

Irradiation for the Novel Radiolytic Formation of Superalloy Nanoparticles

by T. M. Nenoff, K. Leung, D. Berry, J. Knapp, P. Provencio, and J. Jones

Motivation—Superalloys are high temperature, corrosion resistant inorganic materials with both defense and civilian applications. The ability to make them nanoscale allows for a wide variety of nanotechnology applications. We are using radiolysis to develop a universal method to make nanoparticles of metals, alloys and superalloys. The combination of irradiation source, solution electrochemistry, and surface modification by ligands allows for control of size, morphology and composition.

Accomplishment—We are synthesizing metallic and alloy nanoparticles in a novel way that allows for (1) exploration of metastable phase space not accessible by traditional alloy synthesis methods (i.e., melting), (2) synthesis of ultrafine/nanoparticles that enables uniform sintering as opposed to cast melting that grows in defects, and (3) possible controlled anisotropic nanoparticle growth through selective capping. We are combining basic research and an iterative feed-back loop of density functional theory (DFT) modeling, which is then applied directly to variables of materials synthesis. We have successfully designed, built, and utilized reaction setups for both the gamma irradiation facility (GIF) source (dose rate ≈ 75 rads/sec) and ion beam reactors (dose rate is ≈ 4400 rad/sec). Synthetic reaction procedures have also been developed for both irradiation set-ups. In this first year, we tested a number of experimental variables and their effects on nanoparticle formation. They include the role of (1) dose rate, (2) radical inhibitor, (3)

dose, (4) irradiation exposure time, and (5) organic type. Our initial studies were on gold; we then began experimentation on Ni, Pd, Ag, Ag/Ni, Pd/Ni metals of interest for both superalloys and metal-alloy hydrogen membranes. All the variables play a role in determining shape, size, and composition of nanoparticles (Figs. 1 & 2).

Concurrently we are running *ab initio* molecular dynamics (AIMD), which treats the valence electrons of all species quantum mechanically, and is capable of describing chemical reactions and electron transfer events. We have applied AIMD to examine the hydration of mono- and diatomic Ag and Ni species in water. Ag and Ni are found to behave very differently in water. Ag behaves like a hydrophobic sphere, while Ni is highly hydrated (Fig. 3). This helps explain initial synthetic results of nonuniform stoichiometry in nanoparticle-organic cluster formation (Fig. 2).

Modeling combined with experimentation aids in the understanding of critical science issues related to nucleation, alloy formation, and metal clusters-organics binding in water.

Significance—The possibility of synthesizing a wide variety of metastable superalloy phases that can be made only by sintering rather than melting is very exciting. We expect that our successes will be broadly useful in structural applications requiring high strength:fracture ratios.

Sponsors for various phases of this work include: Laboratory Directed Research & Development

Contact: Tina M. Nenoff, Surface & Interface Sciences, Dept. 1114
Phone: (505) 844-0340, Fax: (505) 844-5470, E-mail: tmnenof@sandia.gov



Figure 1. Metal nanoparticles can be synthesized in various shapes based on dose rates and growth time. Gold prism ≈ 30 nm in size.

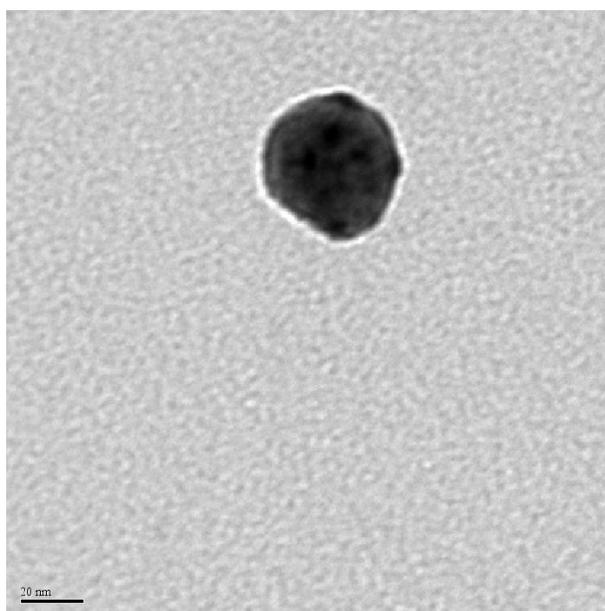


Figure 2. TEM of Ag/Ni/polymer cluster. Dark/light contrast in image suggests nanoparticles of elemental difference. Electron diffraction suggests nanodomains of crystallographic difference.

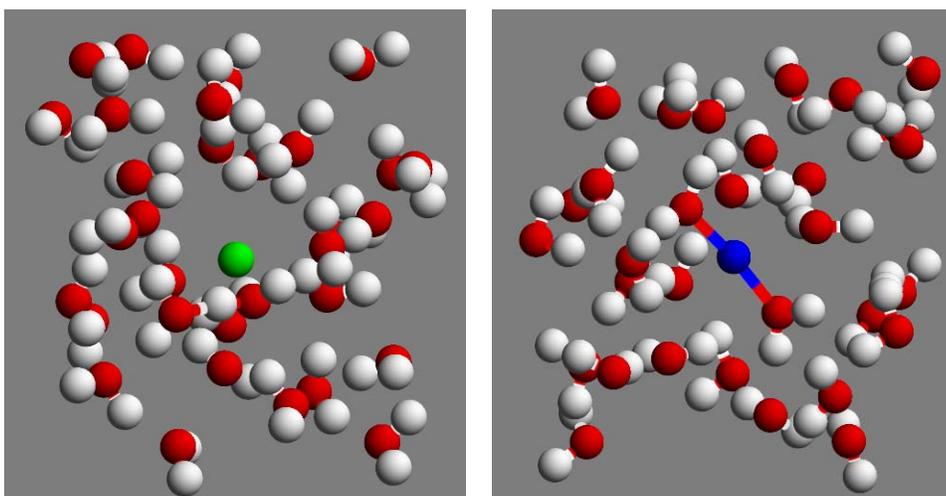


Figure 3. Ag/Ni AIMD snapshots of Ag (green) and singlet Ni (blue) atoms in liquid water. The red and white circles in the ball-and-stick models depict the oxygen and hydrogen sites of H_2O molecules.