

Direct Observation of Boron Nitride Nanocage Growth by the Molecular Beam Nitridation and Liquid-like Motion of Fe-B Nanoparticles

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Summary

Connected chains of BN nanocages have been grown by the molecular beam nitridation of nano-sized Fe-B particles. The particles were exposed to ammonia under high vacuum conditions in the polepiece of an ultrahigh vacuum transmission electron microscope. At a temperature of 1000°C, BN nanocages were observed to form around the Fe-B particles, followed by expulsion of the particles from within the newly formed cages. Expulsion occurred at a critical shell thickness in a liquid-like manner, despite the experiment being conducted well below the Fe-B liquidus and the particles remained crystalline throughout the experiment.

The observations provide direct confirmation of the possibility of nanostructure formation by liquid-like flow of nanocrystalline particles.

Keywords: nanocage, nanoparticle, in-situ TEM, boron nitride, nitridation

Following the discovery of fullerene molecules [1] and related nanostructures [2, 3], the growth of a variety of novel nanostructured carbon-based materials has been achieved in recent years. The formation of 'chains' of hollow spheres or 'nanocages' of carbon has been observed [4, 5], together with nanocages of hexagonal boron nitride (BN) [6].

The mechanism by which nanocages form is not well understood. The goal of the present experiments was to perform direct in-situ observations of the growth of BN nanocages using a modified high resolution ultrahigh vacuum transmission electron microscope (UHV TEM). A variety of growth techniques are available for BN nanocage synthesis including arc discharge [7, 8], excimer laser irradiation [9], low pressure CVD[10,11] and ball milling followed by annealing at high temperatures[12,13] using hexagonal BN powder or finely dispersed nickel boride. In our experiments, we attempted to synthesize FeB nanocages by the direct nitridation of FeB nanoparticles in ammonia under high vacuum conditions.

Nanoparticles of FeB were prepared by ball-milling water-free iron chloride and sodium borohydride (1:3:3 in mole ratio) for 8h followed by annealing in Ar at 500°C for 3hr [14]. The FeB particles were then ultrasonicated in ethanol and cast onto Si supports, 6mm x 2mm x 0.2mm. One side of the support was uniaxially dimpled and chemically thinned to produce multiple perforations prior to casting of the particles. The samples were then loaded into the column of a modified JEOL 2000V UHV TEM.

Electron beam analysis of the particles revealed them to be ~20-50nm in diameter; electron energy loss spectroscopy (EELS) analysis revealed a clear B and C K-edges. The particles were then heated to ~1000°C in a partial pressure of ~5 microTorr of ammonia gas. The formation of thin, faceted shells around the particles was observed. The shells grew to a critical thickness at which point the FeB particle was spontaneously ejected from the shell. EELS analysis revealed the characteristic spectrum corresponding to hexagonal BN.

After further annealing, a second shell was observed to form around the FeB particle; at a similar critical thickness, the particle was again ejected. The process was repeated until a chain of 5 h-BN cages had been formed, the last of which still contained the FeB particle. A bright field image of the sample after cooling to room temperature is shown in Figure 1.

The observations are consistent with a model for nanocage formation whereby the h-BN layers grow at the Fe-B interface by diffusion of nitrogen species through the growing BN layers. At a critical wall thickness, the particle is ejected from the nanocage, relieving compressive strain energy and creating a fresh FeB: vacuum interface. The formation of BN nanocages naturally depletes the B content until further nanocage growth ceases [15].

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Figure 1: Bright-field image showing the series of BN nanocages produced during nitridation of an FeB nanoparticle.

