

## In-Situ Super Rapid Heating of Nano-Aluminum and Nano-Thermmites

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Thermmites are energetic systems comprised of a metal fuel and a metal/metal oxide oxidizer, which give rise to high temperatures and self-propagating reactions upon ignition. When nanoparticles are used in place of larger particles, more homogeneous mixing and interfacial contact can be achieved, leading to several orders of magnitude increase in combustion characteristics[1]. Nano-Al is traditionally used as a fuel due to its high energy density and low cost, and several oxidizers have been studied. These materials are currently being investigated for several applications in propellants, pyrotechnics and explosives, where controlled energy release is a desirable trait. Nano-Al naturally forms oxide shell that is several nanometers in thickness. The interaction of the Al core (MP 933 °K) with the Al oxide shell (MP 2327 °K) is critical to understanding the initiation mechanism. Two different hypotheses have prevailed [2, 3, 4] as to the behavior of nano-Al subjected to rapid heating. However, resolving this issue requires experimental support, which is currently lacking. This research examines the initiation mechanism by replicating a super rapid heating environment in an electron microscope. Both nano-Al and a nano-Al/WO<sub>3</sub> thermite were investigated.

The nano-Al, designated as "50nm ALEX" (70% elemental by mass as measured by thermogravimetric analysis), was purchased from the Argonide Corp. The WO<sub>3</sub> with a size of <100 nm (as specified by the supplier) was purchased from Sigma Aldrich. The thermite was prepared by weighing stoichiometric amounts of nano-Al and WO<sub>3</sub> powders and adding into a 5 ml vial with some hexane. It was then sonicated for ~30 min. to ensure intimate mixing. A few drops of ethanol was then added after the evaporation of hexane, and the suspended sample was pipetted onto a special semiconductor-based heating grid/stage (Protochips, Inc.) that enabled heating of a sample from room temperature up to a maximum of 1575 °K at a rate of 10<sup>6</sup> °K/s. Selected areas of the same particles were examined before and after heating.

Initial TEM heating study of nano-Al depicted a morphological change of many of the particles after one millisecond (1 ms) heating (Fig. 1). No "spallation" or ejection of molten Al was observed, contrary to the prediction of ref. 2. The result is consistent with a cracking/diffusion initiation mechanism for nano-Al. BSE images and EDS mapping of the untreated thermite sample reveal the random distribution of Al and WO<sub>3</sub> particles (Fig. 2). Al particles tended to be spherical and ranged from 50 to 100 nm with some up to 800 nm, whereas WO<sub>3</sub> particles ranged from 100 to 300 nm in general and appeared more euhedral in shape. Larger Al particles were more or less surrounded by WO<sub>3</sub> particles. The BSE image shows that the surface of Al particles appeared relatively clean, though some very small particles seem to be adhered on the surface. The majority of these particles changed instantly after 1 ms of heating to 1573 °K. Most noticeably, Al particles appeared flattened and coated with a thin layer of W and/or WO<sub>3</sub> (Fig. 3). The BSE image and EDS mapping clearly depicted the distribution of high atomic number W from Al. Possible evidence of elemental interdiffusion was observed in the high resolution SEM/EDS images and EDS data. This finding supports heterogeneous condensed-phase reactions as part of the initiation mechanism in the nano-Al/WO<sub>3</sub> thermite. With further additional heating of 1 ms, an even more drastic change was observed (Fig. 4). The small bright spots, observed in the BSE image, may indicate the formation of solid W particles, evidence of further extent of reaction. Other thermite systems are currently being investigated.

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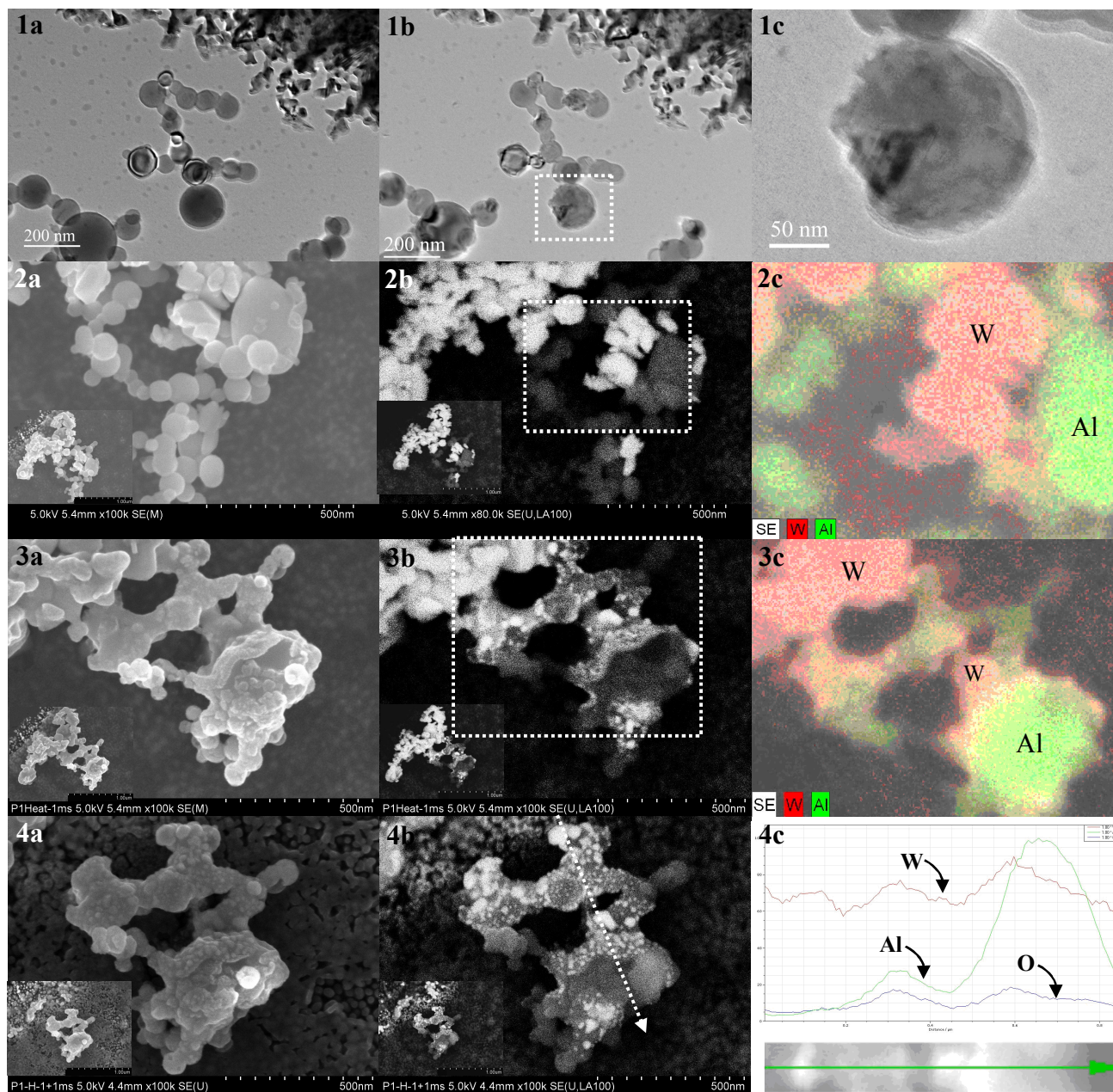


Fig. 1. TEM images of nano-Al particles before (a) and after (b) rapid heating to 1573 °K in 1 ms. High magnification micrograph (c) of the boxed area (in b) illustrates a change in the morphology, indicating a breakdown/cracking of the oxide shell. No “spallation” or ejection of Al was observed.

Fig. 2. Fig. 1. SEM image (a) shows Al and  $\text{WO}_3$  particles. BSE image (b) (bright:  $\text{WO}_3$ ; lighter contrast: Al) and EDS mapping (c) of W and Al, confirms the random distribution of these two elemental nanoparticles. Inserts reveal low magnification view. EDS mapping was obtained from the boxed area.

Fig. 3. SEM (a) and BSE (b) images and EDS mapping (c) show the morphological change after 1 ms heating to 1573 °K. It appears that W/ $\text{WO}_3$  has coated the Al surface.

Fig. 4. SEM (a) and BSE (b) images depict further morphological change, especially volumetric change and particle redistribution after an additional 1 ms heating (2 ms in total). The EDS line profile (dash line on the BSE image) shows possible interdiffusion of Al/ $\text{WO}_3$ . Note the appearance of small bright spots/particles in the BSE images.