



Nanothermite reactions: Is gas phase oxygen generation from the oxygen carrier an essential prerequisite to ignition?

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ABSTRACT

In this study we investigate the role of gas phase oxygen on ignition of nanothermite reactions. By separately evaluating the temperature at which ten oxidizers release gas phase species, and the temperature of ignition in an aluminum based thermite, we found that ignition occurred prior to, after or simultaneous to the release of gas phase oxygen depending on the oxidizer. For some nanothermites formulations, we indeed saw a correlation of oxygen release and ignition temperatures. However, when combined with in situ high heating stage microscopy indicating reaction in the absence of O₂, we conclude that the presence of free molecular oxygen cannot be a prerequisite to initiation for many other nanothermites. This implies that for some systems initiation likely results from direct interfacial contact between fuel and oxidizer, leading to condensed state mobility of reactive species. Initiation of these nanothermite reactions is postulated to occur via reactive sintering, where sintering of the particles can commence at the Tammann temperature which is half the melting temperature of the oxidizers. These results do not imply that gas phase oxygen is unimportant when full combustion commences.

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1. Introduction

Metal–oxidizer mixtures have recently generated considerable interest in the combustion community due to their high energy density on a mass/volumetric basis as compared to traditional organic compounds [1]. When both the metal and the oxidizer comprises of nanoparticles, such mixtures are called nanothermites or metastable interstitial/intermolecular composites (MICs). By using nanoparticles, the fuel and oxidizer can be finely intermixed, thus improving the interfacial contact and greatly reducing the characteristic mass diffusion length between the reactants resulting in enhanced reactivity of the nanothermites as evident from higher flame speeds [2] and lesser ignition delay reported in literature [3].

While fuels like boron [4] and silicon [5] have been explored, nano-aluminum (n-Al) is predominantly the fuel of choice due to a combination of its high energy density, reactivity, low cost, and nontoxic nature. A variety of oxidizers have been studied, and the choice often depends on the particular application. Copper oxide (CuO) [6,7], iron oxide (Fe₂O₃) [6], molybdenum oxide

(MoO₃) [2,8–13], tungsten oxide (WO₃) [11] and bismuth oxide (Bi₂O₃) [11,14] are the commonly used oxidizers in nanothermites.

Nano-aluminum particles typically have a thin (~2–5 nm in thickness) amorphous aluminum oxide shell surrounding the elemental core of aluminum, protecting the particle from further oxidation in air. These particles are typically aggregates of spherical primary particles, although recent work has shown the formation of single domain aluminum crystals [15]. For nanoparticles, the oxide shell can represent a significant portion of the particle mass. Oxidizer particles used in prior studies, on the other hand, display various morphologies. They have been used in the form of platelets [11,13], crystalline sheets [11], spheres [6,14] and nanorods [11,14,16].

An interesting and unresolved question in the study of nanothermites is the way they ignite/react depending on the heating rates involved. At lower heating rates (~1–20 K/min), Trunov et al. [17] has shown the oxide shell to undergo phase transformations making it permeable to the mass transport of aluminum and oxygen across the shell. Since reaction was observed to occur below the melting temperature of bulk aluminum (933 K), the authors suggested that outward diffusion of Al dominates when the oxide is amorphous while inward diffusion of oxygen dominates for crystalline alumina. At faster heating rates (~10³ K/s), Rai et al. [18] showed the formation of hollow aluminum particles after oxidation. They argued that the aluminum in the core must have leaked out by diffusion due to concentration and/or pressure gradient across the shell. Similar experimental evidence have also been

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demonstrated by Nakamura et al. [19]. Pursuing this idea, we have shown in a previous work [20] that diffusion of reactive species is controlling even at heating rates on the order of 10^5 K/s. Based on the observed ignition delay, an effective diffusion rate of $\sim 10^{-10}$ cm²/s was calculated. In another recent study by our group, Sullivan et al. [21] used a specially-designed heating holder to heat n-Al at 10^6 K/s inside a scanning electron microscope. In this particular study, a significant heating pulse (300–1473 K at $\sim 10^6$ K/s, and then held at 1473 K for 10 ms) was necessary before shell breakdown occurred, and outwards migration of Al could visually be identified. A smaller heating pulse, although above the melting temperature of Al, induced no changes within the very fast heating and cooling timescale of this experimental technique. Using Al-WO₃ nanothermite mixture, the authors suggested a condensed phase initiation/reaction. At even higher heating rates ($\sim 10^7$ – 10^8 K/s) Levitas et al. [22] proposed the “Melt Dispersion Mechanism (MDM)” in which the aluminum core melts and exerts mechanical stress on the solid oxide shell. This causes spallation of the shell, and is predicted to happen at or near the melting temperature of aluminum, viz. 933 K. The violent rupture of the shell causes tensile stress on the molten Al core, thus unloading small molten clusters of aluminum at high velocities. The reaction rate in this mechanism is inherently not rate-limited by the diffusion of oxidizer/fuel through the shell. In separate studies using time resolved mass spectrometry of rapidly heated ($\sim 10^5$ K/s) nanoaluminum and nanothermites [23,24], no evidence of aluminum clusters were found but only elemental aluminum was detected. Based on these previous works and the lack of aluminum clusters being detected, our current speculation is that aluminum migrates through its shell via a diffusion mechanism.

The correlation between oxygen release and nanothermite reaction have been suggested by Schoenitz et al. [12]. They conducted thermal analysis at low heating rates on Al-MoO₃ nanothermites and tentatively concluded that the appearance of the first exothermic peak at ~ 470 K is indicative of the decomposition of MoO₃ into MoO₂ and oxygen (O). The authors commented that the in situ oxygen produced due to decomposition of the oxidizer could readily escape if the nanothermite mixture is prepared from the individual components in powder form. Similar suggestions of the possible decomposition of the oxidizer have been put forth to explain the kinetic behavior for Al-CuO nanothermite reactions observed under low heating rates by Umbrajkar et al. [7]. Direct experimental evidence of oxygen release from the oxidizer and its correlation to the ignition of nanothermites was first shown by Zhou et al. [23] using a T-Jump time of flight mass spectrometer (T-Jump TOFMS). Details of the operation of this instrument is available in a previous publication [25]. In short, the nanothermites were ignited on a platinum wire by heating them by an electrical pulse ($\sim 10^5$ K/s) and the species produced during the reaction were sampled every 100 μ s. With a high heating rate ($\sim 5 \times 10^5$ K/s) we detected the release of molecular oxygen (O₂) from CuO and Fe₂O₃ in the reaction of Al-CuO and Al-Fe₂O₃ thermites. The liberated O₂ was one of the first species to be detected temporally thus suggesting that O₂ release played a critical role in the ignition mechanism. This also suggests the role of gas phase oxygen towards ignition of Al-CuO and Al-Fe₂O₃ nanothermites.

Bazyn et al. [26] studied the ignition temperature and burn time of Al-MoO₃ and Al-Fe₂O₃ at high heating rates ($\sim 10^6$ K/s) using a shock tube. They found evidence for ignition of both materials at 1400 K and 1800 K respectively. It is important to note that these temperatures are significantly higher than the melting temperature of aluminum. The findings of ignition temperatures well above the melting temperature of aluminum, and the fact that ignition temperature depends on oxidizer type, indicate that the oxidizer must play some role in the ignition mechanism at high heating rates. The thermal response of a metal oxide to heating depends on the

particular oxidizer: some materials can melt, others decompose into sub-oxides prior to melting, some can even sublime. It has recently been shown [21] by in situ high heating rate electron microscopy ($\sim 10^6$ K/s) that Al-WO₃ nanothermites can react via condensed phase reactions. In a separate study [27], we have used high speed X-ray phase contrast imaging to suggest that reactive sintering may be essential in the initiation of nanothermite reactions. Reactive sintering involves the exothermic release of energy that promotes reaction between two condensed phase species and leads to the formation of product particles with larger characteristic structures than the reactant particles. These larger structures result from the melting and coalescence caused by the exothermicity of the reaction and has been shown to occur very early during the reaction process (approximately within 25–50 μ s after ignition). Furthermore, electron microscopy indicated the importance of reactive sintering through observation of a contact surface between nanoaluminum and the oxidizer, suggesting the existence of a solid-solid/liquid reaction. This mechanism is to be contrasted with the very different conceptual mechanism whereby nanoaluminum reacts with gas phase oxygen liberated by heating the oxidizer [23]. The reactive sintering mechanism implies that oxygen ion transport within the oxidizer should play an important role in the ignition/reaction of nanothermites. So the central question this paper seeks to answer is whether gas phase oxygen is an essential prerequisite to ignition of nanothermite. We will choose a wide range of oxidizers which release oxygen at a widely different range of temperatures, and measure the ignition temperature to verify if gas phase oxygen is necessary for the initiation of nanothermite reactions.

2. Experimental

2.1. Materials

Commercially available n-Al (Argonide Corp.) was used for all the experiments. The nominal size of the particles as specified by the supplier is ~ 50 nm, and was determined to be 70% active using thermogravimetric analysis (TGA). The various materials and the relative size of the primary particles as specified by the manufacturers are given below in Table 1.

For the oxygen release experiments, approximately 10–15 mg of the bare oxidizers were dispersed in hexane, sonicated for 10 min and then heated as described in the experimental approach section below. Additionally, appropriate amounts of n-Al and various oxidizers listed in Table 1 are weighed to make stoichiometric sample, and then dispersed in hexane. The mixture is then sonicated for 25 min before being subjected to ignition tests.

2.2. Temperature-jump rapid heating experiments

To understand the importance of gas phase oxygen, a series of experiments are conducted on rapidly heated fine wires in which the optical emission and vapor phase species can be temporally monitored along with the wire temperature. These experiments are designed to extract the correlation between the oxygen release temperature from the oxidizer, if any, and the ignition temperature for the corresponding nanothermite. A thin platinum wire (length ~ 12 mm, diameter ~ 76 μ m) is joule-heated by a tunable voltage pulse generated by a custom built power source. The transient current passing through the circuit is measured by a current probe. A small portion of the central region of the wire (~ 3 – 4 mm) is coated with the samples by pipeting a dispersion of the samples in hexane onto the wire, then allowing the hexane to evaporate. The amount of material coating the wire is estimated to be around 90 μ g. From the recorded voltage and current data, the temperature of the wire at the point of ignition can be calculated from

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