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Energy release pathways in nanothermites follow through the condensed state

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ABSTRACT

Nanothermite reactions are mechanistically not well understood, due to their ultra-fast transient nature, and the complexity of probing both the vapor-phase and condensed-state chemistries. In this work we examine the combustion product particles of three nano-sized thermite systems (Al/CuO, Al/WO_3, Al/Bi_2O_3) as a probe of the underlying mechanism. Electron Microscopy (EM) and Energy-dispersive X-ray Spectroscopy (EDX) were used to evaluate the combustion product particle size distribution and composition. The results show two distinct product particle size distributions common to all three oxidizers. The larger particles are super-micron (though the precursors were nano-sized) and comprise approximately 90% of the product mass. Simple scaling arguments show that the large population cannot be formed from the vapor given the available residence time. The smaller distribution is sub-100 nm which is primarily the reduced metal formed from vapor phase condensation. This result implies that the majority of the global reaction and thus the energy release is occurring in the condensed phase. Based on these results, a phenomenological mechanism for the nanoaluminum based thermite reaction is proposed.

1. Introduction

Nano-scale reactive composites or metastable intermolecular composites (MIC's) are an increasingly active area of research in the field of propulsion and energetics, resulting from their high energy densities, high propagation velocities and low diffusion length scales. Aumann et al. [1] were the first to show that there is a significant difference in the reactivity of nano-sized thermite mixtures over their micron-sized counterparts. When compared to the conventional micron scale mixtures, their experimentally observed reactivity was much greater owing to the reduction in diffusion length scales. In addition to facilitating increased reactivity, use of MICs boasts higher control over energy densities compared to traditional monomolecular mixtures through the alteration of reactant stoichiometry or by changing the constituents with varying packing densities.

Of all nano-scale reactive composite fuels investigated, the combustion of nanoaluminum has been the most frequently studied. Several mechanisms for its oxidation have been proposed including pressure build-up resulting in quiescent shell rupture [2], oxidizer diffusion into the aluminum core followed by a heterogeneous reaction at the aluminum surface [3], or the Melt Dispersion Mechanism (violent shell rupture followed by molten core spallation) [4,5]. Many researchers consider diffusion of ionic aluminum and oxygen species across the oxide shell to be the controlling process. Trunov et al. [6] have proposed a multi-stage oxidation process for aluminum particles which includes both species transport and phase changes in the oxide shell. More recently, studies have suggested that in addition to the volumetric expansion of the core, strong electric fields induced in the oxide shell can drive cation diffusion across the shell [7,8]. Several studies have also reported the development of reaction models for mechanistic studies of these energetic composites [9,10].

One of the outstanding issues regarding the role of the oxygen carrier in the nanothermite is whether oxygen is directly released from the oxidizer or if oxygen, in the form of an anion, is transported at the interface between the fuel and oxidizer. The latter case may be defined as a condensed state process, in which little or no aluminum–oxygen reaction occurs in the vapor phase. Lynch et al. [11] studied the combustion of nano-sized and micron-sized aluminum particles in a shock tube. Their results explicitly show that there is little Al vapor during an oxidation event of aluminum nanoparticles, which would preclude a vapor phase combustion mechanism. They also observed a sparse AlO signature in the

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nanoparticle oxidation at temperatures below the bulk melting point of aluminum oxide. These results, combined with those of [12] (where the importance of gas phase oxygen for reaction initiation was studied) suggest that a condensed phase reaction is prevalent in these systems. Another proposed mechanism is the mechanochemical Melt Dispersion Mechanism, where the aluminum core is predicted to spallate into nano-sized clusters upon the violent fracture of the alumina shell [4,5]. Other investigations such as Time-of-Flight Mass Spectrometry [10], pressure and optical signature measurements [13–15] have also been conducted, to probe the underlying mechanism of these systems.

Fewer studies [5,16–19] have explored the reaction product distributions to obtain information about the underlying mechanism. One particular study of note is by Drew et al. [16] who studied quenched aluminum particles. We build on this work in a more quantitative manner to evaluate the probable role of condensed vs. vapor phase oxidation through a post-combustion analysis of rapidly quenched product particles. In this study, we observe three different thermite systems that show very different ignition and burning characteristics and conclude that they follow a common reaction mechanism.

2. Experimental approach

The basic approach to this study is to ignite various nanothermite combinations on rapidly heated fine wire. By quenching product particles on a substrate a short distance away from the wire, reaction products could subsequently be inspected by microscopy and surface analytics.

2.1. Material choice and properties

In order to provide sufficient breadth to the analysis, three different nanothermite systems were chosen that have displayed very disparate reaction characteristics. The systems chosen here, exhibit varied combustion characteristics in terms of propagation speeds, pressurization rates and burn times [12,20]. These systems were extensively studied by Sanders et al. [20] employing pressure cell, open tray, and instrumented burn tube methods to study the reaction mechanisms. They concluded the presence of vapor phase/mobile components was important to enhance the propagation velocities and proposed that a shift in the heat transfer mechanism (from convective mode to conductive) occurred when the density of the mixture increased. A particular case of interest was the performance of the Al/Bi_2O_3 mixtures at low densities which displayed a combination of both modes of heat transfer owing to a localized increase in density due to the drastic pressure rise. The adiabatic temperatures vary with the choice of the thermites, with Al/WO_3 mixtures exhibiting a very high adiabatic flame temperature compared to Al/CuO formulations. From the observed pressurization rate and temporal behavior of optical emissions, Sullivan and Zachariah [15] showed significant differences between Al/CuO and Al/WO_3 systems regarding the relative timing of the pressure and optical peaks. Specifically, Sullivan et al. pointed out that the Al/WO_3 nanocomposite does not produce significant gaseous oxidizer species until the system temperatures are very high ($\sim$2800 K). Jian et al. [12] points out that the Al/Bi_2O_3 system ignites almost 700 K below its oxygen release temperature while the Al/WO_3 system does not produce any gas within the experimental temperature range. The Al/CuO mixture is observed to closely follow the expectation that ignition correlates with oxygen release from the oxidizer. Apart from these variations in their respective combustion behavior, these metal oxides exhibit very different physical properties regarding melting and boiling temperatures as outlined in Table 1.

These dissimilarities provide the motivation for choosing these three materials for the current work. All three show significantly different behavior in terms of ignition point, combustion intensity, physical properties and gas release. The question is how the nature of the product distribution varies for these disparate systems and whether analysis of the product distribution will provide insights into the reaction mechanisms.

2.2. Material preparation

Commercially available aluminum nanoparticles (ALEX) with an average particle size of 50 nm, procured from Argonide Corp., were used in this study. These particles had a core–shell structure with an active aluminum content of 70% which was confirmed by thermo gravimetric measurements [21]. These ALEX nanoparticles were ultra-sonicated in hexane for approximately 20 min with three different metal oxide nanopowders. The metal oxide nanopowders used in this study were Copper (II) Oxide (CuO), Tungsten Oxide (WO_3), and Bismuth Trioxide (Bi_2O_3) (all from Sigma Aldrich Corp. and <100 nm). A representative image of the ultrasonicated mixtures (Al/Bi_2O_3) can be seen in Fig. 1, which highlights the intimate mixing with the brighter areas corresponding to the heavier bismuth and the darker areas corresponding to the aluminum particles (Back Scattered Electron imaging). After ultra-sonication, the intimately mixed thermite was micro pipetted onto a platinum wire of 76 μm diameter.

2.3. Temperature-jump wire ignition and particle collection

The experiment consisted of a 12 mm long, 76 μm diameter platinum wire (Omega Engineering Inc.) coated with the nanothermite, which was resistively heated using a high voltage electric pulser. For each run, a pulse width of 3 ms produced a heating rate of 2×10^5 K/s and the experiments were performed in air. The details of the wire heating system comprising the mass spectrometer and power source can be obtained in another work by Zhou et al. [22]. Compared to the method of Zhou et al. [22], the primary modification herein was the ability to reproducibly capture post-combustion material on substrates. This entire assembly was mounted on a bi-axial linear translational stage (Newport Research Corp.). This stage had two manually controlled micrometer actuators with a resolution of 25 μm. The collecting substrate was a separately attached Scanning Electron Microscopy (SEM) stage (15 mm dia. aluminum stage) with a layer of carbon tape on it so as to improve the conductivity of the sample. A high speed digital camera (Phantom V12.1) was used to capture the video of the reaction from which characteristic transit times could be extracted as depicted in Fig. 2. By moving the *Z* direction micrometer, we could collect the product particles on the substrate at various distances on the order of several millimeters away from the wire with accuracy over several micrometers. The impingement criteria were a separation of 1 mm for the "near" substrate condition and 3 mm for the "far" substrate condition. A similar arrangement was used for the Transmission Electron Microscopy (TEM) samples, where a Nickel TEM grid was placed on the SEM stage. The substrates

Table 1
Thermo-physical properties of the nanothermite mixtures.

Thermite mixture (Al/ metal oxide)	Adiabatic flame temperatures (K) [38]	Metal oxide decomposition point [12] (K) (±50 K)	Metal melting point (K)	Metal boiling point (K)
Al/CuO	2843	975	1357	2843
Al/WO_3	3253	–	3695	5933
Al/Bi_2O_3	3319	1620	545	1837