

In situ microscopy of rapidly heated nano-Al and nano-Al/WO₃ thermitesKyle T. Sullivan,¹ Wen-An Chiou,² Richard Fiore,³ and Michael R. Zachariah^{1,a)}¹University of Maryland, College Park, Maryland 20742, USA²NISP Laboratory, NanoCenter, University of Maryland, College Park, Maryland 20742, USA³Protochips Inc., 617 Hutton Street, Suite 111, Raleigh, North Carolina 27606, USA

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The initiation and reaction mechanism of nano-Al and nano-Al thermites in rapid heating environments is investigated in this work. A semiconductor-based grid/stage was used, capable of *in situ* heating of a sample from room temperature to 1473 K, and at a rate of 10⁶ K/s, inside an electron microscope. Nano-Al was rapidly heated in a transmission electron microscope, and before and after images indicate that the aluminum migrates through the shell, consistent with a diffusion-based mechanism. A nano-Al/WO₃ composite was then heated in a scanning electron microscope. The results indicate that a reactive sintering mechanism is occurring for the nano-Al/WO₃ thermite, as the products are found to be in surface contact and significantly deformed after the heating pulse. © 2010 American Institute of Physics. [doi:10.1063/1.3490752]

Thermites are energetic materials which generally involve the reaction of a metal and a metal oxide, and give rise to characteristically high reaction temperatures and low gas production. When nanoparticles are used in place of the more typical micron sized reactants, a large enhancement in reactivity occurs.^{1,2} These materials have been termed nanocomposite thermites³⁻⁵ or metastable intermolecular composites.⁶⁻⁸ Nano-Al has been the most studied fuel, due to a combination of its high energy density and reactivity, low cost, and environmentally benign reaction products.

Aluminum particles naturally form a several nanometer thick oxide shell when exposed to air. The shell is uniform and amorphous⁹ and typically has a thickness of 2–3 nm.¹⁰ As the particle size decreases, the oxide shell represents a significantly large portion of the particle's mass,⁴ and can even exceed 50%. The ignition temperature in nano-Al has been experimentally observed to occur near the melting point of Al (933 K), much lower than the ignition temperature of large aluminum.¹¹ Thus, understanding the interaction of the core and shell during rapid heating is speculated to be critical in understanding the initiation mechanism of nano-Al and nano-Al thermites. Two schools of thought have prevailed; one suggests that the aluminum core expands and ruptures the shell, ejecting small molten clusters of aluminum at high velocities,¹² while the other suggests that aluminum can dif-

fuse through the shell, either through physical cracks or after phase transformations in the oxide shell render it permeable to Al ions.^{10,13,14} This topic was investigated at high heating rates,¹⁵ and the authors found support for a diffusion mechanism. Understanding the thermal response of nano-Al subjected to rapid heating is a necessary prerequisite for understanding the initiation mechanism in composite materials. This work investigates nano-Al and a nano-Al/WO₃ thermite using a novel heating grid/stage (Protochips Inc.), capable of heating the sample from room temperature to 1473 K in 1 ms (10⁶ K/s heating rate), and in an electron microscope. This approach has the advantage that it should enable us to monitor the before and after reaction effects on a particular particle, rather than the more traditional before and after images on ensemble samples.

The nano-Al is designated as “50 nm ALEX,” and was purchased from the Argonide corporation. The nano-Al was found to be 70% elemental by mass, measured using thermogravimetric analysis. The WO₃ was purchased from Sigma-Aldrich, and was specified by the supplier to be <100 nm in size. To prepare the thermite, stoichiometric amounts of Al and WO₃ were weighed and added to a vial with ~5 mL of hexane. The mixture was ultrasonicated for 30 min, and the hexane was then allowed to evaporate. A small amount of ethanol was then added, and the suspension was pipetted directly onto the semiconductor-based grid.

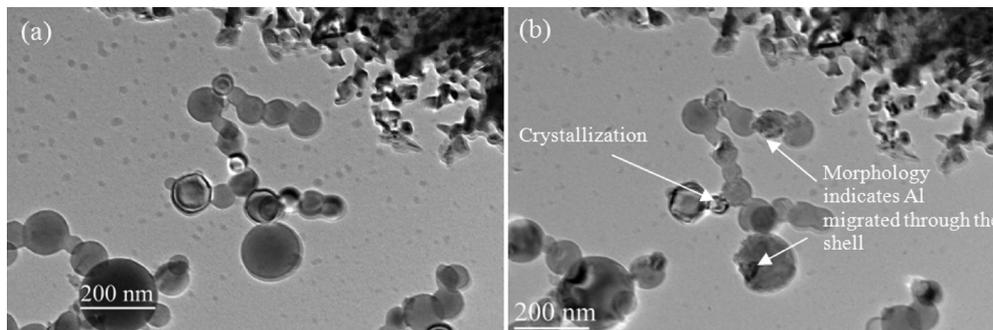


FIG. 1. TEM images of nano-Al before (a) and after (b) heating to 1473 K at 10⁶ K/s. The structure in the upper right corner is from the grid and is not Al.

^{a)}Electronic mail: mrz@umd.edu.

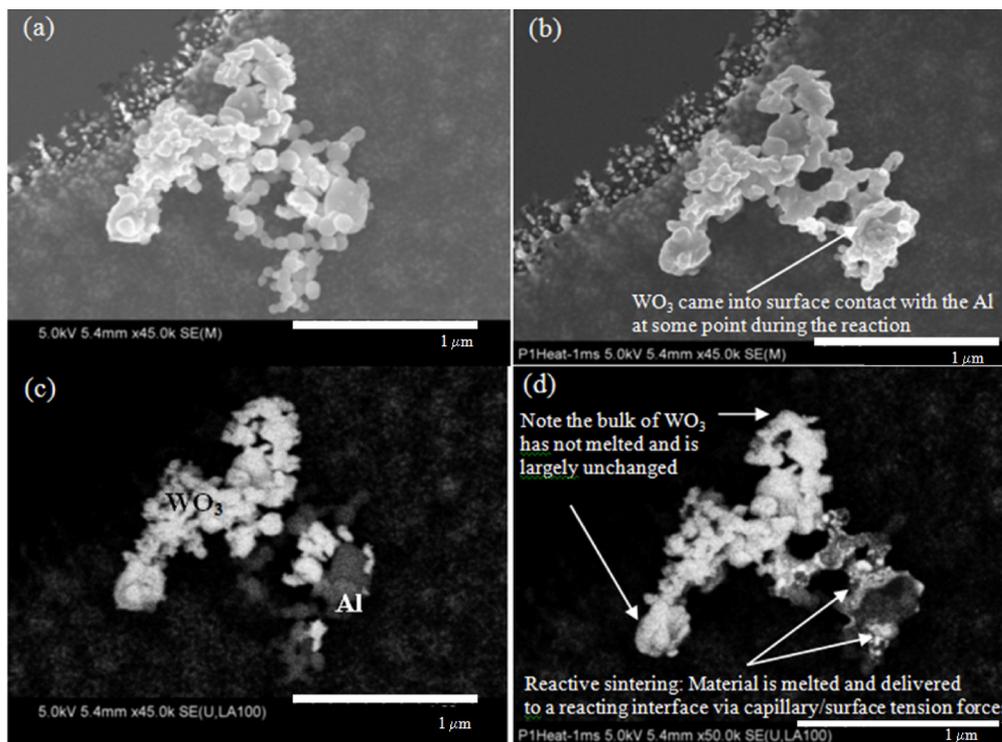


FIG. 2. (Color online) SEM images of nano-Al/WO₃ before (a) and after (b) heating to 1473 K at 10⁶ K/s. Also, the BSE image before (c) and after (d) heating is shown. The bright particles are W/WO₃, the darker particles are Al/Al₂O₃ in the BSE images (confirmed by EDS).

The nano-Al sample was rapidly heated in a high resolution transmission electron microscope (TEM) (JEM-2100, JEOL Ltd.). The images before and after rapid heating are shown in Fig. 1 and would seem to indicate that whatever changes are occurring are subtle. There is certainly nothing indicating any violent “spallating” or ejection of molten Al. The images show that some particles undergo crystallization, whereas others are seen to evolve heterogeneities near the surface as a result of the heating. These heterogeneities indicate the aluminum had in some way diffused through the shell during the heating, and resulted in the observed structures.

To induce more vigorous chemistry a thermite mixture of nano-Al/WO₃ was imaged in high resolution scanning electron microscope (SEM) (SU-70, Hitachi). The SEM was used for this sample because it can be operated in backscattered electron (BSE) mode, which shows heavy species as brighter. Also, this SEM was equipped with an energy dispersive x-ray spectroscopy (EDS) detector, allowing for elemental analysis. The images before and after heating are shown in Fig. 2, and the W/WO₃ and Al can easily be distinguished in the backscattered images (confirmed by EDS).

The Al/WO₃ particles were found to be significantly deformed, and had come into surface contact during the heating. It can also be seen that a large amount of the WO₃ remained unchanged during the heating pulse. In fact, the morphological changes were only dramatic in the regions where fuel and oxidizer were in close proximity, thus indicating the exothermic reaction was primarily responsible for inducing the observed changes. In order to form the observed structures, we propose that the Al/WO₃ reacted at an interface, and the exothermic reaction led to further melting/sintering of adjacent particles as heat is conducted away from the interface. As material is melted, it is rapidly delivered to the interface via strong capillary/surface tension forces. This mechanism is referred to as a reactive sintering mechanism.

In conclusion, we have used a new experimental technique to qualitatively investigate both nano-Al and a nano-Al/WO₃ thermite at high heating rates. The experiments support that nano-Al migrates through the shell but does not violently rupture it. This is consistent with a diffusion mechanism for nano-Al. For the thermite, the results suggest that heterogeneous condensed-phase reactions and large structural changes had occurred in regions where the fuel and oxidizer were in close proximity. The observed morphology after heating is consistent with a reactive sintering mechanism for the nano-Al/WO₃, and other thermites are currently being investigated.

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