increased threat of bioterrorism and various new energetic materials has been developed over the past few decades [1-5]. Preliminary laboratory studies have suggested that an ideal neutralization process should generate not only a high temperature, but also release a long-lasting biocidal agent [6-12]. With the lack of effective biocidal agent release, conventional energetic materials suffer from low neutralization efficiency since the thermal neutralization mechanism is dominant in this case [6]. Therefore, it has been proposed that simultaneously delivering a rapid thermal pulse with a remnant biocidal agent would prolong the exposure time and improve the inactivation process [13].
Iodine-containing energetic materials have shown the most promise because of their excellent biocidal properties [14], compared to other biological energetic materials [15-17]. Different methods have been reported for incorporating elemental iodine into energetic materials [14, 18-20]. Dreizin et al. employed mechanically alloyed aluminum-iodine composites as a fuel in energetic formulations and the initiation and combustion tests in air indicated that higher iodine concentration lowers initiation temperatures and the combustion temperatures were not substantially diminished [12]. They also found improvements in terms of pressurization rate and maximum pressure at constant volume with 15 wt.% and 20 wt.% of I₂ [12]. Wang et al physically incorporated iodine molecules into Al/CuO thermite systems and found that the Al/CuO/I₂ thermite reaction rate was significantly decreased with increasing the iodine content while a decent burn rate could be achieved with high iodine content (67 wt.%) if special laminated structure was used.[19, 21]. Another efficient approach is to use iodine-containing oxy-compounds as an oxidizer, particularly iodine oxides/iodic acids.

Among all the iodine oxides/iodic acids (I₂O₅, I₄O₉, HI₃O₈, HIO₃, H₅IO₆, etc [22-24]), I₂O₅ is the most studied oxidizer in thermite systems [25-29] due to its relatively high iodine content (~76% iodine mass fraction). In these studies, aluminum particles with different sizes were chosen as the fuel due to its high reaction enthalpy, thermal conductivity and availability. With reported propagation velocities of up to ~2,000 m/s for loose ball-milled nano-aluminum and nano-scaled I₂O₅ (~10 nm) [28], I₂O₅ shows its high potential in aluminum-based thermites as an extremely aggressive oxidizer. Constant volume combustion tests also show nano-Al/micro-I₂O₅ outperforms
traditional aluminum-based thermites such as Al/micro-CuO and Al/micro-Fe$_2$O$_3$ [29].
A pre-ignition reaction was proposed to be the ignition trigger in which ionic I$_2$O$_5$ fragments diffused into the alumina passivated shell and to create some reactive complexes exothermically. [27, 30] However, this mechanism is far from clear as Smith et al reported that such pre-ignition reaction was not found for Al/nano crystalline I$_2$O$_5$. [31] I reported that aerosol route synthesized iodine oxides/iodic acids outperform the corresponding commercial ones in combustion cell tests, where in particular Al/a-HI$_3$O$_8$ has the highest pressurization rate and peak pressure and shortest burn time among all iodine-containing composites. [32] Later, I employed carbon as an additive or main fuel into iodine oxides-based energetic materials and reported that carbon addition can lower initiation and iodine release temperatures due to a surface interaction between carbon and iodine oxide. [33]

In this work, I conduct further studies on enhancing the combustion performance of Al/I$_2$O$_5$ thermite materials and understanding the mechanisms. For the fuel, once the aluminum core is heated near its melting point (~660 °C), obtaining sufficient mobility, it can diffuse through the passivated alumina shell and interact with any available oxidizer ultimately leading to initiation [34]. When aluminum combined with iodine oxides/iodic acids, an ignition delay with a constant time period (~0.16 ms) was found in the pressure profiles of all iodine oxides-based energetic materials based on the results in our previously published work. [32] To be more focused on understanding the mechanism behind this ignition delay, I$_2$O$_5$ was chosen as the subject in this work because it is relatively easier to prepare compare to other iodine oxides via aerosol spray pyrolysis and the yield is the highest according to Chapter 3. [18, 32]
The goal of this work is to shorten or even eliminate the ignition delay of Al/I$_2$O$_5$. To achieve that, a secondary oxidizer CuO featuring instant ignition (no delay) when mixed with aluminum is incorporated into the system. Various Al/I$_2$O$_5$ thermites with different CuO addition are prepared and examined in the combustion cell. Meanwhile, the flame temperatures of those employed thermites are also obtained in order to help us understanding the mechanism via two different methods: color camera pyrometry and optical spectrometer measurement. To expand the types of the secondary oxidizer, a weaker oxidizer Ag$_2$O and stronger oxidizer AgFeO$_2$ compared to CuO is also incorporated into Al/I$_2$O$_5$ thermite. Furthermore, a synergetic effect is proposed here to explain the significant enhancement on the reactivity of Al/I$_2$O$_5$ by introducing a secondary oxidizer.

7.2. Experimental

7.2.1 Materials:

The aluminum nanopowders (Al) (Alex, ~80 nm) were purchased from Novacentrix. The active Al was 81% by mass, determined by thermogravimetric analysis. Iodic acid and CuO purchased from Sigma-Aldrich were directly used as received. All the other chemicals were of analytical grade and used as purchased without further treatment.

7.2.2 Preparation of thermites:

Aluminum was stoichiometrically mixed with I$_2$O$_5$ based on the following equation in hexane followed by 30 minutes of sonication.

$$10\text{Al} + 3\text{I}_2\text{O}_5 \rightarrow 3\text{I}_2 + 5\text{Al}_2\text{O}_3$$
After room temperature evaporation of the solvent in a desiccator, the solid thermite powders were used.

7.2.3 T-Jump/TOFMS measurement and high-speed imaging:

The decomposition of oxide particles was investigated using a T-Jump/TOFMS [6]. Typically, a ~1 cm long platinum wire (76 um in width) with a thin layer coating of oxidizer sample was rapidly joule-heated to about 1200 °C by a 3 ms pulse at a heating rate of $5 \times 10^5$ °C/s. The current and voltage signals were recorded, and the temporal temperature of the wire was measured according to the Callendar–Van Dusen equation [34]. Mass spectra were measured every 0.1 ms. The detailed experimental set-up is given in our previous papers [6, 34].

To identify the point of initiation, a high-speed camera (Vision Research Phantom v12.0) was employed to record the combustion on the wire during heating. Initiation temperatures of thermite reactions in vacuum were measured from the correlation of optical emission from high speed imaging and temporal temperature of the wire and were further analyzed in combination with the temporal mass spectra. Each measurement was repeated 3 times.

7.2.4. High speed 32-channel spectrometer

The high-speed 32-channel spectrometer used to collect emission spectra and analyze temperature of combusting samples in the constant-volume combustion cell has been previously described and is only done so briefly here.[34] From the inner edge of the vessel, an assembly consisting of a Sapphire window, a plano convex lens (1
from inner edge), an ND2 filter, and 455nm color glass filter are in a 0.5" lens tube which is terminated with a SMA fiber optic adapter. Light is transmitted via the fiber optic cable to a 500mm, triple-grating, Czerny-Turner Imaging Spectrometer (Acton SP 500i) set to 150 groove/mm and slit width of 100µm to give a dispersion of 13nm/mm over 464-867nm wavelengths. The light is then passed into a 32-channel photomultiplier tube (Hamamatsu MC-PMT, H7260) which is interfaced to a high-speed data acquisition system (Vertilon IQSP580) which terminates the MC-PMT to 50Ω and measures current with a 14-bit resolution. The system is capable of measure at rates up to ~390kHz and MC-PMT voltages and spectrometer integration times are chosen to avoid sensor saturation and to remain within the linearity limit of the MC-PMT. Here I would like to acknowledge Dylan Kline for his help on the temperature measurements of thermites in combustion tests.

7.2.5. Combustion cell and optical spectrometer temperature measurement

Combustion properties of thermites were evaluated in a constant-volume combustion cell, with simultaneous pressure and optical emission measurements. In this study, 25 mg of thermite powders was loaded inside the cell (constant volume, ~20 cm³) and ignited by a resistively heated nichrome wire. The temporal pressure and optical emission from the thermite reaction were measured using a piezoelectric pressure sensor and a photodetector, respectively. Another port houses an optical assembly that collects and relays the emission to a spectrometer.[35] The cell was placed inside an artificial environment bag which was purged with argon to eliminate the influence of atmospheric oxygen while operating. More detailed information on the combustion cell
test can be found in our previous publications.[32, 35] Each sample was measured at least 3 times.

7.3. Results and discussion

Different iodine oxides and iodic acids had been studied within aluminum-based and tantalum-based thermite systems previously.[32] However, by comparing their pressure profile obtained from a constant volume combustion cell with that of Al/CuO, I noticed that there is an ignition delay for all Al/iodine oxides and Al/iodic acids thermites after trigger. Unlike those iodine-containing thermite systems, Al/CuO was ignited almost at the same time as the trigger. To present the difference clearer, a zoom-in view of the pressure profiles of Al/CuO and Al/I₂O₅ are shown in Figure 7.1. There is an ~0.3 ms ignition delay between the two pressure history profiles of the two nanothermites systems. Considering the burn time of Al/CuO is 0.31 ms, an ignition delay with a length almost the same as the ignition process itself cannot be ignored. Since aerosol-route synthesized I₂O₅ have particles size at around several micrometers, the ignition delay might be caused by the difference between the particle sizes of these two oxidizers.[32] To prove this theory, we plotted the pressure profiles of Al/micro-sized CuO, Al/a-HI₃O₈, Al/nano-sized CuO and Al/a-I₂O₅, data was obtained from our previous work and the result is shown in Figure S7.1. The fact that all micro-sized oxidizer-based thermites have ignition delay compare to Al/CuO proves our assumption. And the long burn time, about 1.3 ms, of Al/I₂O₅ might also be a consequence due to the size effect of the oxidizer.
To get rid of or even shorten this ignition delay, an obvious method is to incorporate nano-sized CuO into Al/I_2O_5 system. The thermal energy release by the instant ignition of Al/CuO might help ignite Al/I_2O_5 right away.

Figure 7.1. Temporal pressure traces of Al/CuO and Al/I_2O_5.

Thus, nano-sized CuO is incorporated into Al/I_2O_5 formulations with different ratios to form a series of Al/I_2O_5/CuO ternary systems. All thermites remain stoichiometric to avoid uncontrollable influences. Four ternary samples are prepared by varying the mass ratio between these two oxidizers and are referred as Al/I_2O_5/82% CuO, Al/I_2O_5/68% CuO, Al/I_2O_5/42% CuO and Al/I_2O_5/20% CuO (percentages represent the weight ratio of CuO in the oxidizers). Along with Al/I_2O_5 and Al/CuO, these six samples are examined in combustion cell and their pressure profiles are presented in Figure 7.2. As I expected, the ignition delay disappeared for all four ternary systems indicating the addition of nano-sized CuO can overcome the ignition difficulty of
Al/I_{2}O_{5}. However, what I do not expect is the fact that all four ternary systems significantly outperform Al/I_{2}O_{5} and Al/CuO in term of the peak pressure.

**Figure 7.2.** Temporal pressure traces of different Al/I_{2}O_{5}/CuO thermites. The number listed after the series name represent the weight fraction of CuO within oxidizers in each thermite.

To have a close look at the combustion performance of these thermites, the combustion cell results of all six samples are summarized and presented in Figure 7.3. Al/CuO with a lower peak pressure features a higher pressurization rate compare to
Al/I₂O₅ indicates the ignition delay/burn time of the later is much longer than the former. Again, strengthening our proposed method by incorporating CuO into Al/I₂O₅ to eliminate or shorten the ignition delay and hence further boost its combustion performance.

Figure 7.3A and 7.3B implies that the addition of CuO remarkably increase the peak pressure and pressurization rate of Al/I₂O₅. Apparently, these improvements are independent on the amount of incorporated CuO. As long as CuO is included in Al/I₂O₅, its combustion performance will be improved no matter how much CuO is added.

Surprisingly, by adding 20% of CuO within the oxidizers part, the peak pressure and pressurization rate of Al/I₂O₅ increased by about 4 and 26 times, respectively, the strongest improvement among all. Thus, a ternary system significantly outperforms each binary system. A similar result has been published previously as Al/Fe₂O₃/70% WO₃ outperforms both Al/Fe₂O₃ and Al/WO₃ in term of combustion cell results.[35] The authors explained: the lower ignition temperature of Al/WO₃ help igniting the ternary composite and its higher flame temperature promoting the further decomposition of Fe₂O₃, thus more gaseous oxygen participating the combustion, all those factors are the reason why Al/Fe₂O₃/70% WO₃ outperforms both Al/Fe₂O₃ and Al/WO₃. However, the peak pressure increase is only about 1.5 times compare to 4 times in this work and let alone with 26 times boost for the pressurization rate.

Among those ternary thermites systems, peak pressure and pressurization rate decreases when the CuO content increases. However, they all outperform the other binary thermite systems. With higher weight ratio of CuO in the oxidizers, the overall
combustion performance weakens within these four ternary systems. It could mean that Al/CuO combustion is acting as an on-site trigger to help the ignition of Al/I\textsubscript{2}O\textsubscript{5} thermite, but excessive amount could weaken the overall combustion performance of Al/I\textsubscript{2}O\textsubscript{5}/CuO system.

From Figure 7.3C, it could be seen that all four Al/I\textsubscript{2}O\textsubscript{5}/CuO thermites have a shorter burn time compare with Al/I\textsubscript{2}O\textsubscript{5}, indicating CuO addition can also accelerate the combustion of Al/I\textsubscript{2}O\textsubscript{5}. However, the results are more complicated when comparing with Al/CuO. In particular, the burn times of the Al/I\textsubscript{2}O\textsubscript{5}/CuO composites with more than 40% of CuO addition is almost the same as to Al/CuO indicating the rest iodine oxide plays no or insignificant effect on elongating burn time. As for Al/I\textsubscript{2}O\textsubscript{5}/20% CuO, it features a burn time three quarters of Al/CuO. With less incorporated CuO, the combustion of Al/I\textsubscript{2}O\textsubscript{5}/CuO composite is more violent and gives higher pressurization rate as well. Therefore, CuO and I\textsubscript{2}O\textsubscript{5} apparently are responsible for different functions in the ignition/reaction of Al/I\textsubscript{2}O\textsubscript{5}/CuO. The reaction process of these ternary systems could be summarized as follows: first Al/CuO helps shortening the ignition delay and overall burn time; then Al/I\textsubscript{2}O\textsubscript{5} ignites by the thermal shock of Al/CuO and then further combust violently contributing to the pressurization of the cell. To better understand the causes behind these phenomena, we need to turn our focus on the max emission results.

As discussed in our previous works, maximum optical emission in combustion cell test is positively correlated with the temperature in the system.[36] As shown in Figure 3D, the maximum optical emission of Al/I\textsubscript{2}O\textsubscript{5} is much higher than the others, demonstrating Al/I\textsubscript{2}O\textsubscript{5} reaction release lots of heat. This result is in a good correlation
with the thermal dynamic calculated data shown in Table 7.1 where Al/I$_2$O$_5$ reaction feature a very high adiabatic temperature (3952 °C). Even though Al/I$_2$O$_5$ reaction lasts a longer burn time, it can potentially lift the temperature inside the combustion cell up to a very high value. On the opposite, with a much lower adiabatic temperature, Al/CuO addition significantly lowers the maximum optical emission and in other word temperature. For Al/I$_2$O$_5$/20% CuO, its maximum optical emission (~2 V) lowers to half of Al/I$_2$O$_5$ reaction (3.6 V). And all the other three Al/I$_2$O$_5$/CuO composites give a similar maximum optical emission (0.8 V) as to Al/CuO. Thus, it is reasonable to conclude that the amount of CuO addition can affect the value of the temperature inside the combustion cell and probably the overall combustion performance even though it reaches a plateau when more than 40% of CuO is added. To prove these perspectives, temperature measurements were performed, and the results are going to be discussed below.
Figure 7.3. Combustion cell results of Al/I$_2$O$_3$ with different amount of nano-sized CuO addition.

Table 7.1. Thermodynamic equilibrium predictions of Al/I$_2$O$_3$, Al/CuO and Al/Ag$_2$O thermitesa.

<table>
<thead>
<tr>
<th>Thermite Reaction</th>
<th>Adiabatic Temperature (C)</th>
<th>Gas Production (mmol/g)</th>
<th>Major Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10\text{Al} + 3\text{I}_2\text{O}_3 \rightarrow 5\text{Al}_2\text{O}_3 + 3\text{I}_2$</td>
<td>3952</td>
<td>6.3</td>
<td>I$_2$</td>
</tr>
<tr>
<td>$2\text{Al} + 3\text{CuO} \rightarrow \text{Al}_2\text{O}_3 + 3\text{Cu}$</td>
<td>2570</td>
<td>5.4</td>
<td>Cu</td>
</tr>
<tr>
<td>$2\text{Al} + 3\text{Ag}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{Ag}$</td>
<td>2163</td>
<td>4.3</td>
<td>Ag</td>
</tr>
</tbody>
</table>

a: Assumptions: constant enthalpy and pressure with phase changes; without taking account of the oxide shell of aluminum. Data is taken from Fisher and Grubelich.[36]
The ignition temperature measurements were performed inside a T-Jump/TOFMS chamber and the whole event was simultaneously recorded by a high-speed color camera. Then the flame temperatures were obtained by color ratio pyrometry following a previously published method.[35] The typical snapshots and corresponding flame temperature map of Al/I₂O₅ are shown in Figure S7.2 as an example to show the process of color ratio pyrometry. The summarized average flame temperatures of all tested samples are plotted and presented in Figure 7.4. Consistent with the result shown in Figure 7.3D, Al/CuO thermite has the lowest flame temperature. However, all four ternary thermites have either similar or higher flame temperature than Al/I₂O₅. These results indicate the maximum optical emission results have some relation to the flame temperature but not in a significant way. As results shown in Figure 7.4, the addition of CuO into Al/I₂O₅ system affects its flame temperature differently according to the amount of additive secondary oxidizer. With less than 68% CuO addition, the flame temperature of Al/I₂O₅ reaches the maximum increase about 500 K for Al/I₂O₅/42% CuO sample. When the amount of CuO addition increases to 82%, the flame temperature of Al/I₂O₅ remains almost the same as its original value indicating Al/I₂O₅ could remain the flame temperature to a high value even with only 18% of I₂O₅ in the oxidizer. A more convincing result could be seen if we change the subject to Al/CuO. The flame temperature of Al/CuO jumps from 3500 K to 4760 K with just 18% of incorporated I₂O₅ within the system, again confirms the reaction between aluminum and I₂O₅ generates much more heats than that of aluminum and CuO.
To verify whether the flame temperature data obtained from color camera pyrometry is solid, the flame temperature of Al/I₂O₅ and Al/I₂O₅/20% CuO thermites in a combustion cell were obtained according to a previous published method and the results are presented in Figure 7.5.[35] The average flame temperatures of Al/I₂O₅ and Al/I₂O₅/20% CuO thermites are both located at ~5000 K, which is very close to the temperatures obtained from the color camera pyrometry method.

Therefore, the reasons for the significant enhancement of the combustion performance of Al/I₂O₅ by addition of a small amount of CuO could be summarized as follows: the additive Al/CuO shortens the ignition delay of Al/I₂O₅ (as shown in Figure 7.2); that leads to enormous amount of gas formation for aluminum to react with and then the extremely high flame temperature of Al/I₂O₅ boost the pressure inside the combustion cell further. All those events happen around the same time and produce a synergetic effect on enhancing the overall combustion performance of Al/I₂O₅.
As for the ignition mechanism of Al/I\textsubscript{2}O\textsubscript{5}/CuO thermites, heat released from the instant ignition of Al/CuO helps igniting Al/I\textsubscript{2}O\textsubscript{5}; then the enormous amount of heat released from Al/I\textsubscript{2}O\textsubscript{5} thermite reaction further promoting the decomposition of the oxidizers; with more oxygen gas and higher temperature, the oxidization of aluminum is further accelerated.

To expand the option for the secondary oxidizer, a previously reported very weak oxidizer Ag\textsubscript{2}O was incorporated into Al/I\textsubscript{2}O\textsubscript{5} system to investigate its effect on the combustion performance of Al/I\textsubscript{2}O\textsubscript{5}.[2] Three Al/I\textsubscript{2}O\textsubscript{5}/Ag\textsubscript{2}O ternary thermites were prepared and tested, including Al/I\textsubscript{2}O\textsubscript{5}/19% Ag\textsubscript{2}O, Al/I\textsubscript{2}O\textsubscript{5}/41% Ag\textsubscript{2}O and Al/I\textsubscript{2}O\textsubscript{5}/68% Ag\textsubscript{2}O. Along with Al/CuO, Al/I\textsubscript{2}O\textsubscript{5} and Al/Ag\textsubscript{2}O, their pressure profiles are plotted in Figure S7.3. and the combustion cell results are summarized in Figure 6. The fact that the pressure profile of Al/Ag\textsubscript{2}O is almost like a flat line implies the additive Al/Ag\textsubscript{2}O is very much a dead weight for the ternary thermites. In other words, the Al/Ag\textsubscript{2}O addition could not assist the combustion performance of Al/I\textsubscript{2}O\textsubscript{5}. 

**Figure 7.5.** Temporal reaction temperature profiles of Al/I\textsubscript{2}O\textsubscript{5} (A) and Al/I\textsubscript{2}O\textsubscript{5}/20% CuO (B) obtained via high speed spectrometer temperature measurement.
However, all three Al/I₂O₅/Ag₂O thermites outperform Al/I₂O₅, just like what CuO has done for Al/I₂O₅.

Similar to Al/I₂O₅/CuO thermites, the peak pressure and pressurization rate of Al/I₂O₅/Ag₂O thermite decreases when the amount of Ag₂O increases. As shown in Figure 7.6A and 7.6B, although Al/I₂O₅/68% Ag₂O thermite has a similar peak pressure as to Al/I₂O₅, its pressurization rate is still higher than either Al/I₂O₅ or Al/Ag₂O, implies the combustion performance of Al/I₂O₅ can be enchanted even with incorporating a much weaker secondary oxidizer. The burn time of Al/I₂O₅/Ag₂O thermites is very close to that of Al/Ag₂O and is slightly shorter than that of Al/I₂O₅, except for Al/I₂O₅/68% Ag₂O thermite that feature a burn time twice longer than that of Al/I₂O₅. A longer burn time means less violent thermite reactions probably due to the inefficient decomposition of Ag₂O and/or the bad thermal conductivity of I₂O₅.[32] In addition, the pressure profile (the purple dotted line) of Al/I₂O₅/68% Ag₂O thermite (Figure S7.3) shows a similar trend as to Al/Ag₂O but with a higher peak pressure. The appearance of an obvious ignition delay indicates the combustion performance of Al/I₂O₅/Ag₂O thermite would be further weakening with increasing Ag₂O amount. Considering no ignition delay was found in the pressure profiles of Al/I₂O₅/CuO thermites, a much weaker oxidizer does have its limitation on influencing the ignition and combustion performance of Al/I₂O₅.

The ignition/reaction mechanism of Al/I₂O₅/Ag₂O thermite should be very similar to that of Al/I₂O₅/CuO thermite with only one exception that Ag₂O being a much weaker oxidizer and affecting the gas formation and the oxidization of aluminum. What interesting is that ignition delay exists in both Al/I₂O₅ and Al/Ag₂O cases but not for
Al/I\(_2\)O\(_5\)/Ag\(_2\)O thermite. The ignition temperature results shown in Figure S7.4 indicate Al/I\(_2\)O\(_5\) and Al/Ag\(_2\)O have almost the same ignition temperature; however, Al/I\(_2\)O\(_5\)/Ag\(_2\)O thermites feature a lower ignition temperature especially for Al/I\(_2\)O\(_5\)/41\% Ag\(_2\)O that has a ignition temperature of \(~350\) °C. Therefore, it has to be Al/Ag\(_2\)O thermite the one who ignites first and the generated heat help igniting Al/I\(_2\)O\(_5\) thermite. Otherwise, Al/I\(_2\)O\(_5\) thermite could not be ignited instantly based on the results shown in Figure S7.2. Even though the limitation is there, an enhancement on the combustion performance of Al/I\(_2\)O\(_5\) is still observed when Ag\(_2\)O is incorporated into the system.

AgFeO\(_2\), a stronger oxidizer than CuO, is also tested in this work and the combustion results are presented in Figure 7.6 as well. As I expected, AgFeO\(_2\) shares a similar effect as to CuO. Therefore, it is reasonable to assume that the combustion performance of Al/I\(_2\)O\(_5\) can always be enhanced by addition of a secondary metal oxidizer. However, more oxidizers are needed to be added into Al/I\(_2\)O\(_5\) system to further verify this argument.
A secondary oxidizer CuO was incorporated into Al/I\textsubscript{2}O\textsubscript{5} system to shorten or eliminate the ignition delay of the combustion of Al/I\textsubscript{2}O\textsubscript{5}. By investigating the combustion performance of four different Al/I\textsubscript{2}O\textsubscript{5}/CuO thermites varying the mass ratio between two oxidizers and the other two Al/I\textsubscript{2}O\textsubscript{5} and Al/CuO thermites in a constant volume combustion cell, significant enhancement is observed for all four thermites and their peak pressures and pressurization rates are much higher than that of Al/I\textsubscript{2}O\textsubscript{5} or Al/CuO. The disappearance of the ignition delay in their pressure profiles...
and the shortened burn time imply CuO addition indeed does work on accelerating the ignition of Al/I\textsubscript{2}O\textsubscript{5} thermite and the overall reaction. In addition, the flame temperatures of the thermites while reacting were obtained and the results indicate the flame temperature of Al/I\textsubscript{2}O\textsubscript{5}/CuO thermites are almost the same as to Al/I\textsubscript{2}O\textsubscript{5}, indicating the CuO addition will not sacrifice the high flame temperature of Al/I\textsubscript{2}O\textsubscript{5} system.

Therefore, a mechanism was proposed in this work to account for this unexpected improvement: the additive Al/CuO shortens the ignition delay of Al/I\textsubscript{2}O\textsubscript{5}; that leads to enormous amount of gas formation for aluminum to react and then the extremely high flame temperature of Al/I\textsubscript{2}O\textsubscript{5} boost the pressure inside the combustion cell further. All those events happen around the same time and produce a synergetic effect to enhance the combustion performance of Al/I\textsubscript{2}O\textsubscript{5}.

A weaker oxidizer Ag\textsubscript{2}O and stronger oxidizer AgFeO\textsubscript{2} compared to CuO is also incorporated into Al/I\textsubscript{2}O\textsubscript{5} thermite, respectively, in order to potentially expand the options for the secondary oxidizer. The results demonstrate both Ag\textsubscript{2}O and AgFeO\textsubscript{2} have similar effects on promoting the combustion performance of Al/I\textsubscript{2}O\textsubscript{5}. Although more oxidizers need to be examined furthermore, it is reasonable to assume the combustion performance of Al/I\textsubscript{2}O\textsubscript{5} could be enhanced by just incorporating a secondary oxidizer, which make the iodine-containing energetic materials more tunable and controllable.
7.5. Supplemental Information

**Figure S7.1.** Temporal pressure traces of different thermites from ref (combustion and flame paper).

**Figure S7.2.** The typical snapshots and corresponding flame temperature map of Al/I$_2$O$_5$. 
Figure S7.3. Temporal pressure traces of different Al/I₂O₅/CuO thermites. The number listed after the series name represent the weight fraction of CuO within oxidizers in each thermite.

Figure S7.4. The ignition temperatures of Al/I₂O₅/Ag₂O thermites within T-Jump/TOFMS.
Chapter 8: Silver Ferrite: a superior oxidizer for thermite-driven biocidal nanoenergetic materials*

Overview

Silver-containing oxidizers are of interest as biocidal components in energetic application such as thermites due to their biocidal agent delivery. In this study, AgFeO$_2$, was evaluated as an oxidizer in aluminum-based thermite system. This novel oxidizer AgFeO$_2$ particles were prepared via a wet-chemistry method and the structure, morphologies and thermal behavior were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis and differential scanning calorimetry, and time-resolved temperature-jump time-of-flight mass spectrometry (T-Jump/TOFMS). The results indicate the decomposition pathways of AgFeO$_2$ vary with heating rates from a two-step at low heating rate to a single step at high heating rate. Ignition of Al/AgFeO$_2$ at a temperature just above the oxygen release temperature and is very similar to Al/CuO. However, with a pressurization rate three times of Al/CuO, Al/AgFeO$_2$ yields a comparable result as to Al/hollow-CuO or Al/KClO$_4$/CuO, with a simpler preparation method. The post combustion products demonstrated that the Al/AgFeO$_2$ thermite reaction produces a fine dispersion of elemental nanosized silver particles which coats the larger alumina particles and is thus bioavailable.

8.1. Introduction

High efficiency neutralization of biological warfare agents has become of increased importance due to the enhanced threat of bioterrorism [1-4]. Preliminary laboratory studies have suggested that an ideal neutralization process should contain not only a high thermal event but also a long-lasting biocidal agent release [5-11]. The main problem with conventional energetic materials is low neutralization efficiency since a thermal neutralization mechanism is nominally dominant [5]. Therefore, it has been proposed that simultaneously delivering a rapid thermal pulse with a remnant biocidal agent would prolong the exposure time and improve the inactivation process [12].

Reactive materials are a class of energetic materials containing separated fuels and oxidizers and featuring an extremely high exothermicity, intensive light emission and shock generation by the self-sustained reaction [13-15]. When metal and metal oxide are employed as the fuel and oxidizer, respectively, the intense exothermic metal/metal oxide reaction is commonly referred to a thermite reaction. This reaction is self-propagating once the ignition starts and the kinetics of the reaction are known to be accelerated when the fuel and oxidizer are at the nanoscale, resulting from the increased interfacial contact and reduced characteristic diffusion length scale. The most widely adopted metal is aluminum due to its abundance and competitive reactivity when compared with other metals [16]. Various oxidizers, such as metal oxides [17-25], iodine oxides [26-31], sulfates [32, 33], iodates [12, 34, 35], potassium salts [36, 37] and etc, have been employed in formulation of thermites. Among all, halogens-containing and silver-containing oxidizers have drawn attention because of their excellent biocidal properties [38-42]. For halogens, iodine stands out owing to its
strong neutralization effect and different iodine-containing oxy-compounds, such as metal iodates and iodine oxides [5, 12, 18-32, 34-36, 43], have been studied in thermite systems.

As to silver, it has been pointed out that silver exhibits biocidal properties in the forms of metallic Ag particles and silver ions in a humid environment [44]. Since most of the products of thermite combustion tend to be primarily in the condensed phase [2], metallic silver particles are the focus of this work. As indicated by Morones et al [45] and Smetana et al [46], small particle sizes are necessary for silver particles to perform well in biocidal activities. To deliver not only a high thermal event but also a large amount of small silver particles as the active biocidal sites is the goal of this work.

When it comes to silver-containing oxidizers, Ag_2O was the obvious choice to be considered as an oxidizer in an aluminum-based thermite system. In 2010, Clark et al [47] investigated the combustion performance and biocidal abilities of both Al/I_2O_5 and Al/Ag_2O thermites using a homemade biocidal reaction chamber. They concluded Al/I_2O_5 thermite exhibited significant spore neutralization owing to the generation of lot of iodine gas. In 2011, Russell et al [48] further studied the flame propagation behaviors of Al/I_2O_5 and Al/Ag_2O thermites using mechanical impact and thermal initiation. The results show that Al/Ag_2O features a lower average flame propagation by about 2.5 times in thermal ignition tests but produce much more energy than Al/I_2O_5 in impact-driven ignition tests. They also argued that the energy release of the thermite reactions is significantly enhanced by reducing the sizes of the oxidizers particles. In the same year, Sullivan et al [5] investigated the performance of AgIO_3 as an oxidizer in aluminum-based thermite because it decomposed to O_2, O and I gases when heated.
at an ultra-high heating rate. Silver was not observed in the mass spectra probably because the temperature was high enough to reach the adiabatic flame temperature and thus could not vaporize silver. However, Al/AgIO₃ considerably outperformed Al/CuO in pressurization rate due to a large number of gaseous products released from AgIO₃; however, its high combustion performance was mitigated by the fact that the reaction products were found to form AgI instead of elemental silver and iodine, thus obstructing its usage in biocidal applications.

Sullivan et al [2] subsequently synthesized nano-Ag₂O particles and investigated its reactivity as an oxidizer in biocidal energetic systems since it produces high yields of antimicrobial silver as one of the combustion products. They found that Ag₂O alone performs poorly in terms of pressurization rate and burn time, but its performance is significantly improved when combined with one more reactive oxidizer, such as AgIO₃ or CuO. The morphology of the final products was also studied and indicated that abundant active sites of silver particles were sacrificed since some silver particles were trapped within the interior of other products, which might to some extent affect its biocidal activity. Inspired by the fact that CuO addition improve the performance of Al/Ag₂O extensively, I embed the extra oxidizer into Ag₂O molecularly, which means the oxidizer used in this work is going to be a composite metal oxide. Lately, NiCo₂O₄ [49] and NiFe₂O₄ [50] have been employed as oxidizer in aluminum-based thermites and both feature excellent heat release and intense thermite reaction. Among all Ag-containing composite metal oxides, AgFeO₂ as a molecularly mixed oxidizer of Ag₂O and Fe₂O₃ with a delafossite structure becomes the first one to explore this idea here. In addition, Fe₂O₃ has been proven to be very poor oxidizer in Al-based thermite system
[36], it could potentially make our point even more sound if AgFeO₂ made of two poor oxides (Ag₂O and Fe₂O₃) became a strong oxidizer.

A wet-chemistry method was adopted here for the preparation of AgFeO₂ and its thermal behavior were investigated using a low heating rate thermogravimetric analysis and differential scanning calorimetry in an argon environment. Time-resolved temperature-jump time-of-flight mass spectrometry (T-Jump/TOFMS) was also employed to evaluate the decomposition behaviors of bare AgFeO₂ or Al/AgFeO₂ thermites under rapid heating rates, enabling me to probe the reaction process on a time scale close to that of a combustion event. The results indicate that the decomposition pathways of AgFeO₂ vary in term of heating rates. For a comparison purpose, Al/CuO, Al/Ag₂O and Al/Ag₂O/Fe₂O₃ were also included in this chapter. A high-speed camera coupled with T-Jump/TOFMS simultaneously captured optical emission from the ignition/reaction of the thermites allowing us to obtain the ignition time, and corresponding ignition temperature. In addition, constant volume combustion cell tests were performed on aluminum-based thermites. The post combustion products were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and energy-disperse X-ray spectroscopy. The results demonstrated that the Al/AgFeO₂ thermite reaction produce an enormous amount of nanosized silver particles and feature the best combustion performance in this work.
8.2. Experimental Details

8.2.1. Materials

The aluminum nanopowders (Al) (Alex, ~80 nm) was purchased from Novacentrix. The active Al was 81 % by mass, determined by TGA. All metal oxide nanopowders (< 50 nm) purchased from Sigma-Aldrich was directly used as received. All the other chemicals were of analytical grade and used as purchased without further treatment.

8.2.2. Preparation of AgFeO₂

AgFeO₂ powders were prepared via a co-precipitation method. For this, 2.66 mmol of Fe(NO₃)₃•9H₂O and 2.66 mmol of AgNO₃ were dissolved in 20 mL of water and stirred for 30 minutes. The solution was then heated to 80 °C and stirred for one hour. Then, 1.5 M of NaOH solution was added dropwise into the solution until its pH reaches 13, followed by another 6 hours of stirring on a hot plate (80 °C). The prepared AgFeO₂ powders could be easily isolated from the solution by vacuum filtration and were purified by successively washing with copious amount of distilled water and absolute ethanol. Finally, the product was dried in an oven at 70 °C.

8.2.3. Preparation of Ag₂O

Ag₂O powders were prepared by adding 0.025 M NaOH solution dropwise into 80 mL of AgNO₃ solution (0.005 M) with stirring until the solution become a grey-yellow colloidal suspension. The suspension was kept at 60 °C for another 2 hours to ensure complete reaction. The prepared Ag₂O powders were collected by centrifugation and
washed with distilled water and then absolute ethanol three times. The solid pure Ag$_2$O was obtained after being dried in an oven at 70 °C for 10 hours.

8.2.4. Preparation of thermites

Aluminum nanopowders was stoichiometric mixed with AgFeO$_2$, Ag$_2$O, CuO and Fe$_2$O$_3$ based on the following equations, respectively, in dry hexane followed by 30 minutes sonication. After room temperature evaporation of the solvent the solid thermite powders were collected.

\[
\begin{align*}
4\text{Al} + 3\text{AgFeO}_2 & \rightarrow 3\text{Ag} + 3\text{Fe} + 2\text{Al}_2\text{O}_3, \Delta H_{\text{calculated}} = -1760 \text{ kJ/mol} \\
2\text{Al} + 3\text{Ag}_2\text{O} & \rightarrow 6\text{Ag} + \text{Al}_2\text{O}_3, \Delta H_{\text{calculated}} = -1374 \text{ kJ/mol} \\
2\text{Al} + 3\text{CuO} & \rightarrow 3\text{Cu} + \text{Al}_2\text{O}_3, \Delta H_{\text{calculated}} = -1109 \text{ kJ/mol} \\
4\text{Al} + 3\text{Ag}_2\text{O} + \text{Fe}_2\text{O}_3 & \rightarrow 6\text{Ag} + 2\text{Fe} + 2\text{Al}_2\text{O}_3, \Delta H_{\text{calculated}} = -2125 \text{ kJ/mol}
\end{align*}
\]

8.2.5. T-Jump/TOFMS measurement and high-speed imaging

The decomposition of oxides particles was investigated using a custom T-Jump/TOFMS [5] Typically, a ~1 cm long platinum wire (76 um in width) with a thin coating of oxidizer or thermite sample was rapidly joule-heated to about 1200 °C by a 3 ms pulse at a heating rate of ~$10^5$ °C/s. The current and voltage signals were recorded, and the temporal temperature on the wire was measured according to the Callendar–Van Dusen equation. MS spectra were measured every 0.1 ms. The detailed experimental set-up is given in our previous papers [5, 32].

To identify the point of ignition a high-speed camera (Vision Research Phantom v12.0) was employed to record the combustion on the wire during heating. Ignition temperatures of thermite reactions in vacuum were measured from the correlation of
optical emission from high speed imaging and temporal temperature of the wire and were further analyzed in combination with the temporal mass spectra. Each experiment was repeated 3 times.

8.2.6. X-Ray Diffraction (XRD) measurement and Rietveld refinement

The as-prepared samples were characterized by powder X-ray diffraction. Diffraction pattern was measured using Cu Kα radiation in Bragg-Brentano geometry on Bruker D8 Advance powder diffractometer equipped with incident beam Soller slits, Ni β-filter and LynxEye position sensitive detector. Data were collected from 10° to 90° 2θ with a step size of 0.01578° and counting time of 1 sec per step (total exposure time of 180 sec per step).

8.2.7. Thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) measurement

Thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) was performed using a TA Instruments SDT Q600. The analysis was performed under a 100 mL min⁻¹ argon flow with ~ 1.0 mg samples placed into an alumina pan and heated from room temperature up to 1000 °C at a rate of 10 °C min⁻¹ in argon atmosphere.

8.2.8. Morphologies and structures characterizations Transmission Electronic Microscopy (TEM)

Transmission electronic microscopy (TEM, JEOL JEM 2100 FEG) and scanning electronic microscopy (SEM, Hitachi Su-70) were used to investigate morphologies
and structures of thermites. Elemental distribution in the thermites was analyzed by Energy-disperse X-ray spectroscopy (EDS) on both SEM and TEM.

8.2.9. Combustion test

Combustion properties of thermites were evaluated in a constant-volume combustion cell, with simultaneous pressure and optical emission measurements. In this study, 25 mg of thermite powders was loaded inside the cell (constant volume, ~13 cm³) and ignited by a resistively heated nichrome wire. The temporal pressure and optical emission from the thermite reaction were measured using a piezoelectric pressure sensor and a photodetector, respectively. More detailed information on the combustion cell test can be found in our previous publications [21, 25, 29]. Each experiment was repeated at least 3 times.

8.3. Results and discussions

8.3.1. Synthesis and characterization of AgFeO₂

XRD of as-prepared materials shown in Figure 8.1A indicates that silver ferrite was successfully prepared. The particles have an oval shape with particle size of ~40 nm based on the SEM image shown in Figure 8.1B, and suggests it might be a very good oxidizer in a thermite system due to its small size [32].
The thermal stability of AgFeO$_2$ was studied with a TGA in Ar at a heating rate of 10 °C/min. The result shown in Figure 8.2 indicates a ~4% weight loss at around 650 °C, corresponding to O$_2$ gas release based on equation (8.1). To determine the composition of the remaining material, XRD shown in Figure 8.2B indicates the formation of both Fe$_2$O$_3$ and Ag.

$$2\text{AgFeO}_2 \rightarrow 2\text{Ag} + \text{Fe}_2\text{O}_3 + \frac{1}{2}\text{O}_2$$  \hspace{1cm} \text{Equation (8.1)}

**Figure 8.1.** XRD spectrum (A) and SEM image (B) of AgFeO$_2$ prepared via co-precipitation

**Figure 8.2.** TGA result of AgFeO$_2$ in Ar at a heating rate of 10 °C/min (A); AgFeO$_2$ decomposed product after heated to 1000 °C (B).
High heating rate decomposition of AgFeO$_2$ was investigated using TOFMS/T-Jump (3 ms, heating rate $\sim$5×10$^5$ °C/s). Figure 8.3 shows the temporal evolution of O$_2$ from AgFeO$_2$ during rapid heating. Oxygen was first detected at around 685 °C which is slightly higher than the onset decomposition temperature under low heating rate TGA. Only one O$_2$ signal stage is observed indicating the decomposition of AgFeO$_2$ is a one-step event at high heating rates conditions, as compared to its multistage decomposition behavior at low heating rates as discussed previously.

Time-resolved T-jump mass spectra from rapid heating of AgFeO$_2$ at 1.6-2.2 ms is shown in Figure S8.1 to further explore its decomposition process. Apparently, the onset decomposition of AgFeO$_2$ started at around 1.8 ms (685 °C) with the appearance of a small O$_2$ peak. For mass spectra taken at prior times, H$_2$O$^+$, OH$^+$, CO$^+$/N$_2$$^+$ peaks are attributed to the background [18]. Above the decomposition temperature, no new peak except for O$_2$ peak is found again suggests a one-step decomposition of AgFeO$_2$ at high heating rate. CO$_2^+$ was also observed we attribute to decomposition products of the precursor salt residue on the AgFeO$_2$ surface [17].

![Figure 8.3. Temperature and O$_2$ temporal profile of AgFeO$_2$.](image)
8.3.2. Ignition of Al/AgFeO$_2$ nanothermite

To evaluate the performance of AgFeO$_2$ as an oxidizer in Al-based thermite, physical mixtures of nanosized aluminum and AgFeO$_2$ were made, following 30 min sonication of the mixture in dry hexane. Sequential snapshot of Al/AgFeO$_2$ ignition during high-rate heating under vacuum were captured using a high-speed camera and is shown in Figure 8.4. Optical emission from Al/AgFeO$_2$ reaction was first observed at 1.662 ms with a corresponding wire temperature of ~740 °C as a sign of ignition. Multiple ignition points are observed in the prior time and then merge into a large bright flame indicating the generation of a lot of heat. One should also notice that, upon ignition, thousands of bright dots were rapidly ejected out from the reactants coated on the Pt wire (even more bright dots appeared when ignited in an argon environment as shown in Figure S8.2). The burn time of the thermite in T-jump chamber could be roughly obtained based on the visual flame and is about 0.3 ms, which is almost the same as the value obtained from the combustion cell test discussed below.

Ag$_2$O was included as an oxidizer in Al-based thermites as a control. As the most common used oxidizer, CuO was also included as a standard reference. Since AgFeO$_2$ (Ag$_2$Fe$_2$O$_4$) can be molecularly written as Ag$_2$O and Fe$_2$O$_3$, a binary mixture Ag$_2$O-Fe$_2$O$_3$ with 1/1 molar ratio is also included for comparison.

Figure 8.5 shows the relationship between O$_2$ release temperature in neat oxides and the ignition temperature of corresponding thermites under vacuum. There is a good correlation between the oxygen release from the bare oxidizer and ignition of Al/Fe$_2$O$_3$ and Al/AgFeO$_2$. Al/Fe$_2$O$_3$ has a very high ignition temperature due to the poor performance of Fe$_2$O$_3$ as an oxidizer [24]. On the other hand, Al/Ag$_2$O thermite ignited
at around ~660 °C, essentially the melting temperature of aluminum. Considering Ag$_2$O releases oxygen at around 520 °C, it is reasonable to conclude that the ignition of Al/Ag$_2$O thermite is limited to the melting phase of aluminum like most Al/metal oxides systems [19]. In fact, the ignition temperatures of the other three samples are all higher than the melting point of aluminum indicates that gaseous oxygen released from the decomposition of oxidizers, was insufficient to ignite aluminum when it is still in the solid phase.

Al/Ag$_2$O/Fe$_2$O$_3$ ternary thermite ignited at around 800 °C much higher than its oxygen release temperature (520 °C). Considering Al/Ag$_2$O and Al/Fe$_2$O$_3$ ignited at around 660 and 940 °C, respectively, an ignition temperature of about 800 °C is reasonable for the ternary system Al/Ag$_2$O/Fe$_2$O$_3$. The Fe$_2$O$_3$ addition is more likely hindering/weakening the ignition/reaction of the ternary system due to its weak reactivity in Al-based thermites [36].

As to Al/AgFeO$_2$, it ignited at a temperature close to the oxygen release temperature of the corresponding oxidizer and higher than the melting temperature of aluminum following an ignition mechanism similar to Al/Fe$_2$O$_3$ and Al/CuO [18, 19]. Moreover, the fact that the ignition temperature of Al/Fe$_2$O$_3$ is much higher than that of Al/AgFeO$_2$ implies the oxygen involved with Al/AgFeO$_2$ ignition come from AgFeO$_2$ rather than the first-stage decomposed product Fe$_2$O$_3$ as indicated in TGA. Since only one oxygen release stage appeared at the mass spectra and the violent reaction of Al/AgFeO$_2$ at 1.7 ms (~780 °C) implies decomposition of AgFeO$_2$ is a one-step process during Al/AgFeO$_2$ thermite reaction at high heating rate.
Figure 8.4. Sequential snapshots of Al/AgFeO$_2$ burning on a high-rate heating Pt wire in T-Jump chamber (in vacuum). The labels in each image are the time elapse after triggering.

Figure 8.5. Ignition temperature vs. oxygen release temperature from the corresponding oxidizer. The diagonal dash line presents a perfect correlation.
8.3.3. Combustion performance of Al/AgFeO$_2$ nanothermite

The combustion performance of Al/AgFeO$_2$ at room atmosphere was studied using a constant volume combustion cell, and the results are summarized in Table 8.1. The pressurization rate and peak pressure in Al/AgFeO$_2$ reaction are 6200 kPa/ms and 325 kPa, respectively, which are considerably higher than those of nanothermite reaction of Al/CuO. A direct comparison between the temporal pressure traces of Al/AgFeO$_2$ and Al/CuO was shown in Figure 8.6A in which the first peak was used to determine the corresponding pressurization rate. Clearly, Al/AgFeO$_2$ reaction reaches its first peak with a faster rate and higher peak value compared with Al/CuO. It has been claimed in our previous works that gaseous species release from the decomposition of the oxidizer is the main cause for the pressurization, which can occur much earlier than ignition/combustion [36, 51]. The fact that AgFeO$_2$ (~16%) which has a lower oxygen weight ratio than CuO (~20%) suggests the O$_2$ release rate of AgFeO$_2$ must be higher than that of CuO in order to output such high pressure. In addition, the optical signals peak much later than the corresponding pressure peaks for both Al/CuO (~0.5 ms) and Al/AgFeO$_2$ (0.9 ms) implying a similar mechanism [51, 52]. Therefore, similar to Al/CuO [36], the ignition/reaction mechanism of Al/AgFeO$_2$ is summarized as follows: AgFeO$_2$ releases O$_2$ gas (~690 °C) and the aluminum core becomes mobile (~633 °C); and the mixture ignites (~740 °C, Figure 8.5) and the generated heat further promote the decomposition of AgFeO$_2$ to pressurize the system.

Moreover, with a pressurization rate three times of Al/CuO, Al/AgFeO$_2$ yields a comparable result as prior work on Al/hollow-CuO [25] or Al/KClO$_4$/CuO [36], which
make AgFeO$_2$ a powerful replacement owing to its simpler and cheaper preparation method.

Sullivan et al [2] has previously reported that Al/Ag$_2$O suffers a poor combustion performance in terms of both pressurization rate and peak pressure and incorporation of a small fraction of CuO into the Al/Ag$_2$O system improved its combustion performances extensively to even close to the reactivity of Al/CuO. An explanation was provided by Sullivan et al that CuO addition can increase the reaction temperature and thus further enhance the performance of Ag$_2$O as an oxidizer. Consistent with this reported result, Al/Ag$_2$O performs poorly in the combustion cell test due to to early a release of O$_2$ [2]; however, Fe$_2$O$_3$ addition does not show much improvement to Al/Ag$_2$O system as CuO does. Instead of improving, Fe$_2$O$_3$ even weaken the combustion performance of Al/Ag$_2$O system considering Al/Ag$_2$O/Fe$_2$O$_3$ features the worst pressurization rate and burn time. Thermodynamic equilibrium predictions of Al/CuO, Al/Ag$_2$O and Al/Fe$_2$O$_3$ thermites by Fisher and Grubelich [2, 26, 53] are shown in Table 8.2 where we can see that both CuO and Ag$_2$O should perform significantly better than Fe$_2$O$_3$ in terms of gas production. And this is consistent with our experimental data shown in Table 8.1. In detail, unlike CuO that can rapidly release O$_2$, Fe$_2$O$_3$ cannot efficiently decompose and upon decomposition most of the oxygen is still fixed as solid FeO [36], which leads to its decomposition as the rate-limiting step for Al/Ag$_2$O/Fe$_2$O$_3$ reaction and therefore weakened combustion performance. In fact, Fe$_2$O$_3$ has been introduced previously as a moderator to weaken the reactivities of Al/KMnO$_4$ [24] and Al/KClO$_4$ [36].
Al/AgFeO$_2$ significantly outperforms Al/Ag$_2$O/Fe$_2$O$_3$ by a scale of almost 100 in pressurization rate and about 4 in peak pressure. The fact that Al/AgFeO$_2$ and Al/Ag$_2$O/Fe$_2$O$_3$ share the exact same elemental compositions indicates molecularly incorporation of Ag$_2$O into Fe$_2$O$_3$ outperforms the mechanically mixed Ag$_2$O/Fe$_2$O$_3$ when they were employed as oxidizers in aluminum-based thermites.

The burn time of the thermite reactions measured in the combustion cell are shown in Table 8.1. Clearly, Al/AgFeO$_2$ features the shortest burn time which makes it the most violent thermite among the four examined. A direct comparison of the optical emission trace of Al/AgFeO$_2$ and Al/CuO was shown in Figure 8.6B. The Al/CuO reaction has a four-times higher peak optical emission but 0.1 ms longer burn time compare with those of Al/AgFeO$_2$. This result indicates that Al/AgFeO$_2$ is a weaker heat generator than Al/CuO; but reacts more rapidly. In general, AgFeO$_2$ is the best oxidizer among those four in the aluminum-based thermite system from both pressurization and optical emission perspectives.

<table>
<thead>
<tr>
<th>Thermites</th>
<th>Peak Pressure (Kpa)</th>
<th>Pressurization rate (Kpa/ms)</th>
<th>Burn time (ms)</th>
<th>Peak optical emission (Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/n-CuO</td>
<td>226</td>
<td>2045</td>
<td>0.46</td>
<td>4.3</td>
</tr>
<tr>
<td>Al/Ag$_2$O</td>
<td>75</td>
<td>25.7</td>
<td>3.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Al/Ag$_2$O/Fe$_2$O$_3$</td>
<td>74</td>
<td>21</td>
<td>5</td>
<td>0.4</td>
</tr>
<tr>
<td>Al/AgFeO$_2$</td>
<td><strong>325</strong></td>
<td><strong>6200</strong></td>
<td>0.3</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 8.6. Direct comparison between the pressure and optical trace of Al/AgFeO2 and Al/nCuO.

Table 8.2. Thermodynamic equilibrium predictions of Al/CuO, Al/Ag2O and Al/Fe2O3 thermites. Data is taken from Fisher and Grubelich\textsuperscript{a} [53].

<table>
<thead>
<tr>
<th>Thermite reaction</th>
<th>Adiabatic</th>
<th>Gas (mmol/g)</th>
<th>Major species</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2Al + 3CuO \rightarrow Al_2O_3 (l) + 3Cu (l, g)$</td>
<td>2570</td>
<td>5.4</td>
<td>Cu</td>
</tr>
<tr>
<td>$2Al + 3Ag_2O \rightarrow Al_2O_3 (l) + 6Ag (l, g)$</td>
<td>2163</td>
<td>4.3</td>
<td>Ag</td>
</tr>
<tr>
<td>$2Al + Fe_2O_3 \rightarrow Al_2O_3 (l) + 2Fe (l, g)$</td>
<td>2862</td>
<td>1.4</td>
<td>Fe</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Assumptions: constant enthalpy and pressure with phase changes; without taking account of the oxide shell of aluminum.

8.3.4. Post-combustion-product characterization

It has been pointed out previously that the nature and dispersion of the products from a thermite combustion plays an important role in biocidal applications [26]. XRD evaluation of crystalline product species is shown in Figure 8.7 and show no evidence of the parent starting materials, but five new strong peaks indexed to elemental silver.
are seen. The fact that no peak corresponding to Al$_2$O$_3$ or Fe was observed might suggest they are both amorphous.

![XRD pattern](image)

**Table 8.3.** The XRD pattern of Al/AgFeO$_2$ reaction product.

For SEM evaluation of the reaction product a 7 mm × 5 mm rectangular double-sided carbon tape was placed inside the combustion cell chamber. Two representative SEM images of the product were shown in Figure 8.8A-B, show there are mainly two populations of product particle sizes. One has relatively larger dimension and another with a dimension as small as ~80 nm. 2D elemental mapping using EDS shown in Figure 8.8, indicate the larger spherical particles are Al$_2$O$_3$ while the smaller particles are Ag. This was also confirmed with 1D elemental line-scan coupled with elemental analysis shown in Figure S8.3. Most importantly for the application as a biocide, is that the smaller Ag particles randomly decorate the larger Al$_2$O$_3$ particles.

Overall, the intensity of iron signal is the weakest among those four elements under EDS mapping implying the random distribution of iron.
Table 8.4. Representative SEM images (A and B) of the Al/AgFeO$_2$ reaction product collected inside the combustion cell; 2D elemental mapping (Ag, Fe, Al and O) of Figure 8B using EDS.

TEM of the reaction product along with an EDS elemental mapping result is shown in Figure 8.9. As can be seen, there are two different types of particles similar to the SEM result. One has a spherical shape with a relatively larger particle size and low
contrast; another has a spherical/oval shape with smaller size and dark contrast. In the EDS elemental mapping, red represents silver, blue iron, yellow aluminum and green oxygen. Clearly, the three larger spherical particles are Al$_2$O$_3$. Since the mixing of red and blue gives purple, it is reasonable to conclude that the silver and iron positions are mostly overlapped. It could mean a formation of Ag-Fe alloy; however, the SEM results indicate the iron signal is much weaker and always appears with the presence of both aluminum and oxygen signals. To clarify this speculation, an EDS line-scan analysis was employed, and the result will be discussed below. It should also be noted that some white pixels were found in the purple area, implying the presence of oxygen (green plus red and blue equals to white). Thus, those silver- and iron-containing particles might be partially oxidized that could be a result from handling the product in air.

![TEM image and 2D elemental mapping](image)

**Figure 8.7.** TEM image (A) and 2D elemental mapping (B) of the Al/AgFeO$_2$ reaction product. Red represents Ag, blue represents Fe, yellow represents Al and green represents O.

As one can see from the EDS line-scan result shown in Figure 8.10, except for the small oxygen signal peak at ~0.4 um, the aluminum and oxygen signals are almost synchronous in positions indicating Al$_2$O$_3$. Like the SEM EDS mapping result, iron is
the weakest among all four elements. It overlaps with aluminum and silver, respectively, implying the iron is randomly distributed and excluding the hypothesis of Ag-Fe alloy formation.

Figure 8.8. A representative TEM image and the corresponding EDS line-scan data of the Al/AgFeO$_2$ reaction product.

Comparing these two representative TEM images Figure 8.9A and Figure 8.10A, the morphologies of the silver particles are quite different. The ones in Figure 8.9A are nanosized with spherical/oval shapes and are decorated on/near the Al$_2$O$_3$ surface that suggests silver product had vaporized and re-condensed [2]. This mechanism is beneficial to biocidal applications due to the wide distribution of small sized silver particles during the violent combustion event. As to the one in Figure 8.10A, particles
at the bottom right with oddly shapes clearly underwent some sintering while silver. Those results are consistent to a previously reported sintering reaction mechanism of Al-based thermites [54, 55]. However, it seems much less reactants were following the sintering mechanism according to the SEM image shown in Figure 8.8 where the majority of silver product has small particle size and distributed randomly.

### 8.4. Conclusions

In this study, the AgFeO$_2$ was prepared via a wet-chemistry method to yield phase pure ~ 40 nm particles. The decomposition pathways of AgFeO$_2$ were found to depend on heating rates: decomposition to Ag, O$_2$ and Fe$_2$O$_3$ at ~600 °C at low heating rate and direct decomposition ~685 °C at high heating rates.

The ignition of Al/AgFeO$_2$ was found to slightly higher than the oxygen release temperature and thus with a similar mechanism to Fe$_2$O$_3$ although ignites at a much lower temperature. Fast video imaging indicates a fine smoke dispersing particle.

Combustion cell test showed that Al/AgFeO$_2$ outperformed other thermites in maximum pressure, pressurization rate and burn time. Moreover, with a pressurization rate three times and 5% less oxygen content of Al/CuO, Al/AgFeO$_2$ yields a comparable result as to Al/hollow-CuO or Al/KClO$_4$/CuO. The fact that Al/AgFeO$_2$ and Al/Ag$_2$O/Fe$_2$O$_3$ share the exact same elemental compositions but feature the highest and lowest pressurization rate, respectively, indicates molecularly incorporation of Ag$_2$O into Fe$_2$O$_3$ outperforms the mechanically mixed Ag$_2$O/Fe$_2$O$_3$ when they were employed as oxidizers in aluminum-based thermites. Post combustion products indicate the formation of elemental silver nanoparticles (~ < 80 nm) decorating larger Al$_2$O$_3$ and is this bioavailable.
8.5. Supplemental Information

**Figure S8.1.** Multiple mass spectra of AgFeO₂

**Figure S8.2.** A snapshot of Al/AgFeO₂ burning on a high-rate heating Pt wire in T-Jump chamber (in argon).
Figure S8.3. One-dimensional elemental line-scan using EDS of the Al/AgFeO$_2$ reaction product collected inside the combustion cell.
Chapter 9: Understanding Ignition Mechanism of boron-based Nanothermites

Overview

The goal of this work is to explain why boron-based thermites show the lowest ignition temperature comparing with other fuel-based thermite systems when using the same oxidizers. To do so, boron as the one feature the highest maximum combustion enthalpy when it was employed as the fuel is stoichiometrically mixed with CuO, Bi$_2$O$_3$, KIO$_3$, Fe$_2$O$_3$, Co$_3$O$_4$ and MoO$_3$ to form boron-based nanothermites. Time-resolved temperature-jump time-of-flight mass spectrometer (T-Jump/TOFMS) was used to study the ignition and decomposition of boron-based thermites. A high-speed camera simultaneously captured optical emission from the ignition/reaction of the thermites allowing for the ignition time, and corresponding ignition temperature. In addition, the ignition behaviors of bare boron nanopowders and boron-based nanothermites at various gaseous oxygen pressure were investigated using the T-Jump method. High-heating rate transmission electron microscopy studies were performed on both B/CuO and B/Bi$_2$O$_3$ nanothermites to evaluate the ignition process. I propose a co-sintering effect between B$_2$O$_3$ and the oxidizer play an important role in the ignition process of boron-based nanothermites.

9.1 Introduction

Reactive materials are a class of energetic materials containing separated fuels and oxidizers and featuring an extremely high exothermicity, intensive light emission and
shock generation by the self-sustained reaction [1-3]. When metal and metal oxide are employed as the fuel and oxidizer, respectively, the intense exothermic metal/metal oxide reaction is commonly referred to a thermite reaction. This reaction is self-propagating once the ignition happens and the kinetics of the reaction are known to be accelerated when the fuel and oxidizer are at the nanoscale, resulting from the increased interfacial contact and reduced characteristic diffusion length scale. The most widely adopted metal is aluminum due to its abundance and competitive reactivity when compared with other metals [4]. It has been used as an additive in numerous types of rocket propellants and pyrotechnic mixtures. However, aluminum is currently not the only commercially available nanosized metal fuel [2]. Investigating other fuels, such as boron, tantalum and carbon, with different properties than aluminum can be used to tweeze out mechanisms for ignition and combustion. Figure 9.1 shows the maximum reaction enthalpy for different metal fuels in a thermite composition with copper (II) oxide (CuO) [5] as the oxidizer. It is obvious that boron features the highest maximum combustion enthalpy when it was employed as the fuel. Thus, boron theoretically could be an attractive alternate for aluminum.

![Figure 9.1. Maximum combustion enthalpy for the reaction of various metals with CuO.](image-url)

198
Like aluminum, boron particles also have a passivated oxide shell, $\text{B}_2\text{O}_3$. Since $\text{B}_2\text{O}_3$ melts at a much lower temperature (450 °C) than the core (2100 °C), the burning scenario of boron is very different from aluminum. Upon heating, the molten $\text{B}_2\text{O}_3$ shell will surround the outside which prevent oxygen source from diffusing through. Over the last few decades, the ignition and combustion of boron particles were extensively studied both theoretically and experimentally.

Prentice [6] observed a two-stage combustion process for the ignition of boron particles in air and in oxygen-argon mixtures at atmospheric pressures. The low-temperature stage involves a surface burning process followed by a high-temperature stage is corresponding to gas-phase combustion. Later, Macek and Semple [7] investigated combustion of boron particles at atmospheric pressure in hot oxidizing gases of different compositions and found that boron combustion always happens in a two-stages process verifying what Prentice has claimed previously. The first short stage involves the removal of the oxide layer and can be a kinetic and/or diffusion-controlled process. The second stage involves the burnout of a bare boron particle is controlled by gas-phase diffusion of oxidants. The burn time of each stage is found to be inversely proportional to the oxygen molar ratio and merge as the mole fraction of oxygen decreases. Macek and Semple [8] then studied the combustion of boron particles at elevated pressures and found that the low-temperature stage was nonreproducible at pressure above ~10 atm.

There are contradictory theories about the mechanism that dominate species diffusing into the liquid boron oxide layer during the first stage of boron particles
ignition. Glassman et al [9] claimed that boron oxide production during first ignition stage results from boron diffusion across the oxide layer rather than oxygen diffusion claimed by King [10, 11]. Yeh and Kuo [12] later verifies that the diffusion of dissolved boron into molten boron oxide dominates the diffusion process. They also found the boron oxide layer of boron particles changed from a crystalline to an amorphous structure at elevated temperatures and its chemical composition was identified as a polymeric vitreous \((\text{BO})_n\) complex through the reaction between dissolved boron and molten boron oxide. Theoretical models were also developed to simulate each of the two-stages combustion of boron particles by Knipe [13], Mohan and Williams [14] and others.

The influence of initial thickness of boron oxide layer on ignition and combustion of boron particles was studied by Ao et al [15]. They reported the oxide layer has little effect on the reactivity of the oxidation of boron particles below 775 °C. With increasing boron oxide layer thickness, the combustion efficiency decreases, and the time required for complete removal of the oxide layer is longer, while the ignition delay time significantly increases, and the oxide layer removal rate is raised.

In recent years, more efforts have been devoted to the ignition and combustion of boron-based thermites system. As mentioned previously, thermites involve an exothermic reaction of a metal fuel and a metal oxide. Sullivan et al [16] studied the reaction of nano-B/Al/CuO metastable intermolecular composites and reported the addition of nanoboron to Al/CuO can enhance the reactivity when the boron is less than 50 mol% of the fuel, while no enhancement was observed for microboron. From both experimental and theoretical results, they speculated that the sensible heating, removal
of the oxide shell and the melting of the boron are all critical for fast reaction. Liu et al[17] prepared B/CuO nanothermite through a chemistry precipitation method. They reported an improved thermochemistry behavior of boron particles with a coating of nano-CuO and a lower onset reaction temperature. Recently, Wang et al[18] reported a clear relationship between molecular properties of the oxidizer and ignition temperature as well as combustion performance of boron-based nanothermites in which larger oxygen vacancy concentration and smaller metal-oxygen bond energy lead to lower ignition temperature.

In this work, boron nanopowder stoichiometrically mixed with CuO, Bi₂O₃, KIO₃, Fe₂O₃, Co₃O₄ and MoO₃ were evaluated. Time-resolved temperature-jump time-of-flight mass spectrometer (T-Jump/TOFMS) was used to study the ignition and decomposition of boron-based thermites. A high-speed camera simultaneously captured optical emission from the ignition/reaction of the thermites allowing for the ignition time, and corresponding ignition temperature. In addition, the ignition behaviors of bare boron nanopowders, B/CuO, B/KIO₃ and B/Bi₂O₃ nanothermites at various gaseous oxygen pressure were investigated using the T-Jump method. High-heating rate transmission electron microscopy studies were performed on both B/CuO and B/Bi₂O₃ nanothermites to evaluate the ignition process. Pressure cell tests evaluated combustion performance.
9.2. Experimental

9.2.1 Materials:

The aluminum nanopowders (Al) (Alex, ~80 nm) were obtained from Novacentrix. The active Al was 81% by mass, determined by TGA. The nanoboron powders were obtained from the SB Boron Corporation [16]. The active B was 72% by mass, determined by TGA. All metal oxide nanopowders (< 50 nm) purchased from Sigma-Aldrich were directly used as received. All the other chemicals were of analytical grade and used as purchased without further treatment.

9.2.2. Preparation of thermites:

Nanoboron was stoichiometrically mixed with CuO, Bi$_2$O$_3$, KIO$_3$, Fe$_2$O$_3$, Co$_3$O$_4$ and MoO$_3$ based on the following equations, respectively, in hexane followed by 30 minutes sonication. After room temperature evaporation of the solvent the solid thermite powders were collected for use.

\[
2B + 3CuO \rightarrow 3Cu + B_2O_3
\]

\[
2B + Bi_2O_3 \rightarrow 2Bi + B_2O_3
\]

\[
2B + KIO_3 \rightarrow KI + B_2O_3
\]

\[
2B + Fe_2O_3 \rightarrow 2Fe + B_2O_3
\]

\[
8B + 3Co_3O_4 \rightarrow 9Co + 4B_2O_3
\]

\[
2B + MoO_3 \rightarrow Mo + B_2O_3
\]
9.2.3. T-Jump/TOFMS measurement and high-speed imaging:

The decomposition of oxides particles was investigated using a custom T-Jump/TOFMS [19]. Typically, a ~1 cm long platinum wire (76 um in width) with a thin layer coating of oxidizer sample was rapidly joule-heated to about 1200 °C by a 3 ms pulse at a heating rate of ~10^5 °C/s. The current and voltage signals were recorded, and the temporal temperature on the wire was measured according to the Callendar–Van Dusen equation. MS spectra were measured every 0.1 ms. The detailed experimental set-up is given in our previous papers [19, 20].

To identify the point of ignition a high-speed camera (Vision Research Phantom v12.0) was employed to record the combustion on the wire during heating. Ignition temperatures of thermite reactions in vacuum were measured from the correlation of optical emission from high speed imaging and temporal temperature of the wire and were further analyzed in combination with the temporal mass spectra. Each experiment was repeated 3 times.

9.2.4. TGA/DSC characterization

Thermogravametric analysis and differential scanning calorimetry (TGA/DSC) was performed using a TA Instruments SDT Q600. For both nTa and nAl oxidation analysis runs, a heating rate of 20 °C/min and O2 flow rate of 100 mL/min were employed.

9.2.5. In situ high heating rate TEM

Protochips Arduro heating chips were used with a Protochips TEM holder in a JEM 2100 FEG TEM/STEM, equipped with Oxford EDS and Gatan Tridiem EELS systems, with an accelerating voltage of 200 kV. Ta nanopowders were deposited onto an
Arduro chip and heated in air whereas the Ta based nanothermites were heated under vacuum within the TEM. All samples were heated at $10^5 \, ^\circ\text{C} /\text{s}$ and held for a period between 1 and 100 ms.

### 9.3. Results and Discussion

Over the past decades, different fuels such as aluminum, [21-26] carbon, [27-29] tantalum, [30] etc, had been studied in thermite systems and different ignition mechanisms have also been developed to interpret their unique ignitions. Since the same oxidizers have been investigated previously in those fuel systems, the initiation temperatures in vacuum environment of CuO, Bi$_2$O$_3$, Fe$_2$O$_3$ and KIO$_3$, with different fuels are listed in Table 9.1 to demonstrate the particularity of boron-based nanothermites. The measured oxygen release temperatures, and literature melting points of the bare oxidizers are also included in Table 1. It can be clearly seen that boron-based nanothermites give the lowest ignition temperature for those oxidizers.

As previously demonstrated that the ignition of Al-based nanothermites is dominated by the mobility of the aluminum core and the reactive sintering only play a partial role, this explains why Al/oxidizer nanothermites feature the highest initiation temperatures for all the listed oxidizers.[21, 25, 31] Reactive sintering was introduced in our previous works to describe the ignition mechanism of aluminum-based nanothermites where reaction initiates at an Al/oxidizer interface and the exothermic reaction led to further melting/sintering of adjacent particles. Then those newly melted materials are rapidly delivered to the reactive interface via strong capillary/surface tension forces and followed by the formation of the sintered product. [25, 31] As for
carbon, it remains immobile upon heating to a temperature within the regime of our set-up. The reactive sintering of metal oxide increases the effective contact area between carbon and oxidizer and thus further promoting sintering/heating, which helps to initiate condensed phase reaction and expand the effective reaction zone. [32] Those effects are the reasons why carbon/oxidizer nanothermites initiate at a much lower temperature than Al/oxidizer nanothermites. In addition, a rapid oxide shell crystallization of nano tantalum has been proposed to be the dominant factor for the ignition of tantalum-based thermites where the crystallization contributes enough energy to the shell/oxidizer interface and therefore promoting the reactive sintering to take place.[30]

Even though the reactive sintering has been observed in aluminum-based, carbon-based and boron-based nanothermites (boron case will be discussed later), the extremely different ignition temperatures obtained on those different types of nanothermites suggest there are other impactors influencing the ignition except for reactive sintering.

Boron has an oxide shell featuring an extremely low melting point that is very different from either aluminum, carbon or tantalum, and boron-based nanothermites feature the lowest initiation temperature among these four types of thermites. It has been reported in a recent work that B/Bi$_2$O$_3$ shows the second least negative $\Delta G_r$ and $\Delta H_r$ compared to Al/Bi$_2$O$_3$ and Ta/Bi$_2$O$_3$, which eliminating the possibility of ascribing the low ignition temperature of B/Bi$_2$O$_3$ to the thermodynamically causes.[23] Both facts imply the boron oxide shell may play some role in the ignition of boron-based nanothermites.
Ignition temperatures of B/CuO, B/Bi$_2$O$_3$, B/KIO$_3$, and B/Fe$_2$O$_3$ are higher than the melting point of B$_2$O$_3$, and close to the Tamman temperature of corresponding oxidizer, which means both B$_2$O$_3$ shell and the oxidizer are to some extent mobile prior to ignition. Those results are suggesting that the molten B$_2$O$_3$ shell might participate in or even promote the sintering of metal oxides to feature a co-sintering effect in which oxygen can diffuse through the mixed B$_2$O$_3$/metal oxide area and react with the boron core and thus resulting in a low initiation temperature. According to a recent published work, an interface was created due to the wetting of Bi$_2$O$_3$ by the molten B$_2$O$_3$ where high mobility solid-state oxygen can diffuse through and reacts with boron core[18]. However, Bi$_2$O$_3$ is a very special oxidizer that features the highest known oxygen ion conductivity and usually undergoes a condensed phase reaction mechanism in thermites system where oxygen transfers to be in contact with the fuel within solids.[28] Here, I propose that such co-sintering effect is present not just in B/Bi$_2$O$_3$ but also in other boron-based nanothermites and further attributing to their low ignition temperature.

<table>
<thead>
<tr>
<th>Oxidizer</th>
<th>O$_2$ release temperature (°C)</th>
<th>Melting point (°C)</th>
<th>Ignition temperature of nanothermites (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al/Oxidizer</td>
</tr>
<tr>
<td>CuO</td>
<td>730</td>
<td>1325</td>
<td>765</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>965</td>
<td>820</td>
<td>575</td>
</tr>
<tr>
<td>KIO$_3$</td>
<td>630</td>
<td>560</td>
<td>625</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1065</td>
<td>1565</td>
<td>1135</td>
</tr>
</tbody>
</table>
To further prove my proposal, I first look into the boron particles and then move on to boron-based nanothermites.

Figure 9.2 shows the SEM images of the boron nanoparticles are mostly spheroids that are agglomerated with hard aggregates, with average primary particle diameter ~60 nm.

![Figure 9.2. SEM images of boron nanoparticles.](image)

To learn how boron reacts in different systems, the oxidation of boron nanoparticles was first studied in an air environment using standard low heating rate TGA/DSC and the results are shown in Figure S9.1. The one-step exothermic oxidation of boron nanoparticles starts at ~500 °C, which is slightly higher than the melting point of B₂O₃ shell (450 °C, Table S9.1). Thus, the molten phase B₂O₃ shell might play a role in the oxidation and will be discussed below. TEM images of boron nanoparticles before and after in-situ heating up to 800 °C (Figure S9.2) show no significant changes upon heating, indicating the boron nanoparticles do not sinter even with the molten B₂O₃ shell, suggesting that the necking between particles occurred during the synthesis of the boron, and before the passivating shell was created. Considering the boron active content is about 72% in boron nanoparticles, complete oxidation of boron nanoparticles
would result in a final weight % of ~262% (final product is assumed to be B$_2$O$_3$), which is slightly lower than the final weight 280% shown in Figure S9.1.

The oxidation of boron particles at high heating rate was obtained by T-jump system. Boron was ignited in gaseous oxygen at various pressures within a high heating rate T-jump chamber and the measured ignition temperatures as a function of oxygen pressure are shown in Figure 9.3. The fact that boron nanoparticles always ignited at ~850 °C even at elevated oxygen pressures suggests its ignition is not controlled by a gas phase mechanism where the oxidizer first decomposed into gaseous oxygen and then those oxygen diffuse through the molten Al$_2$O$_3$ shell and reacts with the fuel core.[21] This in contrast to what is observed with aluminum which shows a decrease in ignition temperature with increasing oxygen concentration [22]. Considering the B$_2$O$_3$ shell is molten at ~850 °C, it is reasonable to speculate that the ignition of boron nanoparticles is strongly related to the oxide shell. In another words, gas phase oxygen cannot diffuse through B$_2$O$_3$ shell under those pressurized atmospheres. [22]

![Figure 9.3](image)

**Figure 9.3.** Ignition temperature of boron measured using the T-Jump ignition at varying O$_2$ pressures.
Since the ignition of boron nanoparticles is apparently not controlled by gas phase oxygen, different solid oxidizers were stoichiometrically mixed with boron nanoparticles and their ignition temperatures obtained via the high heating rate T-jump method are listed in Table 9.2. The oxygen release temperature and the melting point of each oxidizer are also included in this table. B/MoO₃ and B/Sb₂O₃, ignited at ~650 and 630 ºC, respectively, but since neither of these oxides release any gas upon heating up to 1200 ºC it is reasonable to conclude that they are initiated through condensed phase reactions. [21] For the other boron-based thermites shown in Figure 9.4, I find their ignition temperatures are lower than the oxygen release temperature from the corresponding neat oxidizers. This also implies a condensed phase reaction since reaction occurs before oxygen release.

To further investigate the ignition mechanism of boron-based nanothermites, boron coped with CuO (a known gas phase oxidizer in Al-based thermite systems), Bi₂O₃ (a known condensed phase oxidizer in Al-based thermite systems) and a salt oxidizer KIO₃ were ignited in oxygen atmosphere with different O₂ pressure. Figure 9.5 shows not surprisingly the oxygen has no synergistic effects in ignition and that the ignition temperature is independent of oxygen concentration. Perhaps more interesting is that the ignition temperatures with bonded oxygen is lower than in free oxygen. An integrated oxidizer greatly enhance combustion due to mass transfer limits of free oxygen in a bulk sample, thus in a wire coated sample test, such transport limits were seen. The reader is reminded that reaction with free oxygen leads to the highest adiabatic flame temperature relative to the other oxidizers.
Table 9.2. Ignition temperature of various B based nanothermites with different oxidizers. The oxygen release temperature from neat oxidizer as detected by TOFMS and the melting point of the oxidizers are also included. Heating rate $\sim 5 \times 10^5 \, ^\circ\text{C/s}$.

<table>
<thead>
<tr>
<th>B/Oxidizer nanothermites</th>
<th>Ignition temperature (°C) ± 30 °C</th>
<th>O$_2$ release temperature from neat oxidizer (°C) ± 30 °C</th>
<th>Melting point of the oxidizer (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>640</td>
<td>730</td>
<td>1320</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>550</td>
<td>960</td>
<td>820</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>670</td>
<td>1060</td>
<td>1560</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>660</td>
<td>740</td>
<td>895</td>
</tr>
<tr>
<td>KIO$_3$</td>
<td>510</td>
<td>630</td>
<td>560</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>650</td>
<td></td>
<td>790</td>
</tr>
<tr>
<td>Sb$_2$O$_3$</td>
<td>630</td>
<td></td>
<td>650</td>
</tr>
</tbody>
</table>

Figure 9.4. Oxygen release temperature of various oxidizers vs ignition temperature of various B based nanothermites.
Since $\text{B}_2\text{O}_3$ melts at a much lower temperature (450 °C) than the core (2076 °C) and lower than the measured ignition temperature, for reaction to occur, oxygen must be diffusing through the liquid layer or the boron core must be exposed to the oxygen source in some way, such as by de-wetting. Thus, solid state oxygen must find a way to diffuse into the boron core and initiated the fuel-oxidizer reaction.

To examine the ignition process, high-heating rate in-situ TEM were employed here. Two oxidizers were mixed with boron to form boron-based nanothermites: CuO (gas phase oxide) and Bi$_2$O$_3$ (condensed phase oxide)

Figure 9.6 shows images of B/CuO nanothermites before and after heating, where the lighter aggregates are boron, and the darker particles are CuO. Figure 9.6A shows that all CuO particles are in good contact with boron prior to heating. After rapid in situ
heating to 800 °C for 10 ms, comparing Figure 9.6A and 9.6B, it is clear that those CuO particles that are in good physical contact with boron nanoparticles underwent significant morphological changes, and the isolated boron nanoparticles retain their original form. EELS results show that the darker particles with irregular spherical shape observed in Figure 9.6B are copper particles (Figure S9.3). Similar to the reactive sintering mechanism of aluminum-based thermites[31], the surface contact between the boron and CuO is essential to initiate their reaction.

Similar experiments on B/Bi₂O₃ nanothermites were also conducted. EDS line scans in Figure 9.7A2 indicates the darker particles are Bi₂O₃. After rapid heating, B/Bi₂O₃ nanothermites underwent dramatic morphological changes. All Bi₂O₃ particles aggregated/sintered together and formed much larger particles with irregular shapes that later proved to be bismuth. The EDS line scan (Figure 9.7B2) of the same spots as to those of Figure 7A2 shows that those darker particles are bismuth and the lighter ones are B₂O₃. In addition, it seems that all bismuth atoms are moved to the edge of the plane and formed much bigger particles, where B₂O₃ particles are intended to stay in the middle of the plane.

It has been previously reported the importance of reactive sintering in which the interfacial reaction upon heating can lead to an increased mobility and sintering of the particles into larger structures [25, 31]. As Jian et al points out [21] partial sintering of metal oxides can commence at a much lower temperature; at the Tammann temperature ~½ melting point. Once the metal oxide becomes mobile, the contact area between fuel and oxidizer increases extensively, favoring ignition. However, all boron-based nanothermites except for B/Fe₂O₃ ignited at temperatures higher than the Tammann
temperatures of their corresponding oxidizers. Therefore, the partial sintering of metal oxides might not play a controlling role for the ignition of boron-based nanothermites.

Both B/CuO and B/Bi₂O₃ nanothermites show evidence of reactive sintering having occurred on the interfacial area where boron has good contact with the oxidizers. Once the reaction was initiated, the generated heat will transfer to the adjacent particles and either promote initiation or draw them towards the reacting interface, where the final products are formed.

The major difference between aluminum and boron is that the isolated boron remains almost the same after rapid heating, but aluminum particles either undergoes crystallization of its aluminum oxide shell or evolve heterogeneities near the surface. The rather stable property of boron further indicates the importance of the contact between boron and the oxidizer to ignition. Considering aluminum-based nanothermites show even higher ignition temperature than boron-based nanothermites, it is reasonable to conclude that the co-sintering effect between B₂O₃ and the oxidizer play an important role in its ignition process.
Figure 9.6. TEM images of B/CuO nanothermites prior to (A) and after (B) in situ heating at $4 \times 10^5 \, ^\circ\text{C/s}$ to 800 $^\circ\text{C/s}$ for 10 ms. A and B are the same position.

Figure 9.7. TEM images and elemental line scan of B/Bi$_2$O$_3$ nanothermites prior to (A) and after (B) in situ heating at $4 \times 10^5 \, ^\circ\text{C/s}$ to 800 $^\circ\text{C/s}$ for 10 ms.
9.4. Conclusions

The ignition mechanisms of boron and boron-based nanothermites are investigated in this work. It is noted that boron nanoparticles always ignited at ~850 °C even at elevated oxygen pressures suggests its ignition is not controlled by a gas phase mechanism. Different oxidizers were mixed with boron nanoparticles to examine the possibility of condensed phase reaction mechanism and the results show that boron-based nanothermites have the lowest ignition temperatures compare with that of other fuel-based samples and the ignition of boron-based nanothermites is independent of gaseous oxygen pressure. Therefore, a condensed phase mechanism is controlling the ignition mechanism of boron-based nanothermites. Since the ignition temperatures of boron-based nanothermites are higher than the melting point of B$_2$O$_3$, and close to the Tamman temperature of corresponding oxidizer, where both B$_2$O$_3$ and the oxidizers are to some extent mobile prior to ignition, suggesting that the low ignition temperature of boron-based nanothermites might be contributed to a co-sintering effect between B$_2$O$_3$ and the oxidizers. In detail, the molten B$_2$O$_3$ shell might participate in or even promote the sintering of metal oxides to feature a co-sintering effect in which oxygen can diffuse through the mixed B$_2$O$_3$/metal oxide area and react with the boron core and thus resulting in a low initiation temperature.

Then, High-heating rate TEM measurements B/CuO and B/Bi$_2$O$_3$ nanothermites provide evidence of reactive sintering having occurred on the interfacial area where boron has good contact with the oxidizers, like Al-based nanothermites. However, Al-based nanothermites show even higher ignition temperature than boron-based
nanothermites, it is reasonable to conclude that the co-sintering effect between B₂O₃ and the oxidizer play an important role in its ignition process.

9.5. Supplemental Information

![Figure S9.1](image.png)

**Figure S9.1.** TGA/DSC of boron nanoparticles under 100 mL/min of air at a heating rate of 25 °C/min.

**Table S9.1.** The general properties of boron and B₂O₃.

<table>
<thead>
<tr>
<th></th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Boron</strong></td>
<td>2076</td>
<td>3927</td>
</tr>
<tr>
<td><strong>B₂O₃</strong></td>
<td>450</td>
<td>1860</td>
</tr>
</tbody>
</table>
Figure S9.2. The TEM images of boron nanoparticles before (A) and after (B) heating to 800 C.

Figure S9.3. EELS spectrum of B/CuO (Cu: major edges at 951 and 931 eV).
Chapter 10: Summary

10.1 Conclusions

The objective of this dissertation study was to develop new energetic materials with biocidal capabilities and apply them in various nanothermites systems to explore the relationships between fuel and oxidizer reactions. To achieve this goal, oxidizers that consist of element like iodine or silver were prepared via various synthetic methods and then incorporated into different fuel-based nanothermites for ignition/reaction studies. Various fuels or oxidizers were added into the system to create ternary nanothermites in order to further understand their ignition/reaction properties.

As discussed in Chapter 1, nanothermites have so much potential in various energetic applications because they offer high energy densities and high reaction rates. By employing biocidal agents within the system, they can be the potential solution for counterfeiting the threat of bioterrorism. The detailed experimental techniques are presented in Chapter 2 in order to let the readers know how those experiments were performed.

In Chapter 3, three different products, δ-HIO₃, HI₃O₈ and I₂O₅, were obtained via aerosol spray pyrolysis. Both temperature and humidity control in silica gel preparation were necessary to obtain all three products without post-processing. This chapter demonstrates a facile and environmentally friendly aerosol spray pyrolysis method to prepare various iodine oxides/iodic acids using a single precursor HIO₃. By tuning the furnace temperature and the humidity I was able in a single step to produce near phase pure δ-HIO₃, HI₃O₈ and I₂O₅.
As one of the products produced in Chapter 3, $\delta$-HIO$_3$, was demonstrated to be a new polymorph of iodic acid, which crystallizes in the orthorhombic space group $P2_12_12_1$. Its crystal structure is reported in Chapter 4. Ab initio crystal structure determination of $\delta$-phase reveals that previously known I$_4$O$_9$.xH$_2$O phase is actually HIO$_3$.

In Chapter 5, those prepared iodine oxides/iodic acids, including $a$-I$_2$O$_5$, $a$-HI$_3$O$_8$ and $\delta$-HIO$_3$, were employed as the oxidizer in thermite systems. Their decomposition behaviour was studied using T-Jump/TOFMS, which identified a single decomposition step for all oxides at high heating rates compared with the multi-steps process at low heating rate. The ignition temperatures of nAl-based thermites are all ~650 °C which is at the melting point of aluminum (~660 °C). This suggests that the mobility of the aluminum core is dominating the ignition/reaction while the gaseous oxygen released from the decomposition of the oxidizer does not participate in the ignition until the molten aluminum was available. Unlike nAl-based thermites, the ignition temperatures of nTa-based thermites are lower than the oxygen release temperatures from the corresponding bare oxidizers. In this case, a condensed phase reaction mechanism is proposed to dominate the ignition process. Combustion tests show that nAl/$a$-HI$_3$O$_8$ has the highest pressurization rate and peak pressure and shortest burn time, and since it also has an iodine content of ~75% which is as high as I$_2$O$_5$ on a per mass basis, this material may be a very promising candidate in biocidal application.

In Chapter 6, I employed carbon (CB, CNT and FGS) as both a fuel and as an additive to aluminium and tantalum fuels to study the influence of a fuel without
nascent oxide shell on initiation of iodine oxide-based thermites. I found that the initiation temperature of CB/I$_2$O$_5$ is much lower than the initiation temperature of Al/I$_2$O$_5$ and Ta/I$_2$O$_5$. When CB is used as an additive to other fuels, I observe a decrease in the overall initiation temperature and a lowering of the iodine release temperature to below that of the nascent oxidizer. Other carbon allotropes showed similar results. FTIR analysis indicated that CB lowered the iodine-oxygen bond energy of I$_2$O$_5$ on the surface and thus triggered this condensed phase reaction. These results indicate that CB can be employed as an additive to any metal fuel as a means to lower both the initiation and iodine release temperature.

In Chapter 7, a secondary oxidizer CuO was incorporated into Al/I$_2$O$_5$ system to shorten or eliminate the ignition delay of the combustion of Al/I$_2$O$_5$. By investigating the combustion performance of four different Al/I$_2$O$_5$/CuO thermites varying the mass ratio between two oxidizers and the other two Al/I$_2$O$_5$ and Al/CuO thermites in a constant volume combustion cell, significant enhancement is observed for all four thermites and their peak pressures and pressurization rates are much higher than that of Al/I$_2$O$_5$ or Al/CuO. The disappearance of the ignition delay in their pressure profiles and the shortened burn time imply CuO addition indeed does work on accelerating the ignition of Al/I$_2$O$_5$ thermite and the overall reaction. A mechanism was proposed in this work to account for this unexpected improvement: the additive Al/CuO shortens the ignition delay of Al/I$_2$O$_5$; that leads to enormous amount of gas formation for aluminum to react and then the extremely high flame temperature of Al/I$_2$O$_5$ boost the pressure inside the combustion cell further. All those events happen around the same time and
produce a synergetic effect to enhance the combustion performance of Al/\text{I}_2\text{O}_5.

Although more oxidizers need to be examined furthermore, it is reasonable to assume the combustion performance of Al/\text{I}_2\text{O}_5 could be enhanced by just incorporating a secondary oxidizer.

In Chapter 8, the AgFeO\textsubscript{2} was prepared via a wet-chemistry method to yield phase pure ~ 40 nm particles. The decomposition pathways of AgFeO\textsubscript{2} were found to depend on heating rates: decomposition to Ag, O\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3} at ~600 °C at low heating rate and direct decomposition ~685 °C at high heating rates. The ignition of Al/AgFeO\textsubscript{2} was found to slightly higher than the oxygen release temperature and thus with a similar mechanism to Fe\textsubscript{2}O\textsubscript{3} although ignites and a much lower temperature. Fast video imaging indicates a fine smoke dispersing particle. Combustion cell test showed that Al/AgFeO\textsubscript{2} outperformed other thermites in maximum pressure, pressurization rate and burn time. Moreover, with a pressurization rate three times and 5% less oxygen content of Al/CuO, Al/AgFeO\textsubscript{2} yields a comparable result as to Al/hollow-CuO or Al/KClO\textsubscript{4}/CuO. Post combustion products indicate the formation of elemental silver nanoparticles (~ < 80 nm) decorating larger Al\textsubscript{2}O\textsubscript{3} and is this bioavailable.

In Chapter 9, the ignition mechanisms of boron and boron-based nanothermites are investigated in this work. It is noted that boron nanoparticles always ignited at ~850 °C even at elevated oxygen pressures suggests its ignition is not controlled by a gas phase mechanism. Different oxidizers were mixed with boron nanoparticles to examine the possibility of condensed phase reaction mechanism and the results show that boron-based nanothermites have the lowest ignition temperatures compare with that of other fuel-based samples and the ignition of boron-based nanothermites is independent of
gaseous oxygen pressure. Therefore, based on the experimental results, I proposed a co-sintering mechanism to explain the causes of the low initiation temperature of boron-based nanothermites: the molten B₂O₃ shell might participate in or even promote the sintering of metal oxides to feature a co-sintering effect in which oxygen can diffuse through the mixed B₂O₃/metal oxide area and react with the boron core and thus resulting in a low initiation temperature.

10.2. Recommendations for future work

10.2.1. The effect of boron addition to iodine release, ignition and combustion of Al/I₂O₅ thermite

In my dissertation, carbon addition has been added into Al/I₂O₅ system and the results show it can lower the iodine release temperature and ignition temperature of Al/iodine oxide thermites owing to a condensed phase interaction between carbon and I₂O₅ according to the FTIR results. Recently, our group also studied the effect of titanium addition to Al/I₂O₅ system and found the ignition temperature decreases as the titanium fraction in the fuel increases and that titanium can accelerate the release of iodine and oxygen gas from Ti/Al/I₂O₅ ternary system. And the reactivity and combustion performance of Al/I₂O₅ thermite was significantly enhanced with addition of titanium. Therefore, carbon, a fuel without an oxide shell and with an extremely high melting temperature core, and titanium, a fuel with a partially reactive titanium (II) oxide shell, have all been proven to be an efficient additive to boost the combustion performance and lower the ignition temperature Al/I₂O₅.
In one of the previous chapters in my dissertation, “Understanding Ignition Mechanism of boron-based Nanothermites”, I found out that B/I₂O₅ cannot ignited in either argon or air environment. The oxide layer outside of boron fuel has a very low melting temperature ~440 °C compare to the boron core that features a very high melting point. This unique property of boron nanoparticles may bring some new insights to improving the ignition and combustion of Al/I₂O₅ system.

Considering boron with other oxidizers do not have this problem, I started looking into the reasons that causing this problem. First, I studied the decomposition behaviors of B/I₂O₅ under both high and low heating rate and the results are shown in Figure 10.1. Figure 10.1A indicates that the boron lowers the iodine release temperature of I₂O₅ from 450 to as low as 280 °C at high heating rate. However, at low heating rate, boron does not affect the thermal behavior of I₂O₅.

![Figure 100.1](image)

**Figure 100.1.** The iodine release temperature (A) and the TGA results (B) of B/I₂O₅ composite with different weight ratio of boron.

Figure 10.2 shows the ignition temperatures and iodine release temperatures of B/Al/I₂O₅ composites with different boron content. The iodine release temperature was determined from the time-resolved mass spectra of thermites. Both ignition and iodine
release temperature decrease when the boron content increases and both reach plateau when 4 w.t.% of boron is incorporated into B/Al/I$_2$O$_5$ system. In addition, the iodine release temperature is always more than 100 °C lower than the corresponding ignition temperature indicating I$_2$O$_5$ decomposes prior to the exothermic reaction between boron and I$_2$O$_5$. The fact all B/Al/I$_2$O$_5$ composites with different boron content can be ignited under argon environment implies boron alone could not exothermically react with I$_2$O$_5$ and it can only be used as an additive for Al/I$_2$O$_5$ system.

![Figure 100.2](image)

**Figure 100.2.** The ignition temperatures and iodine release temperatures of B/Al/I$_2$O$_5$ composites with different weight ratio of boron.

To figure out the reason why addition of boron lower both ignition and iodine release temperature, inert oxides such as Al$_2$O$_3$ and SiO$_2$ were introduced into Al/I$_2$O$_5$ system as comparisons. (Al$_2$O$_3$ and SiO$_2$ have similar particle size as Boron). Giving the fact that addition of both Al$_2$O$_3$ and SiO$_2$ have no discernible effect on either ignition or
iodine release temperatures of Al/I_2O_5 system as shown in Figure 10.3, it is reasonable to conclude that heat transfer among the fuel and oxidizer is not the cause for the lowering effect.

![Graph showing ignition temperatures and iodine release temperatures of Al/I_2O_5 composites with different oxides additives.](image)

**Figure 10.3.** The ignition temperatures and iodine release temperatures of Al/I_2O_5 composites with different oxides additives.

Based on the digital image shown in Figure 10.4 of B/Al/I_2O_5 suspension after sonication treatment, the color of the suspension changes from transparent colorless to purple that indicates the formation of iodine. Thus, iodine somehow was draws out from I_2O_5 compound with the presence of boron and later suspend in the solvent as I_2.

![Digital image of B/Al/I_2O_5 suspensions after sonication treatment.](image)

**Figure 10.4.** Digital image of B/Al/I_2O_5 suspensions after sonication treatment.
To evaluate the interaction between boron and I$_2$O$_5$, I$_2$O$_5$, boron, physical mixed B/I$_2$O$_5$ and sonicate mixed B/I$_2$O$_5$ composites have been characterized by FTIR. The results shown in Figure 10.5 reveal no significant change was found in B/I$_2$O$_5$ compared to the spectra of I$_2$O$_5$, which rule out the possibility of a condensed phased effect. Thus, I$_2$O$_5$ becomes very unstable and can easily decompose and deliver iodine when boron is in the system might be a catalytic effect, which need to be further investigated.

![Figure 10.5](image)

**Figure 10.5.** FTIR results of I$_2$O$_5$, boron, physical mixed B/I$_2$O$_5$ and sonicate mixed B/I$_2$O$_5$ composites.

10.2.2. *Incorporate silver into MnO$_2$ molecularly: silver hollandite*

Ag$_x$(MnO$_2$)$_y$.

In previous chapter, I have proved that the molecularly incorporation of Ag$_2$O into Fe$_2$O$_3$ significantly outperforms the physical combination of Ag$_2$O and Fe$_2$O$_3$. To
further explore this idea, I propose to incorporate silver element, a rather inactive material to the thermite reaction but features biocidal prosperity, into an oxidizer to see the effect. By looking into literature, I finally chose silver hollandite \( \text{Ag}_x(\text{MnO}_2)_y \) as the subject to study here. By breaking silver hollandite formula, one can see it is a combination of silver element and manganese oxide, which would be the perfect materials to test the idea.

Then, the silver hollandite was prepared by refluxing a mixture solution of \( \text{Mn(NO}_3)2 \) and \( \text{AgMnO}_4 \) in an acidic condition. Its XRD pattern shown in Figure 10.6 indicate the crystal structure of silver hollandite match to a previously reported structure, \( \text{Ag}_{1.8}\text{Mn}_8\text{O}_{16} \). And its SEM images show silver hollandite materials are in fiber-like shape with a diameter about 30 nm and length of 500 nm.

![XRD spectrum and SEM image of Ag_{1.8}Mn_8O_{16} prepared via wet chemistry method.](image)

Silver hollandite was heated in an argon environment with a heating rate of 10 C/min up to 1000 C and the decomposition products are collected and characterized. The XRD pattern of the product shown in Figure 10.7 indicates the formation of both silver and
Mn$_3$O$_4$. Considering Mn$_3$O$_4$ is a good oxidizer in aluminum-based thermites and silver is biocidal, it is promising to obtain positive results by further studying the ignition, combustion and biocidal applications of Al/Ag$_{1.8}$Mn$_8$O$_{16}$ system.

![Figure 10.7. XRD spectrum of Ag$_{1.8}$Mn$_8$O$_{16}$ decomposed products after heated to 1000 °C in Ar.](image)

**Figure 10.7.** XRD spectrum of Ag$_{1.8}$Mn$_8$O$_{16}$ decomposed products after heated to 1000 °C in Ar.

10.2.3. **To deliver independent silver and iodine products from a single system for biocidal application.**

As mentioned in previous chapters, both iodine and silver exhibit biocidal properties. Various efforts have been devoted into studying the performance of either iodine-containing or silver-containing oxidizers within thermite systems. Silver iodate, as a highly insoluble salt containing both silver and iodine elements, has been considered and studied for its potential use in thermite-driven biocidal applications. However, Sullivan from our research group had found that the silver and iodine products intends to form silver iodide that leads to inactive biocidal cites. Therefore, to
design a system that could deliver independent silver and iodine elements after thermite reaction could be a major achievement in this field.

Since $I_2O_5$ is the most commonly used iodine oxides, it was chosen as the iodine-containing oxidizer. Then, $Ag_2O$, $AgFeO_2$ and $Ag_{1.8}Mn_8O_{16}$ introduced and studied in previous chapters are employed here for the silver-containing oxidizers. Combines with aluminum fuel, a ternary system is being investigated.

Figure 10.8A shows a snapshot of $Al/I_2O_5/Ag_2O$ thermite burning on a high rate heating Pt wire under vacuum capture by a high-speed camera. Large number of particles formed during the ignition/combustion and could potentially be the biocidal active cites. By applying color ratio pyrometry to the captured image, the corresponding flame temperature map of $Al/I_2O_5/Ag_2O$ thermite is shown in Figure 10.8B. The flame temperature can reach as high as 5500 K guarantees a delivery of a very high thermite release.

![Figure 100.8](image)

**Figure 100.8.** A snapshot of $Al/I_2O_5/Ag_2O$ thermite burning on a high rate heating Pt wire under vacuum capture by a high-speed camera and its corresponding high speed pyrometry frame.

To thoroughly investigate the ternary system, four different mass ratios of iodine oxide and silver-containing oxidizer are used. By characterizing the combustion products of $Al/I_2O_5/Ag_2O$, $Al/I_2O_5/AgFeO_2$ and $Al/I_2O_5/Ag_{1.8}Mn_8O_{16}$, there is only one
sample with no detection of AgI in the combustion products proved by the XRD patterns (Figure 10.9), that is of Al/I$_2$O$_3$/Ag$_{1.8}$Mn$_{8}$O$_{16}$ with 72% I$_2$O$_3$ (weight fraction in oxidizers). Therefore, a system with the potential to deliver two different biocidal cites and a strong thermal shock should be carried on further.

![Figure 10.9](image)

**Figure 10.9.** The XRD result of the combustion products of Al/I$_2$O$_3$/Ag$_{1.8}$Mn$_{8}$O$_{16}$ with 0.72 I$_2$O$_3$ in the oxidizer collected inside the pressure cell chamber.

10.2.4. Florine-containing thermite system; to deliver Florine gas considering it is biocidal.

Besides iodine and silver, fluorine is also known to be a biocide. As proved in previous chapters, molecularly incorporated silver or iodine into oxidizers performs much better than physically adding the elements. Therefore, a promising idea to create an energetic system that delivers not only a long-lasting thermal shock but also fluorine gas is to figure out a way to incorporate fluorine into an oxidizer. By looking into literatures, fluorine-containing oxidizers draw my attention. Especially for bismuth oxyfluoride BiO$_x$F$_{3-2x}$, bismuth oxide alone is a very strong oxidizer and the addition of fluorine (one with an even higher electronegativity) might boost its performance.
even more. Other alternatives include iron oxyfluoride $\text{Fe}_2\text{OF}_4$, selenium oxyfluoride $\text{F}_2\text{OSn}$, etc. By employing those metal oxyfluoride oxidizers in aluminum-based thermite system, it might fulfill the goal of producing both thermal and biocidal events. To prevent the combination of aluminum and fluorine, the content of fluorine should be very excess.
Bibliography

Chapter 1:


Chapter 2:


Chapter 3:


[33] K. Stahl, M-A. Szafranski, Single-Crystal Neutron Diffraction Study of HIO\textsubscript{3} at 295 and 30 K and of DIO\textsubscript{3} at 295 K. *Acta Chemica Scandinavica* 46, 1146 (1992);


[37] A. Fischer, Redetermination of HI\textsubscript{3}O\textsubscript{8}, an adduct of formula HIO\textsubscript{3}\textbulletI\textsubscript{2}O\textsubscript{5}, *Acta Cryst.* E61, i278 (2005).


**Chapter 4:**


Chapter 5:


https://doi.org/10.1017/S0885715617000859


Chapter 6:


252


[33] L. Zhou, Development of ion-mobility and mass spectrometry for probing the reactivity of nanoparticles and nanocomposites, University of Maryland, College Park, Md., 2009.


Chapter 7:


Chapter 8:


Chapter 9:


Chapter 10:


