

# Irradiation for the Novel Radiolytic Formation of Superalloy Nanoparticles

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# Problem: Utilization of Novel NP formation Without Sintering or Oxidation

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Superalloys: Ni-based alloys that are hardened with refractory metals to higher temperatures while retaining superb mechanical strength  
e.g.:  $\gamma$ -phases Ni/(Co, Cr, Mo, or W) or  $\gamma'$ -phases  $\text{Ni}_3(\text{Al, Ti})$

Synthesis of nanoparticles of alloy compositions allows for both nano and bulk scale applications of alloys.

Sintering of nanoparticles of an alloy allows for more defect-free bulk alloys, non-destruction of the refractory elements, and access to meta-stable phase spaces and morphologies.

Radiolysis is a room temperature method to produce kinetically favorable, metastable alloy nanoparticles.

Ability to make homogenous NPs, independent of reaction size, means large quantities are possible

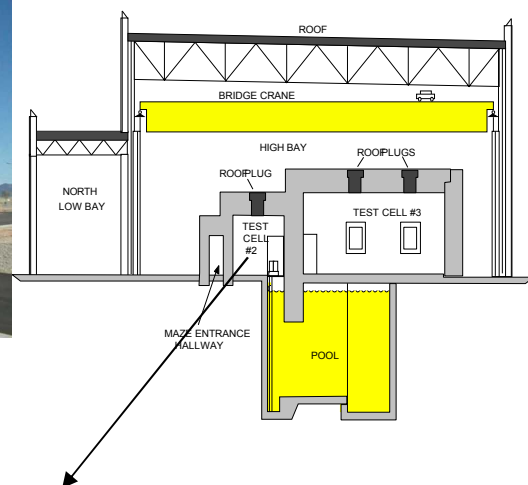
# Approach:

## Room Temp Radiolysis at SNL's GIF Facility

Radiolysis is a method in which metal Ions are reduced in water by Ionizing Radiation:  
The dose rate dictates the  $[e^-]$  in the reaction solution thereby affecting the chemistry of the NP formation.

QuickTime™ and a  
TIFF (Uncompressed) decompressor  
are needed to see this picture.

Sandia's Gamma Irradiation Facility (GIF) is a  
 $^{60}\text{Co}$  source :  $1.345 \times 10^5 \text{ Ci}$ ,  $\approx 300\text{K rad/hr}$ .



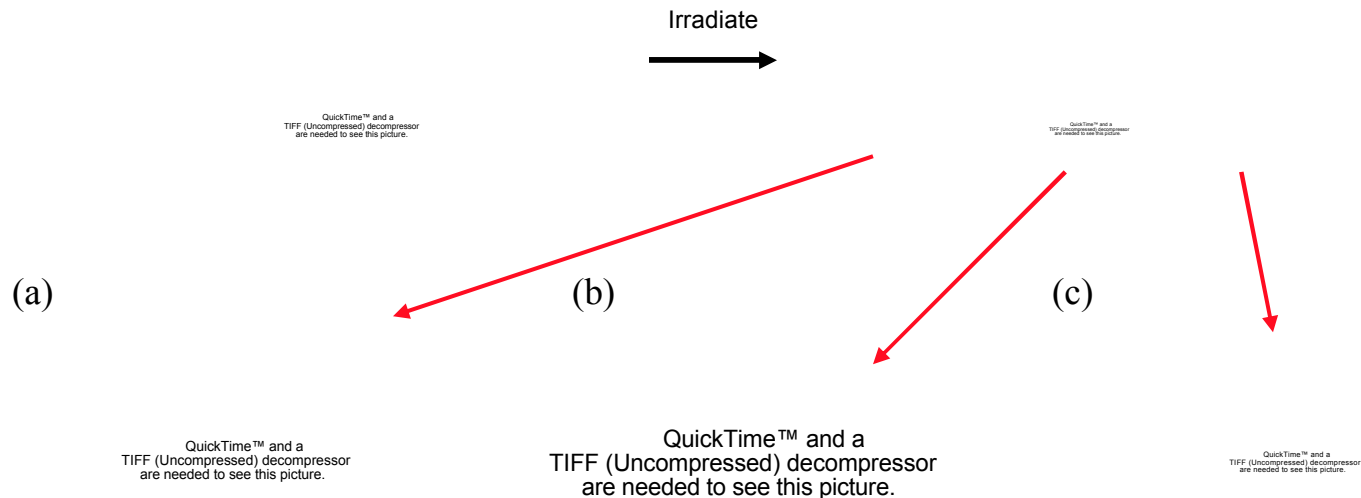
**C**

**A** **B** **Co source**

# Results: Gold Nanoparticles, Morphology Determined by Dose Rate

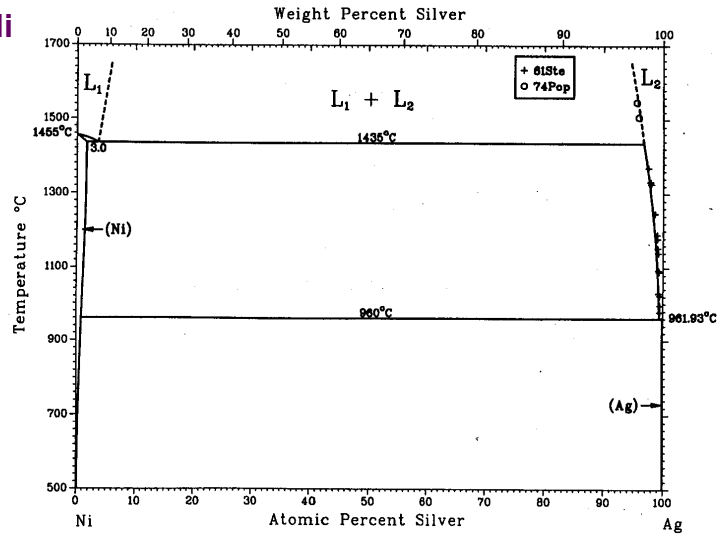
Reaction Conditions: 25ml solutions in 100ml vials  
HAuCl<sub>4</sub>•3H<sub>2</sub>O (1000ppm Au in dilute HNO), poly(vinyl alcohol) (PVA, MW of 88000), DI H<sub>2</sub>O  
Purged solution with N<sub>2</sub>, sealed and stored in dark  
Exposed solutions to  $\gamma$ -irradiation; allowed to age and crystals to grow

(a) 770, (b) 72.3, (c) 7.07 rads/sec for 3 min dose ( $\approx 10^3$  rad)

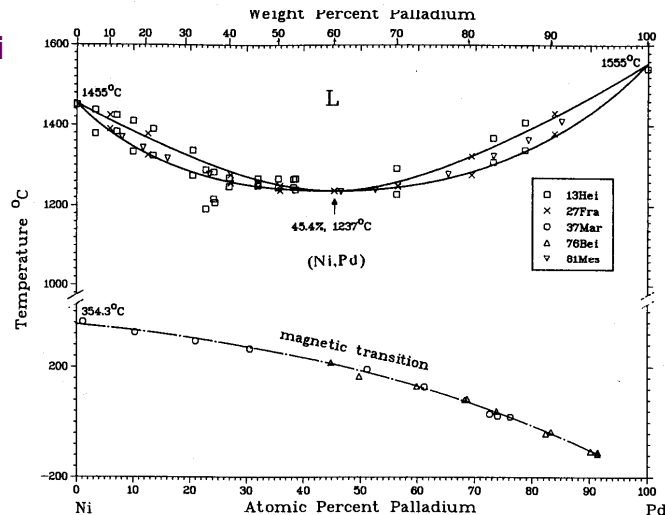


# Kinetically-driven Access to New Phase Spaces: Thermodynamically inaccessible or limited Ni-based NPs

## Ag-Ni



## Pd-Ni



Theory of NP alloy formation via radiolysis

QuickTime™ and a  
TIFF (Uncompressed) decompressor  
are needed to see this picture.

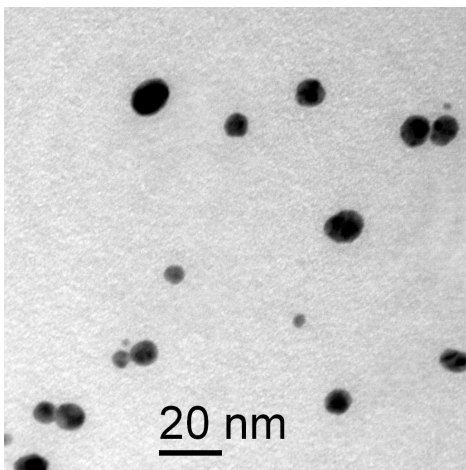
T. B. Massalski, *ASM International*, 2<sup>nd</sup> Ed., 1990

Belloni, *Catalysis Today*, 2006, 113, 141

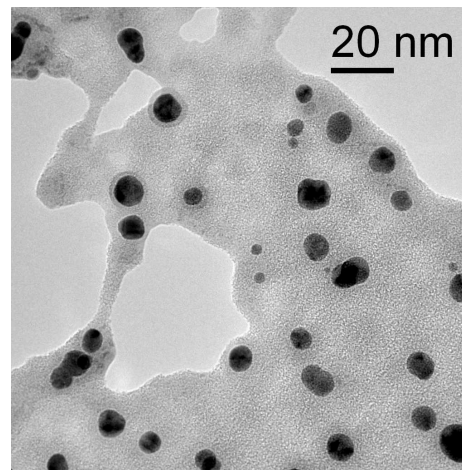
T. M. Nenoff, [tmnenof@sandia.gov](mailto:tmnenof@sandia.gov)

# Reaction Composition Effect on NP sizes: TEM

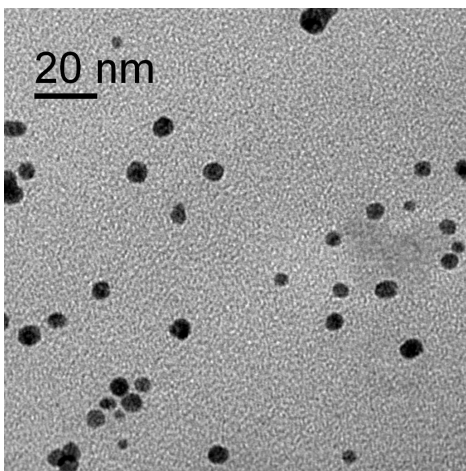
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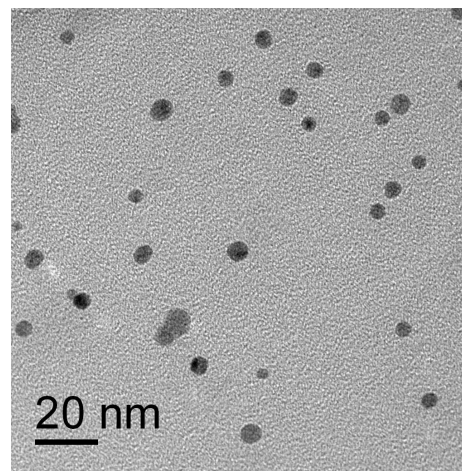
Pure Ag NPs



10% Ni, 90% Ag NPs



30% Ni, 70% Ag NPs



50% Ni, 50% Ag NPs



# AgNi Superalloy Nanoparticles

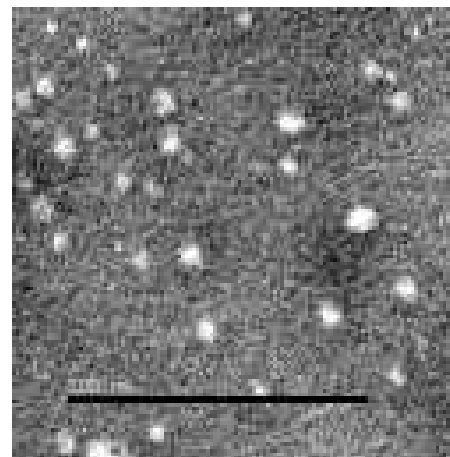
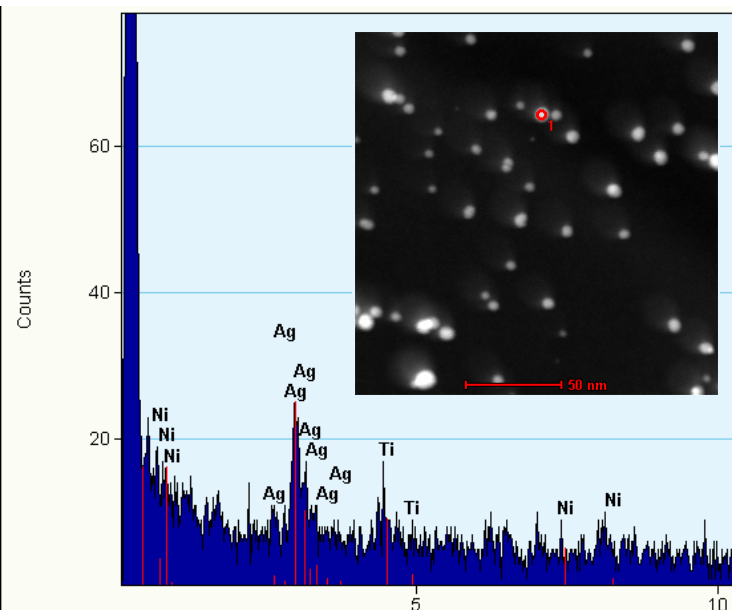
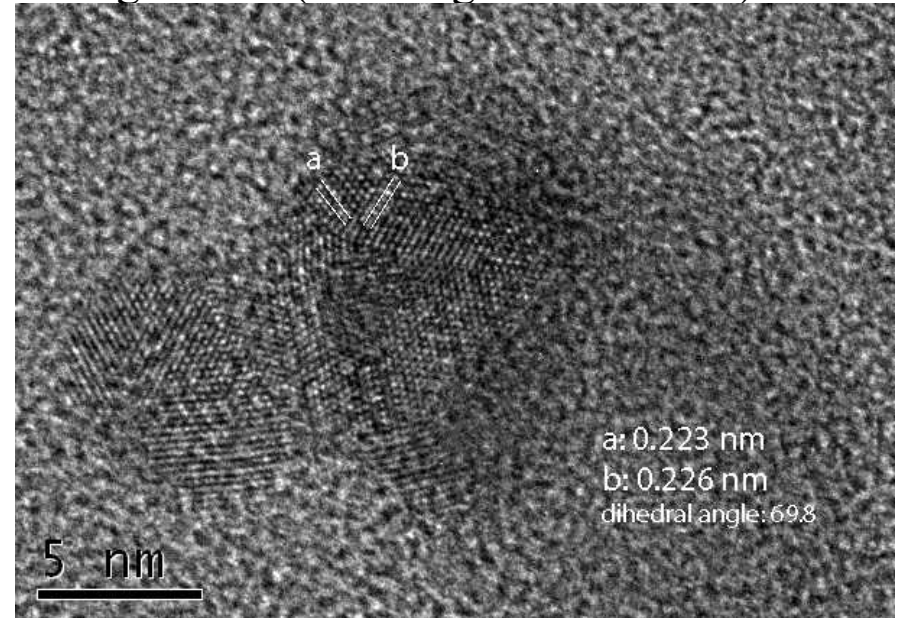
- HRTEM (CINT):

Ni (111) = 0.203 nm, Ag (111) = 0.236 nm

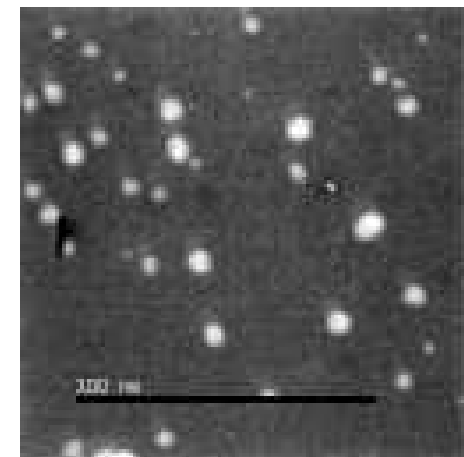
Ag-Ni alloy based on 50% Ni = 0.22 nm

- STEM & EDX: Single particle data indicates homogenous composition of Ag & Ni; confirmed by EELS maps

AgNi NPs ( 50% Ag : 50% Ni rxn)



Ag Map

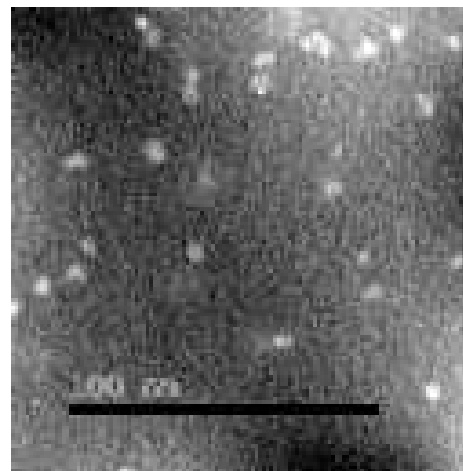
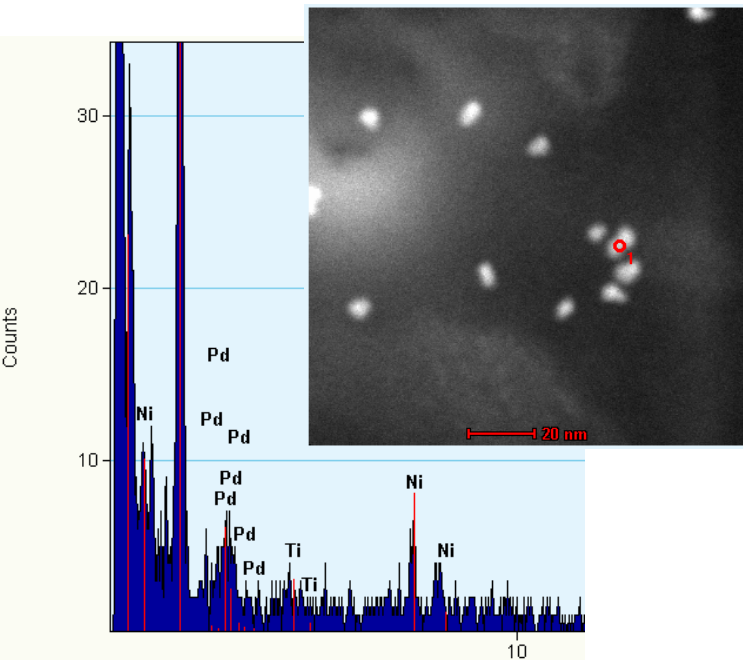
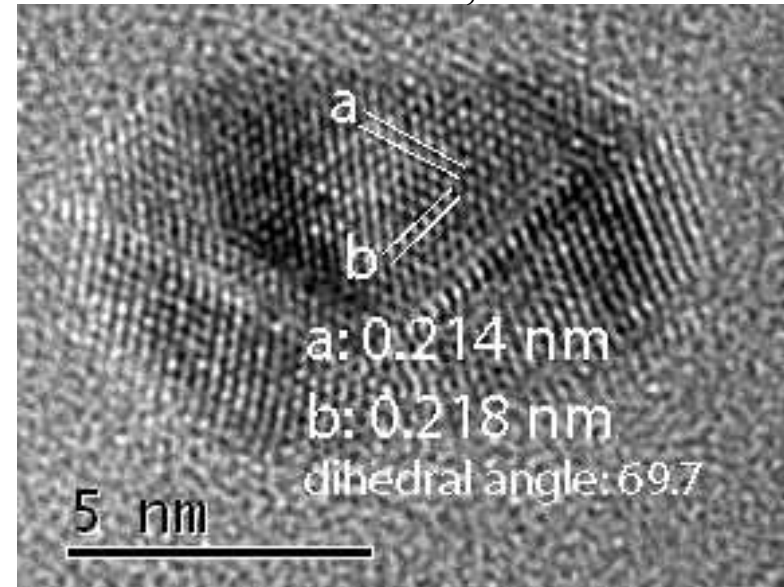


Ni Map

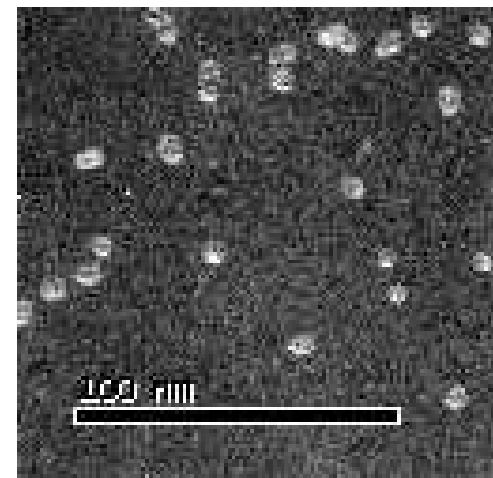
# PdNi Superalloy Nanoparticles

- HRTEM (CINT): (twinned crystal)  
Ni (111) = 0.203 nm, Pd (111) = 0.225 nm  
Pd-Ni alloy based on 50% Ni = 0.214 nm
- STEM & EDX: Single particle data indicates homogenous composition of Pd & Ni; confirmed by EELS maps

PdNi NPs: 50% Ni, 50% Pd



Pd map



Ni map



# Significance:

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Long Term Science for SNL Business SMU's (NTM, ERN) plus  
DOE National Security Mission and Strategic Goals.

Defense, Energy, Science applications require SuperAlloys:  
light weight, corrosion resistant, sintered refractory  
materials (weapons casings & connects, aircraft,  
satellites, power plants, gas turbine engines & burners

Leverage future funding by DOE/NE (nuclear fuel alloys),  
DOE/H<sub>2</sub> (H<sub>2</sub> dissociative membranes), DOD/DARPA/DTRA