

Probing the Oxidation Mechanism of Ta Nanoparticles via *In-Situ* and *Ex-Situ* Ultra-Fast Heating TEM/STEM

Jeffery B. DeLisio¹, Garth C. Egan¹, Sz-Chian Liou², Wen-An Chiou², and Michael R. Zachariah¹

¹ Department of Chemistry and Biochemistry and Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD, USA

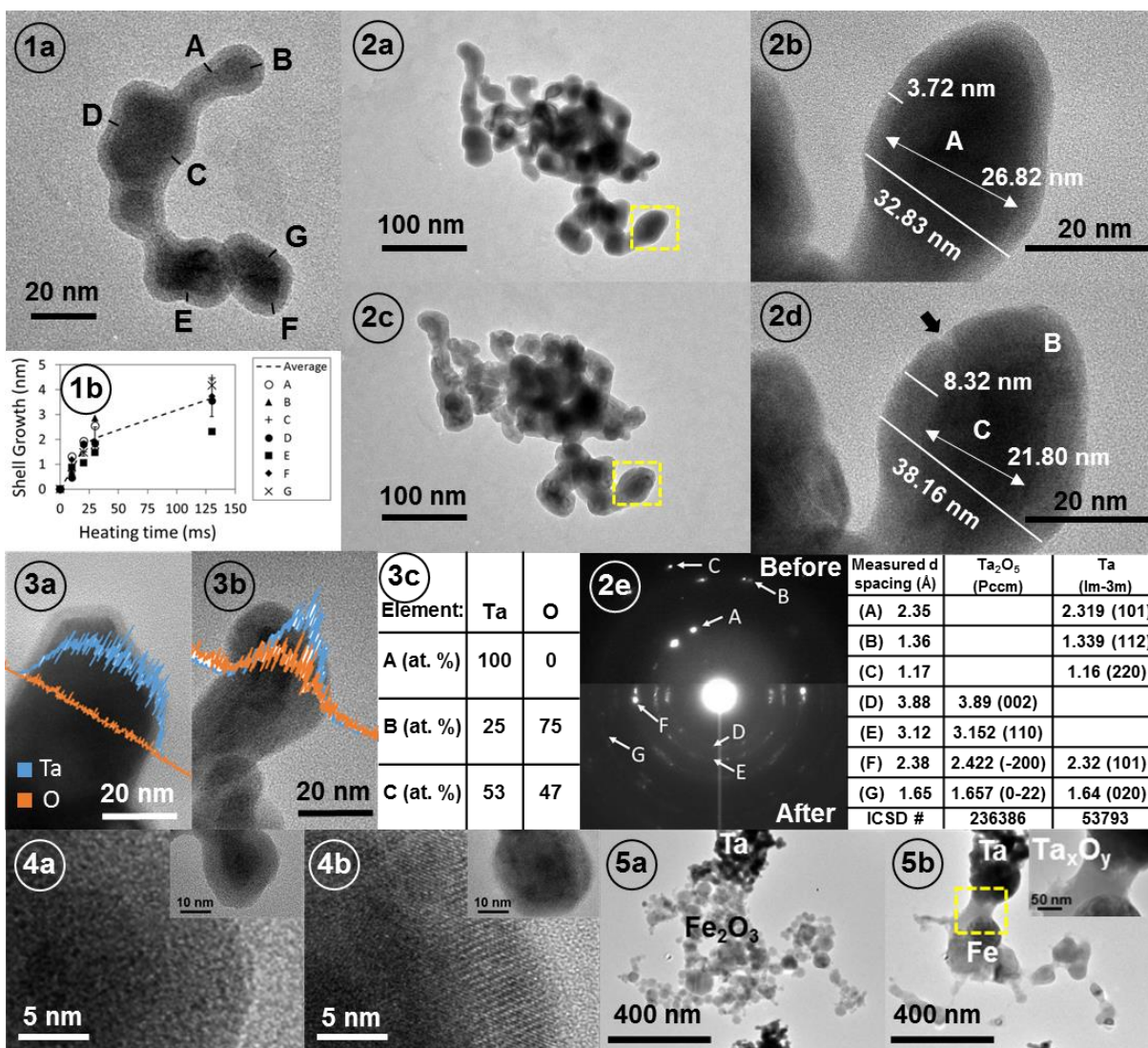
² AIM Lab, NanoCenter, University of Maryland, College Park, MD USA

Aluminum (Al) nanopowders are of significant interest for many propellant, pyrotechnic, and explosive applications due to their high energy density and fast reaction kinetics. The interaction between the Al core (MP 660 °C) and the Al₂O₃ shell (MP 2072 °C) of nano-Al is critical to understanding the initiation mechanism for oxidation, which is currently under debate [1]. Various mechanisms for the oxidation of Al in nanothermites have been proposed that detail the diffusion of oxidizer and fuel through the shell [2], with experimental results showing ignition occurring near the melting point of Al [3]. The crystallization of the oxide shell is an important part of the Al ignition mechanism [4], but is a difficult process to investigate because oxide crystallization occurs at a temperature very close to the melting point of Al. To examine the oxidation mechanisms of nanosized metal fuels, tantalum (Ta) was chosen due to its high melting point in comparison to Al (3017 °C vs. 660 °C). This research examines the oxidation mechanism of nano-Ta by replicating an ultra-fast heating environment in an electron microscope as well as in an oxygenated atmosphere.

Ta (<50 nm in diameter, Global Advanced Metals) and iron oxide (Fe₂O₃) nanopowders (Sigma Aldrich) were homogeneously mixed via sonication in ethanol for 30 minutes prior to deposition onto the TEM grids. Protochips Arduro heating chips were used with a Protochips TEM holder in a JEM 2100 FEG TEM/STEM, equipped with Oxford EDS and Gatan Tridiem EELS systems. To examine the ignition behavior of Ta, Ta nanopowders deposited onto an Arduro chip were heated in air whereas the Ta/Fe₂O₃ nanothermite was heated in vacuum within the TEM. All samples were heated at 10⁵ K/s and held for a period between 1 and 100 ms.

Both Al and Ta nanoparticles are passivated by a thin (~3-5 nm) oxide shell/layer that creates a barrier between the active core and any oxidizer (Fig. 1a). The thickness of Ta's oxide layer increased after consecutive heating experiments in air to a maximum temperature of 500 °C. Oxide growth rates varied at different locations on the aggregate (Fig. 1b). Drastic surface changes of the oxide shell are clearly shown when Ta nanoparticles were heated to and held at 850 °C for 1 ms in air (Fig. 2). During oxidation, the oxide shell diameter of the Ta nanoparticles increased from 32.83 to 38.16 nm (Figs. 2b and 2d), while the Ta core shrank by nearly 4nm. The SAD pattern after rapid heating indicates Ta₂O₅ has a preferred orientation during crystalline oxide growth (Fig. 2e). EDS point and line scan analyses at various positions show increased oxygen concentration throughout the particle after heating (Fig. 3). HRTEM images reveal little crystallization in the oxide shell after a series of heating ramps to 500 °C (30 ms in total), but crystallization is clearly observed after being heated to 850 °C for 1 ms (Fig. 4). This rapid crystallization and the stress on the particle result in cracking of the oxide shell (arrow in Fig. 2d), which may enhance oxygen diffusion into the core. The Ta/Fe₂O₃ nanothermite was heated in the TEM to 1200 °C and held for 1 ms. The Fe₂O₃ appears to wet the surface of the Ta, allowing oxygen to diffuse through the Ta₂O₅ shell to oxidize the Ta. Unlike Al, Ta does not sinter at areas that are not in contact with the Fe₂O₃, as shown by the nanostructure of the unreacted parts of the Ta aggregate [5] (Fig. 5).

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 [6] This work was supported by the Army Research Office, the Defense Threat Reduction Agency and the AIM Lab, NanoCenter (MRSEC Shared Facility, NSF DMR 05-20741) at UMD.



- Fig. 1.** TEM image of Ta aggregate (a) with labeled locations where oxide shell was measured, and the corresponding oxide shell growth for each location vs. heating time (b).
Fig. 2. TEM images before (a, b) and after (c, d) being heated in air to 850 °C at 10⁵ K/s and held for 1 ms, SAD patterns before and after heating (e).
Fig. 3. EDS line scans before (a) and after heating to 850 °C (b) and EDS at points in Figs. 2b and d (c).
Fig. 4. HRTEM images of Ta nanoparticles after being heated in air to 500 °C multiple times (30 ms in total) (a) and to 850 °C for one time only (b); both at a heating rate of 10⁵ K/s.
Fig. 5. TEM images of Ta/Fe₂O₃ mixture before (a) and after (b) being heated to 1200 °C at a heating rate of 10⁵ K/s and held for 1 ms, and HRTEM image of interface after heating (inset).