Abstract

Thermite reactions with high energy release and biocidal agents’ production are of interest for their potential applications in bio-agent defeat. In this work, we investigated the ignition and combustion of nano-Al/micro-I$_2$O$_5$ thermite, and studied its potential use in biocidal applications. Cyro-milling technique was used to produce micro-sized I$_2$O$_5$ (~2-4 $\mu$m) which were used as the oxidizer in this study. The ignition and reaction of the prepared nano-Al/micro-I$_2$O$_5$ thermite were systematically studied by a rapid fine wire heating technique using a high speed digital camera and a temperature-jump/time-of-flight (T-Jump/TOF) mass spectrometer. The ignition temperature of nano-Al/micro-I$_2$O$_5$ thermite in air at atmospheric pressure was found to be ~810 K, lower than ignition temperature ~940 K in vacuum. Time-resolved mass spectra results confirmed that nano-Al/micro-I$_2$O$_5$ thermite reaction can produce a lot of iodine species which were suggested to be good biocidal agents. Thermal decomposition of the I$_2$O$_5$ oxidizer under rapid heating conditions were investigated by T-Jump/TOF mass spectrometer, and was found to release significant O$_2$ before its thermite ignition. Constant-volume combustion cell tests were carried out to characterize the pressure rise and optical emissions during the thermite combustion events, and the performance of the I$_2$O$_5$ containing thermites was compared with other metal oxides thermite systems. The results show that Al/I$_2$O$_5$ thermite composite outperform the traditional Al/CuO and Al/Fe$_2$O$_3$ thermite systems in terms of peak pressure, pressurization rate and burning time. Additionally, we observed the concurrent pressure and optical rising for all nano-Al/micro-oxidizer thermites in this study. The results indicate that the pressure rise in nano-Al/micro-I$_2$O$_5$ thermite reaction should be from the produced hot biocidal species by very exothermic thermite reactions other than from the decomposition of oxidizers, suggesting the beneficial of using microsized I$_2$O$_5$ as the biocidal oxidizer. Transmission electron microscope with X-ray compositional microanalysis characterization was performed to analyze the post-combustion products and the production of iodine and aluminum oxides were found as main products. Additional studies of hygroscopic properties of I$_2$O$_5$ on its thermite reaction will also be discussed. Our study of Al/I$_2$O$_5$ thermites show that these I$_2$O$_5$ containing thermite reactions are very reactive and suggested to effectively produce iodine gas which can be used in microbial agent defeat applications.
1. Introduction

Global terrorist threats involving the usage of biological agents highlight the need for preemptive neutralization of biological agent munitions, stockpiles and production facilities. The approaches for effective destruction of biological agents are being considered and an ideal neutralization of biological agents is suggested to possess both a thermal and long-lasting biocidal agent release. [1] Recently, one class of thermite reactions which exhibit both thermal and chemical defeat characteristics was proposed to be a promising approach to effectively neutralize this threat. [1-6]

The thermite reaction is a highly exothermic reaction between a metal fuel and metal oxide oxidizer. Aluminum is most often the choice of fuel, due to its high reaction enthalpy, high thermal conductivity and availability. [7-8] A variety of oxidizers have been used in formulation of thermites, with the most studied oxidizers including Fe₂O₃, CuO, MoO₃, Bi₂O₃, WO₃, etc. [9-12] On the other hand, other oxidizers, such as KMnO₄, [13] KClO₄, [14] AgIO₃, [1] are found to be highly reactive. Among these oxidizers, AgIO₃ has been considered as a potential biocide due to the high thermal release and the reaction products. Sullivan et al. found that both silver and iodine species, which are known biocides, produced in the Al/AgIO₃ thermite reactions were predominantly found in the exterior of the product particle, and thus were bio-available. [1] Another class of oxidizers containing iodine, such as I₂O₅ et al., [3, 6, 15] have been suggested, as a means to release significant quantities of gas phase iodine. Martirosyan et al. found that Al/I₂O₅ nanothermite produced much higher transient pressure pulse than traditional metal oxides based nanothermites. [6, 16] Clark and Pantoya tested the biocidal effects of different thermite reactions (Al+I₂O₅, Al+Ag₂O, and Al+Fe₂O₃) on spore neutralization, and found that only the iodine containing thermite demonstrated significant spore neutralization. [3]

In this paper, we aim to further explore the Al/I₂O₅ thermite reaction. In particular, ignition and combustion performance along with the final state of the products will be studied. The ignition and reaction process of nano-Al/micro-I₂O₅ were characterized by a high speed digital camera and a temperature-jump/time-of-flight mass spectrometer (T-Jump/TOFMS) and whereby thermite reactions can be initiated from a rapidly heated fine wire. The decomposition of iodine pentoxide during rapid heating was also characterized by T-Jump/TOFMS. Constant-volume combustion tests were performed and compared with traditional thermites formulations. The post combustion products were characterized using transmission electron microscopy and X-ray analysis. The results demonstrate that the iodine containing thermites can produce a lot of iodine species and possess a good combustion performance, indicating their potential applications in biocide and energetic gas generators.

2. Methods

2.1. Sample preparation

The nano-aluminum samples used in this study were purchased from the Argonide Corporation, and designated as “50 nm ALEX”. The active aluminum was measured by TGA to be 70% by weight, and was considered when preparing the stoichiometric samples. Iodine pentoxide powder (I₂O₅) was purchased from Sigma-Aldrich (99.99 % purity) and stored in a glove box to prevent water adsorption. Powder X-ray diffraction (XRD, Bruker D8 Advance using Cu Kα radiation) results in Figure 1 show that the as received I₂O₅ contains small amount of H₃IO₈ which either from
manufacturing process or water adsorption during XRD characterization. Microsized \( \text{I}_2\text{O}_5 \) samples were prepared by mechanical milling 1 hour (Cyromill, Retsch) of the as-received \( \text{I}_2\text{O}_5 \) in hexane to prevent water uptake.

![XRD pattern of as received \( \text{I}_2\text{O}_5 \) from Sigma-Aldrich and standard XRD patterns of \( \text{I}_2\text{O}_5 \) and \( \text{H}_3\text{O}_8 \). Note: All other peaks without marks in as received \( \text{I}_2\text{O}_5 \) are from \( \text{I}_2\text{O}_5 \) phase.](image1)

**Figure 1.** XRD pattern of as received \( \text{I}_2\text{O}_5 \) from Sigma-Aldrich and standard XRD patterns of \( \text{I}_2\text{O}_5 \) and \( \text{H}_3\text{O}_8 \). Note: All other peaks without marks in as received \( \text{I}_2\text{O}_5 \) are from \( \text{I}_2\text{O}_5 \) phase.

The milled \( \text{I}_2\text{O}_5 \) samples, as well as as-received \( \text{I}_2\text{O}_5 \) were characterized by scanning electron microscopy (SEM, Hitachi SU-70 FEG-SEM), and the images show the particle sizes go down to 2-4 \( \mu \text{m} \) after milling , as shown in Figure 2. The milled \( \text{I}_2\text{O}_5 \) particles were used in the following tests. Microsized Fe\textsubscript{3}O\textsubscript{3} and CuO powders (<5 \( \mu \text{m} \) as specified) used in this study were purchased from Sigma-Aldrich, and summarized in Table 1. For these thermite formulations, we can take them as composites comprised of nanosize fuel and microsize oxidizers.

![SEM images of as received (a) and milled (b) \( \text{I}_2\text{O}_5 \) particles.](image2)

**Figure 2.** SEM images of as received (a) and milled (b) \( \text{I}_2\text{O}_5 \) particles.
Thermite samples were prepared by mixing of nano-aluminum and I$_2$O$_5$ powder in stoichiometric ratio. The mixed samples were ultrasonicated in ~10 ml hexane for about 30 min to ensure the mixing between the fuel and oxidizer. For the wire heating experiments, the prepared sample suspension was coated onto a ~10 mm long, 76 µm diameter platinum wire with a micropipette. For the constant volume combustion cell tests, the ultrasonicated thermites sample suspension were kept in a vacuum oven at 333 K (60 °C) to allow the hexane to fully evaporate. The dry powder was then gently broken apart to a loose powder.

2.2. Time-resolved mass spectrometry measurement and wire ignition with high speed imaging

The recently developed temperature-jump/time-of-flight mass spectrometer (T-Jump/TOFMS) [17] was used to characterize the decomposition of I$_2$O$_5$ and the thermite reaction between nano-Al and I$_2$O$_5$. The T-Jump probe (76 µm Pt wire) is directly inserted close to the electron ionization (EI) region of the TOF mass spectrometer, which enables continuously monitoring of a reaction event with a temporal resolution of 100 µs per mass spectrum. Typically, the T-Jump filament (Pt wire, length ~12 mm, diameter ~76 µm) was coated with a thin layer of sample powder (~0.1 mg) and directly inserted close to the electron ionization (EI) region of the mass spectrometer. The coated Pt wire can be rapidly joule heated up to ca. 1800 K in 3 ms, corresponding to a heating rate of ~5×10$^5$ K/s. The Pt wire was replaced after each heating event. From the voltage and current trace, a resistivity measurement can be obtained and related to the instantaneous temperature of the Pt wire, which can be mapped against the time resolved mass spectra. Time-resolved mass spectra combined with temperature profile were then used for characterization of decomposition or thermite reaction. A detailed experimental description of T-Jump/TOFMS can be found in our previous papers. [17, 18]

High speed imaging of sample burning on the wire was conducted with a Vision Research Phantom® v12.0 digital camera. The high speed video was taken at a resolution of 256×256 and frame rate of 67065 fps (14.9 µs per frame). The ignition temperature of the thermite sample reaction was obtained from the correlated high speed imaging of the ignition events with temperature profile of the Pt wire.

2.3. Pressure cell combustion tests: Simultaneous pressure and optical characterization

A constant volume combustion cell [13, 19] was used to characterize the reactivity of bulk thermite samples with the capability of simultaneous pressure and optical measurements. Typically, a fixed mass (25 mg) of the loose thermite sample was placed inside a constant-volume (~13 cm$^3$) pressure vessel, and ignited by joule heating of a nichrome coil. A piezoelectric pressure transducer on the port of the cell, together with an in-line charge amplifier and signal conditioner were employed to measure the temporal pressure change and the pressurization rate (dP/dt). The pressurization rate has been used as a measure of reactivity in thermites since it has been found to correlate with flame propagation velocity, [20] another widely used measurement of thermite reactivity. The optical signal was simultaneously collected by a lens tube assembly attached on the port of the cell, containing a planoconvex lens (f = 50 mm) and a photodetector to collect the broadband emission. The characteristic burn time of thermites in the pressure cell was represented by the full width at half-maximum (FWHM) of the recorded optical signal. For the detailed combustion cell measurement, you can refer to our previous papers. [13, 19]
The measurement of reactivity of the thermites is usually reported as a relative value, which indicates that both the pressurization rate and optical emission measurements should only be thought of in terms of relative performance at the present time.

2.4 Post-combustion characterization

The post-combustion products were collected after combustion test in the combustion cell. The collected sample was dry ground by rubbing between two very clean glass slides. The powder adhered onto a TEM grid (Au mesh/carbon film) for analysis in transmission electron microscope (TEM, JEOL JEM 2100 FEG). This TEM sample preparation technique was used to avoid any interaction between the combustion products (e.g. iodine) and solvent. The TEM is equipped with an energy dispersive X-ray spectrometer (EDS, Oxford INCA 250) for elemental analysis, which can be operated in scanning mode to perform 1D elemental line scanning and 2D elemental mapping of the sample.

3. Results and Discussion

3.1 Time resolved mass spectrometry of iodine pentoxide decomposition and reaction with nano-aluminum

![Image of mass spectrometry spectra](image)

**Figure 3.** Time-resolved mass spectra from I$_2$O$_5$ decomposition (a) milled sample prepared in glove box and (b) milled sample exposed to air for one day.

I$_2$O$_5$ particles as well as thermite samples of nano-Al/micro-I$_2$O$_5$ were rapidly heated in ~3 ms and up to ~1800 K, at a heating rate of $5 \times 10^5$ K/s, and the species formed were examined by the time-resolved mass spectrometry. We begin by examining the time resolved mass spectra of milled I$_2$O$_5$ sample (microsize) decomposition under rapid heating, shown in Figure 3a. For spectrum taken at t<1.0 ms (also seen in t=0 s in Figure 5), primary peaks of H$_2$O (m/z=18) and N$_2$ (m/z=28), together
with a small amount of $O_2$ (m/z=32) are from the background species in the ionization chamber. At $T$=800 K (t=1.0 ms), we found a strong signal assigned to $O_2^+$ and other signals assigned to $I^-$, $IO^-$, $IO_2^-$, $I_2^+$, and $I_2O^+$. It is noted that $I^-$, $IO^-$, $IO_2^-$ were previously reported as the primary species of iodic acid (HIO$_3$) decomposition using mass spectrometer. [21] Given the fact that I$_2$O$_5$ is hygroscopic, this suggests that the spectrum taken at ~800 K might be from the decomposition of HIO$_3$ (also denoted as HIO$_3$I$_2$O$_5$) [22] which forms from reaction between iodine pentoxide and water (3I$_2$O$_5$+H$_2$O→2HIO$_3$). At higher temperatures >910 K (t=1.3 ms), only a very strong $O_2^+$ signal, as well as $I^-$, $I_2^+$ are observed. We also plot $O_2^+$ and H$_2$O$^+$ temporal intensity obtained during the rapid heating of milled I$_2$O$_5$ sample as a function of time and wire temperature shown in Figure 4a. From Figure 4a, the onset temperature of oxygen release for milled I$_2$O$_5$ particles is found to be ~760 K.

![Figure 4](image)

**Figure 4.** Temporal profile of oxygen and water peak intensity from heating of I$_2$O$_5$ samples. (a) milled sample prepared in glove box and (b) milled sample exposed to air for one day. (Heating rate ~5×10$^5$K/s)

In Figure 3b, we show the mass spectra taken at rapid heating of another milled I$_2$O$_5$ sample which was exposed to air for one day and expected to absorb much more water than milled I$_2$O$_5$ sample shown in Figure 3a. Comparison of the two samples (Figures 4a-b) clearly shows that water evolution in the air exposed sample is significantly above the background. Since the I$_2$O$_5$ sample shown in Figure 4b contains more water, it is not surprising to see a higher intensity of IO$^-$, IO$_2^-$. In Figure 3b. Similar with milled I$_2$O$_5$ samples shown in Figure 3a, only strong $O_2^+$ signal and $I^-$, $I_2^+$ species which are from the decomposition of I$_2$O$_5$ (2I$_2$O$_5$→5O$_2$+2I$_2$) can be seen at higher temperature. The onset oxygen release temperature is ~740 K, as shown in Figure 4b.

Figure 5 shows the time resolved mass spectra taken at 100 μs intervals for a nano-Al and milled I$_2$O$_5$ (microsize) thermite reaction. In addition to the mass spectrometry measurement conducted for the thermite reaction, a high speed camera system was coupled with the mass spectrometer to simultaneously capture the emission from the ignition and combustion process. The thermite sample was found to ignite at ~940 K (t=1.70 ms) as optically observed by the high speed camera. We also observe O$_2^+$, $I^-$ and $I_2^+$ prior to ignition, consistent with the straight decomposition of I$_2$O$_5$. Post
ignition, we find strong signals for $O_2^-$ and $I^-$ and weaker signals from $I_2^+$ and $I^{2+}$. A very weak $IO^+$ peak was also observed after ignition, presumably from some water in the sample. The species observed are consistent with the global reaction presented in Eq. 1 and 2. One point of note is that the amount of oxygenated iodine species is reduced in the thermite as compared with the straight decomposition, implying not surprisingly that the iodine sub-oxides can also act as an aluminum oxidizer.

Secondarily, we also see that ignition (~940 K) occurs after the point of gas phase release of $O_2$ from $I_2O_5$ (~740 K) and essentially at the point that aluminum melts (933 K).

$$2I_2O_5 \rightarrow 2I_2 + 5O_2$$  
Eq. (1)  
$$Al + I_2O_5 \rightarrow Al_2O_3 + I_2$$  
Eq. (2)  

Figure 5. Time-resolved mass spectra from nano-Al+micro $I_2O_5$ thermite reaction.

3.2. Combustion characterization of nano-Al/micro-$I_2O_5$ thermites

The ignition behavior of nano-Al/micro-$I_2O_5$ thermites samples were examined in atmospheric conditions by high-speed imaging. In Figure 6, we show selected temporal snapshots of the violent Al/$I_2O_5$ thermite reactions at atmospheric pressure. The images allow us to assign the point of ignition at $t=1.491$ ms, corresponding to the wire temperature of ~810 K. The images also show two ignition points that propagate toward each other and are suggestive of a flame propagation mechanism, consistent with hot $O_2$ convective heat transfer effects. In fact, this explanation has been previously suggested to explain high propagation rates for Al/Ag$IO_3$ burning on the wire. [1] Herein,
we noted that the ignition temperature for Al/I_2O_5 system in air at atmospheric pressure is found to be 100 degrees lower than the melting point of the aluminum. The low ignition temperature might be explained by the possible exothermic reaction between producing iodine from the oxidizer decomposition and the aluminum oxide shell surrounding the Al nanoparticles. [4]

![Figure 6](image)

**Figure 6.** Sequential snapshots of Al/I_2O_5 burning on fast-heating wire in air, as captured by a high-speed video camera. The labeled numbers are time elapsed (µs) after triggering. The thermite is nano-Al (ALEX) and milled I_2O_5 (microsize) with an equivalence ratio of 1.0.

In the ionization chamber of mass spectrometer (~10^-6 Torr), the nano-Al/micro-I_2O_5 thermites displayed a much less violent reaction and burning than at atmospheric conditions. It is worth noting that a higher ignition temperature was found for the nano-Al/micro-I_2O_5 thermite in vacuum (940 K), compared to ~810 K in air at atmospheric pressure. However, ignition temperatures in both cases are still higher than the oxygen release temperature from the I_2O_5 particles (~760 K). The differences of reactivity and burning in vacuum and air can be further explained from the following approach. The mean free path of gas released from the oxidizers in vacuum is orders of magnitude higher than in air, and so some oxygen released from the I_2O_5 particles may simply escape from the thermite mixture before it reacts with the aluminum nanoparticles.

Constant volume combustion cell tests were performed to evaluate the relative performance of nano-Al/micro-I_2O_5 thermites against other thermites under atmospheric conditions. It should be noted that all thermite formulations in this investigation use the same nano-Al fuel. To compare the effects of particle size we plot simultaneous pressure and optical traces for both nano-Al/as received I_2O_5 and nano-Al/micro-I_2O_5 in Figure 7a-b. Quite clearly the micro-I_2O_5 thermite outperforms the as received I_2O_5 thermite in terms of a higher pressure peak, shorter pressure rise and burning time.

Direct comparison of the combustion cell tests of Al/I_2O_5 and nano-Al/micro-CuO are shown in Figure 7c-d. The plots show that I_2O_5 has a higher overpressure by a factor of ~ 4 relative to CuO and a shorter burning time. The same trend is also reported elsewhere that Al/I_2O_5 displays a much higher peak pressure than Al/CuO combustion in which both fuel and oxidizers are at the nanoscale. [6]

The experimental results of pressure and optical emission data are further tabulated for Al/I_2O_5 thermites along with other metal oxides thermite mixtures in Table 1. Clearly, the micro-I_2O_5
thermite exhibits the highest overpressure and pressurization rate, and shortest burning time among all other nano-Al/micro-oxidizer thermite samples and even a nano-Al/nano-Fe$_2$O$_3$ thermite.

**Figure 7.** (a) pressure and (b) optical traces for nano-Al+as received I$_2$O$_3$ and nano-Al+milled I$_2$O$_3$ thermites reactions; (c) pressure traces and (d) optical emission traces for nano-Al+milled I$_2$O$_3$ and nano-Al+micro-CuO thermites reactions. All of the results measured during combustion in a constant-volume combustion cell.

In a previous study of nanothermites, we found that for the Al/CuO nanothermite the pressure peaks earlier than does the optical emission. i.e. a rapid pressure signal followed by a prolonged optical signal. [17] The result can also be seen in Table 1 for nano-CuO, which shows a very short pressure rise time (13 μs) and a relative long burn time (192 μs). We have argued that the pressurization occurs as a result of the oxygen release from CuO nanoparticles, which can occur well before significant combustion as associated with the optical emission. This was contrasted in the same study with Al/Fe$_2$O$_3$, for which the pressure and optical signals occur concurrently for which we concluded that the oxidizer decomposition was the rate-limiting step in Al/Fe$_2$O$_3$. However, for all nano-Al/micro-oxidizer thermites formulations tabulated in Table 1, we can see the pressure and optical signals occur almost concurrently, or even earlier. This is very different than that observed in Al/CuO nanothermite system, indicating that the reaction mechanism in the nano-Al/micro-oxidizer system is quite different. Given the only difference for Al/CuO nanothermites and nano-Al/micro-CuO system is the particle size of the CuO oxidizer, it is reasonable to conclude that the oxidizer decomposition has become the rate-limiting step in nano-Al/micro-CuO thermite reaction. By
extension then this argument implies that oxidizer decomposition is limiting in the nano-Al/micro-I_2O_5 thermite reaction for which pressure and optical signals occur concurrently.

Table 1. Combustion cell test data for thermites samples prepared with different oxidizers. All oxidizers were mixed with nano-Al (ALEX). Thermites samples were prepared stoichiometrically assuming complete conversion to Al_2O_3.

<table>
<thead>
<tr>
<th>Oxidizers (w/Al, ( \phi = 1 ))</th>
<th>( P_{\text{rise}} ) (KPa)</th>
<th>Pressure rise time (( \mu \text{s} ))</th>
<th>Pressurization Rate (KPa/( \mu \text{s} ))</th>
<th>FWHM burn time (( \mu \text{s} ))</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_2O_5 ) (A)</td>
<td>237</td>
<td>944</td>
<td>0.251</td>
<td>1579</td>
<td>As received, Sigma-Aldrich, 99.99 %</td>
</tr>
<tr>
<td>( I_2O_5 ) (M)</td>
<td>366</td>
<td>397</td>
<td>0.922</td>
<td>293</td>
<td>After 1 hour milling</td>
</tr>
<tr>
<td>Micro-CuO</td>
<td>152</td>
<td>732</td>
<td>0.208</td>
<td>514</td>
<td>&lt;5 ( \mu \text{m} ), 98%, Sigma-Aldrich</td>
</tr>
<tr>
<td>Micro-Fe_2O_3</td>
<td>51.7</td>
<td>8350</td>
<td>0.00619</td>
<td>4394</td>
<td>&lt;5 ( \mu \text{m} ), \geq 99%, Sigma-Aldrich</td>
</tr>
<tr>
<td>Nano-CuO</td>
<td>800</td>
<td>13</td>
<td>61.5</td>
<td>192</td>
<td>&lt;50 nm, Sigma-Aldrich</td>
</tr>
<tr>
<td>Nano-Fe_2O_3</td>
<td>92.4</td>
<td>800</td>
<td>0.116</td>
<td>936</td>
<td>&lt;50 nm, Sigma-Aldrich</td>
</tr>
</tbody>
</table>

Thermodynamic equilibrium data for Al, Fe_2O_3, CuO and I_2O_5 based thermites taken from Fischer and Grubelich’s theoretical calculations [23] are shown in Table 2. From the data both the Cu and I based systems should be significant gas producers relative to Fe, and is in fact consistent with the pressurization data presented in Table 1. The experiments however show that I_2O_5 generates a pressure rise more than four times that of of nano-Al/micro-CuO system, indicating the faster reaction kinetics. The higher maximum pressure can be explained by the fact that the evaporation of low boiling point iodine (457 K) could increase the pressure inside the reactor while the boiling point of metal product formed during Al/CuO thermite reactions is much higher than iodine. [6]

Table 2 Constant enthalpy and pressure thermodynamic equilibrium calculations of stoichiometric thermite systems. Data is taken from Fisher and Grubelich (1998) without taking account of the oxide shell on Al.

<table>
<thead>
<tr>
<th>Thermite reaction</th>
<th>Adiabatic Temp. (K)</th>
<th>Gas production (mmol/g)</th>
<th>Major gas species</th>
<th>State of metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2\text{Al+Fe}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe} )</td>
<td>3135</td>
<td>1.4</td>
<td>Fe</td>
<td>liquid-gas</td>
</tr>
<tr>
<td>( 2\text{Al+3CuO} \rightarrow \text{Al}_2\text{O}_3 + 3\text{Cu} )</td>
<td>2843</td>
<td>5.4</td>
<td>Cu</td>
<td>liquid-gas</td>
</tr>
<tr>
<td>( 10\text{Al+3I}_2\text{O}_3 \rightarrow 5\text{Al}_2\text{O}_3 + 3\text{I}_2 )</td>
<td>&gt;3253</td>
<td>6.3</td>
<td>I_2</td>
<td>gas</td>
</tr>
</tbody>
</table>

For all thermites reactions limited by the decomposition of oxidizers, the pressure rise is largely dependent on the final state of the products other than the gas produced during the decomposition of oxidizers. Next, it will be very straightforward for us to understand why the nano-Al/micro-CuO and nano-Al/micro-I_2O_5 can even outperform the nano-Al/nano-Fe_2O_3 thermite reactions in terms of relative combustion performance shown in Table 1.

In addition, from the point of view of Al/I_2O_5 thermite’s potential application as biocides, it has been expected that the pressure rise is from the produced hot biocidal species by very exothermic
thermite reactions other than species from the decomposition of oxidizers. Hence, the nano-Al/micro-I$_2$O$_5$ thermite formulations with concurrent pressure and optical rise signal should be a very good candidate for effective biocides. Since nano-Al/micro-CuO and nano-Al/micro-I$_2$O$_5$ behave similarly in the combustion cell tests, we would expect similar combustion behavior for nanosized oxidizers. That is to say, the higher pressure rise occurs much earlier than optical emission signal. Of course, we cannot rule out the possibility that two oxidizers at nanoscale might behavior very differently, and more experimental studies are needed to verify this.

3.3. Post-combustion characterization of Al+I$_2$O$_5$ thermites

Not only the combustion performance of thermites, but also the nature and dispersion of the products matter in biocidal applications. Numerous toxicological studies have shown that small nanoparticles have higher cell cytotoxicity. [24, 25] So, a good biocide system should be a reaction producing biocidal products which have a high surface area and can be exposed to the environment.

The post combustion products of Al/I$_2$O$_5$ thermite reaction were collected and added up with the ethanol, the resulted solution displayed a brown color indicating the iodine formed after reaction. The sample was also dry ground by rubbing between two very clean glass slides and prepared for TEM analysis. A representative transmission electron microscopy (TEM) image along with the elemental map of Al, O and I is shown in Figure 8 for products from the combustion cell test of Al/I$_2$O$_5$ thermite. From the elemental mapping, we see particles that contain Al and O, and other particles only contain I. Selected particles with an elemental linescan coupled also confirmed the products are aluminum oxide and iodine, as shown in Figure 9. The produced iodine species exists as small nanoparticles (with dark contrast) confirmed by EDS in Figure 8-9. The results also excluded the possibility of the AI$_3$ formation in the final products. In simple, Al/I$_2$O$_5$ thermite reaction is an effective way to produce iodine gas via condensed phase reaction. Furthermore, upon cooling the iodine condenses to form the high surface area nanoparticles with surface explosion to the environment thus maximize its killing potential as a biocidal agent.

![Figure 8](image_url)

**Figure 8.** Representative TEM image and 2D elemental mappings (Al, O, and I, using EDS) of post-combustion products after Al+I$_2$O$_5$ thermite reaction in the combustion cell. The thermite was nano-Al (ALEX) and milled I$_2$O$_5$ particles (microsize) with an equivalence ratio of 1.0. Note: Iodine element has a dark contrast in TEM image because of its high atomic number.
4. Conclusions

The ignition and combustion behavior of nano-Al/micro-I$_2$O$_5$ thermite was systematically studied. Mechanical milling was successfully applied to prepare microsize I$_2$O$_5$, and the milled I$_2$O$_5$ thermite system was found to have a higher reactivity compared before mechanical milling. Time resolved mass spectrometry shows that I$_2$O$_5$ oxidizer starts to decompose at 760 K to produce a lot of oxygen and iodine species, mainly I$^+$ and I$_2$$^+$. The ignition temperature of nano-Al/micro-I$_2$O$_5$ thermite reaction in air at atmospheric pressure was determined to be $\sim$810 K. Combustion cell tests show that nano-Al/micro-I$_2$O$_5$ system outperforms nano-Al/micro-CuO system in both pressurization rate and burning time. Concurrent pressure and optical rising was observed for all nano-Al/micro-oxidizer systems in this study. This suggests that the burning of nano-Al/micro-oxidizer systems in this study is possibly limited by the decomposition of oxidizers. Different than the nano-Al/nano-CuO system, the pressure rise in nano-Al/micro-I$_2$O$_5$ in this study is from the produced hot biocidal species by very exothermic thermite reactions other than species from the decomposition of oxidizers. TEM coupled with EDS analysis was performed to analyze the post combustion products, and the results indicated that the produced iodine species condensing as small nanoparticles. Considering its potential application as biocides, nano-Al/micro-I$_2$O$_5$ thermite reaction is an effective way to produce iodine gas via condensed phase reaction. Furthermore, upon cooling the iodine condensed to form the high surface area nanoparticles with surface explosion to the environment thus could maximize its killing potential as a biocidal agent.

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References


