Titan + Protochips Atmosphere = Environmental TEM

APPLICATION NOTE | Hydrogen Bubbles Formation and Evolution in Aluminum Nanoparticles

The formation of voids and successive growth of hydrogen bubbles in solid metals have attracted extensive attention, mainly because the existence of such bubbles and/or blisters can significantly deteriorate the mechanical properties of the host metals. Various kinds of treatments have been found to be able to introduce cavity, bubbles or blisters in different metals, such as high energy and high dose proton implantation, quenching in H_2/H_2O gas, and cathodic reaction. However, the initiation of cavity, dynamic evolution of bubbles, and how the mechanical properties of metals decay are still not well understood. In this application note, *in situ* environmental scanning/transmission electron microscopy (S/TEM) experiments are employed to investigate the formation and evolution of hydrogen bubbles in Aluminum (Al) nanoparticles (NPs) dynamically.

The *in situ* experiments are carried out in Protochips Atmosphere^{TM} TEM environmental gas cell in a probe aberration corrected FEI Titan G2 60-300 kV S/TEM operated under 200 keV. High purity 5% H_2 (with balancing gas 95% Ar) is introduced into the cell as hydrogen source. The gas pressure in the environmental cell could be controlled from 1 Torr to 760 Torr by using Atmosphere^{TM} manifold. Under the irradiation from high energy electron beam, hydrogen molecules are ionized to generate atomic H to facilitate its entrance through the surface native Al_2O_3 layer on Al NPs. Once the cavity at the interface of Al_2O_3 shell and Al core has nucleated, hydrogen gas bubbles grow by absorbing more hydrogen atoms.

Figure 1 shows the STEM high-angle annular dark-field (HAADF) images from a cluster of Al NPs under 200 kV electron irradiation in 700 Torr 5% H_2/95% Ar gas

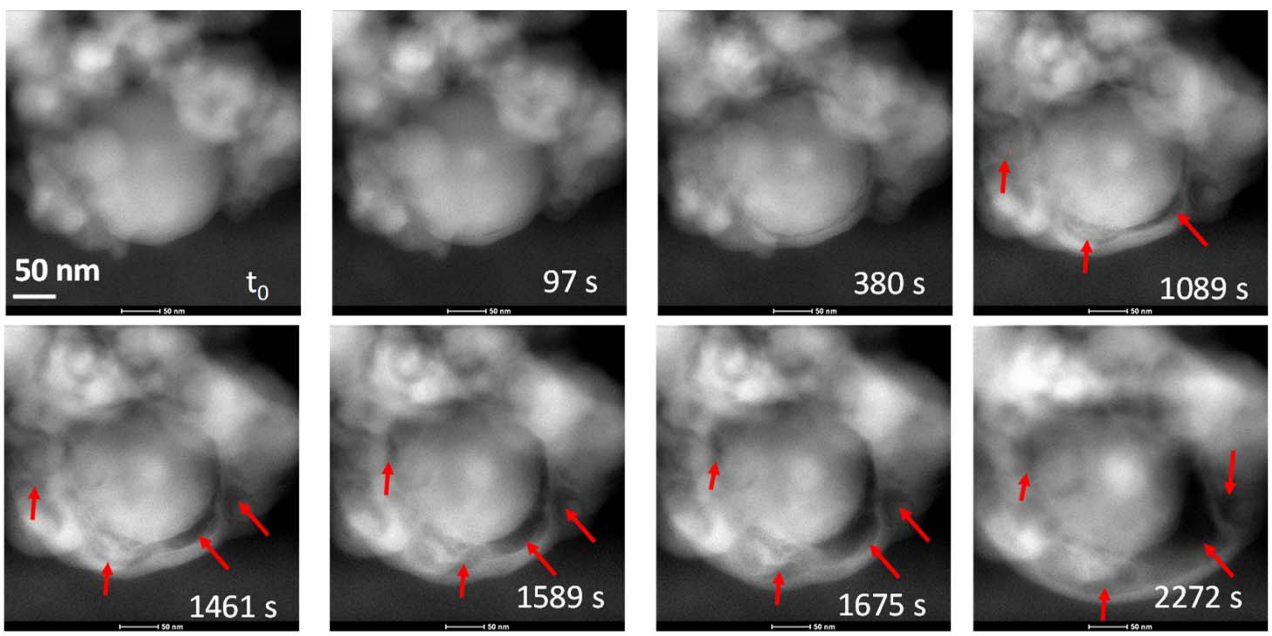

Figure 1. *Time-elapsed HAADF-STEM images showing the formation and evolution of hydrogen bubbles at the interface of surface Al_2O_3 shell and inner Al core in each individual NPs, as indicated by red arrows.*

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AIF analytical instrumentation facility

College of Engineering
Analytical Instrumentation Facility

www.aif.ncsu.edu

Campus Box 7531
2410 Campus Shore Drive
Raleigh, NC 27695-7531
P: 919.515-8887

environment. It is very interesting that the hydrogen bubbles are formed first at the interface of surface Al_2O_3 shell and inner Al core in each individual NPs. The size of each hydrogen bubbles increase as the electron beam keeping irradiation on the NP. Some of the bubbles are indicated by red arrows in Figure 1.

This phenomenon is also confirmed in the bright field TEM imaging, as shown in Figure 2a. After continuing beam irradiation on Al NPs in hydrogen environment, the size of hydrogen bubbles keep increasing and the neighboring bubbles merge to bigger bubbles. Moreover, the Al core starts to become porosity, as shown in Figure 2b. The generation of porosity inside solid Al core can be attributed to the formation of H-vacancies clusters, and the aggregation of these clusters to form pores inside the solid Al.

The effects of beam intensity, hydrogen pressure, and size of NPs on the evolution of hydrogen bubbles and porosity will be studied in details for future work. Other metal particles with/without surface oxide layers and in different gas environments can also be investigated using this technique.

The combination of the Protochips Atmosphere cell and state-of-the-art microscope essentially provides the ability to do environmental TEM (ETEM) experiments, with the advantage of control of much higher pressure (up to 760 Torr) inside the Atmosphere cell than a dedicated ETEM (typically up to 15 Torr).

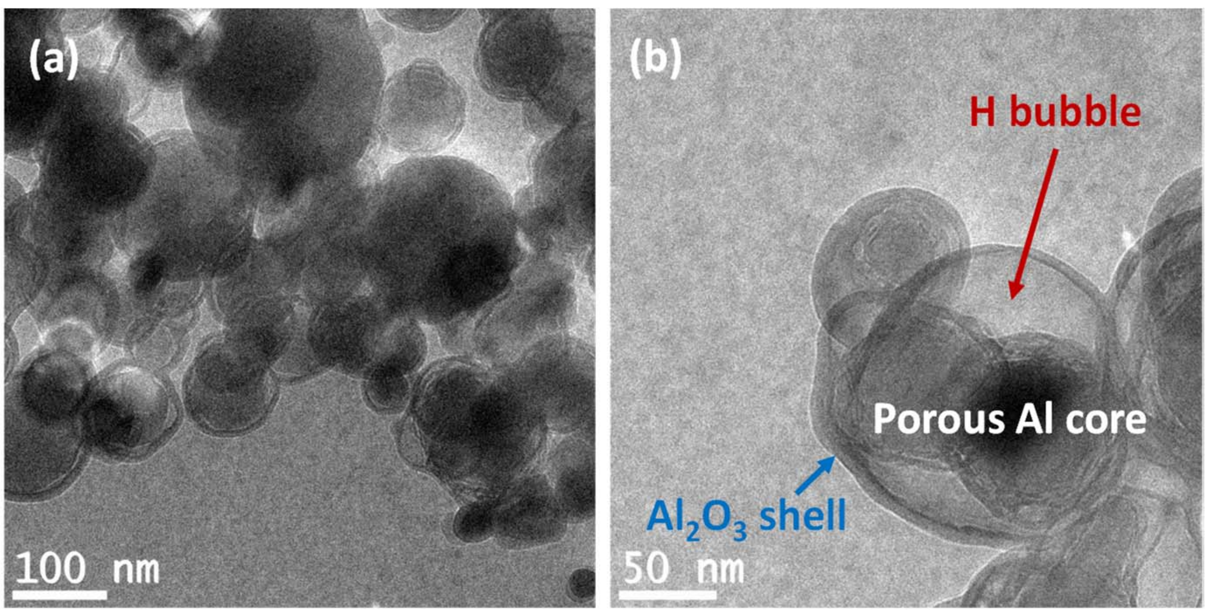

Figure 2. *(a) Conventional TEM image showing the formation of hydrogen bubbles at the interface of surface Al_2O_3 shell and inner Al core in each individual NPs after exposure under parallel electron beam in conventional TEM mode. (b) The morphology of Al NPs after intensive electron beam irradiation in hydrogen environment, showing the hydrogen bubbles and the porosity of inner Al core.*

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