1. REPORT DATE (DD-MM-YYYY) 2. REPORT TYPE 3. DATES COVERED (From - To)

Technical Report

- 

4. TITLE AND SUBTITLE
THE ROLE OF METAL OXIDES IN NANOTHERMITE REACTIONS: EVIDENCE OF CONDENSED PHASE INITIATION

5a. CONTRACT NUMBER
W911NF-09-1-0214

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

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7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of Maryland - College Park  
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20742 -5141

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office  
P.O. Box 12211  
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
55832-EG.2

12. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
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15. SUBJECT TERMS
Nanoenergetic materials

16. SECURITY CLASSIFICATION OF:

a. REPORT
UU

b. ABSTRACT
UU

c. THIS PAGE
UU

17. LIMITATION OF ABSTRACT
UU

15. NUMBER OF PAGES
19a. NAME OF RESPONSIBLE PERSON
Michael Zachariah

19b. TELEPHONE NUMBER
301-405-4311

Standard Form 298 (Rev 8/98)  
Prescribed by ANSI Std. Z39.18
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THE ROLE OF METAL OXIDES IN NANOTHERMITE REACTIONS: EVIDENCE OF CONDENSED PHASE INITIATION

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Abstract

This work is a culmination of several corresponding studies designed to probe the initiation and reaction of aluminum nanothermite systems. The main diagnostic tool used in this study is a Temperature-Jump/Time-of-Flight Mass Spectrometer (T-Jump/TOFMS), which uses a filament heating method capable of very high heating rates up to $10^6 \, ^\circ C/s$, while spectra are simultaneously obtained at a time resolution of 100 µs. Nanothermites of Al/CuO, Al/Fe$_2$O$_3$, Al/WO$_3$, and Al/Bi$_2$O$_3$ were all tested with this system along with the neat Al and metal oxide powders. High speed imaging was also used to visually compare reaction rates of each sample showing that, contradictory to some previous works, Al/Bi$_2$O$_3$ reacts much faster than the other nanothermites. The nanothermites Al/CuO, Al/Fe$_2$O$_3$, and Al/WO$_3$ showed a correlation of ignition with the neat oxide’s decomposition to gas phase products. However, the Al/Bi$_2$O$_3$ sample clearly ignites at a temperature well below the decomposition of Bi$_2$O$_3$ to gaseous products, which strongly suggests a condensed phase initiation mechanism for Al/Bi$_2$O$_3$. To further investigate this mechanism, C/Bi$_2$O$_3$ was also tested as, unlike aluminum, carbon will remain in the solid phase in the temperature regime of our experiments. This work showed similar results as the Al/Bi$_2$O$_3$ where C/Bi$_2$O$_3$ clearly reacts before Bi$_2$O$_3$ decomposes. In a complimentary study a high-heating rate TEM grid was also used to probe the behavior of individual nanoparticles under these experimental conditions. While testing Bi$_2$O$_3$ it was seen that the material reacted with the carbon coating of the TEM grid, again displaying a condensed phase reaction. The TEM studies provide evidence that other nanothermites may follow this mechanism as well. Furthermore, a T-Jump/PMT setup was used to optically determine the burn times and ignition temperatures in filament heating experiments, and was also used at the Argonne National Laboratory’s Advanced Photon Source. This work provided unique high speed phase contrast imaging that offers further insight into the aluminum nanothermite reactions.

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Introduction

Nanocomposite thermite reactions are attracting increased interest in the field of energetic materials due to high energy densities and adiabatic flame temperatures, which are comparable or greater to those of traditional organic based energetics (e.g. RDX). However, due to large characteristic diffusion length scales, traditional thermites burn at a much slower rate than those of organic energetics which have the fuel and oxidizer essentially mixed at the atomic level. Nanothermites, which are typically made with aluminum nanoparticles of size less than 100 nm, drastically reduce diffusion lengths compared to microscale particles and demonstrate burn rates up to several orders of magnitude higher.[1-5] Given the central role that nanoaluminum plays, much attention has been given to understanding the transport of aluminum with respect to its \( \text{Al}_2\text{O}_3 \) shell. If the aluminum nanoparticle is rapidly heated, the nearly instantaneous melting of the aluminum could have considerable effects in aiding of aluminum transport. The exact nature of aluminum transport is not known, but several models have been proposed including aluminum and oxygen diffusion through the alumina shell[6], pressure build up due to melting of the aluminum, which ruptures the shell allowing Al to leak out[7] and extreme pressure build up causing eruption of the alumina shell that spallates the molten aluminum[8]. Regardless of the argument, it can be agreed that rapid heating of an aluminum particle will have a positive effect on the transport of aluminum. In recent studies interest has shifted towards understanding the effect of different oxidizers on the nanothermite reaction.[9-11]

Because of the large variety of metal oxides available, each with different physical, chemical, and electrical properties, the potential to change the energy release profile becomes feasible. Our group has done some previous work characterizing nanothermite reactions.[9, 12, 13] In particular, our work has highlighted the dependence of nanothermite ignition on the gaseous oxidizer release from the metal oxides CuO, Fe\(_2\)O\(_3\), and ZnO.[14] However, there is uncertainty as to whether oxidizer release to the gas phase is a necessary mechanistic step for all nanothermite compositions. In chemical looping combustion (CLC) systems, condensed phase reaction between carbon and CuO has been demonstrated.[15] In this work Siriwardane and co-workers suggests that the surface of the CuO, which has a Tammann of \( \sim 405 \) °C, melts and provides a pathway for oxygen distribution to the solid coal. There
are significant differences between the phase transitions of carbon and aluminum in the temperature ranges of a combustion system. Aluminum has a melting point of 660 °C and boiling point of 2520 °C, whereas carbon will not change phase until over 3800 °C.[16] These differences will have effects on transport properties between the two systems, but some aspects of the reaction mechanism may be transferrable.

Another metal oxide of particular interest in nanothermite formulations is bismuth trioxide, which has a relatively low vapor pressure and unique conducting properties when heated. Bi₂O₃ is well known as a good oxide ion conductor, and has been highly researched for use in electrochemical cell applications.[17-21] The δ-phase of Bi₂O₃, which is stable from 1002-1097 K [18, 21], shows an advanced ion conductivity up to two orders of magnitude greater than that of its other phases.[17] It has been observed that when combined with aluminum nanoparticles, a very reactive Bi₂O₃ nanothermite is formed. Sanders et al.[10] investigated the difference between four different aluminum nanothermites Al/CuO, Al/Bi₂O₃, Al/MoO₃, and Al/WO₃. Each of these thermite mixtures was subjected to tests in a closed bomb pressure cell, open tray burn, and burn tube experiments. Their results show that Al/Bi₂O₃ produces the greatest peak and average pressure, as would be expected from equilibrium calculations that indicate it produces the most gaseous species during combustion when compared to other oxidizers.[10, 11, 22] However, Al/Bi₂O₃ had the lowest propagation velocity in burn tube experiments, and had a slightly lower propagation rate than Al/CuO in the open tray experiments. Differing results were seen in open tray experiments by Puszynski et al where Al/Bi₂O₃ produced higher burn rates than Al/CuO, Al/MoO₃, or Al/WO₃.[22] This group also performed DSC traces at slow heating rates of 1-20 K/min and determined the decomposition temperature to be in the range of ~839-861 K depending on the size of the Bi₂O₃ particles used in the mixture. We have also investigated the formation of ionic species during the nanothermite reaction in Al/Bi₂O₃, Al/CuO, Al/Fe₂O₃, and Al/WO₃, demonstrating that the bismuth oxide thermite produces the highest rate of ion release of the samples.[12]

Because of the interesting and in some cases contradictory behavior of the Bi₂O₃ and carbon nanocomposite systems, and the fact that no studies are available at high heating rates, we show in this paper our results at heating rates greater than 10⁵ K/s, of time resolved mass-spectrometry, and high
heating rate SEM. These results suggest that both Bi$_2$O$_3$ and carbon containing nanocomposites show a primary reaction pathway that is consistent with condensed phase reactions.

**Experimental**

Nanocomposite samples were prepared by mixing aluminum and Bi$_2$O$_3$ nanoparticles particles to obtain a stoichiometric mixture.

$$2Al + Bi_2O_3 \rightarrow Al_2O_3 + 2Bi$$  \hspace{1cm} (1)

Oxidizers were purchased from Sigma Aldrich, and were spherical and agglomerated. These include Bi$_2$O$_3$ (90-210 nm), Fe$_2$O$_3$ (<50 nm), and CuO (<50 nm), with the sizes specified by the supplier. The aluminum was purchased from Argonide, Corp. and has an average particle size of ~50 nm. C/metal oxide samples were also stoichiometrically mixed. The C/Bi$_2$O$_3$ reaction is given as an example,

$$3C + 2Bi_2O_3 \rightarrow 3CO_2 + 4Bi$$ \hspace{1cm} (2)

where the carbon is "regal 300" carbon black attained from Cabot Corp. When calculating stoichiometry, the Al$_2$O$_3$ shell which makes up 30% of the mass of the aluminum sample is taken into account as previously determined through thermogravimetric analysis. The samples are initially placed in a hexane solution and sonicated for ~20 min to ensure a fine mixing of materials. The primary instrument used is a Temperature-Jump/Time-of Flight Mass Spectrometer (T-Jump/TOFMS). The system and experimental procedure has been described in detail elsewhere.[23] In brief, the sample slurry is coated on a ~1 cm long, 76 µm diameter platinum filament, which can be heated at a very high rate of up to $10^6$ K/s with the use of a tunable voltage pulse from an in-house built power supply. The essence of the experiment is that the T-Jump filament is directly inserted close to the electron ionization region of a custom time-of-flight mass spectrometer (MS). This allows for a very short delay (~20 µs) between product species evolution and ionization and subsequent detection by the micro-channel plate (MCP) detector of the TOFMS. Ionization of the gaseous product species is performed by an electron-impact (EI) ionization source with an energy of 70 eV. For a typical heating event, a sequence of 95 spectra with m/z (mass to
charge ratio) up to 400 are recorded with a temporal resolution of 100 µs. Furthermore, the current and voltage through the filament are simultaneously recorded during heating to determine the onsite filament temperature. The experimental procedure for our nanothermite self-ionization study is given elsewhere, [12] but in short, the setup is the same as for a normal T-Jump/TOFMS run, except that the e-gun is turned off. Therefore any ions that are detected by the MCP are strictly from ionization during the reaction. Several experiments were conducted with the addition of simultaneous high speed imaging using a Phantom 12.1 camera for select T-Jump experiments using an imaging rate of ~33,000 fps. Aside from the nanocomposite samples, the carbon, aluminum, and metal oxide samples were each tested separately in the T-Jump/TOFMS system to investigate each material’s role in the nanocomposite initiation. In a complimentary study, Al/Bi₂O₃, Al/CuO, and Al/Fe₂O₃ nanothermites were tested in a constant volume pressure cell that has its experimental details described elsewhere.[24]

A unique heating holder (Protochips, Inc.) was also used to visually investigate the morphological changes of Bi₂O₃ inside a scanning electron microscope (SEM). This holder can heat the sample in-situ from room temperature to a maximum of 1473 K, at a rate of 10⁶ K/s. The before and after images can be compared to draw some conclusions about how the reaction occurred. In the context of the mass-spectrometry results we can consider this as “T-Jump microscopy”.

Results and Discussion

T-Jump Mass Spectrometry

We begin our analysis by first investigating the time resolved mass spectra of the reaction products from rapid heating of Al/Bi₂O₃ and neat Bi₂O₃ nanothermite mixtures. For each case the heating rate was set to ~5x10⁵ K/s which for a pulse time of ~3 ms, gave a final temperature of ~1870 K. It should be noted that our TOFMS has a background signal at m/z 18, (H₂O⁺) and minor peaks at m/z 17, 28, and 32, representing OH⁺, N₂⁺, and O₂⁺ respectively. A typical spectrum obtained during Bi₂O₃ heating is shown in Figure 1. It shows a peak at m/z 32 for O₂⁺, m/z 44 for CO₂⁺, m/z 104.5 for Bi⁺², m/z 209 for Bi⁺, and m/z 216 for BiOH. A full time-resolved set of spectra of the Al/Bi₂O₃ reaction is shown in Figure 2 where each spectrum is separated by 100 µs. The detailed Al/Bi₂O₃ spectrum in Figure 3 shows
peaks at $\text{Al}^+$, $\text{Bi}^+$, $\text{Bi}^{+2}$, $\text{O}_2^+$, and $\text{CO}_2^+$. One interesting feature not observed in our mass spectral characterization of other thermites is the doubly charged Bi in the Bi$_2$O$_3$ system.[9, 12] This is likely due to Bismuth having low first and second ionization potentials of ~7.29 and 16.69 eV respectively.[25]

![Image of Bi$_2$O$_3$ mass spectrum]

**Figure 1:** Time-of-flight mass spectrum for Bi$_2$O$_3$ sample.

![Image of Al-Bi$_2$O$_3$ spectrum]

**Figure 2:** Full spectrum for Al-Bi$_2$O$_3$ nanothermite reaction. Each spectrum is separated in time by 100 µs.

Our self-ionization work also demonstrated unique ion formation properties for the Bi$_2$O$_3$ thermite as it had a higher ionization rate than the other thermites tested.[12] Another interesting feature of Al/Bi$_2$O$_3$ nanothermite is the amount of Bi vapor formed compared with metal vapor formed in other reactions. If Bi$_2$O$_3$ goes through reaction (1), then Bi would be in gas phase due to its relatively low boiling
temperature of 1837 K and an adiabatic flame temperature for the system of 3253 K.[25, 26] Al/CuO and Al/Fe$_2$O$_3$ reactions form very high temperature boiling metals (Cu: 2835 K; Fe: 3134 K) [25], and have adiabatic flame temperatures of 2843 K and 3135 K respectively, thus we should expect more vapor phase Bi. This trend can be confirmed through comparison of Al/Bi$_2$O$_3$, and Al/CuO systems in Figure 4, which shows bismuth and copper gas release from their respective nanothermite systems during T-Jump/MS experiments.

![Figure 3: Time-of-flight mass spectrum for Al/Bi$_2$O$_3$ sample (TOP: m/z 0-100, BOTTOM: m/z 100-200).](image)

![Figure 3: Time-of-flight mass spectrum for Al/Bi$_2$O$_3$ sample (TOP: m/z 0-100, BOTTOM: m/z 100-200).](image)

![Figure 3: Time-of-flight mass spectrum for Al/Bi$_2$O$_3$ sample (TOP: m/z 0-100, BOTTOM: m/z 100-200).](image)
To further investigate the nature of Al/Bi$_2$O$_3$ combustion, high speed imaging was used to capture the nanothermite reaction while simultaneously sampling with the T-Jump/MS. Figures 5 and 6 show selected images of the T-Jump experiments under vacuum for Al/Bi$_2$O$_3$ and Al/CuO respectively at a framing rate of ~33,000 fps (every 30 s). From these images we concluded that Al/Bi$_2$O$_3$ burns about twice as fast as Al/CuO as these samples had burn times of ~0.09 ms and ~0.18 ms, respectively.

**Figure 4:** Bi and Cu gas release from Al/Bi$_2$O$_3$ and Al/CuO nanothermites.

**Figure 5:** High speed images of Al/Bi$_2$O$_3$ during heating in the TOFMS.
Figure 6: High speed images of Al/CuO during heating in the TOFMS.

Previous burn tube and open tray experiments testing thermite performance have given mixed results as to whether Al/CuO or Al/Bi₂O₃ exhibits a higher burn rate because of the difficulty in controlling experimental parameters. Packing density, particle size, tube diameter, and pressure are just a few critical experimental parameters that greatly influence burn rate results. For comparison in this paper, we consider the work by Son and co-workers on aluminum nanothermites of CuO, Bi₂O₃, MoO₃, and WO₃ in both open tray and burn tube setups.[10] Their results show that Al/CuO has the fastest burn rate in open tray experiments followed by Al/Bi₂O₃, while in the burn tube, Al/Bi₂O₃ was the poorest performer followed by Al/CuO. So in both the burn tube and open tray experiment Al/CuO outperformed Al/Bi₂O₃, however, in our filament tests it is clear that the opposite is true. To resolve this discrepancy we refer to the work of Weismiller et al who reported on the dependence of pressure and atmosphere on Al/CuO in a burn tube experiment.[27] They reported that higher pressures have a significantly detrimental effect on the burn velocity of a nanothermite, and ascribed this as a shift from a convective mode of heat transfer to a conductive one with an increase in pressure.[27] We can compare those results with our pressure cell data in Table 1, which shows maximum pressure, pressure rise time, pressurization rate, and overall burn time, for various nanothermite composites. Clearly Al/Bi₂O₃ has the highest maximum pressure followed by Al/CuO and Al/Fe₂O₃. This result, which has also been reported in other works, corresponds to the predicted high gas release for Al/Bi₂O₃.[26] In burn tube experiments it is reasonable to believe that the slower burn rate for the bismuth thermite is due to the increased local pressure while burning, which shifts the heat transfer to a conductive mode. The thermite reaction in the mass spectrometer is at a much lower pressure and thus as expected, the reaction in the bismuth oxide system is more rapid.

Table 1: Pressure cell results for various nanothermites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pmax (psi)</th>
<th>Pressure Rise Time (µsec)</th>
<th>Pressurization Rate (psi/µsec)</th>
<th>Burn Time (µsec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>T-Jump</td>
<td>Thermal</td>
<td>Mass</td>
<td>Temp</td>
</tr>
<tr>
<td>--------------</td>
<td>--------</td>
<td>---------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Al/Bi₂O₃</td>
<td>157</td>
<td>10.0</td>
<td>15.7</td>
<td>197</td>
</tr>
<tr>
<td>Al/CuO</td>
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<td>8.8</td>
<td>11.1</td>
<td>170</td>
</tr>
<tr>
<td>Al/Fe₂O₃</td>
<td>13.4</td>
<td>800</td>
<td>.017</td>
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</table>

The temporal nature of the T-Jump mass-spectrometer experiment allows us to draw some conclusions about the initiation steps that may be involved with the bismuth nanothermite and how it differs from some other systems. In our previous work, we studied the nanothermite reaction of Al/CuO, Al/Fe₂O₃, and Al/ZnO.[9] For each of these materials we investigated the decomposition of the thermite, as well as decomposition of the metal oxide and aluminum nanopowders.

![Image](image-url)

**Figure 7:** (A-C) Products from Al/Bi₂O₃. (D-E) Products from Bi₂O₃. (A) Al, (B) O₂, (C) Bi, (D) O₂, (E) Bi.
We found from comparing the metal oxide spectra and the thermite spectra that the thermite reaction initiates at a time in close proximity to the point of release of gaseous $O_2$ from the respective oxidizer. In comparison, Al/Bi$_2$O$_3$ shows a much different reaction characteristic. Figure 7 shows the filament temperature, as well as reaction product concentrations as detected by the mass spectrometer for Al/Bi$_2$O$_3$, and Bi$_2$O$_3$ in the current study. If we compare the reaction products in Figure 7 from the thermite (parts A-C) and the oxide (parts D-E) heating, we see that unlike other nanothermites, there is a significant difference in times between thermite ignition, and gas phase $O_2$ release from the oxide. Although these two samples were tested in separate heating runs, the experimental conditions were replicated in a similar fashion so that qualitative conclusions can be confidently made. We see that when the oxide is heated by itself, Bi and $O_2$ are released very late at $\sim$3.1 ms and $T = 1940$ K. This compares to the thermite case where combustion starts at $\sim$1.6 ms and $T = 1273$ K, as signified by the appearance of Bi, $O_2$, and shortly after, Al. Clearly, unlike the iron oxide and copper oxide thermite reaction systems, where ignition occurs very close to the point that the oxide releases gaseous $O_2$, the initiation of the Al/Bi$_2$O$_3$ occurs before the Bi$_2$O$_3$ decomposes to release gaseous oxygen. This evidence strongly suggests that the initiation of the Al/Bi$_2$O$_3$ reaction occurs in the condensed phase.

To further investigate this mechanism we consider a fuel which cannot vaporize at these temperatures. For this purpose we employ a C/Bi$_2$O$_3$, C/CuO, and C/Fe$_2$O$_3$, composites using nanometer scale carbon particles. To observe reaction within this system, the only feasible reaction pathway is for the oxygen from the oxide to heterogeneously react with the carbon particles. Figure 8 shows the individual spectra for A. C/CuO, and B. CuO.

**Figure 8:** Individual spectra for A. C/CuO, and B. CuO
To investigate the reaction products from rapid heating of the carbon nanocomposites, the neat metal oxides and nanocomposites were individually heated in separate experimental runs. Figures 8a and 8b show individual detailed spectra for the nanocomposite C/CuO, and the neat oxide CuO, respectively. A typical background spectrum for our mass spectrometer consists of peaks at mass to charge ratios (m/z) 18 (H₂O) and 28 (N₂), with smaller peaks at m/z 32 (O₂) and 17 (OH). The main reaction product for the carbon nanocomposite combustion in vacuum is CO₂ (m/z 44) as can be seen in both Figure 8a. There are several smaller peaks observed at m/z 12 (C) and 16 (O) as well as an increase in m/z 28 (CO), which are all considered to be due to fragmentation of the CO₂ molecule during ionization. This corresponds well to what is reported for the CO₂ mass spectrum in the NIST spectral library.[28] The small peaks at m/z 32 (O₂) are due to a small amount of oxygen not consumed in the reaction that is released to the gas phase. For the neat nanopowder, there is a significant difference in the amount of CO₂ and O₂ as compared to the nanocomposite. In Figure 8b the intensity of O₂ is greater than that in the nanocomposite, and the CO₂ is substantially decreased. This trend was also confirmed for the C/Bi₂O₃ and C/Fe₂O₃ nanocomposites. It is clear from comparison of the nanocomposites vs. neat oxide nanopowders that the O₂ formed by the metal oxides is almost entirely consumed in the reaction with carbon to form CO₂.

![Figure 9](image_url): Detected CO₂ and O₂ concentration from C/CuO and CuO, respectively.
With carbon dioxide detected as the prominent gaseous product species, it is unclear how the carbon is oxidized to form this. To further investigate the reaction pathways, comparison is made between time-resolved concentration profiles for the neat metal oxide nanopowders and the nanocomposites. The oxygen release profile from the neat copper oxide is compared with the carbon dioxide release from the C/CuO nanocomposite in Figure 9.

**Figure 10:** Detected CO$_2$ and O$_2$ concentration from C/Fe$_2$O$_3$ and Fe$_2$O$_3$, respectively.
This gives a correlation between what time/temperature the $O_2$ is released from the oxide, and when the reaction starts to progress in the C/CuO nanocomposite. From Figure 9 it can be seen that the CO$_2$ is produced from the C/CuO at a lower temperature than $O_2$ is released to the gas phase from the CuO. This strongly suggests that there is a condensed phase reaction mechanism driving the CO$_2$ producing reaction. Figure 10 plots the CO$_2$ production from C/Fe$_2$O$_3$ along with the $O_2$ release from Fe$_2$O$_3$, and Figure 11 does the same for Bi$_2$O$_3$. This Figure shows the same trend as that for C/CuO, the carbon dioxide is produced well before gaseous $O_2$ is available, therefore the initiation of this reaction must be in the condensed phase.

**T-Jump Microscopy**

To further explore the idea of a condensed phase combustion mechanism, we investigate the morphological changes, using in-situ rapid heating within a scanning electron microscope (SEM, Hitachi SU-70). The sample grids, which have a few nanometer thick holey carbon film deposited over a silicon carbide substrate, offer the opportunity to study the heating of Bi$_2$O$_3$ as well as the reaction with the
underlying carbon substrate. Figure 12 shows an SEM image of the sample on the grid before heating. The dark background is the thin carbon film, and the grainy looking areas are the holes in the carbon film which expose the underlying silicon carbide. The Al/Bi$_2$O$_3$ was sparsely placed on the grid so that in certain instances the Bi$_2$O$_3$ and Al are isolated as shown in Figure 12.

The sample was given a heating pulse from room temperature to 1250 K at a rate of $10^6$ K/s, and then held for 1 ms the results of which are shown in Figure 13. Elemental analysis of the sample after heating is shown in Figure 14. Despite the fact that we were well above the melting point of aluminum, it is clear that the aluminum aggregate did not undergo any sintering. However, the Bi$_2$O$_3$ showed significant changes within the 1 ms timescale of the heating pulse. It should be noted that with a longer heating pulse the aluminum will also show significant morphological change. One would expect that since aluminum melts at 933 K and bismuth trioxide melts at 1097 K that we would see some changes in aluminum before Bi$_2$O$_3$. These results suggest that either the timescale of heat conduction is significantly lower in Al than in Bi$_2$O$_3$, or that the alumina shell is not immediately rupturing upon melting of the aluminum core. Figure 14 confirms that during heating the Bi$_2$O$_3$ forms a film of Bi$_2$O$_3$ with spheres of Bi on its surface. If we consider regions where Bi$_2$O$_3$ is only in contact with the carbon film but not near any aluminum we can observe a region where we have a Bi$_2$O$_3$ film over which a much larger elemental Bi particle sits.
This strongly suggests that the Bi$_2$O$_3$ liquid reacts with the carbon which can be indicated by the recession of the hole in the carbon film from Figure 12 to Figure 13. The C/Bi$_2$O$_3$ reaction produces liquid Bi (MP 545 K), which appears to be immiscible in liquid Bi$_2$O$_3$ allowing it to phase separate and form larger spherical particles. This result appears to be highly consistent with the condensed phase reaction model deduced from the T-Jump/TOFMS experiments. The fact that the liquid Bi$_2$O$_3$ melts and wets the surface of the carbon further suggests that there is a transfer of oxygen through the liquid Bi$_2$O$_3$ phase.

We also note that the reaction has proceeded to completion within the timescale of the heating pulse, <1 ms. The reaction may have actually occurred even faster, however, 1 ms was the minimum pulse which could be applied. This may imply that very thin carbon is a viable fuel to use in a thermite formulation, so long as the length scales are sufficiently small and the oxidizer can heterogeneously react with carbon.
If carbon could be utilized as a fuel, then much higher overpressures could be realized via the formation of a gaseous CO$_2$ product, thus greatly improving the performance. Carbon is also unique in that it will not have a passivating oxide shell like that of metal surfaces. With no oxide shell, there would be no loss of mass due to partial oxidation, but also, there should be little to no ignition delay caused by diffusion of species through the shell, as has been reported for nano-Al.[13] As a performance test a C/Bi$_2$O$_3$ sample was placed in the pressure cell, but the sample failed to initiate. It is possible that this was due to high agglomerate particle size, despite primary particles being on the order of 10’s of nanometers. Despite this failed test, the lack of a passivating shell, and high possible pressure outputs make carbon an attractive additive to metals, however, much more work will have to be done to test its viability.
Discussion

In our previous works, the difference in ignition points for various aluminum thermites suggests a strong dependence on the oxidizer for triggering the ignition point.[14] It is likely that for the Al/CuO and Al/Fe₂O₃ nanothermites, which ignite at higher temperatures than Al/Bi₂O₃, the aluminum was already exposed at the time of oxygen release from the oxidizer. Bi₂O₃ will likely have free O²⁻ ions within its lattice as soon as it enters its ion conducting phase at 1002 K, just above the melting point of aluminum at 933 K. If we take into account our high heating rate, this temperature change will happen on the order of 10 μs. Our temperature for ignition of the bismuth oxide thermite is determined to be slightly higher in temperature than the δ-phase transition in Bi₂O₃, however, this high ignition temperature could be a result of implementing such a high heating rate. Our ignition temperature for Al/Bi₂O₃ is also higher than that reported by other groups. From Figure 7 we determine the temperature at ignition to be the point where
reaction products are first observed at ~1273 K, while Puszynski observed an exotherm in the Al/Bi₂O₃ reaction at temperatures of ~839-861 K. At this point we are not able to resolve this discrepancy but it is clear that we are probing different reaction kinetics than most of the previous works. High heating rates clearly result in a much more rapid exothermic event as compared to the slower heating rate studies which show a broad temporal exotherm.[22] Slow heating rates apparently also allow for the reaction to start at a temperature below the melting point of Al. Since the aluminum remains in the solid phase, the reaction is likely limited by the diffusion of oxygen through the Al₂O₃ shell.[6] If we take the case for the bismuth oxide sample, if a high heating rate is applied, once the temperature reaches the point where the δ-phase is reached, we suddenly have an abundance of free, mobile oxygen ready to react, as well as aluminum in the liquid phase which can diffuse out of the Al₂O₃ shell.

This mechanism can be combined with our recently proposed reactive sintering mechanism,[29] and can also be applied to the carbon nanocomposites. In our previous T-Jump microscopy experiment with an Al/WO₃ nanothermite, we observed that during certain heating pulses neat WO₃ would undergo little to no morphological changes. However, under the same heating pulse, when the WO₃ was in contact with aluminum, significant melting of the WO₃ occurred. We believe that a condensed phase exothermic reaction between the Al and WO₃ aided in the heating of the material and caused these morphological changes. For the carbon based reactions this is likely a similar mechanism, where reactive sintering creates an intimate contact between the fuel and oxidizer to allow for a rapid condensed phase reaction. This also corresponds with the prediction by Siriwardane that the surface of the metal oxide particle can melt at the Tammann temperature, and create a pathway for oxide transfer to the fuel.[15] This would explain the reactions occurring in the condensed phase before the gaseous oxidizers are released.

Conclusion

T-Jump/TOFMS experiments were used to investigate the initiation and reaction of various aluminum and carbon nanocomposites. Time resolved spectra were compared with those from previous nanothermite studies as well as spectra of the neat oxides and fuels. It was observed that both aluminum and carbon nanocomposites react well before gaseous oxygen release from the oxide, and all evidence
points to a condensed phase initiation of the reaction. This was also confirmed by heating rate SEM
experiments where the Bi₂O₃ oxide reacted with the carbon film of the SEM grid. It was also seen that
bismuth oxide nanothermites reacted faster than copper oxide nanothermites within our T-Jump/MS
experiments. This suggests that the condensed phase initiation reactions in nanocomposites are capable
of being extremely rapid.

Acknowledgment

This work was supported by the Army Research Office and the Defense Threat Reduction Agency. The
authors also acknowledge support from the University of Maryland Center for Energetic Concepts
Development.

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