57th Annual SAS/ACS/MSNO May Conference

Revealing Interfaces and Nanostructure: The Application of Atom Probe Tomography to Nickel Based Superalloys

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1. Background in nickel-based superalloys
2. Background in atom-probe tomography
3. Decomposition behavior of model Ni-Al-Cr alloy when aged at 600 °C

Acknowledgements: Prof. David Seidman, Kevin E. Yoon , Zugang Mao (Northwestern); Ronald Noebe (NASA GRC); Georges Martin (Comm. à l'Energie Atomique); Northwestern University Center for Atom Probe Tomography (NUCAPT)

Poster: The effect of prior exposures on the notched fatigue behavior of disk superalloy ME3

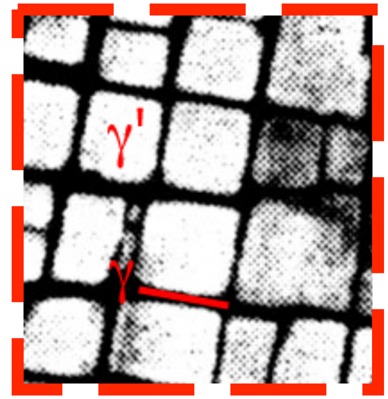
Co-authors: Susan L Draper[1], Timothy T Gorman[2], Jack Telesman[1], Timothy P Gabb[1], David R Hull[1], Daniel E Perea[3] and Daniel K Schreiber[3] : 1. NASA Glenn 2. NASA USRP 3. PNNL

May 15, 2013

Ni-Based Superalloys

Due to an unusual combination of properties, Ni-based superalloys are used in many applications which require structural integrity at elevated temperatures

Precipitate strengthened



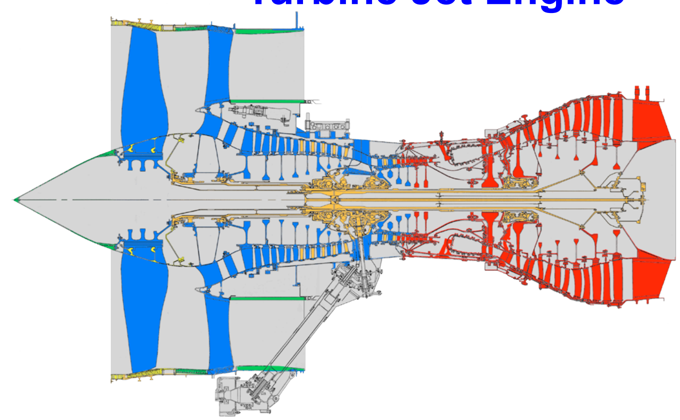
<u>Mechanical properties</u>

- Capable of bearing loads at T/T_M = ~0.85-0.9 ($T_{M(Ni)}$ = 1453˚C) without significant deformation
  - γ' strengthening (precipitatestrengthening)
  - Solid solution strengthening in the γ-matrix
- Damage Tolerance (Ductility and Toughness)

<u>Requirements</u>:

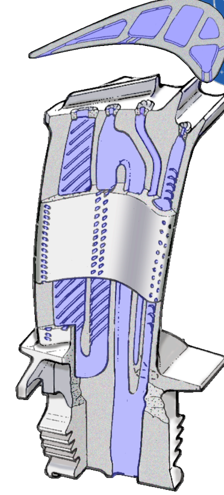
- Resistance to Environmental Degradation
  - Hot corrosion and oxidation

Turbine Jet Engine

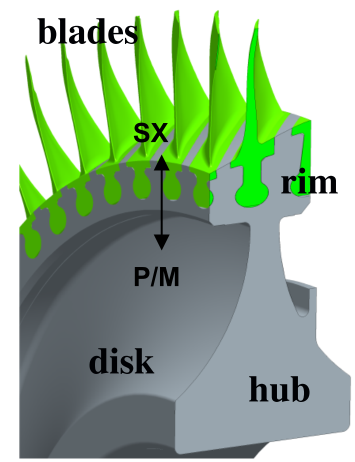


Titanium Steel Nickel

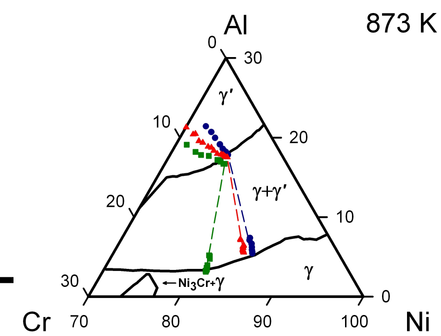
- **Single Crystal Ni-Based Superalloys**
  - Engineered for Extreme Temperature Capability - Creep, Thermal Fatigue and Environmental Protection
  - Anisotropic Properties
  - Turbine Blade and Nozzle Applications *NASA GRC*



- **Polycrystalline Ni-Based Superalloys**
  - Intermediate Temperature Capability – Fatigue, Tensile, Crack Growth and Environmental Resistance
  - Isotropic Properties
  - Turbine Disk Applications *NASA GRC*
  –



- **Model Ni-Based Superalloys**
  - Fundamental thermodynamic and kinetic underpinning of γ'-precipitation

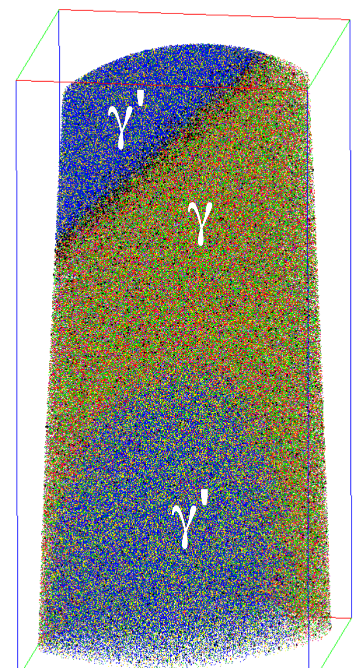


Atom-probe tomography measurements

APT: post-mortem atomic imaging technique in direct space with sub-nanometer spatial resolution (static snapshots of dynamic process)

1. **Short-range ordering, clustering, impurity concentration & distribution**
2. **Morphological development**
3. **Dimensional and nanostructural quantification**
   - Variations in layer thicknesses
   - Radius, number density, volume fraction of precipitates
4. **Compositional characterization**
   - Bulk phases
   - Fine scale nanostructure
   - Buried interfaces (e.g. grain boundaries):
     - Chemical interdiffusion, chemical roughness, segregation, transients

~50 million atoms



98 nm x 97 nm x 152 nm

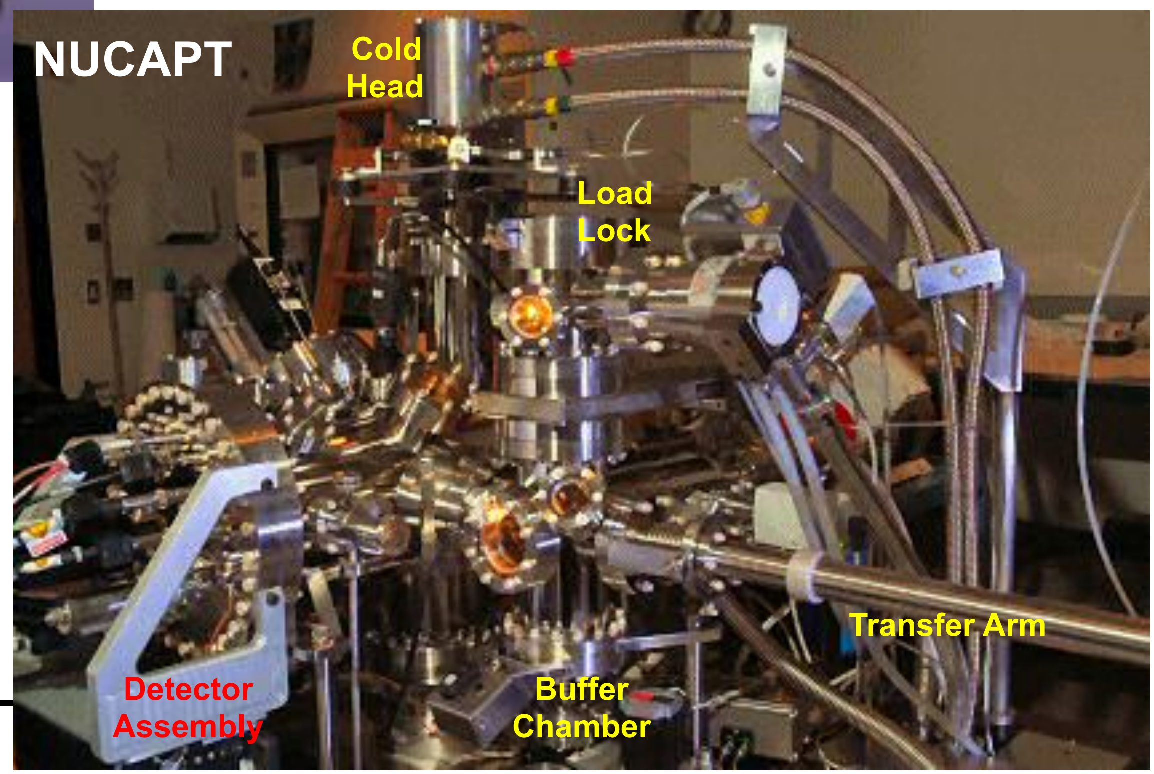
3-D Atom Probe Tomography

- **Analyze data with 3D visualization software, IVAS, from Cameca (formerly Imago Scientific)**

Determines the spatial position of individual atoms and their chemical identities with sub-nanometer scale resolution

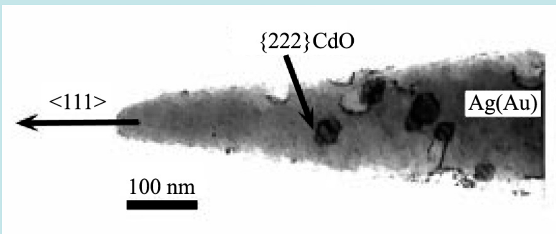
Ion detection efficiency: 40-60%, Depth positioning: 0.02-0.05 nm, Lateral positioning: 0.2-0.3 nm

- ***Analyze volumes >10^6 nm^3***
  0.1 x 0.1 x 0.5 μm^3
- ***5 x 10^{-11} torr ultrahigh vacuum***
- ***Specimen T: 20 to 300 K***
- ***Equipped with both electrical and thermal-assisted pulsing:***
  - ***250 kHz electrical pulse***
  - ***500 kHz picosecond laser (green: 532 nm, 10 ps)***



APT specimens are needle shaped

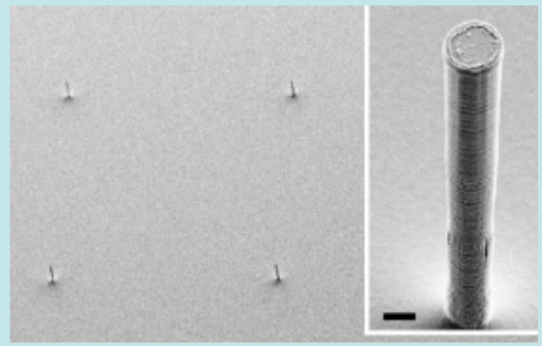
Metals: Electrochemical wire sharpening from APT blank ($0.25 \times 0.25 \times 10$ mm^3)



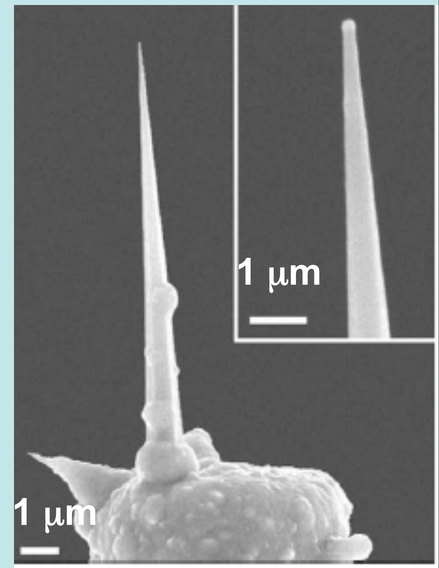
D. A. Shashkov, M. F. Chrisholm and D. N. Seidman Acta. Mater, 47, 3939-3951 (1999).

Nanowires: Direct growth on a micropost

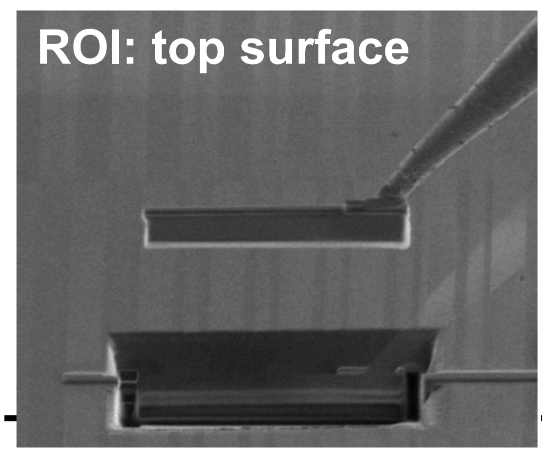
Silicon Micropost Array

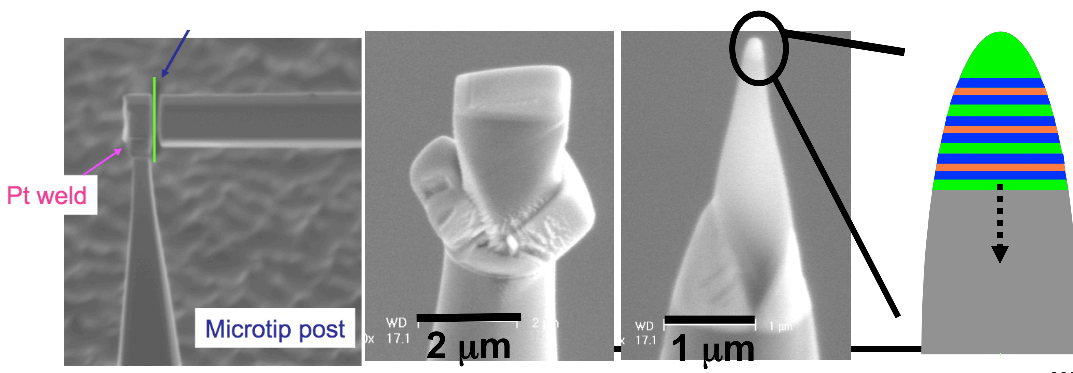


Perea et al. J. Solid State Chem, 181 (2008) 1642



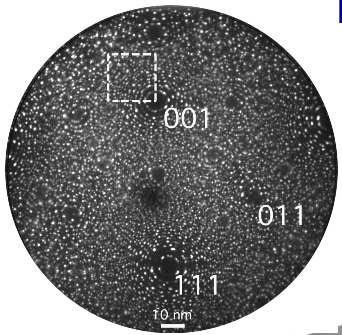
Multilayers: FIB preparation / Lift-out to micropost

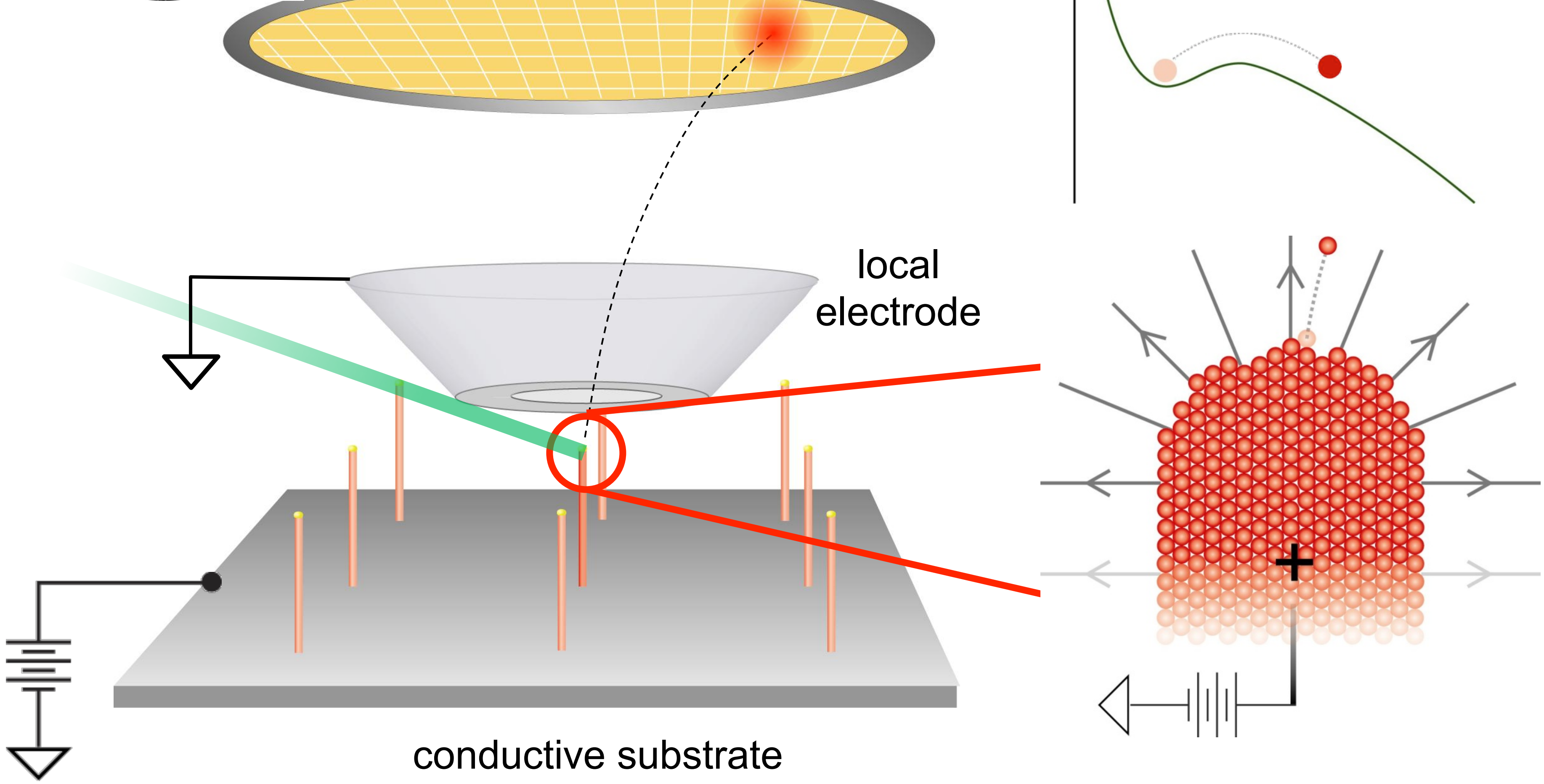




Tip radius is 50-100 nm

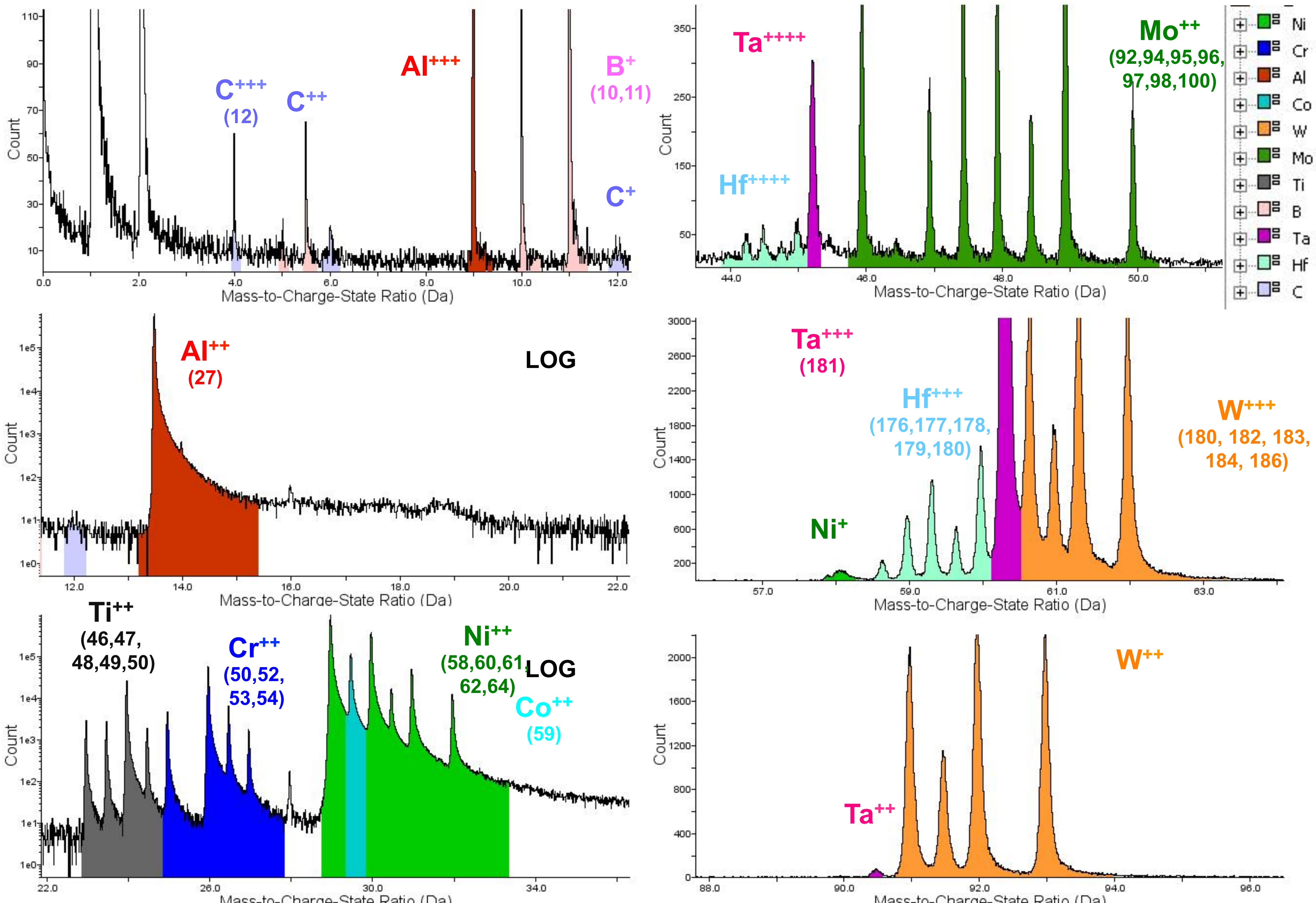
Pulsed-laser Atom Probe Tomography





Courtesy of NUCAPT

Ions identified from their m/n signature (time-of-flight)



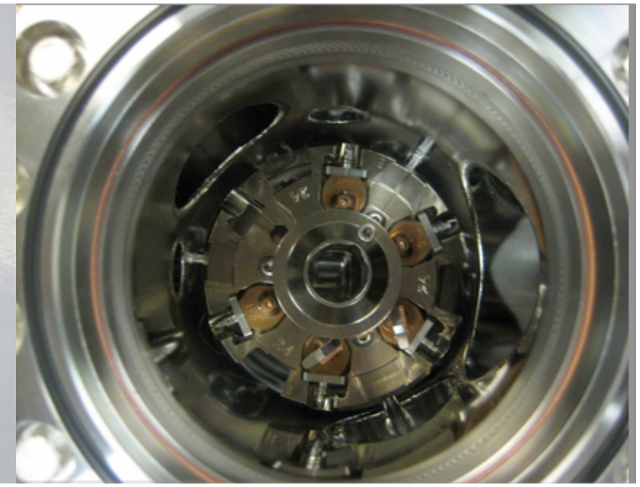
PL-APT Mass Spectrum for a Commercial Ni-based Superalloy

3-D LEAP™ Tomography

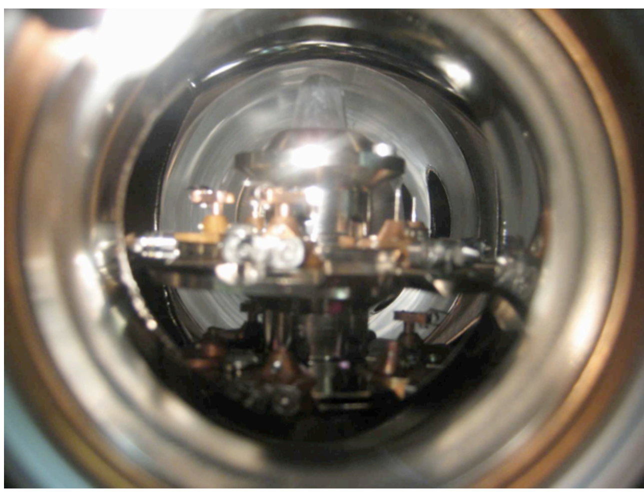
Specimens & Pucks

Specimen Carousel

Load Lock Chamber (Top Entry)

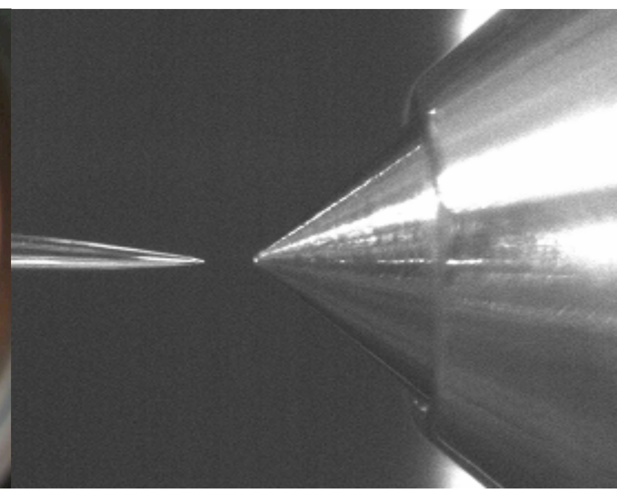


Analysis Chamber (Side Viewport)

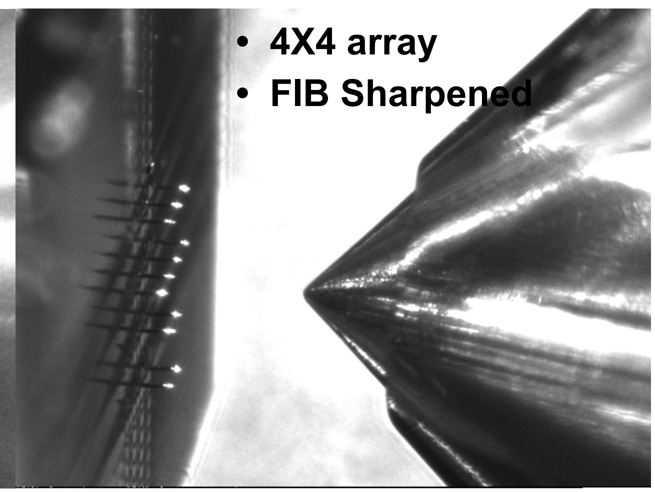


Courtesy of NUCAPT

Needle Geometry



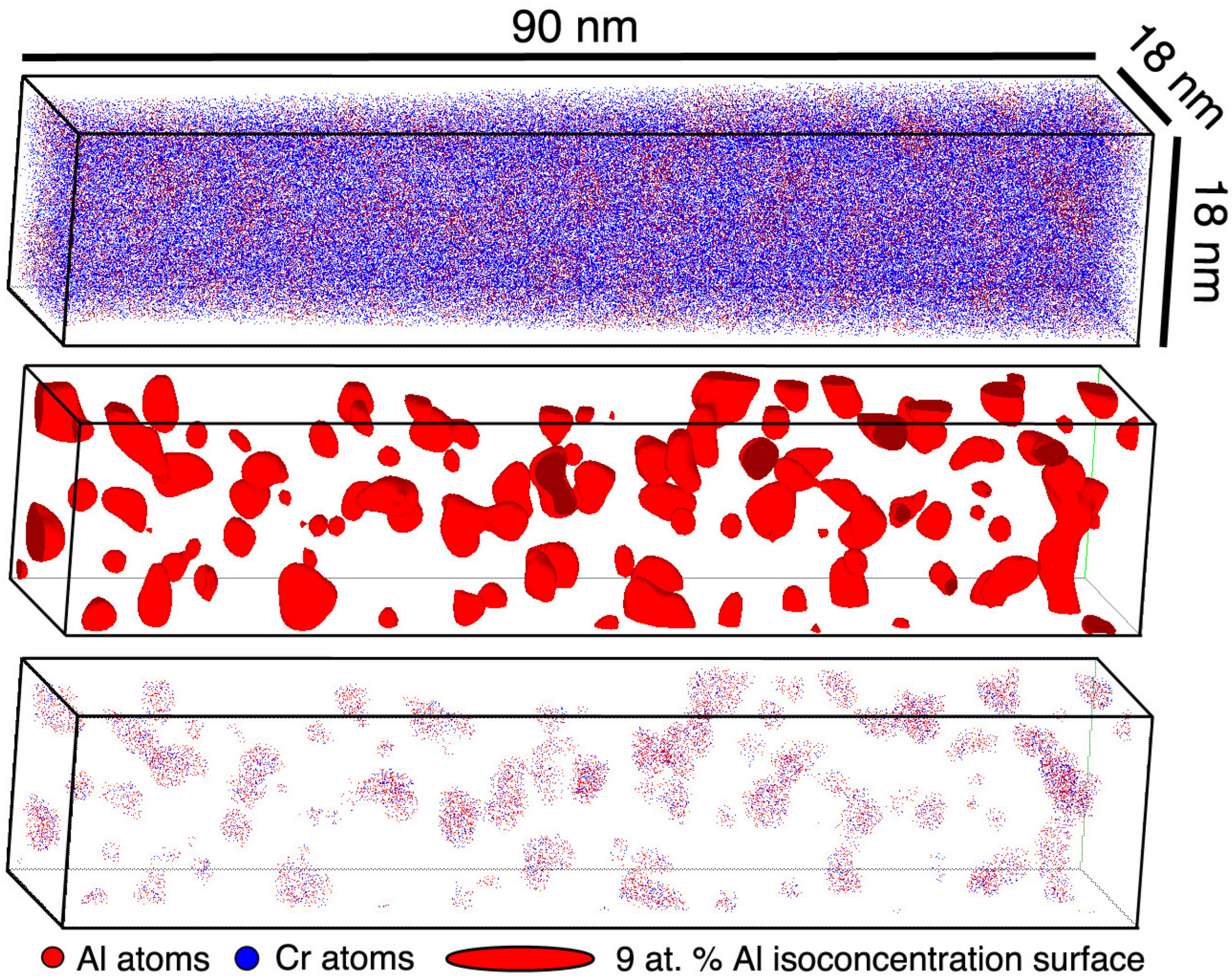
Microtip Geometry



Courtesy of Imago

Fine scale microstructural analysis with APT

Ni-5.2 Al-14.2 Cr (at. %) aged at 600°C for 4 hours



APT reconstructed volume

Isoconcentration surface

Selected volume

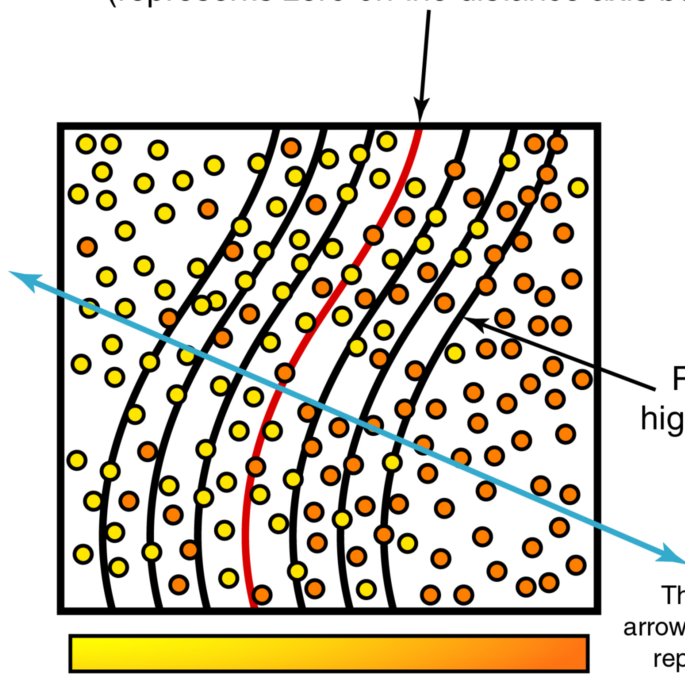
Proximity Histogram Concentration Profile

Data analysis in IVAS 3D visualization software

Proximity Histogram or "Proxigram" is a 3D nonlinear compositional profile with respect to isoconcentration surface (interfaces).

Three steps

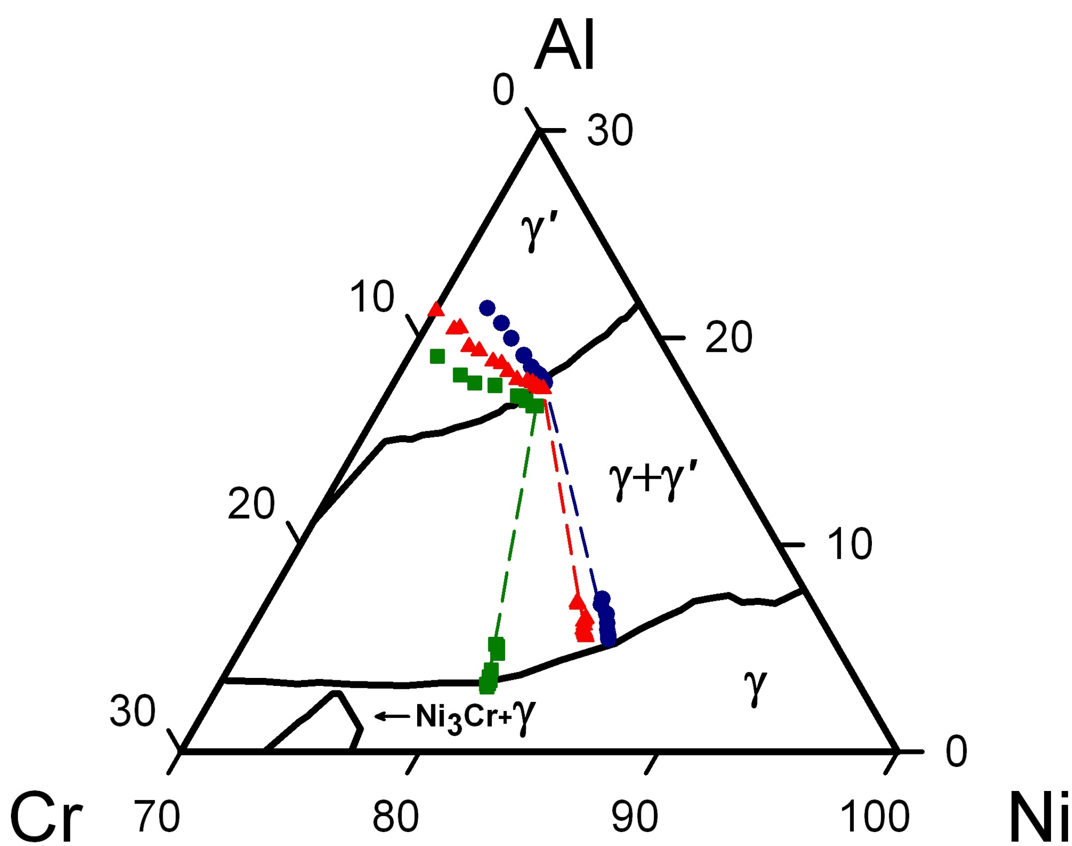
1. **A sampling to generate a regular grid of concentration points**
2. **An interpolation to identify an isoconcentration surface**
3. **A correlation of the isoconcentration surface to the original set of discrete atomic positions**



- Analyzes all the concentrations of the same value in a data set in parallel, invaluable for large data sets
- Invariant to interfacial geometry

Hellman, Seidman et al. *Micro. Microanal.* ***6****, 437 (2000)*

Decomposition behavior of model Ni-Al-Cr alloy when aged at 600 °C



T= 600 °C aging studies of Ni-5.2 Al-14.2 Cr at. %

Atomic-scale mechanisms that drive the early stage precipitation

Moderate solute supersaturations, ϕ^{eq} = 15.6 %
(nondilute, nonideal)

$$\gamma\ (\text{fcc}) \xrightarrow[600°C]{T} \gamma\ (\text{fcc}) + \gamma'\ (L1_2)$$

Ni-Al-Cr → Ni-Al-Cr + $Ni_3(Al_xCr_{1-x})$

1st-order ordering transformation

Increased aging

Short-range order and clustering → *Nucleation of γ' (mechanism)* → *Temporal evolution of the γ'-nuclei*

Nanostructural & Compositional Evolution

Atom Probe

Lattice Kinetic Monte Carlo

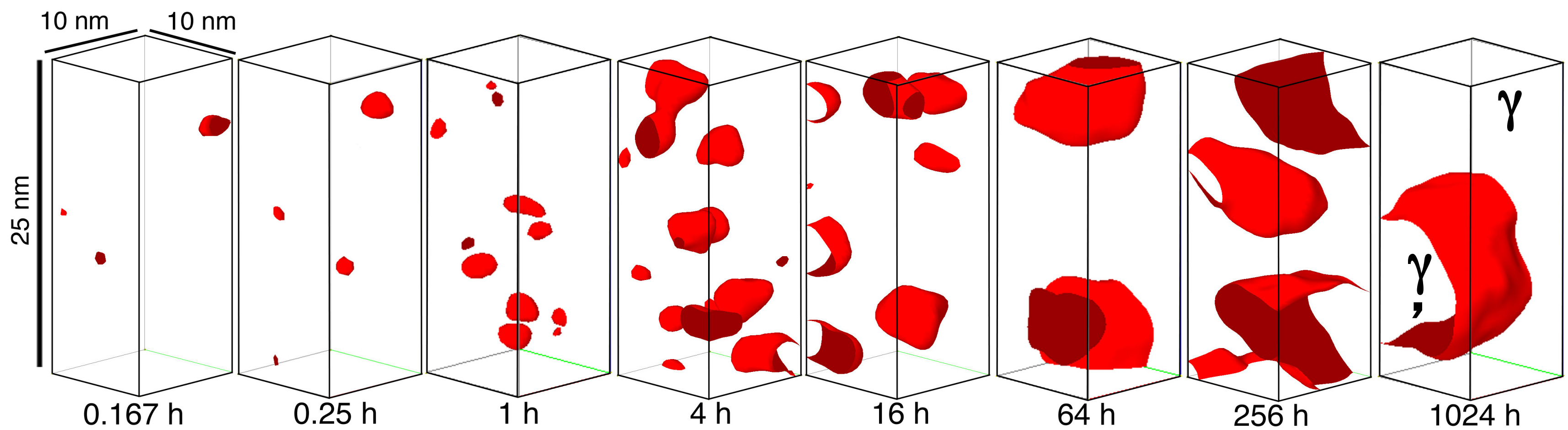
Clusters to precipitates radii up to ~10 nm

Seminal research of Schmuck *et al.* (Phil. Mag. A **76**, 1997, p.527) and Pareige *et al.* (Acta mat. **47**, 1999, p.1889)

Temporal evolution of γ'-precipitation in 3D

10 x 10 x 25 nm³ sub-volumes of APT reconstructions

9 at. % Al isoconcentration surfaces (atoms omitted for clarity)



Ni-5.2 Al-14.2 Cr aged at 600°C

- **Precipitates as small as R = 0.45 nm are resolved, 20 detected atoms, which is close to lattice kinetic Monte Carlo (LKMC) predictions for critical nuclei size of 0.485 nm**
- **Dimensions and orientation of each precipitate are determined using best-fit ellipsoid**
- **Buried interfaces: generate average compositional profiles across the γ/γ' interfaces using proximity histogram compositional profiles**

Sudbrack et al, Acta Mater 54 (2006) 3199.

APT measurements of the mean precipitate radius

t (h)	Nb. of ppts. analyzed	$\langle R \rangle \pm \sigma$ (nm)
0.17	7.5	0.74 ± 0.24
0.25	74	0.75 ± 0.14
1	100	0.89 ± 0.14
4	173.5	1.27 ± 0.21
16	101	2.1 ± 0.4
64	46	2.8 ± 0.6
256	81	4.1 ± 0.8
1024	6	7.7 ± 3.3

nucleation

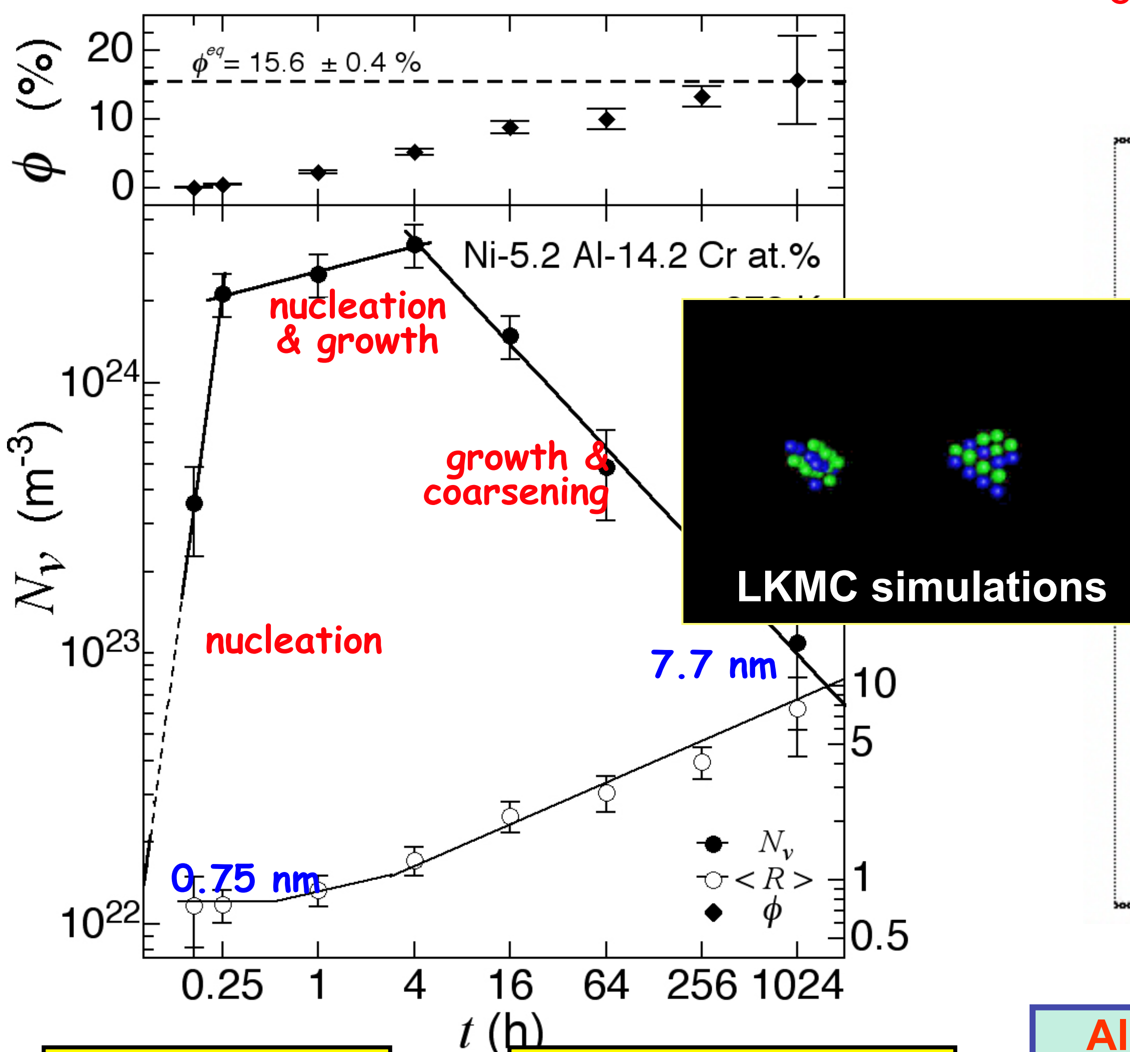
nucleation and growth

growth and coarsening

Sudbrack et al, Acta Mater 54 (2006) 3199.

Growth regimes established by APT measurements

Volume fraction of γ' (ϕ)

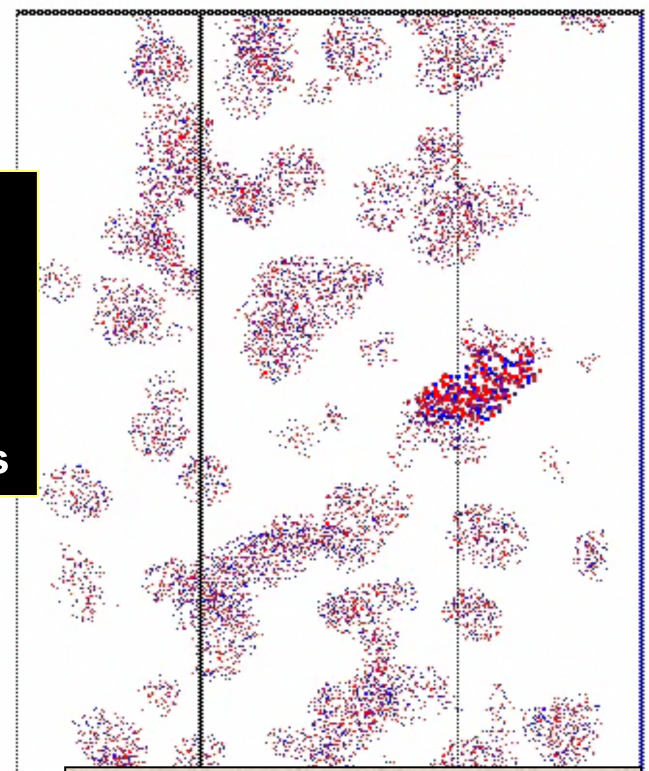


Ppts. per unit volume (N_v)

Mean precipitate radius (<R>)

Example of γ' -precipitate pair connected by necked region

***t* = 4 h at peak N_v**



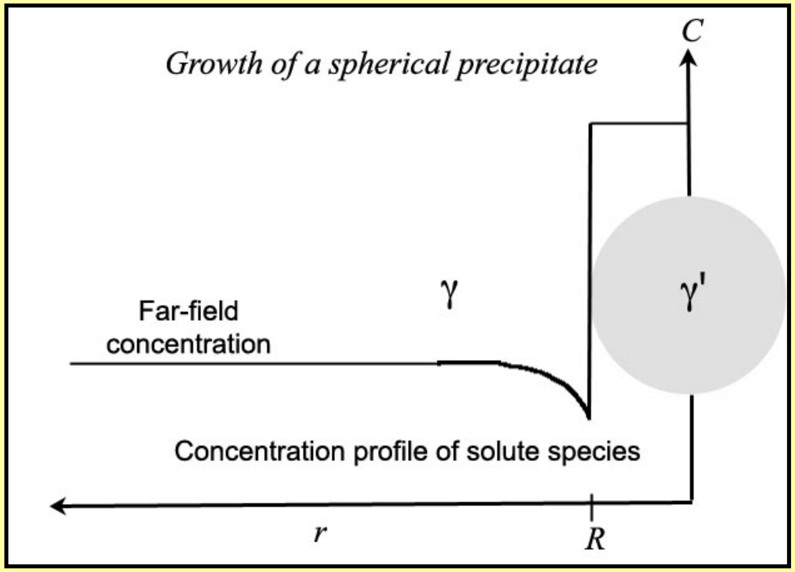
24 nm × 20 nm × 38 nm

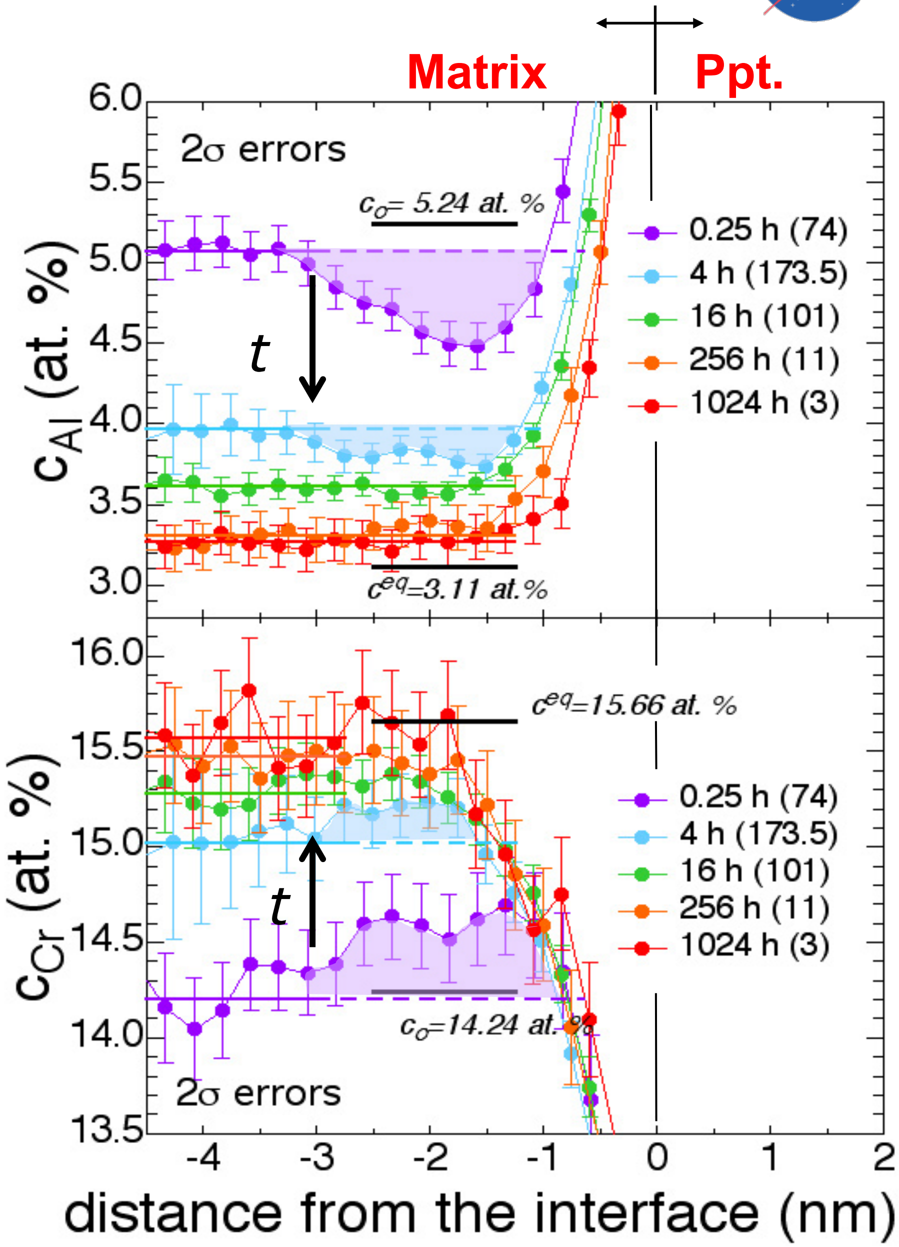
Al and Cr atoms within the 9 at. % Al isoconcentration surface displayed

Sudbrack et al, Acta Mater 54 (2006) 3199.

Concentration profile evolution in the matrix

Schematic: **Growth of stable nucleus** occurs by solute diffusion **driven by chemical potential gradient** due to supersaturated matrix





Transients disappear after 16 h
∴ quasi-steady state obtained

F. S. Ham, J. Phys. Chem. Solids, 6 (1958) 335

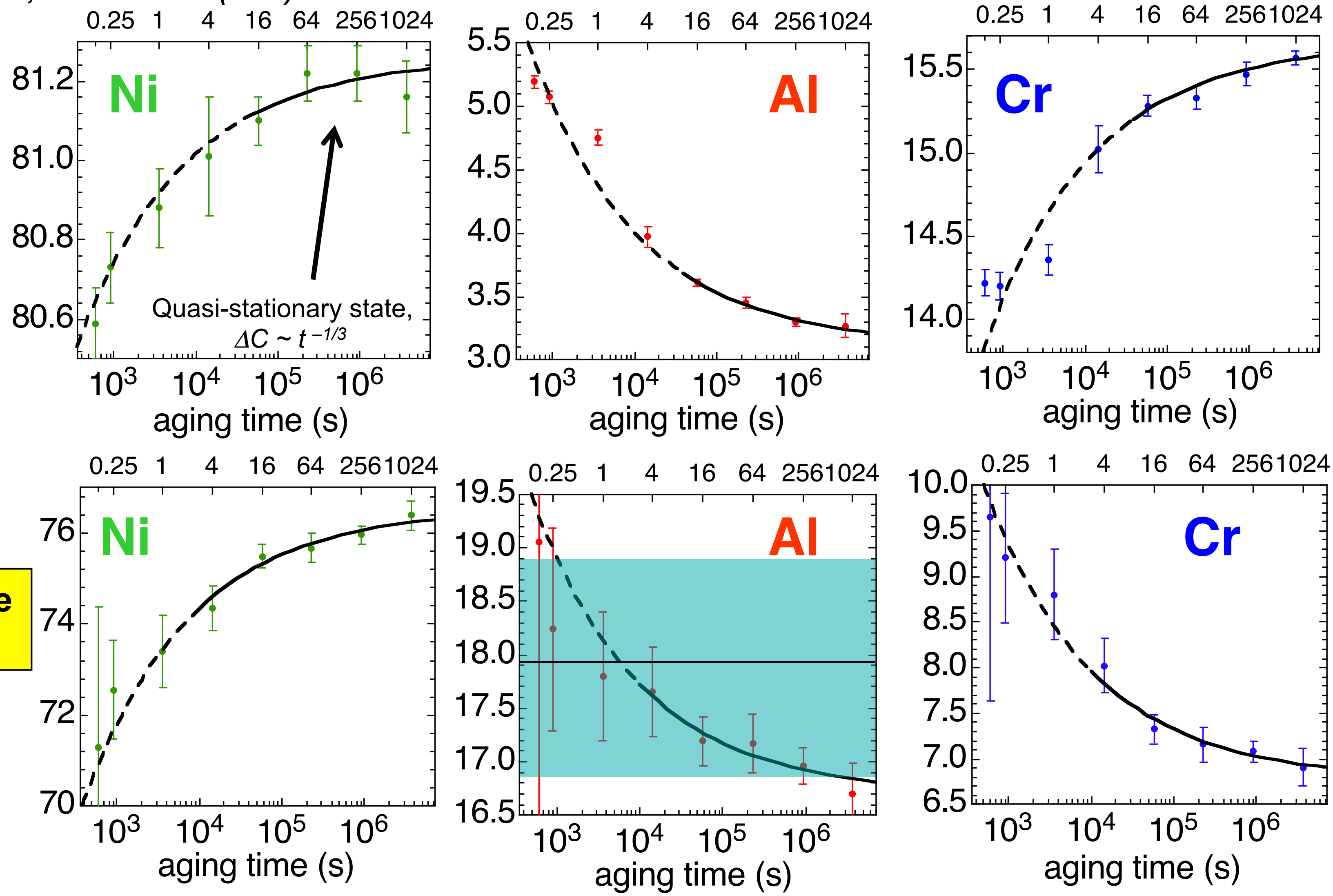
**** Proxigram method, which averages over all interfaces in the analysis volume***

Compositional evolution

Sudbrack et al, Acta Mater 54 (2006) 3199.

Matrix in the far-field

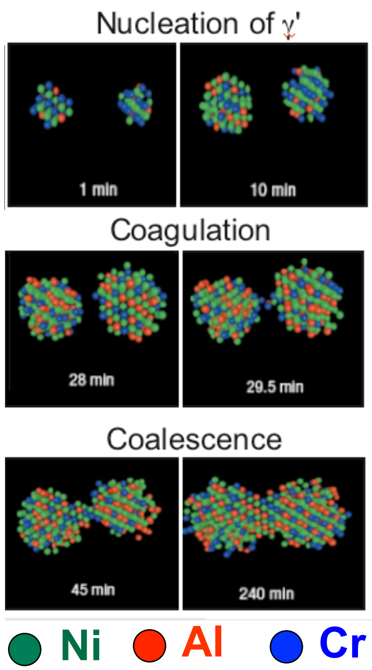
Precipitate Cores



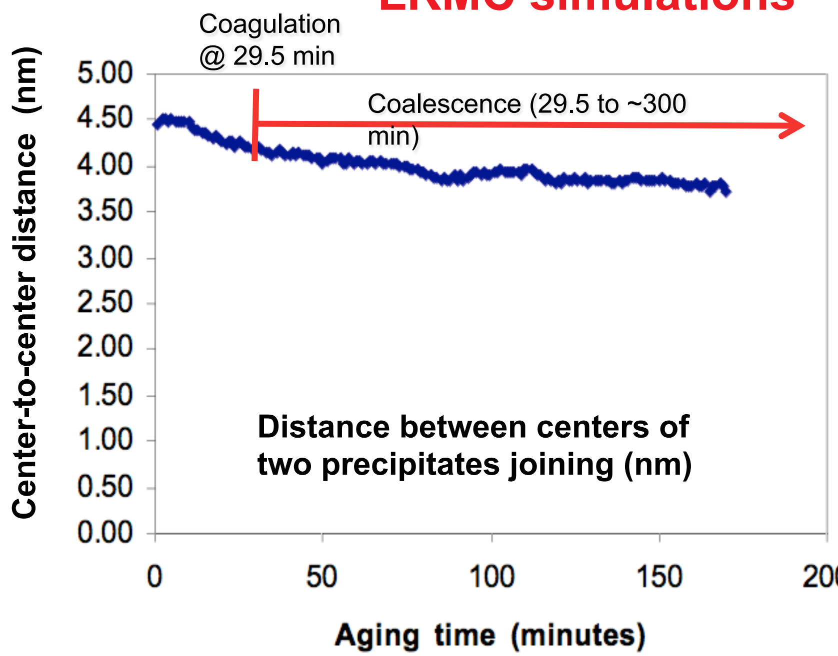
Gibbs-Thomson effect: predicts an increase in solid-solubility at an interface due its curvature. It is non-negligible when precipitate dimensions are on the of the order capillary length, typically 1-2 nm

See: Sudbrack et al, Acta Mater 55 (2007) 119.

Confirmation of early-stage coagulation & coalescence



LKMC simulations



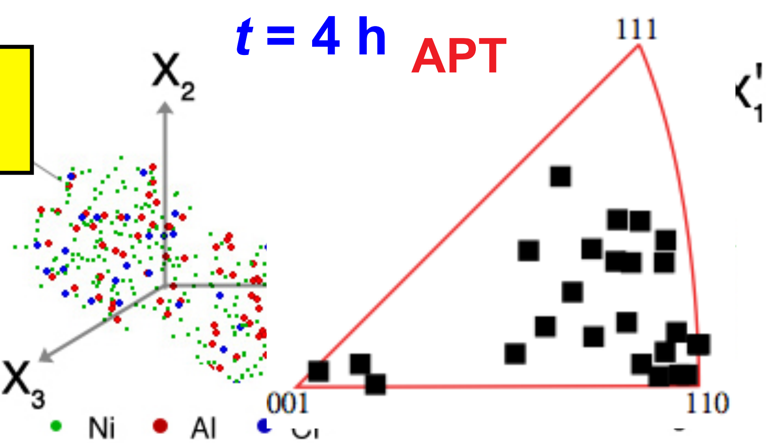
There are four $L1_2$ ordering variants

APB energy for two variants to join is 3-4 times larger than interfacial energy

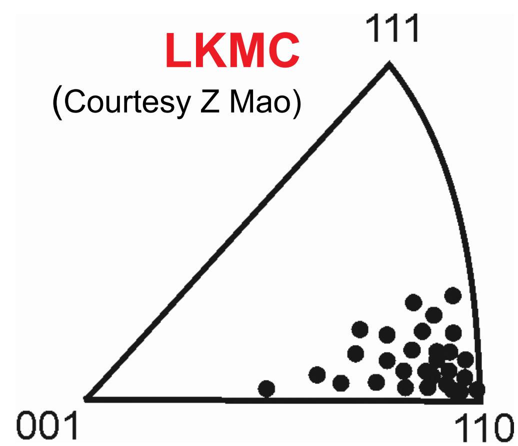
--> Two precipitates must match variants to join

As much as 30% coalesced

Neck orientation distribution



RA Karnesky, CK Sudbrack and DN Seidman, APL (2007).



In FCC structure of the γ-matrix, <110> is fastest diffusion path for solute clusters

- **Atom probe tomography is a powerful characterization technique**

- **The combined APT/LKMC approach has been particularly helpful in:**
  - Nanometer scale characterization of morphological development in 3D
  - Precise compositional analysis of buried interfaces
  - Insight into diffusional processes that drive phase transformations

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