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Room Temperature Synthesis of Alloy Nanoparticles

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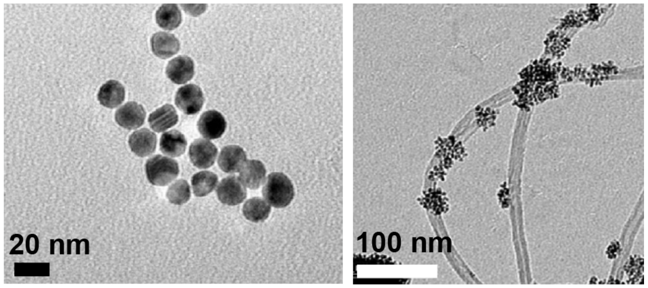
Radiolysis to Form Novel Alloys Meta-Stable Phase Spaces

Radiolysis by γ-radiation is used to access new alloys

By varying the dose rate, we vary the structure of nanoparticle growth in solution over a wide composition range in alloys

Reactions occur at room temperature allowing for growth on various substrates

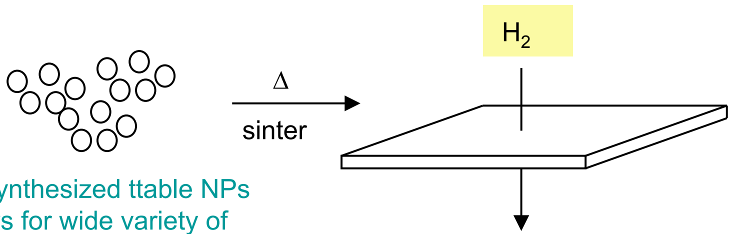


Oh, S. D., et al. *Materials Letters* ***2005***

Pt-Ru NP grown and deposition on SWCNT

Sintered materials for: H_2 membranes, gas turbine microengines, lightweight aircraft, etc.

- ***State of the Art: Pd and Pd-alloys for durable H_2 dissociative membranes operate at high temperatures and are CO and sulfur tolerant***



RT synthesized ttable NPs allows for wide variety of compositions with minimized defects

metal/alloy H_2 membrane

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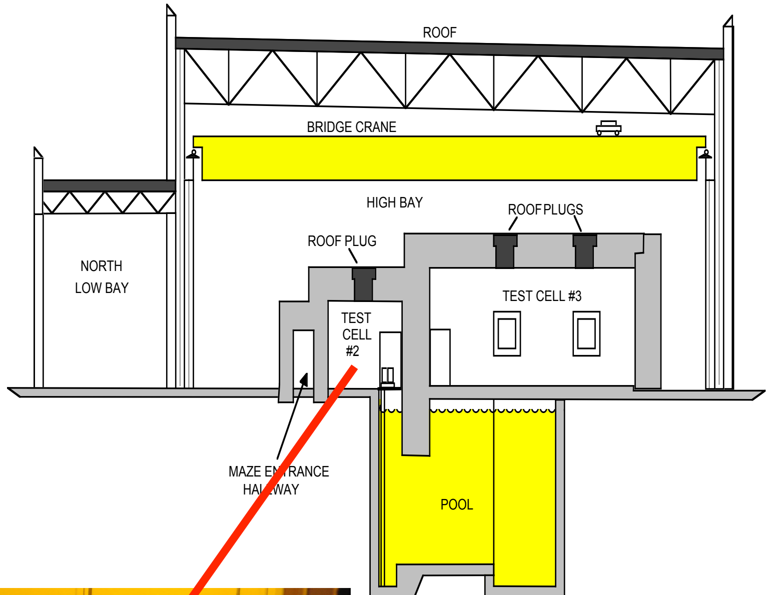
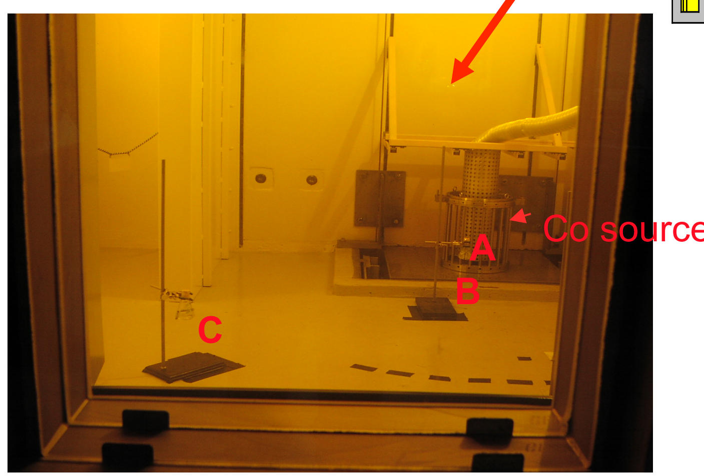
Room Temp Radiolysis at Sandia (SNL) GIF Facility

Sandia Gamma Irradiation Facility (GIF) is a
^{60}Co source : 1.345 x 10^5 Ci, ≈ 300K rad/hr.





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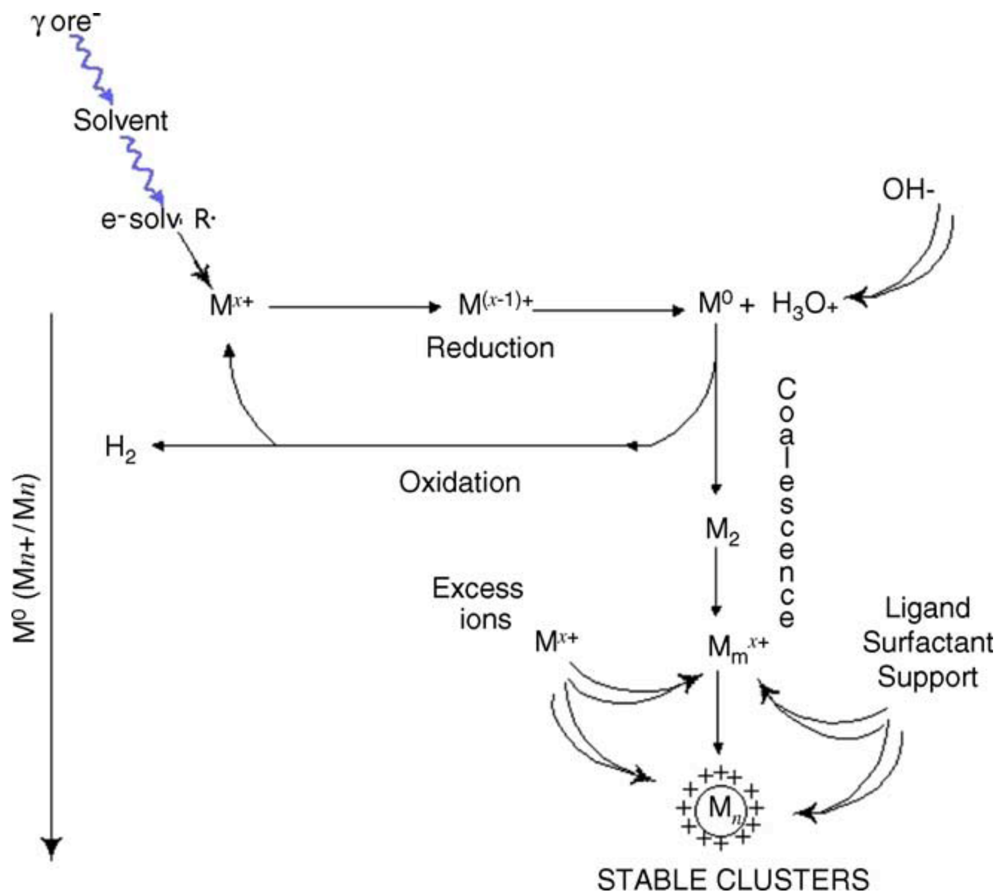
Radiolysis for Nanoparticle Formation

Metal ion reduction by ionizing radiation:
Dose rate dictates [e-] in reaction solution thereby affecting the chemistry of the NP formation

$$H_2O \Rightarrow e^-_{aq}, H_2, OH^\bullet, H^\bullet, H_3O^+, H_2O_2, HO_2^\bullet$$



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

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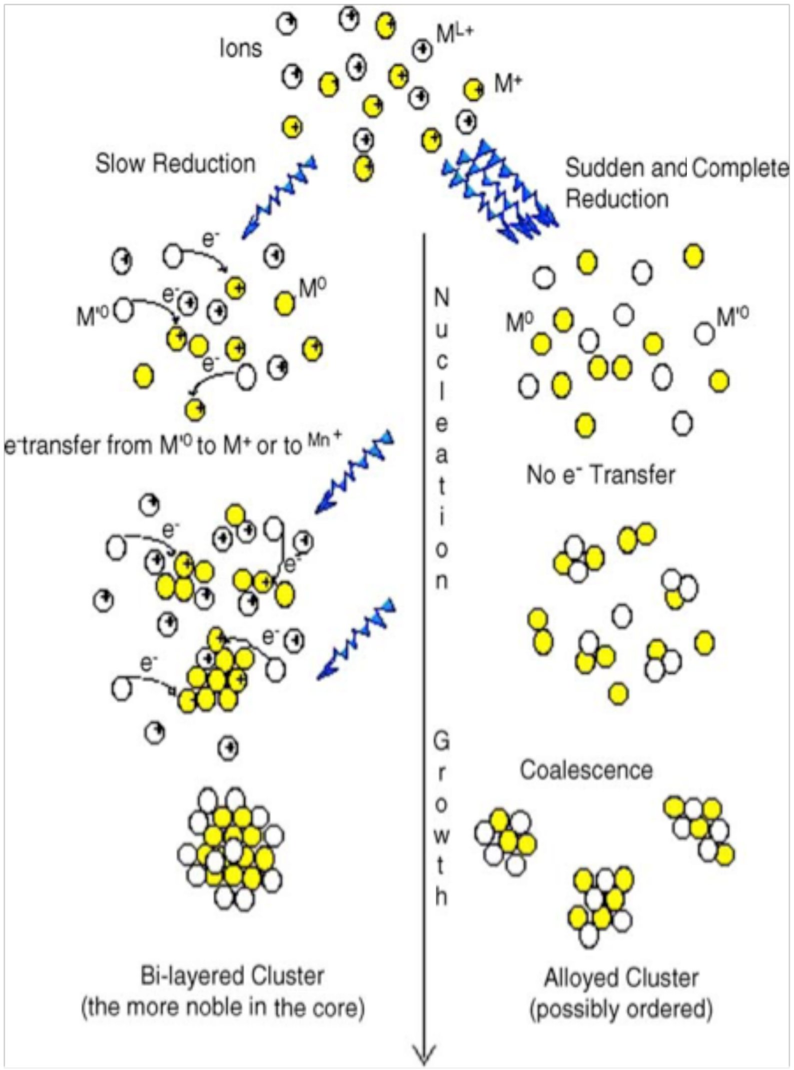
Methodology to Access Ni-based Alloy Phase Spaces

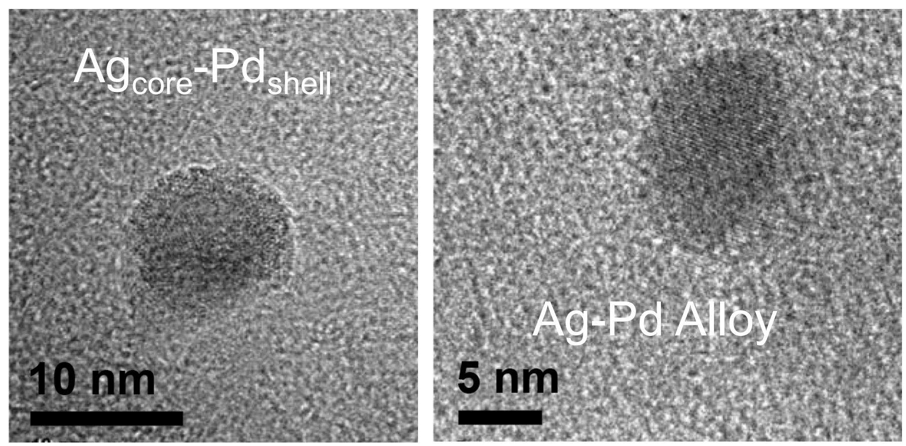


Belloni, *Catalysis Today*, **2006**,*113*,141

Alloys: Possibility to access different phase space than with traditional melting

Using high radiation dose and High dose rate, we pursue nanoparticle alloy formation

Slow Reduction | Sudden Reduction



Redjala, T. et al. *Oil Gas Sci. Technol.* ***2006***

$AgNO_3$, $HAuCl_4$, $Pd(NO_3)_2$ and poly (vinyl alcohol) (PVA, 99% hydrolysed, MW = 86000); Dose rate of 1.75 $Gy.s^{-1}$

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Nanoparticle (NP) Synthesis & Analysis

Experimental NP Synthesis:

Into 25ml solutions in 100ml vials add dilute metal salt solutions, alcohol (MeOH), organic polymer (PVA) and DI H_2O.

Purged solution with N_2, sealed and stored in dark.

Exposed solutions to γ-irradiation.

NP Analysis:

(1) UV-vis: Varian Cary 300 Scan UV-visible Spectrophotometer

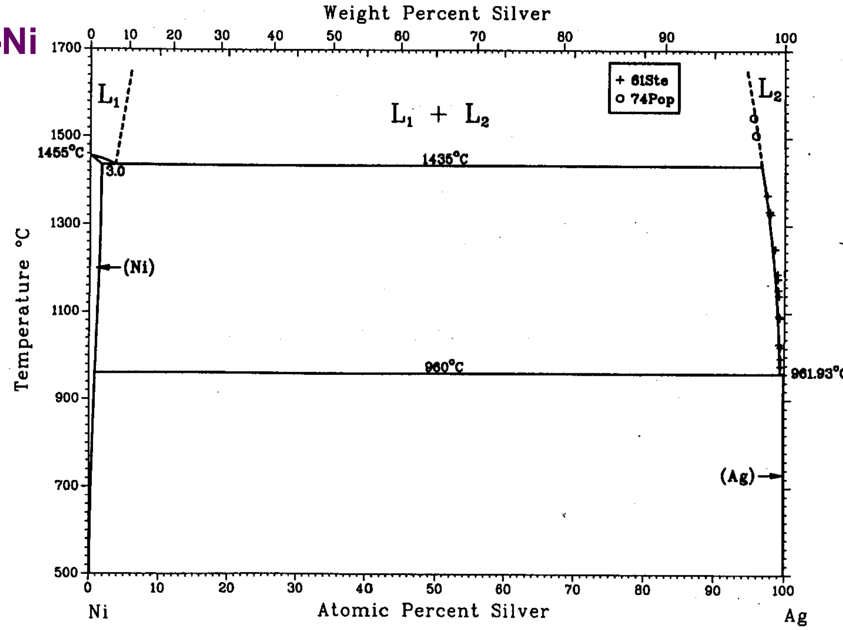
(2) Transmission Electron Microscopy (TEM): JEOL 1200EX (120 kV) bright-field

(3) High Resolution TEM and scanning TEM: FEI Tecnai G(2) F30 S-Twin (300 kV) TEM at Sandia's Center for Integrated Nanotechnologies (SNL CINT)

- 0.14 nm resolution in high-angle annular dark-field (HAADF) mode
- equipped with energy-dispersive X-ray (EDX) & electron energy-loss spectrometer (EELS)

Ag-Ni Alloy Particle Formation – Kinetically Driven Access to New Phases

Thermodynamic Phase Diagram



T. B. Massalski, *ASM International*, 2nd Ed., **1990**

High Dose Radiolysis: RT Kinetic Phase Growth

Dose Rate ≈ 300 rad/sec

Particle Formation via radiolysis (γ-irradiation)

$^{\cdot}OH(^{\cdot}H) + e_{aq}^{-} + CH_3OH \longrightarrow e_{aq}^{-}/\ ^{\cdot}CH_2OH + H_2O\ (H_2)$

$e_{aq}^{-}/\ ^{\cdot}CH_2OH + Ag^{+}(Ni^{2+}) \longrightarrow Ag^{0}(Ni^{0}) + {}^{\cdot}CH_2OH$

Particle Growth

$x\,^{\cdot}CH_2OH + (AgNi)_n \longrightarrow (AgNi)_n^{x-} + xCH_2O + xH^{+}$

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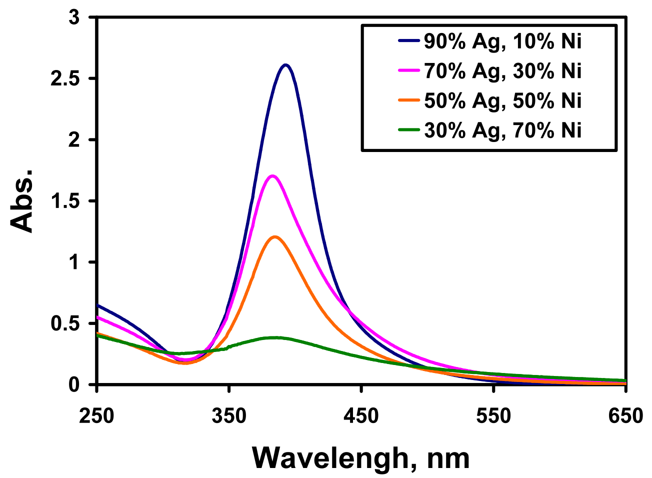
Ag-Ni Alloy NPs – Characterization

Different stoichiometries of Ag^{+} and Ni^{2+} used to prepare Ag-Ni alloy NPs

	Ag	$Ag_{0.9}$-$Ni_{0.1}$	$Ag_{0.7}$-$Ni_{0.3}$	$Ag_{0.5}$-$Ni_{0.5}$	$Ag_{0.3}$-$Ni_{0.7}$	Ni
$[Ag^{+}]$, × 10^{-4} M	2	1.8	1.4	1	0.6	0
$[Ni^{2+}]$, × 10^{-4} M	0	0.2	0.6	1	1.4	2
$[Ag^{+}] + [Ni^{2+}]$, × 10^{-4} M	2	2	2	2	2	2
$[Ag^{+}]:[Ni^{2+}]$	pure Ag NPs	9:1	7:3	5:5	3:7	pure Ni NPs

UV-Vis



Ag plasmon band dampens from $Ag_{0.9}$-$Ni_{0.1}$ to $Ag_{0.3}$-$Ni_{0.7}$

$AgClO_4$ and $NiSO_4$ are used to synthesize Ag-Ni particles by radiolysis. UV-vis spectroscopy supports varied stoichiometries in NPs.

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Ag-Ni Alloy NPs – TEM Images

pure Ag
8.5 nm

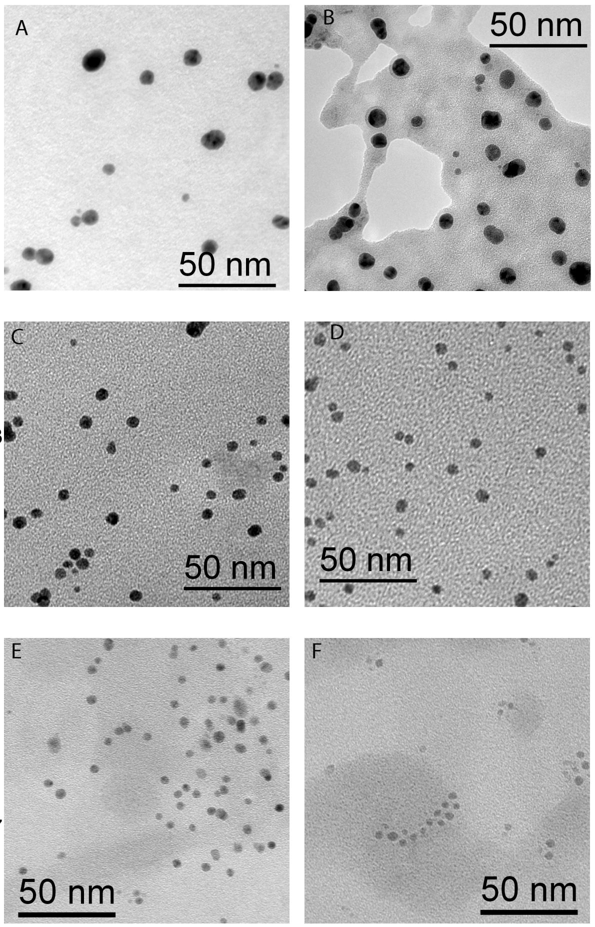
$Ag_{0.9}$-$Ni_{0.1}$
7.4 nm

$Ag_{0.7}$-$Ni_{0.3}$
5.7 nm

$Ag_{0.5}$-$Ni_{0.5}$
5.4 nm

$Ag_{0.3}$-$Ni_{0.7}$
4.0 nm

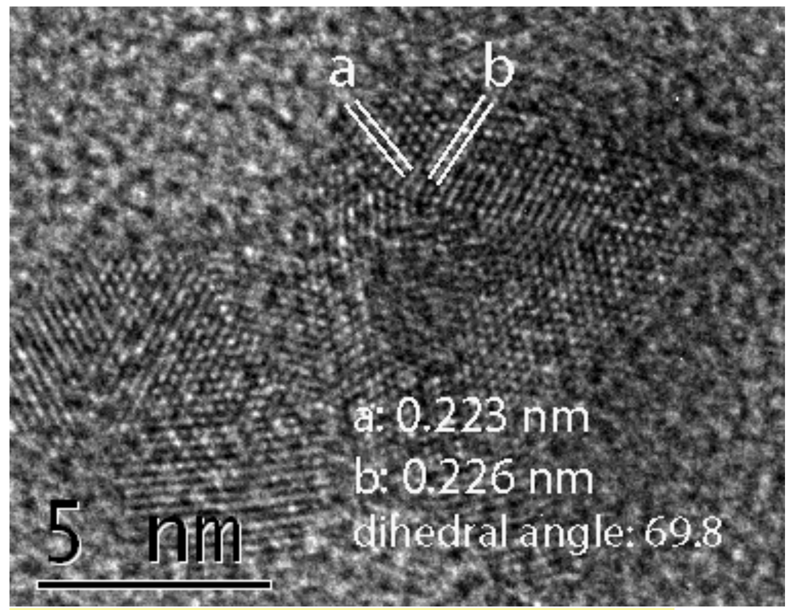
pure Ni
3.4 nm



The size of Ag-Ni NPs is decreased with higher Ni ratio

Particle size in diameter and size distribution of Ag, Ag-Ni, and Ni NPs

	Ag	$Ag_{0.9}$-$Ni_{0.1}$	$Ag_{0.7}$-$Ni_{0.3}$	$Ag_{0.5}$-$Ni_{0.5}$	$Ag_{0.3}$-$Ni_{0.7}$	Ni
size in diameter, nm	8.5	7.4	5.7	5.4	4.0	3.4
size distribution	24%	24%	20%	15%	18%	19%



Ni: 0.203 nm, Ag: 0.236 nm Ag-Ni

Lattice spacing of 50% Ag and 50% Ni may be present. Theory: 0.220 nm

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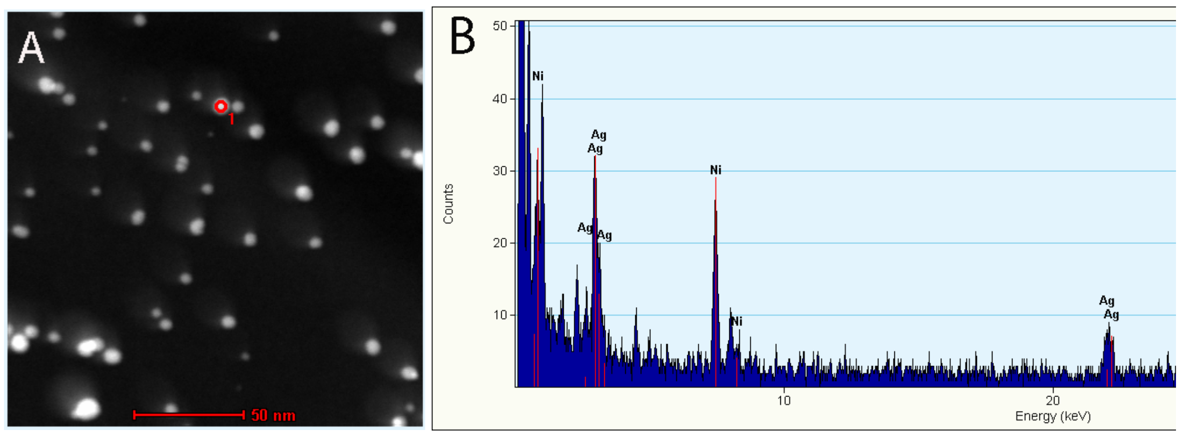
Ag-Ni Alloy NPs – HAADF Images

HAADF-STEM and single particle EDX images



$Ag_{0.5}$-$Ni_{0.5}$ NPs

The size of Ag and Ni peaks from single particle EDX are comparable in intensity

JPCC, 2009, *113*, 1155; US Patent Tech Advance, 2008: SD10767

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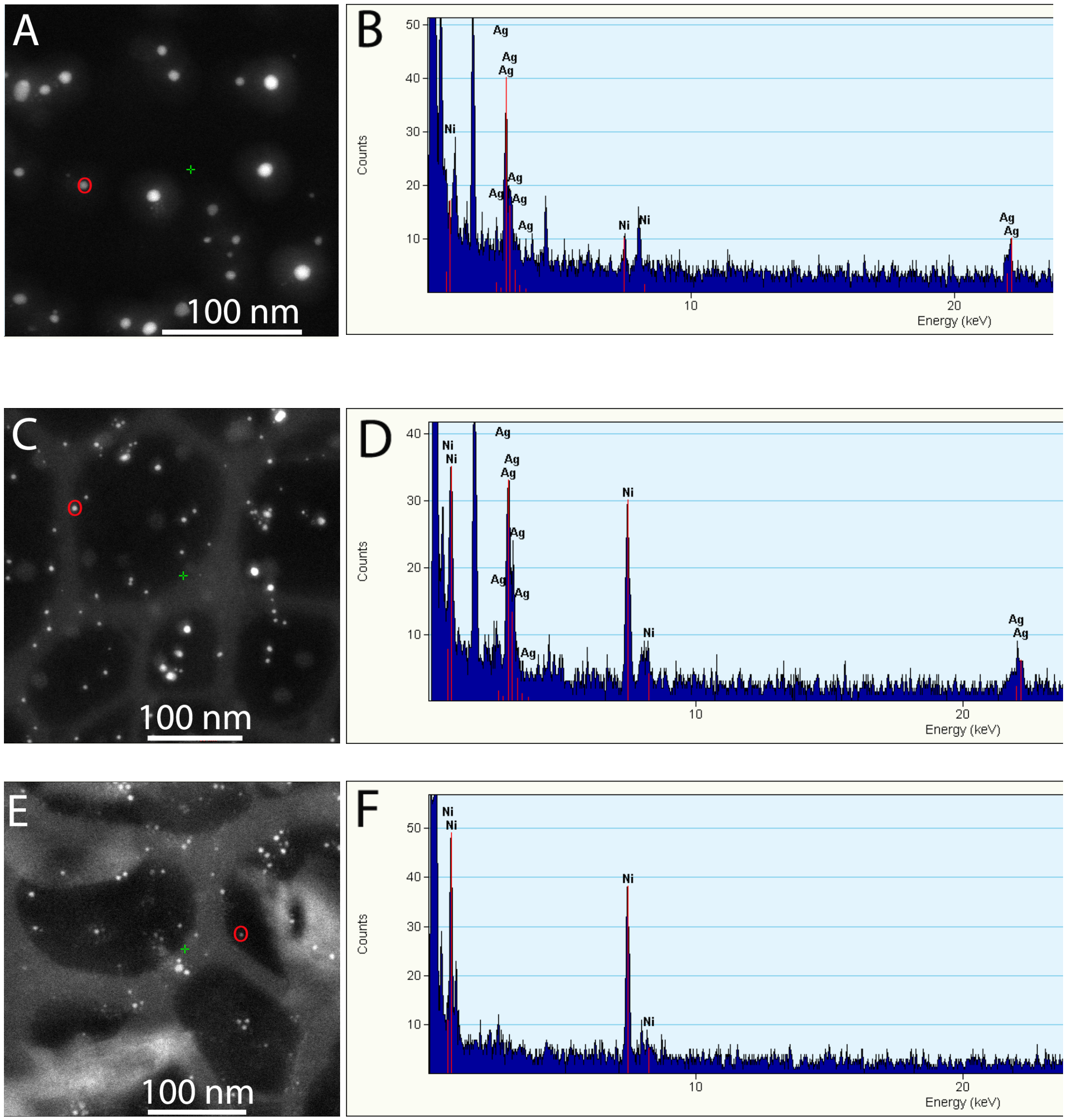
Ag-Ni Alloy NPs – HAADF Images



$Ag_{0.7}$-$Ni_{0.3}$ NPs

$Ag_{0.3}$-$Ni_{0.7}$ NPs

pure Ni NPs

The size of Ag and Ni peaks qualitatively correspond to initial ion ratios

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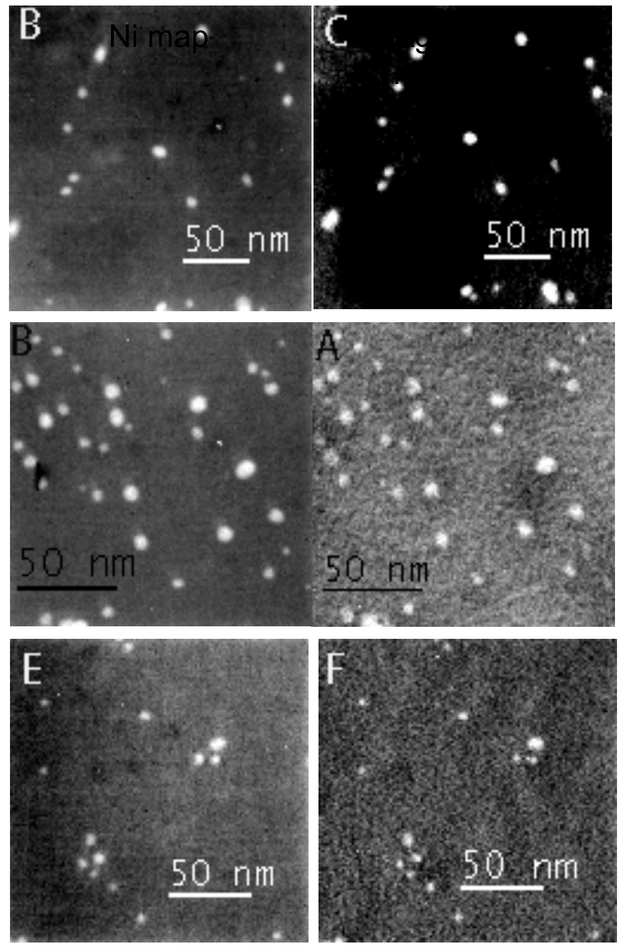
Ag-Ni Alloy NPs – EFTEM Mapping

EFTEM maps

$Ag_{0.7}$-$Ni_{0.3}$ NPs

$Ag_{0.5}$-$Ni_{0.5}$ NPs

$Ag_{0.3}$-$Ni_{0.7}$ NPs



Ag map Ni map

Elemental mapping shows Ag and Ni concentrated uniformly in NPs

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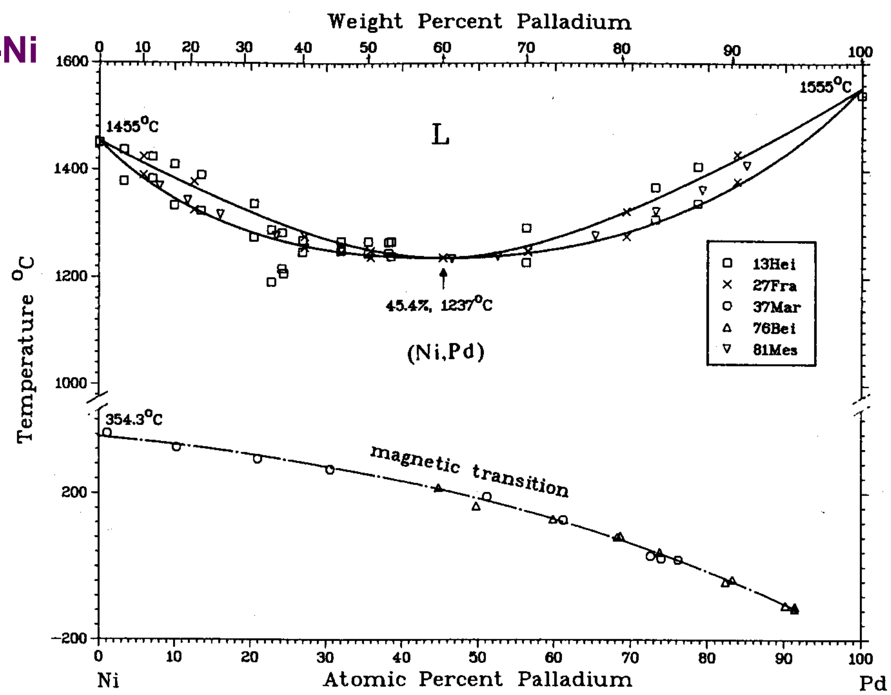
Pd-Ni Alloy Nanoparticles

Pd-Ni NPs: 50% Ni, 50% Pd

Pd-Ni

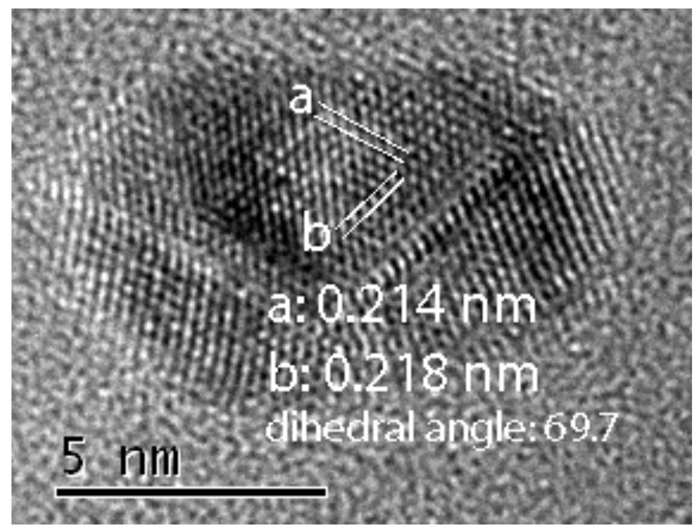


T. B. Massalski, *ASM International*, 2nd Ed., **1990**

HRTEM (CINT): (twinned crystal)

Ni (111) = 0.203 nm, Pd (111) = 0.225 nm

Pd-Ni alloy based on 50% Ni = 0.214 nm



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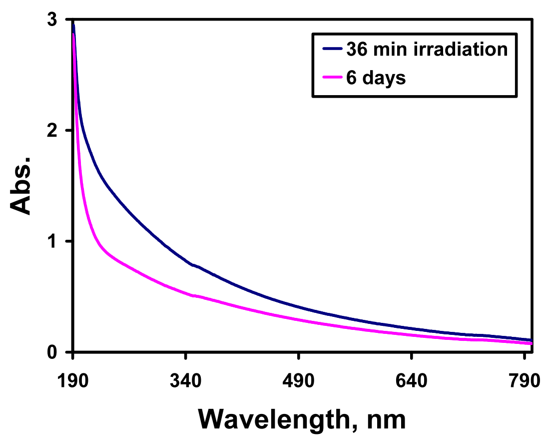
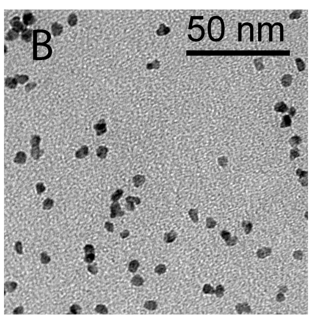
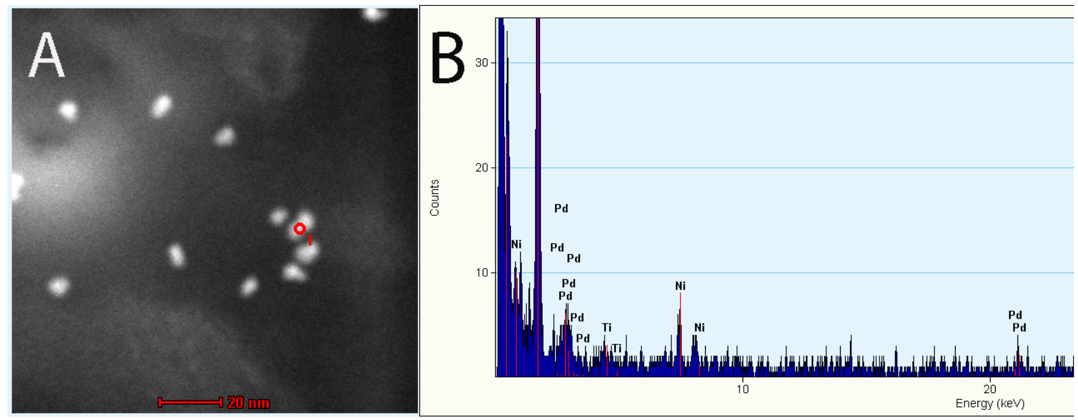
Characterization of Pd-Ni Alloy NPs

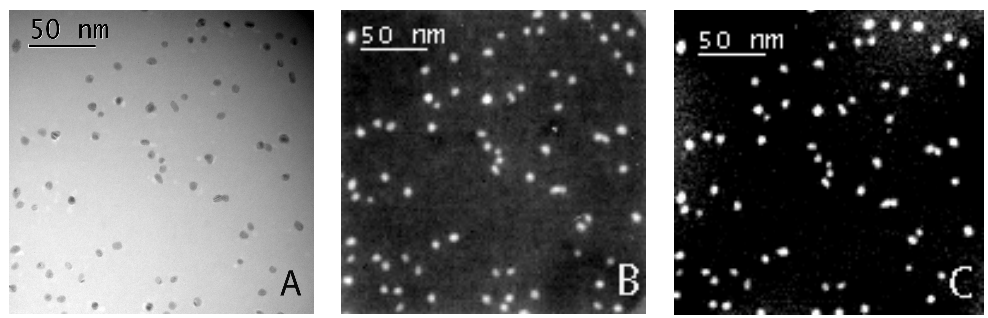
$Pd(NH_3)_4Cl_2$ and $NiSO_4$ are used to synthesize $Pd_{0.5}$-$Ni_{0.5}$ particles by radiolysis (high dose rate, 300 rad/s)







HAADF-STEM and single particle EDX images



zero loss image

Ni map

Pd map

EFTEM maps

• STEM & EDX: Single particle data indicates homogenous composition of Pd & Ni

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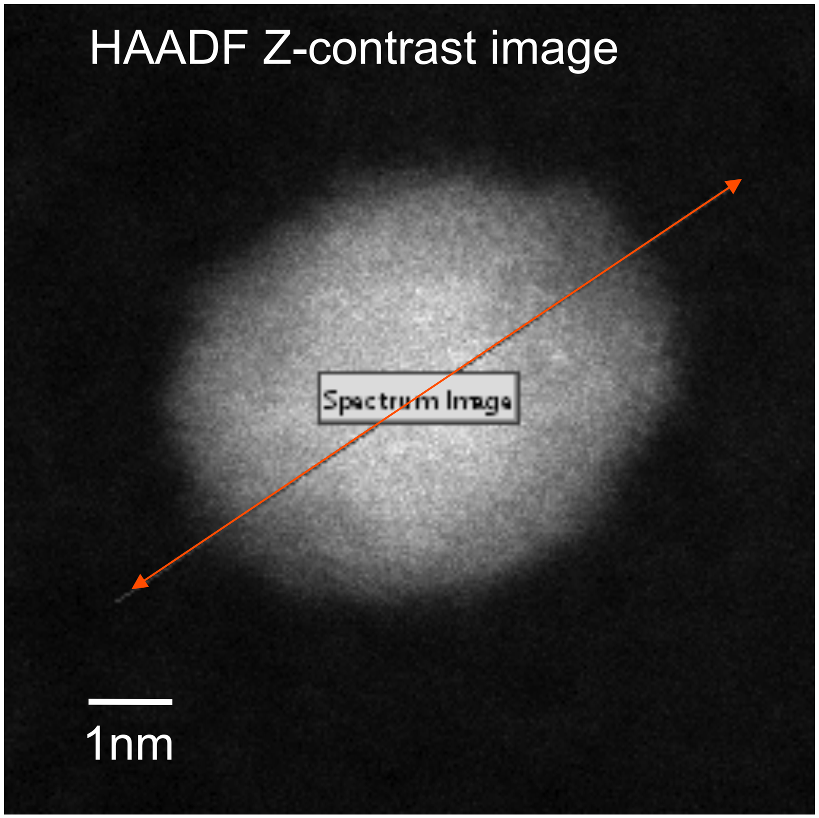
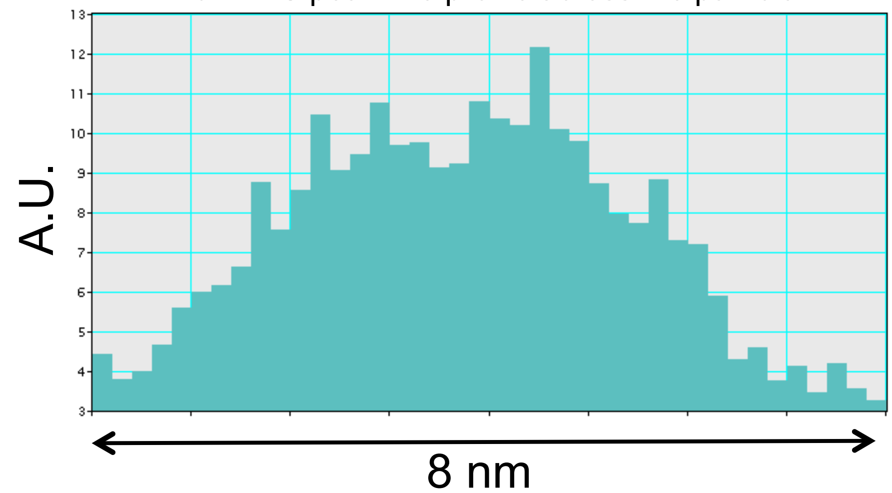
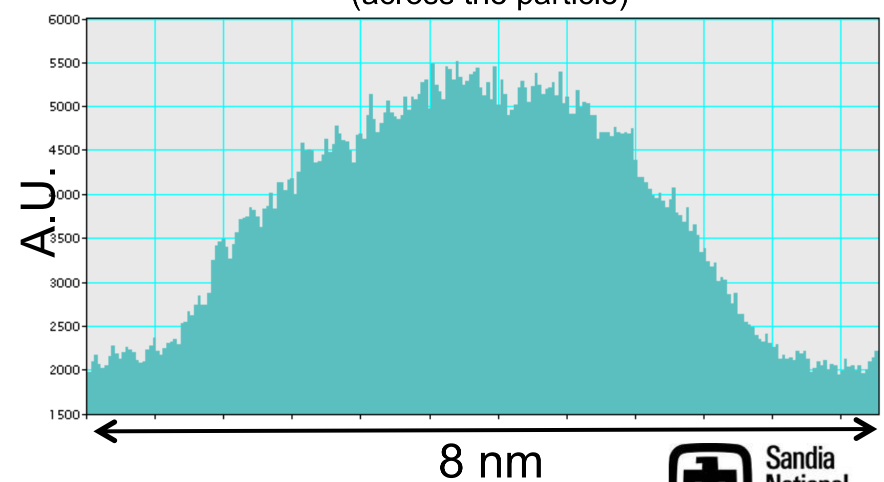
Atomic resolution compositional analysis by EELS



Pd EELS peak line profile across the particle



Intensity line-profile in the Z-contrast image (across the particle)



The Z contrast profile and the Pd EELS peak profile have a very similar shape, indicating the uniform distribution of Pd atoms in the particle

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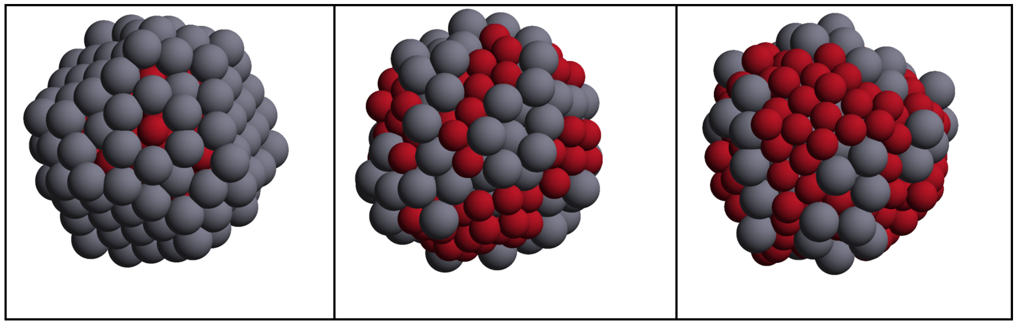
Kinetically Driven Alloy Phase Formations – Confirmed with 1st Principles Modeling

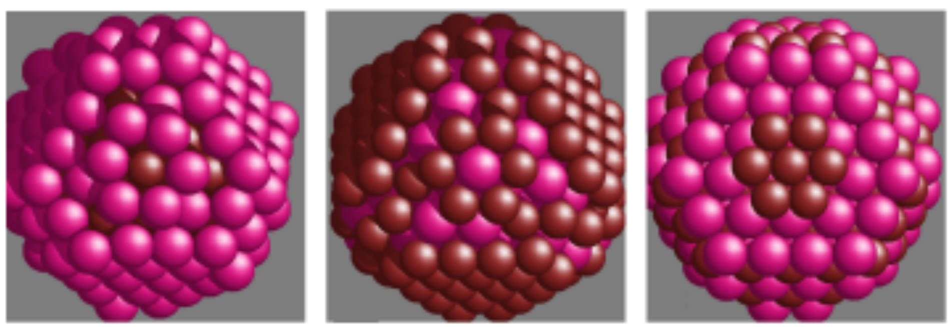
DFT Modeling using the VASP Code; FCC simulation using 240 atoms/NP

Optimized Ni_{core}-Ag_{shell}, alloy, Ag_{core}-Ni_{shell}



Potential Energy = 0eV, 43.7eV 57.2eV

Optimized Ni_{core}-Pd_{shell}, alloy, layered Ni-Pd



Potential Energy = 0eV, 16.6eV 16.7eV

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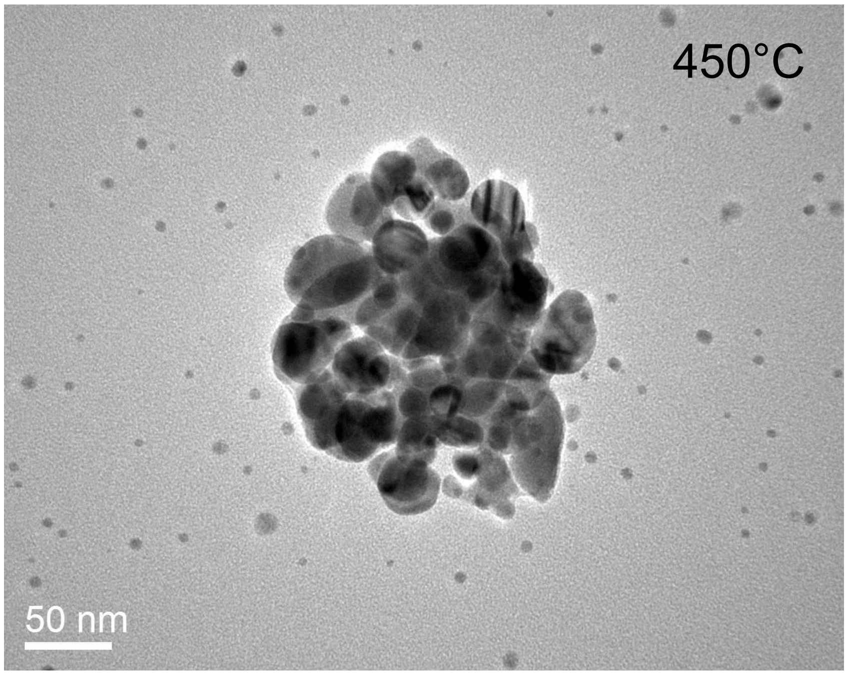
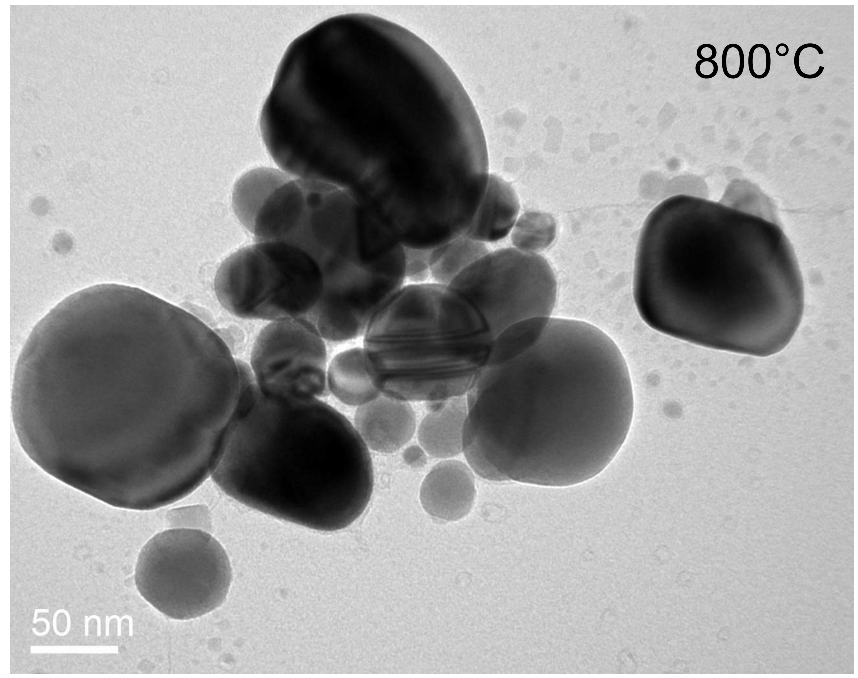
Sintering Ag-Ni NPs: 25°C – 800°C on heated TEM stage





50/50 AgNi, small scale ripening from RT - 450°C in first 25 min

Rapid large scale sintering, possibly *via* Oswald Ripening processes, occurs in ≈ 15 min. between 450 – 800°C

Melting Points: Ag 962 °C
Ni 1453 °C

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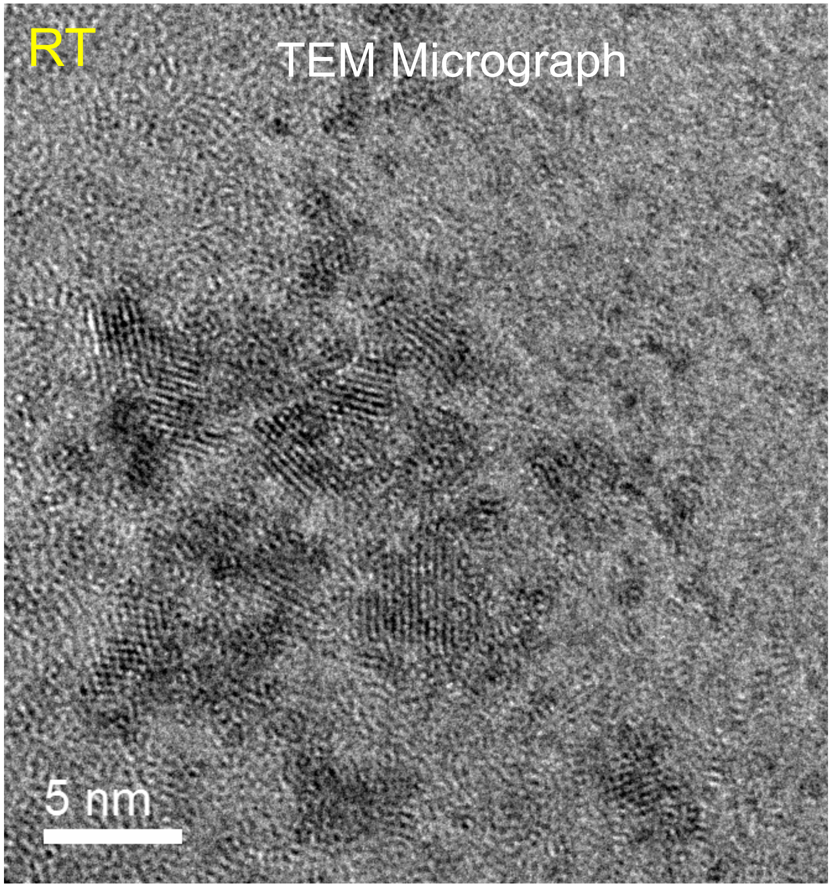
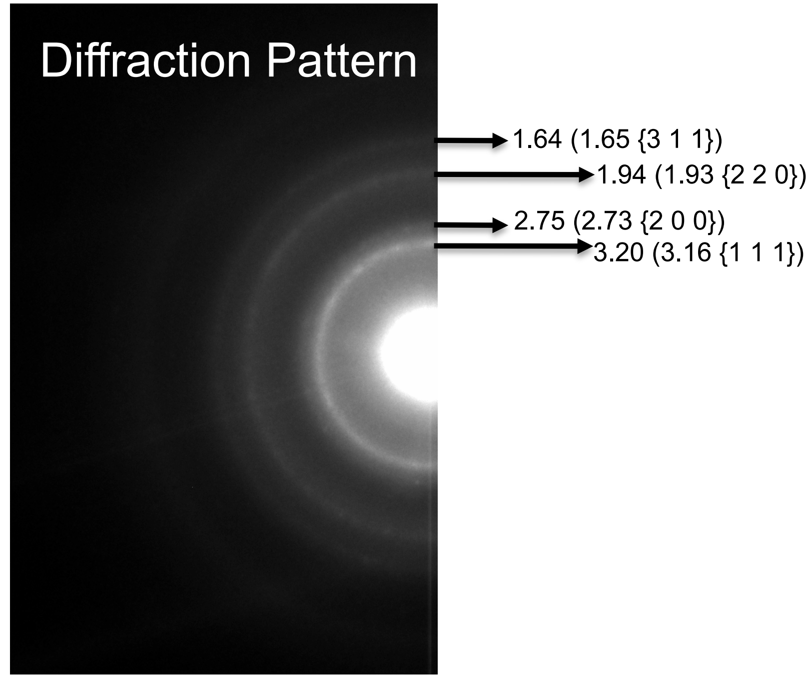
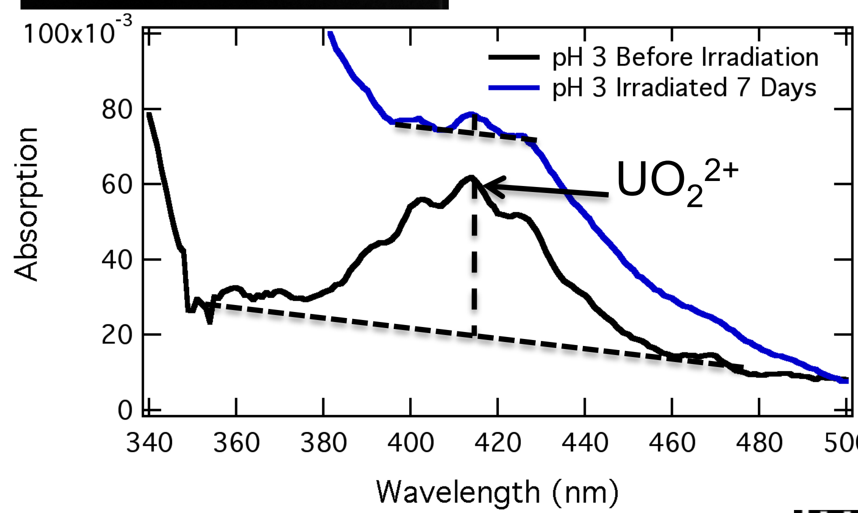
Characterization of U containing NPs

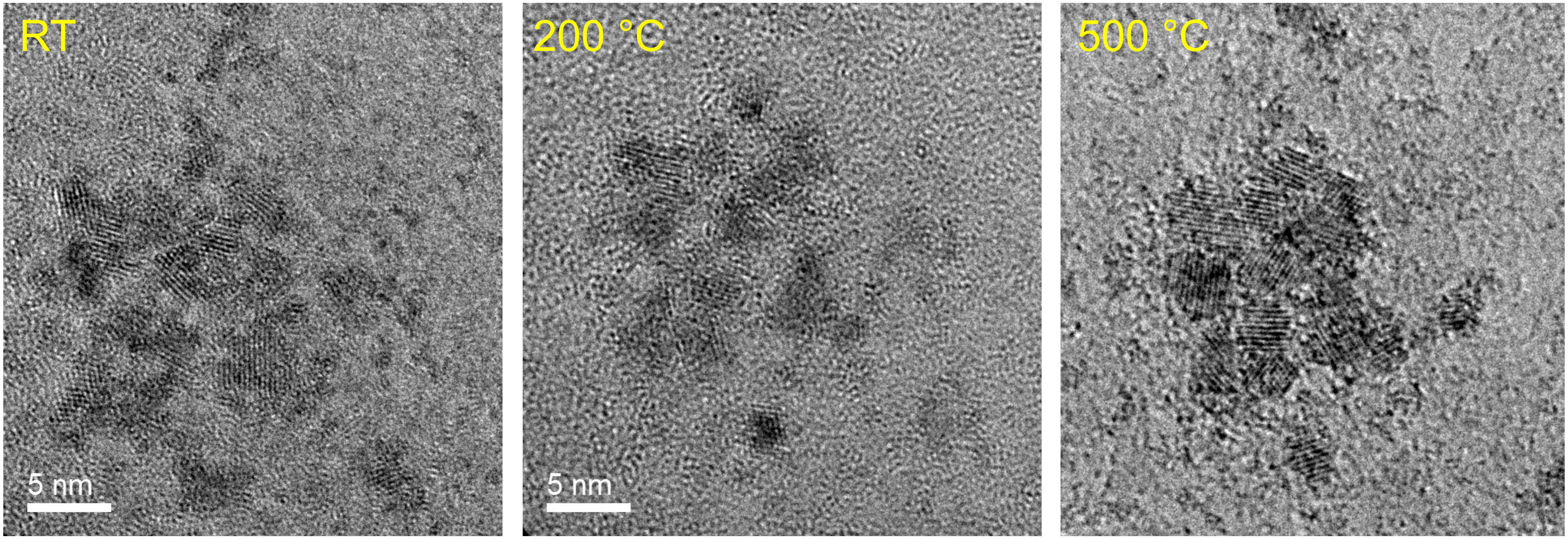


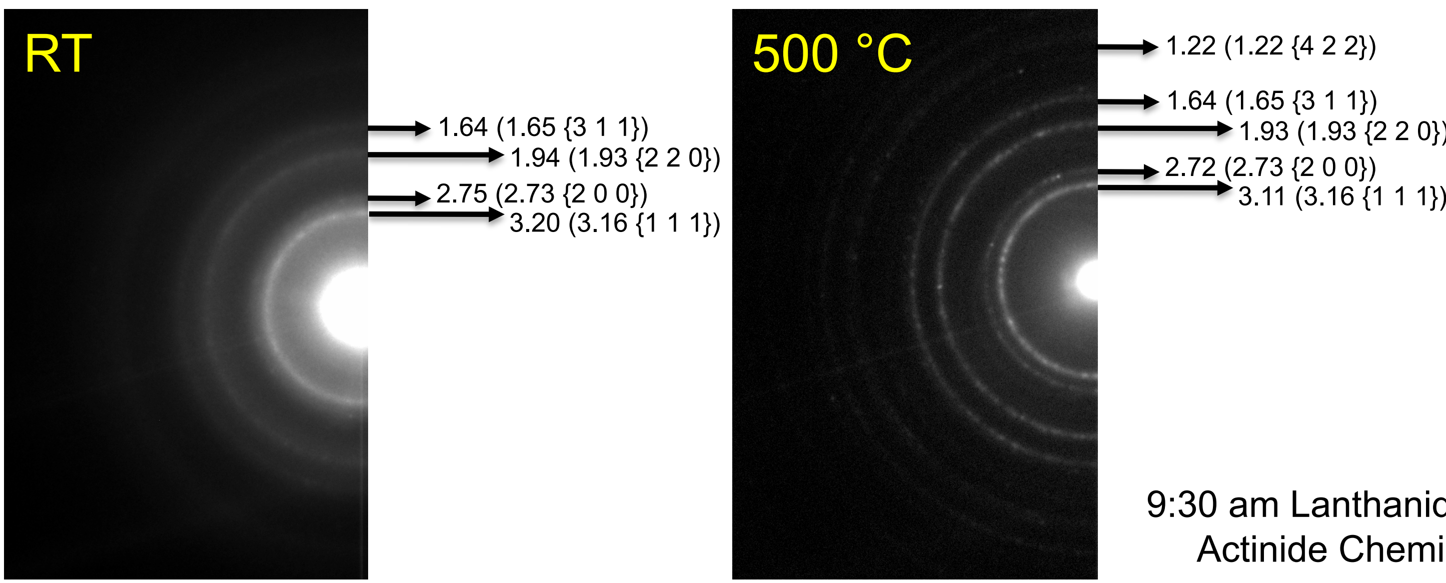




UO_2 NP formation confirmed by UV-vis, bright-field TEM and diffraction

UO_2 NP Sintering at 500 °C





Low T NP sintering achieved at 500 °C; ~1000 °C lower than reported

9:30 am Lanthanide and Actinide Chemistry

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Conclusions

- **Ag and Ni are immiscible. Ag-Ni NPs are considered a core-shell structure from both experiments and simulations.**
- **Low dose rate** intermetallic electron transfer causes core-shell formation
- **High dose rate, alloyed Ag-Ni & Pd-Ni NPs are formed.** Rate overrides electrochemical or thermodynamic process, and competes with possible intermetallic electron transfer.

  High dose rate reduces ions very fast, so high dose rates favor alloy formation

- **DFT modeling supports alloy formation at high dose rate**
- **Sintering of alloy NPs from ≈ 5nm NPs to large / mesoscale bulk formation**

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Acknowledgements

Team Members

Synthesis: Zhenyuan (Mark) Zhang, Donald T. Berry

TEM: Jianyu Huang, Paula Provencio

NP Sintering/ Heated Stage TEM: David Robinson, Benjamin Jacobs

Modeling: Roland Stumpf, Kevin Leung

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