Study of Nanocluster Stability Nanostructured Ferritic Alloys (NFAs) Under High Dose Irradiation

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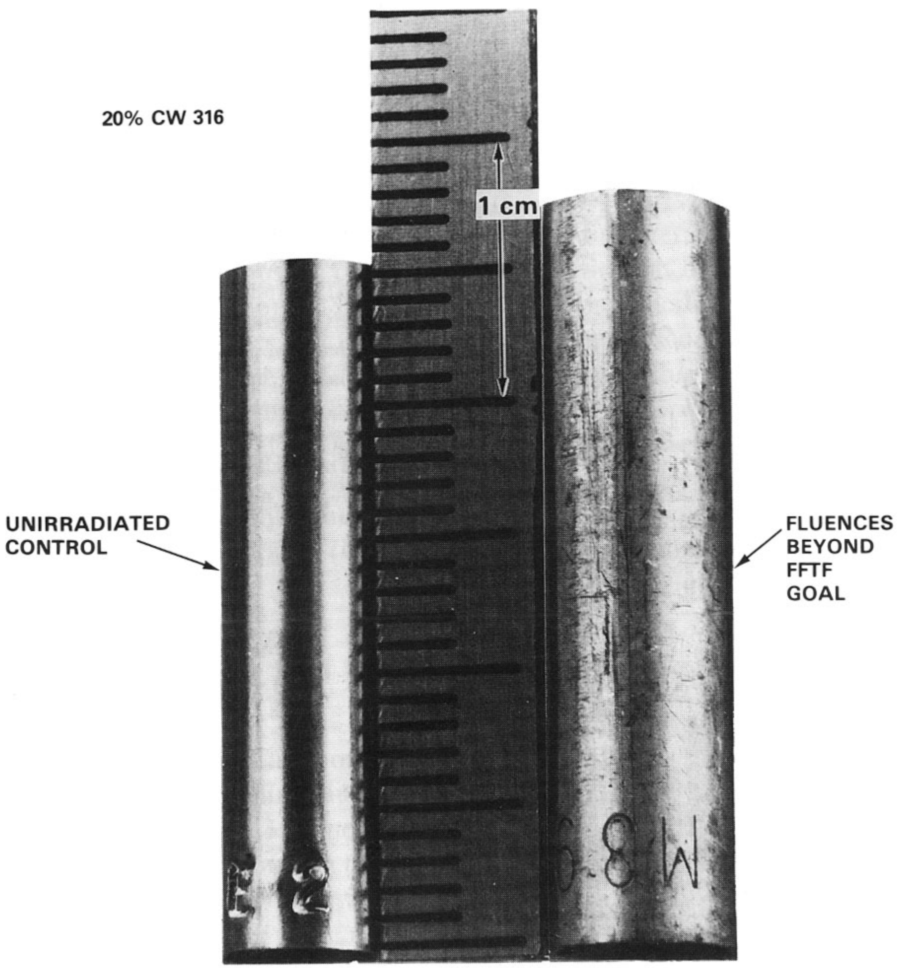
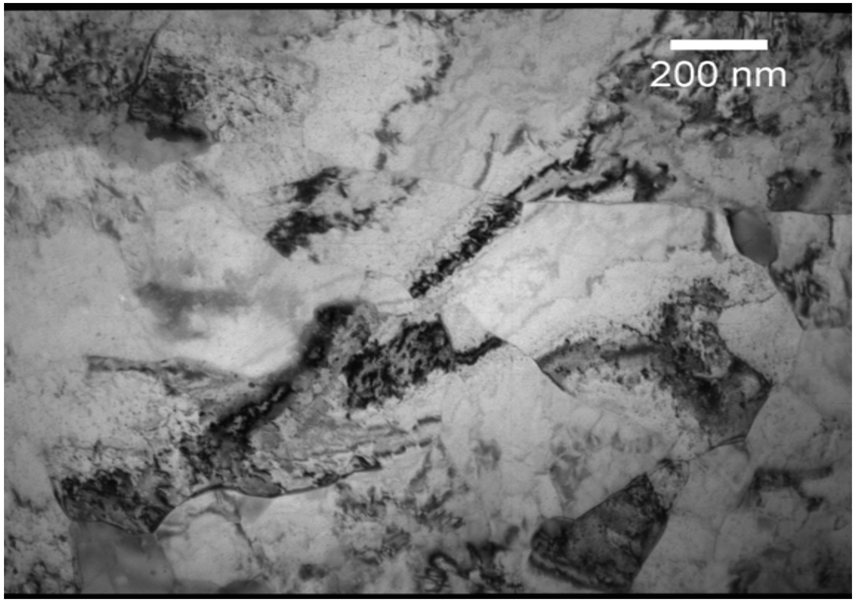
Motivation



- Intense radiation damage environment
- Changes in microstructure
  - Swelling
  - Element segregation
- Changes in properties
  - Hardening
  - Embrittlement
  - Irradiation assisted creep
  - Irradiation assisted stress corrosion cracking

Motivation



Bright field TEM image of an NFA

- Ferritic/martensitic (F/M) steels
  - Resist swelling
  - Less than ideal high temp creep strength
- Nanostructured ferritic alloys (NFAs)
  - Nanoclusters act as pinning points for dislocations
  - Improves high temp creep strength
  - Nanoclusters stable under irradiation?

Cluster stability theory

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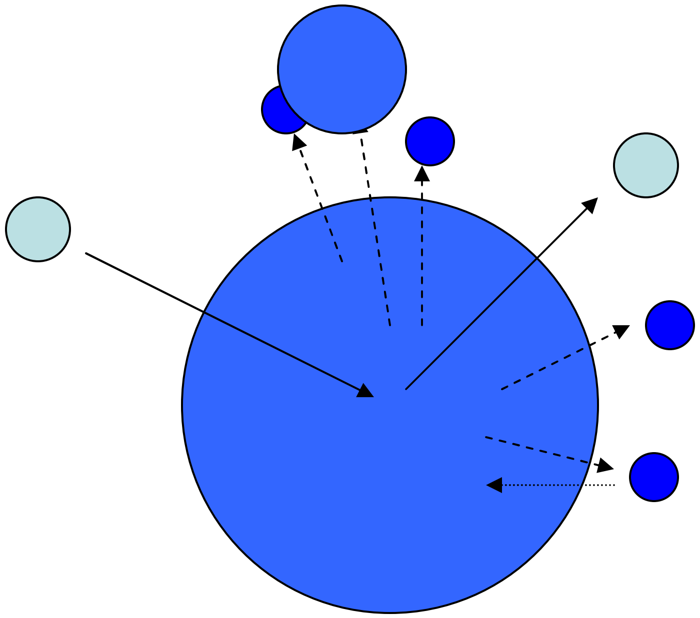
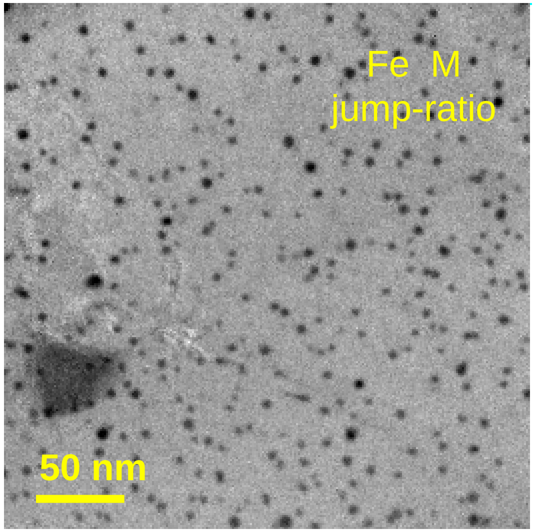


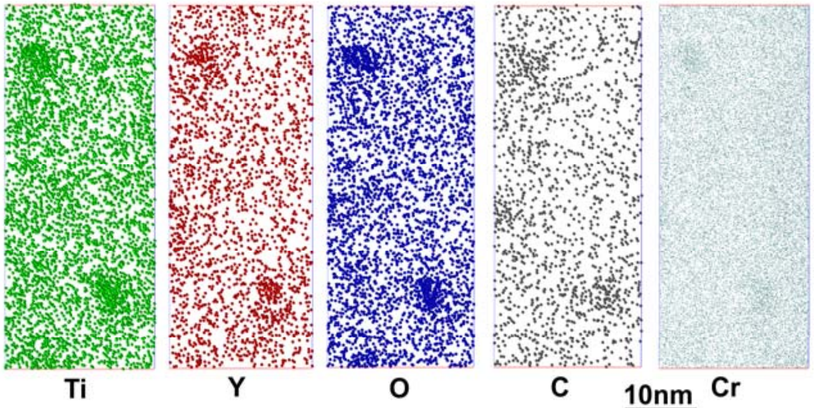
- Material leaves clusters due to:
  - Ballistic ejection
  - Radiation enhanced diffusion
- Material re-joins clusters due to
  - Back diffusion
- New clusters precipitate

Analysis techniques

- Observe 'group' effects and 'individual' effects
- Energy filtered transmission electron microscopy (**EFTEM**)
  - Increased confidence in nanocluster identification
  - Is not affected (much) by defect structure or bend contours
- Atom probe tomography (**APT**)
  - Smallest of the nanoclusters (< 2 nm) can be detected
  - Element composition
  - Radiation induced seg.



EFTEM iron jump ratio image of an Fe9Cr NFA. Areas of iron depletion correspond to Y-Ti-O clusters.



APT 2-D maps of nanoclusters in a 9Cr NFA

Previous results

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- EFTEM and APT performed on 9CrODS steel
  - Control samples
  - 1 dpa, 525 °C proton irradiated samples
- Conditions favored cluster stability
  - Low dose
  - Low dose rate (1×10^{-6} dpa/s)
  - Relatively high temperature
- Heterogeneous cluster distribution, effects subtle to non-existent
- 14YWT alloy chosen for its more uniform cluster distribution

EFTEM	Unirradiated	Irradiated 1 dpa, 525 °C
Mean size (nm)	3.35	3.11
Standard deviation of the mean (nm)	0.04	0.05
Standard deviation	3.40	4.15
Skewness	3.4	4.15
Mean number density (nanoclusters/nm^3)	9.4×10^{-5}	1.18×10^{-4}
Standard deviation of the mean	1.7×10^{-5}	3.4×10^{-5}
Standard deviation (nanoclusters/nm^3)	4.1×10^{-5}	8.2×10^{-5}

APT	Guinier radius, R_g (nm)	Standard deviation (nm)
Unirradiated	0.9	0.5
Irradiated 1 dpa, 525 °C	1.1	0.6
Irradiated 1 dpa, 700 °C	1.4	0.2

Ni^{2+} Irradiations

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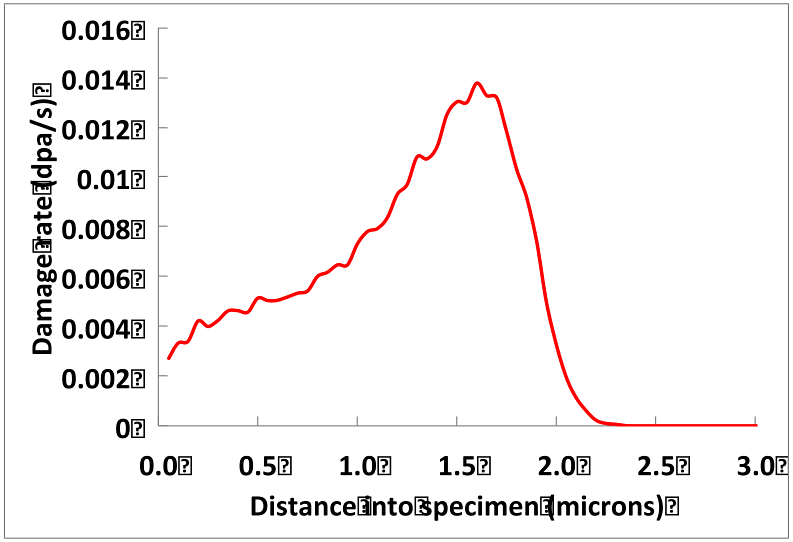
- Irradiations were conducted at Pacific Northwest National Laboratory (PNNL)
- Equipment
  - Source of Negative Ions by Cesium Sputtering (SNICS) source
  - NEC Pelletron® tandem accelerator
- Irradiation parameters
  - 14WYT: 5, 50, 100 dpa at -75 ºC
  - 14YWT: 5, 50, 100 dpa at 600 ºC
  - 5.0 MeV Ni^{2+}
  - ~ $1x10^{-3}$ dpa/s
- Temperature regulation
  - Sample heated by beam ~ 50 ºC
  - Filament heater
  - Temperature uncertainty ±50 ºC



- Damage rates calculated by SRIM 2006 for Fe14Cr matrix
- Samples prepared using focused ion beam (FIB) at ~ 0.5 micron depth

EFTEM – Unirradiated 14YWT

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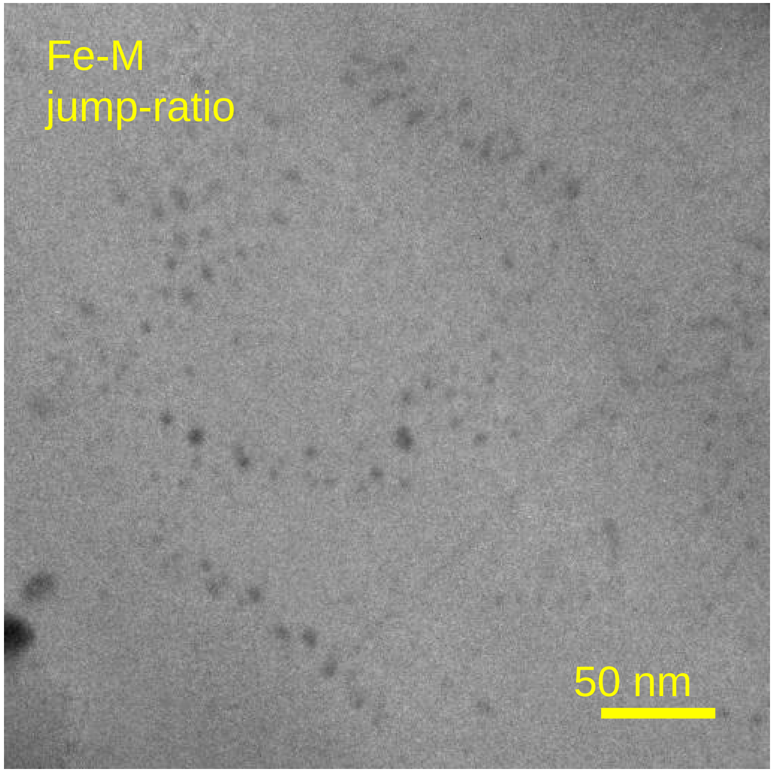
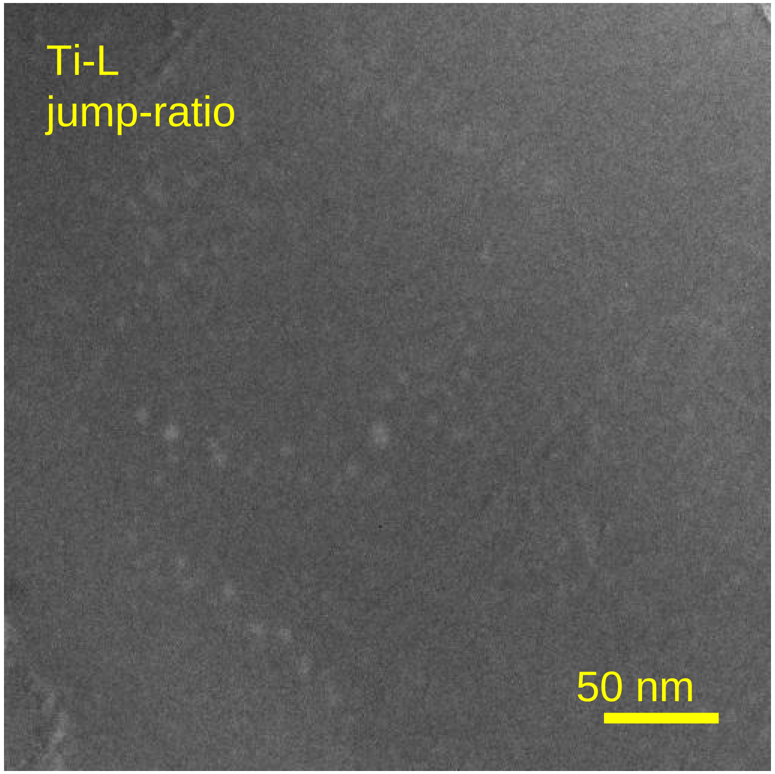
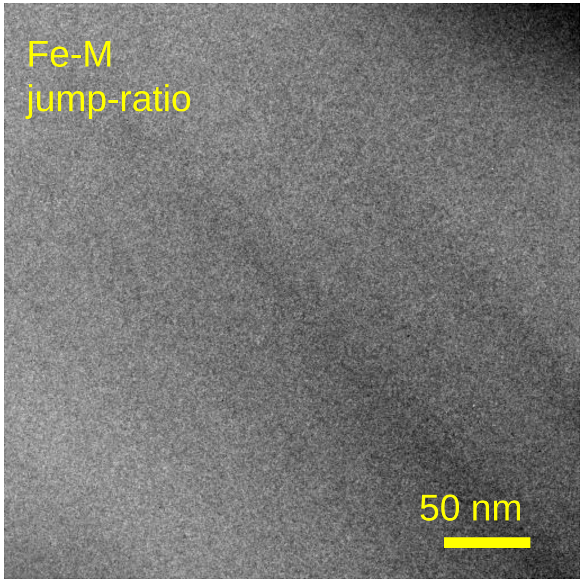


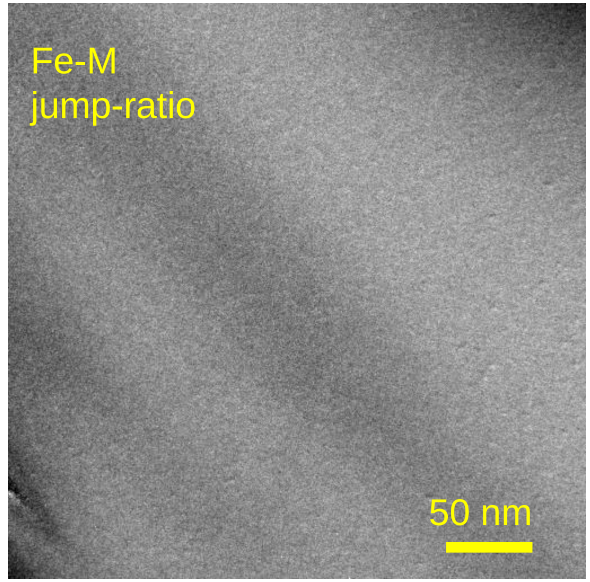


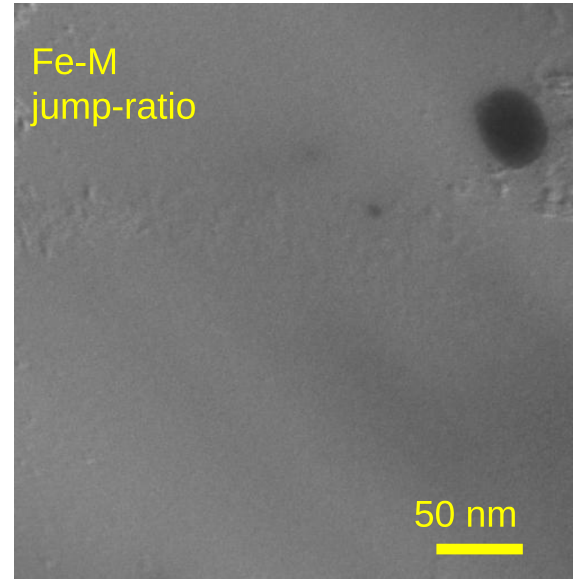
Average cluster size – 2.7 nm (1σ = 1.9 nm)
Number density – 3×10^4 clusters/μm^3 (1σ = 1.5×10^4 clusters/μm^3)*
Total volume analyzed – 0.055 μm^3
Total clusters analyzed – 1855

*Number density standard deviation from variation in 300 nm x 300 nm x 10 – 40 nm volume measurements (i.e. each image)

EFTEM – 100 dpa, -75 ºC irradiated 14YWT





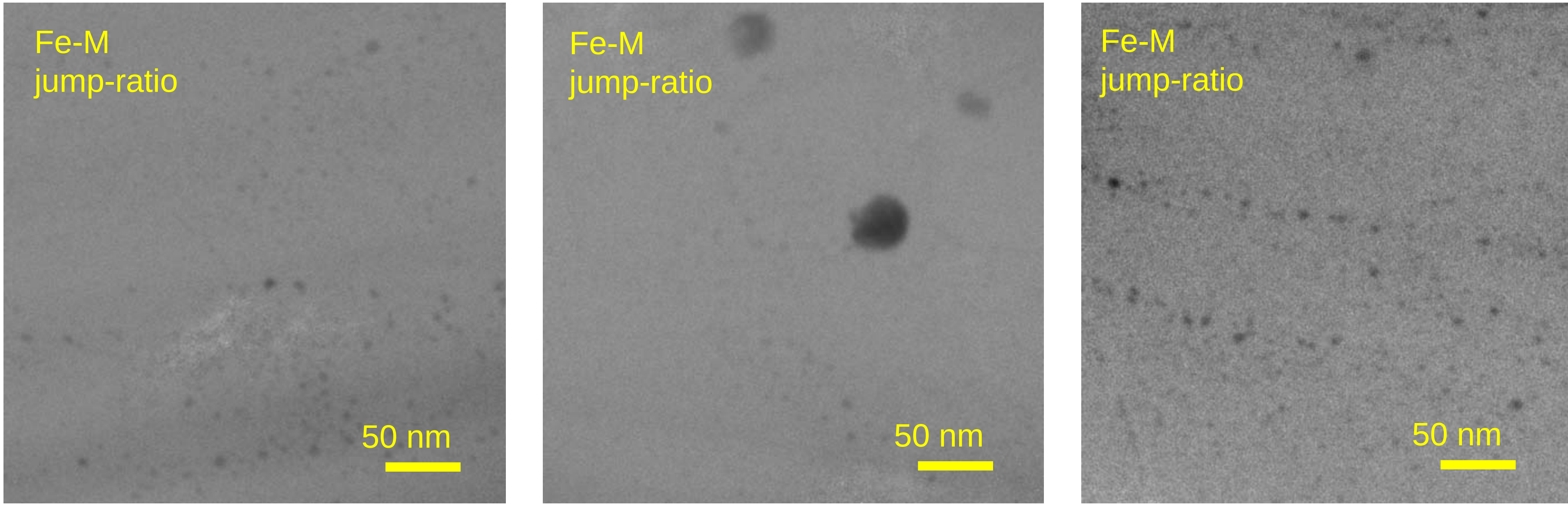


~50% images examined had NO NC visible

Average cluster size – 18.3 nm (1σ = 14.0 nm)
Number density – $3x10^2$ clusters/μm^3 (1σ = 4 $x10^2$ clusters/μm^3)*
Total volume analyzed – 0.057 μm^3
Total clusters analyzed – 15

*Number density standard deviation calculated from variation in 300 nm x 300 nm x 10 – 40 nm volume measurements (i.e. each image)

EFTEM – 100 dpa, 600 ºC irradiated 14YWT



Average cluster size – 2.9 nm (1σ = 1.9 nm)
Number density – 3×10^4 clusters/μm^3 (1σ = 1.9×10^4 clusters/μm^3)
Total volume analyzed – 0.043 μm^3
Total clusters analyzed – 1372

*Number density standard deviation calculated from variation in 300 nm x 300 nm x 10 – 40 nm volume measurements (i.e. each image)

EFTEM data summary

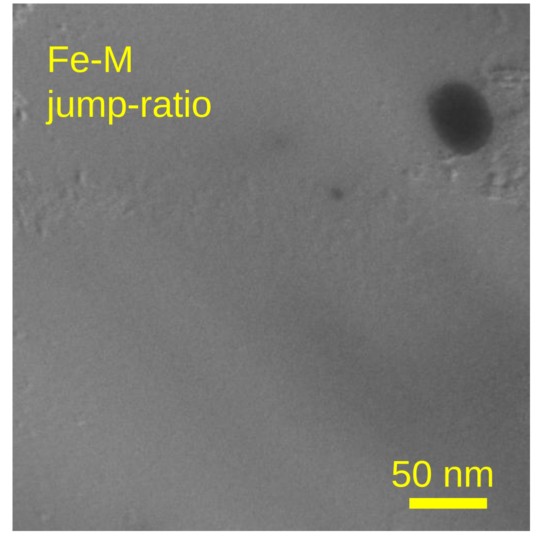
Dose (dpa)	None	50	100	100	None*	1*
Temperature (ºC)	n/a	-75	-75	600	n/a	525
Ave diameter (nm)	2.7	7.3	18.3	2.9	3.3	3.1
1σ Ave diameter	1.9	8.0	14.0	1.9	3.4	4.2
# density (#/μm³)	$3x10^4$	$2x10^3$	$2x10^2$	$3x10^4$	$9x10^4$	$1x10^5$
1σ # density	$2x10^4$	$1x10^3$	$4x10^2$	$2x10^4$	$1x10^4$	$3x10^4$

*Previous results from proton irradiation and EFTEM study of 9CrODS steel from JAEA. Dose rate ~1x10-6 dpa/s.

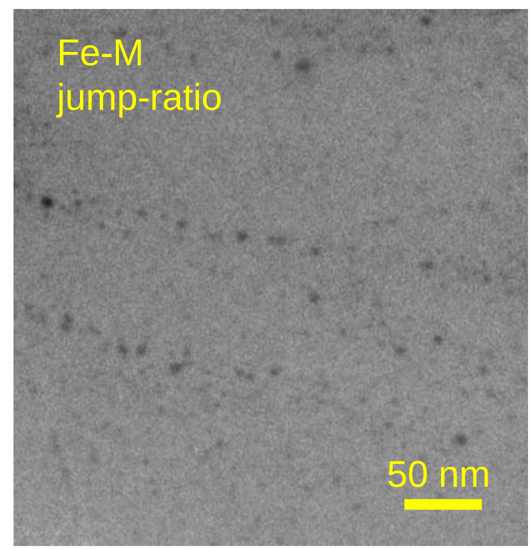
Drastically different results from low to high temperature at high dose and high dose rate.

Cluster stability theory

- Dramatic difference in cluster stability between 100 dpa -75 ºC and 100 dpa 600 ºC samples indicates diffusion plays a key role in stability
- Destruction of clusters at low temperature (no diffusion) indicates that ballistic ejection the primary mechanism for re-solution
- Clusters are 'healing' at high temperature
  - No indication that clusters are nucleating after re-solution rather than back diffusing to existing clusters
  - Size distribution of unirradiated and 100 dpa, 600 ºC samples similar



100 dpa, -75 ºC



100 dpa,600 ºC

ATR UW Pilot Project

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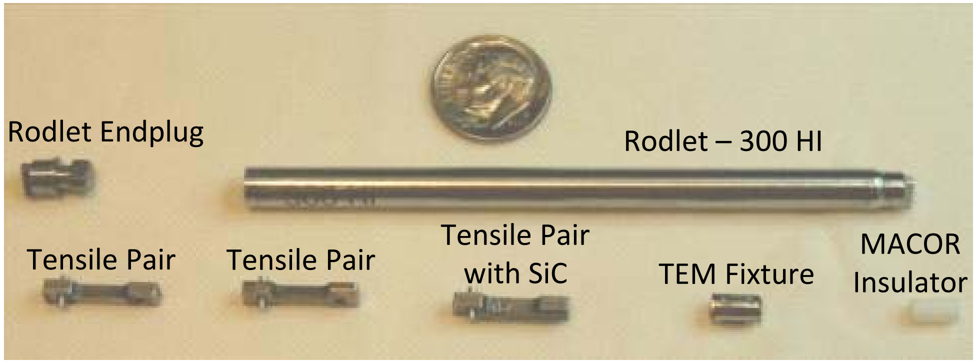
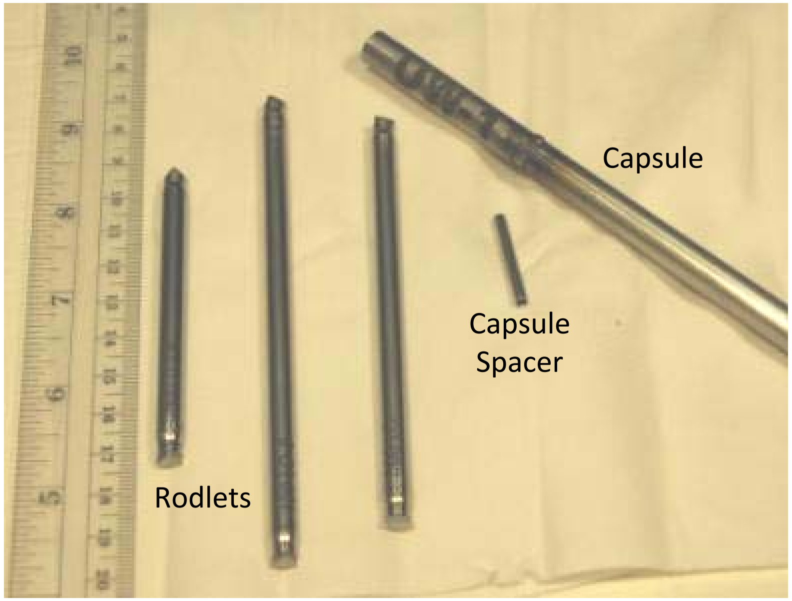
- Various alloys prepared as 3 mm TEM disks- including 9CrODS from the previous proton irradiation cluster stability study
- Samples loaded in rodlets, rodlets stacked in capsules
- Temps range from 300 – 700 °C
- Planned doses – 3 and 6 dpa





Planned PIE

- Use advanced transmission and scanning transmission electron microscopy techniques to investigate irradiation affects on F/M steels
  - EFTEM Imaging
    - Determine large scale nanocluster oxide stability in ODS steels
  - Atom Probe Topography (APT)
    - Determine small scale nanocluster oxide stability and chemical composition in ODS steels
- Use SANS to couple APT and EFTEM studies for ODS Steels
  - Initial work on SANS in progress
- Use traditional PIE studies to provide more insight on F/M steel stability under neutron irradiation
  - Microhardness
  - Shear punch

SANS at NIST

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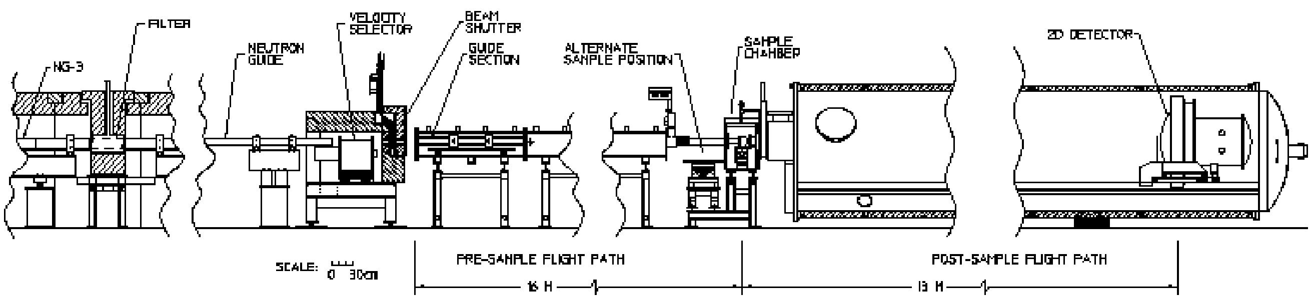
- 9CrODS steel irradiated to 3 dpa at 500 °C was analyzed
- Four specimens at this condition, 3 mm disks with a thickness of ~750 microns, were shipped to the National Institute of Standards and Technology (NIST)
  - Analysis using small angle neutron scattering (SANS) was performed
  - Neutron scattering is useful because of the ability to non-destructively analyze nanoscale features over a large sample volume
  - 9CrODS creep strength depends on nanocluster oxides

CHRNS 30 METER SANS INSTRUMENT



SANS at NIST

- All specimens were stacked - sample volume was still small in comparison to a typical SANS experiment, but clusters scattered strongly enough that data was easily collected within the time frame of a few hours.
- An electron magnet was used in order to negate magnetic effects
- Data was collected from a blank beam, a control sample, and the irradiated specimens
  - Detector distances of ~1 m, 4 m, and 15 m.
  - Q range ~ 0.0015 to 6 nm^{-1}, corresponds to cluster diameters ranging from ~ 1 nm to 500 nm.
- Qualitative analysis of the live data indicated a bimodal distribution of nanofeatures in the control specimen. Initial results indicate the destruction of the cluster population during irradiation, but quantitative analysis is still pending.
- Energy-filtered transmission electron microscopy is planned on the specimens to confirm any results.

Conclusions and future work

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- Heavy ion irradiations
  - Nanoclusters were unstable for high dose/dose-rate, and low temperature
  - Nanoclusters were stable for high dose/dose-rate, and high temperature
  - Initial APT agrees with EFTEM results
    - APT will continue on the rest of the current specimens
    - Wanted: composition information
  - Irradiations have been conducted at 100 ºC, 300 ºC, and 450 ºC to 100 dpa have been performed on 14YWT to examine effects of intermediate temperatures on cluster stability
- Neutron irradiations
  - 3 dpa, 500 C specimens have been analyzed by SANS
  - Initial results contradict ion irradiations: low dose, low dose rate, and high temperature conditions in ATR should favor cluster stability, but SANS shows cluster destruction
  - More analysis needed!

Acknowledgements

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- The Ni irradiation and APT research was performed using EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.
- FIB preparation of TEM samples was performed at Oak Ridge National Laboratory was sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, by the Advanced Fuel Cycle Initiative, Office of Nuclear Energy, Science and Technology, and at the SHaRE User Facility sponsored by the Division of Scientific User Facilities, Office of Basic Energy Sciences, US Department of Energy.
- 14YWT steel sample material was generously provided by ORNL.
- EFTEM research was performed at the University of Las Vegas, Nevada (UNLV) – special thanks to Longzhou Ma.

Backups

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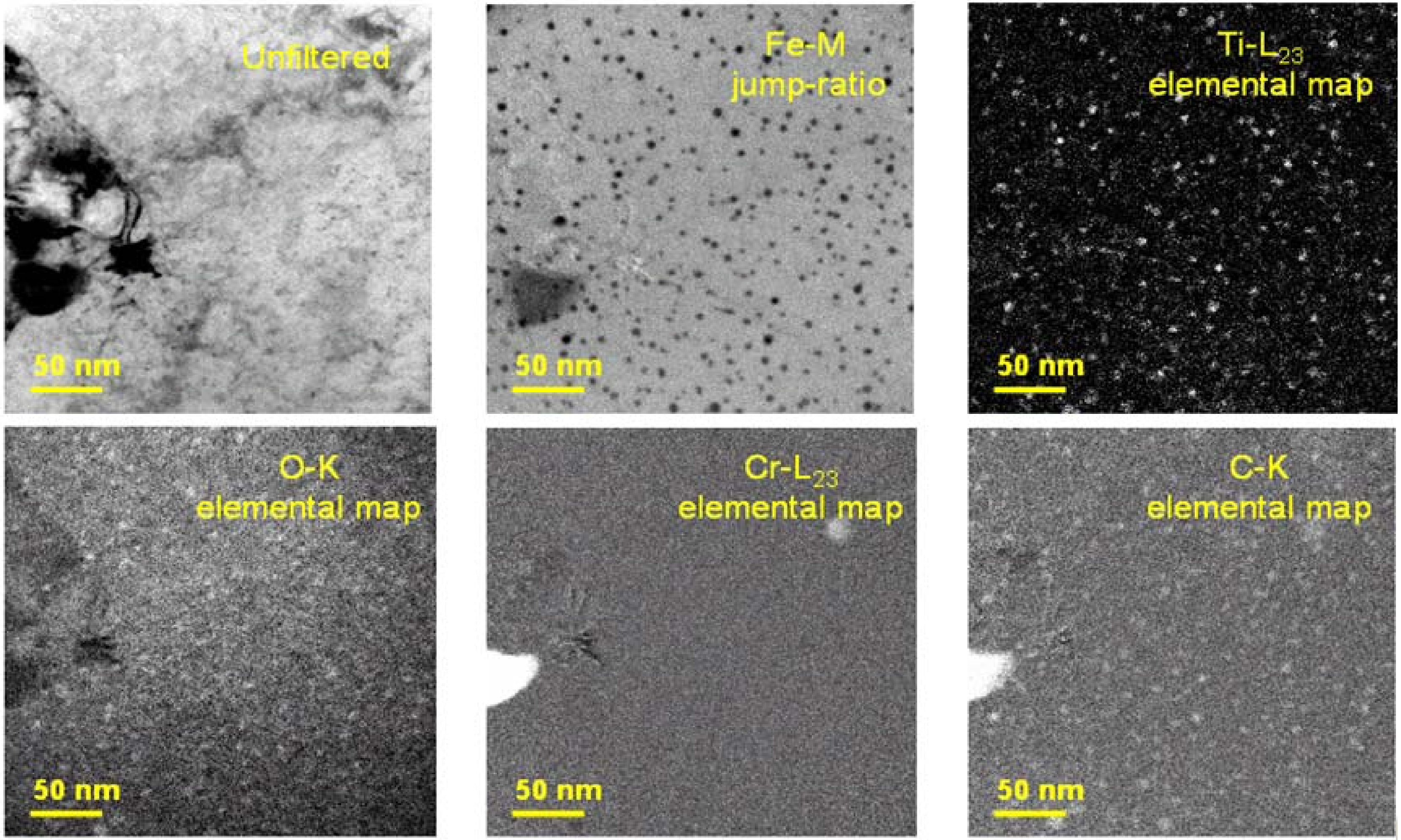
EFTEM
Unirradiated NFA (9Cr)



Energy Filtered TEM (EFTEM)

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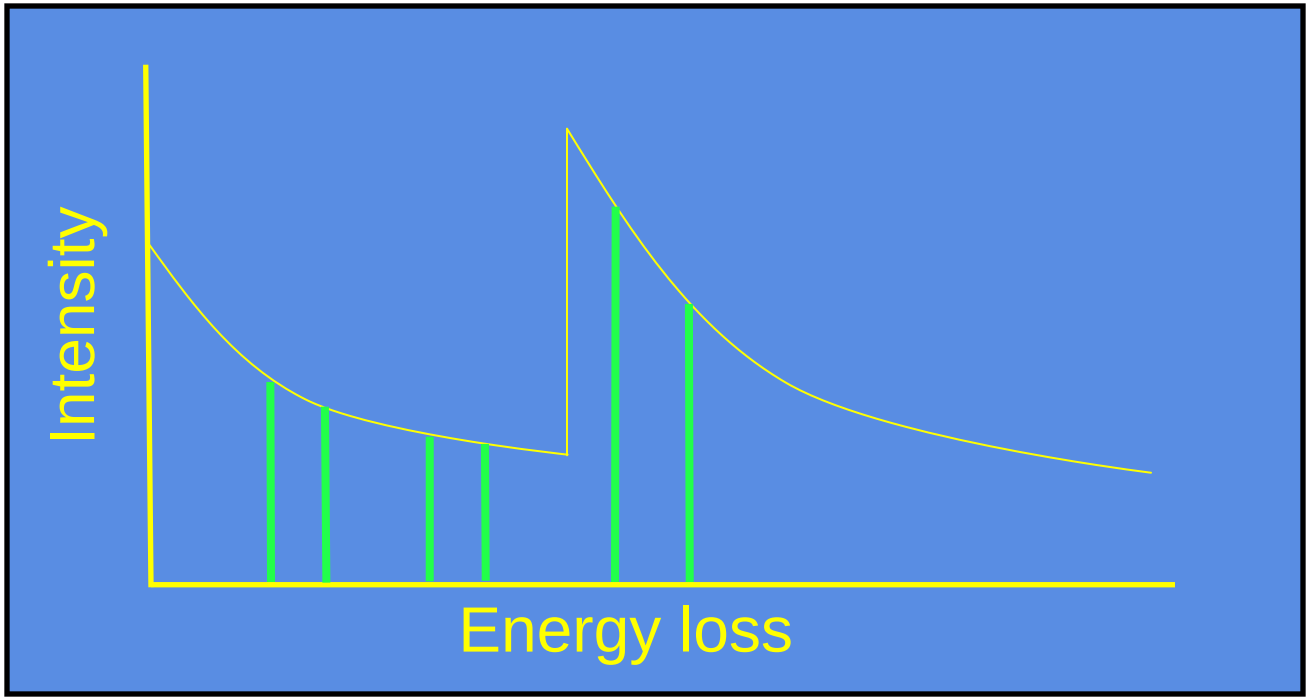

- Three-window method ('element map')
  - Extrapolated background calculated from pre-edge windows
  - Background subtracted from edge image
- Two-window method ('jump ratio')
  - Post-edge image divided by pre edge image
  - Often provides clearer image

Atom probe tomography (APT)

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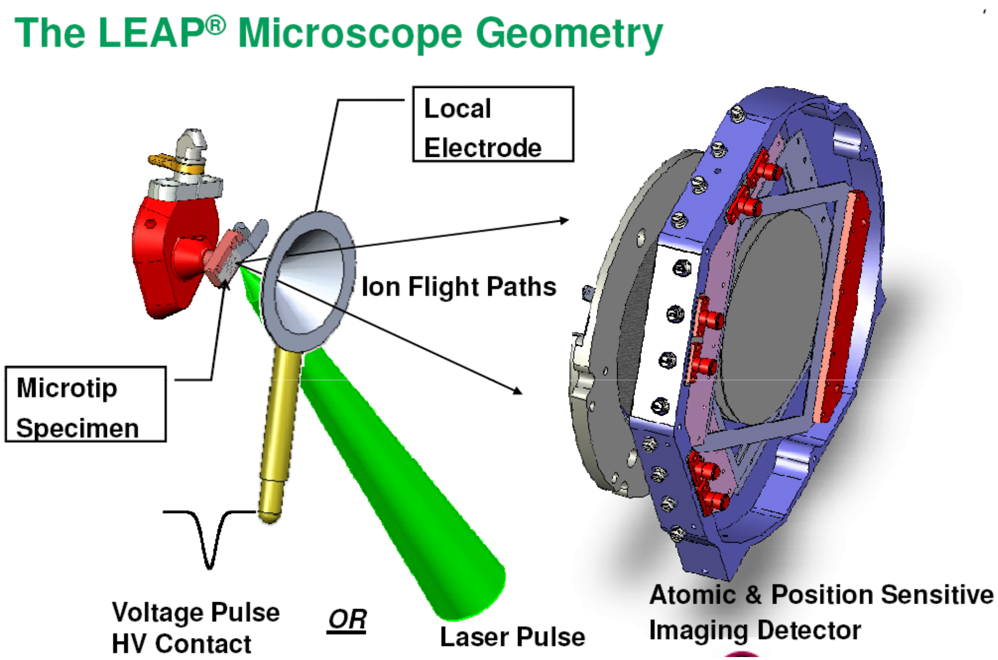
- Atoms are field emitted from a sharp sample tip by high-voltage or laser pulses
- Time-of-flight spectrometer determines mass to charge ratio
- Detector measures spatial coordinates of atoms
- Typical sample volume
  - 10 nm x 10 nm x 100 to 250 nm
  - 10^5 to 10^6 atoms



LEAP v. LEAP 4000X

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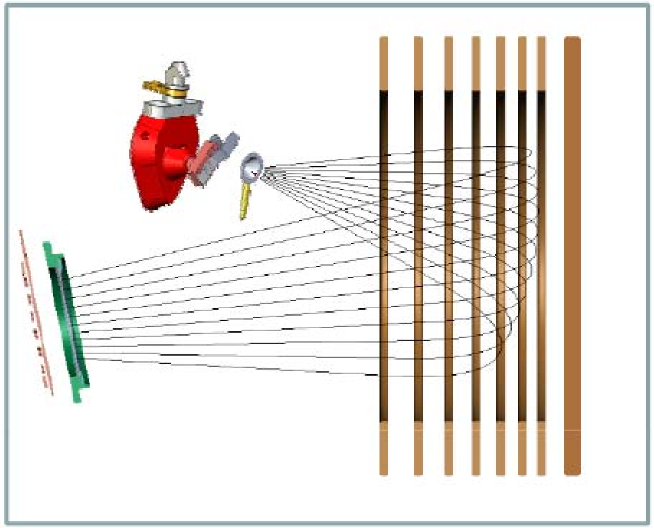
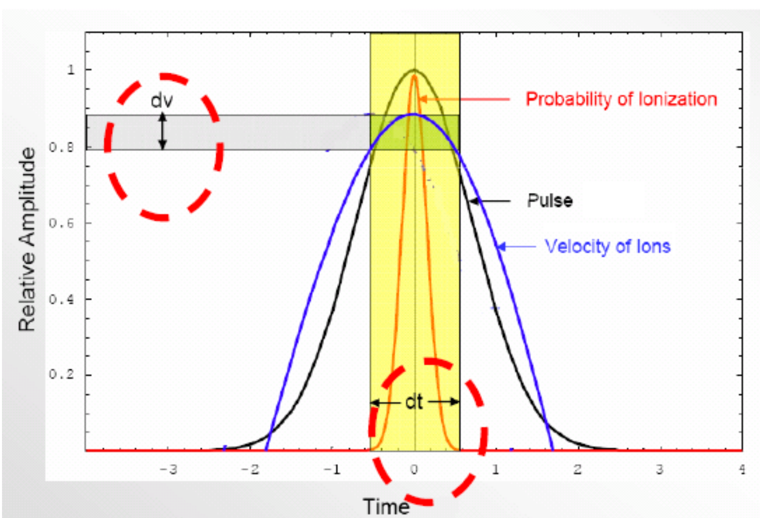
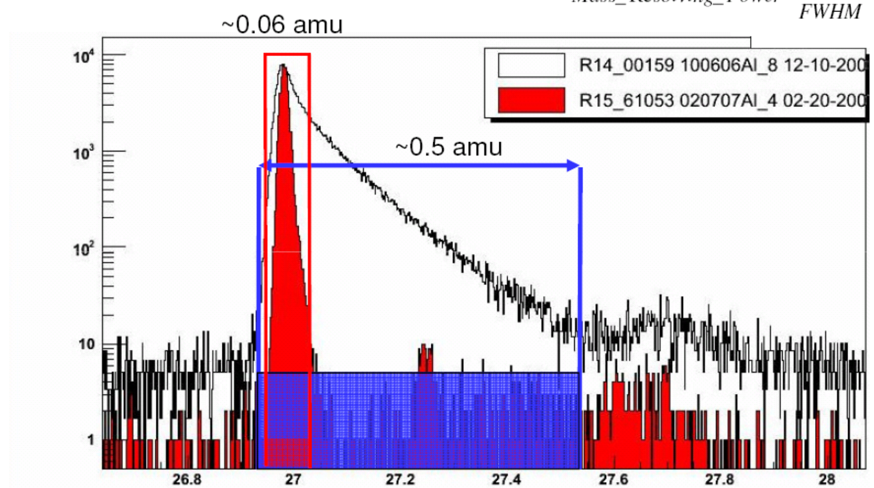


- Large angle reflectron setup yields energy compensated flight path
- Minimizes effects of variation in velocity of departing ions (dv)
- Allows resolution of Y



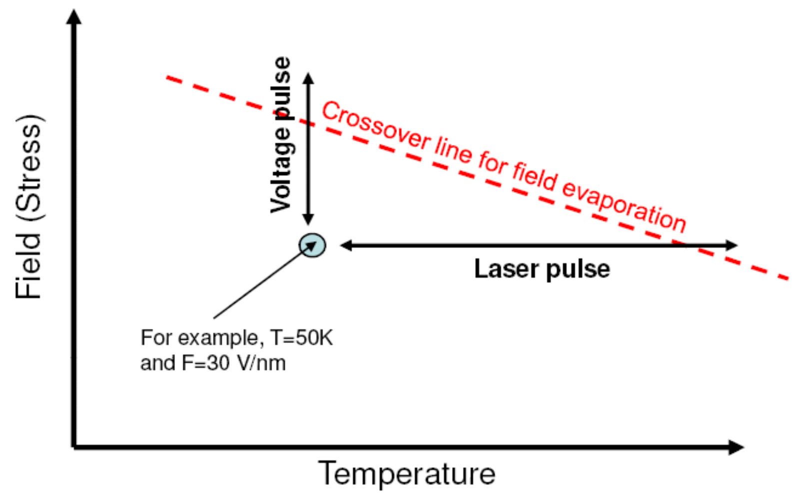
- Enhanced signal to noise performance (Aluminum Data)

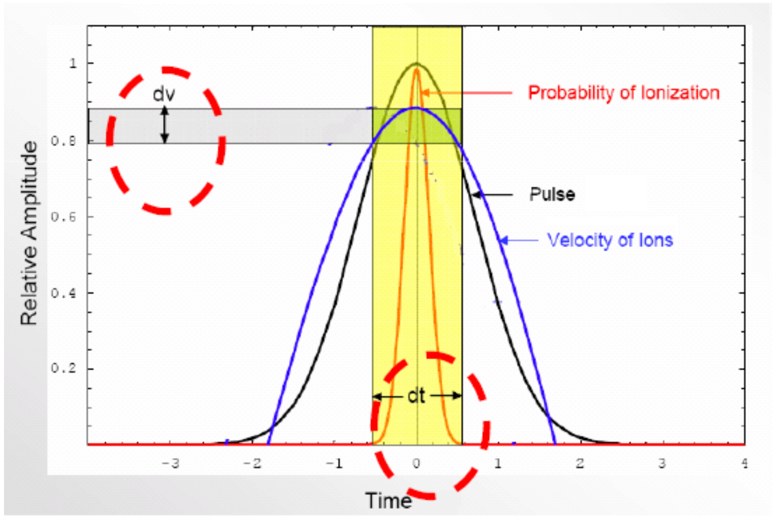
$$Mass\_Resolving\_Power = \frac{m/q}{FWHM}$$



Laser v. Voltage pulsing

- Laser pulsing
  - Easier on the sample
  - Allows for analysis of semiconductors and insulators
  - Uncertainty in time is greater, so spatial resolution is worse
- Voltage pulsing
  - Greater certainty in time, better spatial resolution
  - More uncertainty in velocity of ions, so mass resolving power is usually worse



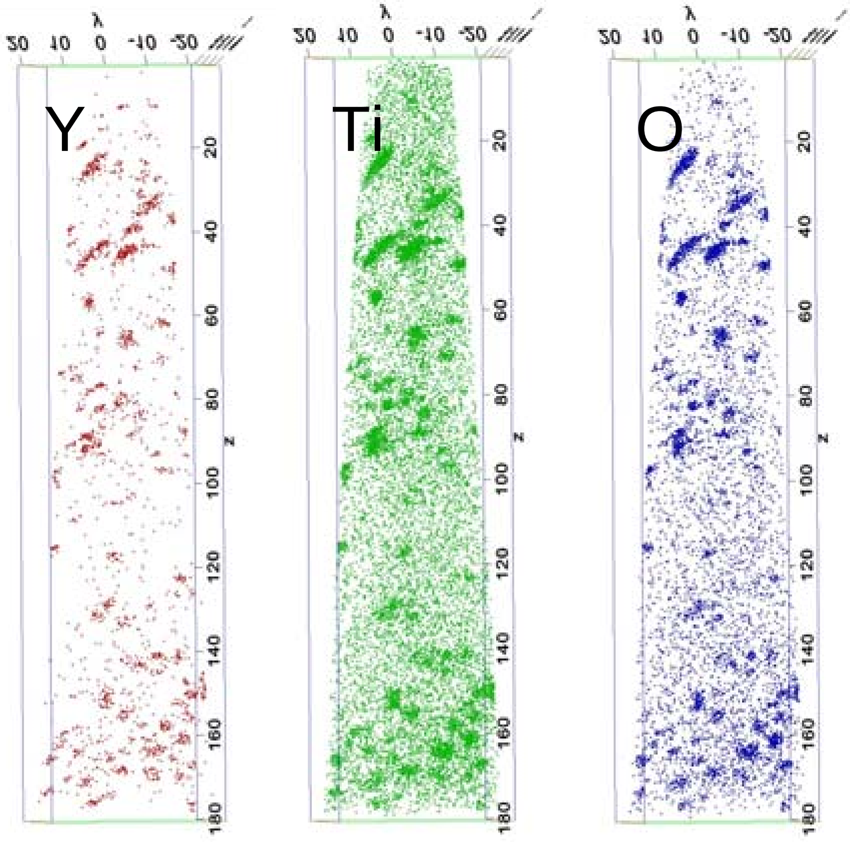


APT – data collection

- APT performed at the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory(PNNL)
- LEAP 4000X
- Samples were prepared in a FEI Quanta FIB – microtip array utilized
- Voltage pulsed runs first attempted – specimens kept fracturing, so switched to laser pulsing

APT – data analysis

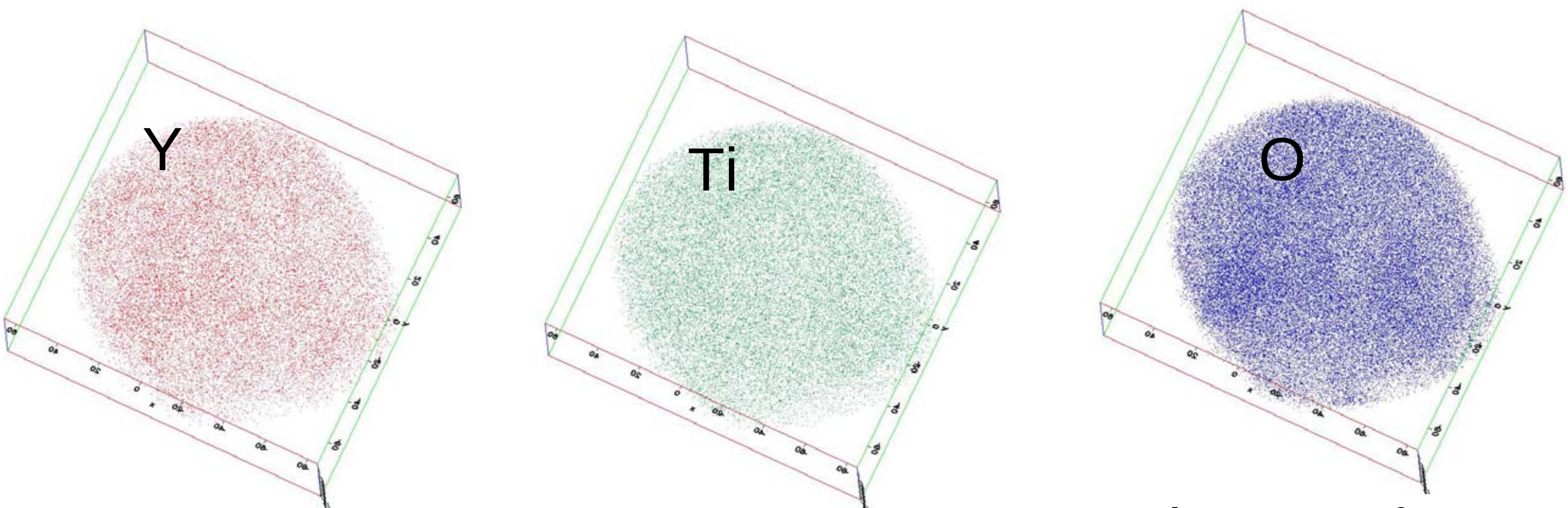
- Data has successfully been collected from unirradiated 14YWT and 100 dpa, -75 °C
- Nanoclusters observed in control sample
- Measured using IVAS built in cluster finding algorithms – maximum separation distance, etc.
- Ave. radii ~ 1 nm



Unirradiated

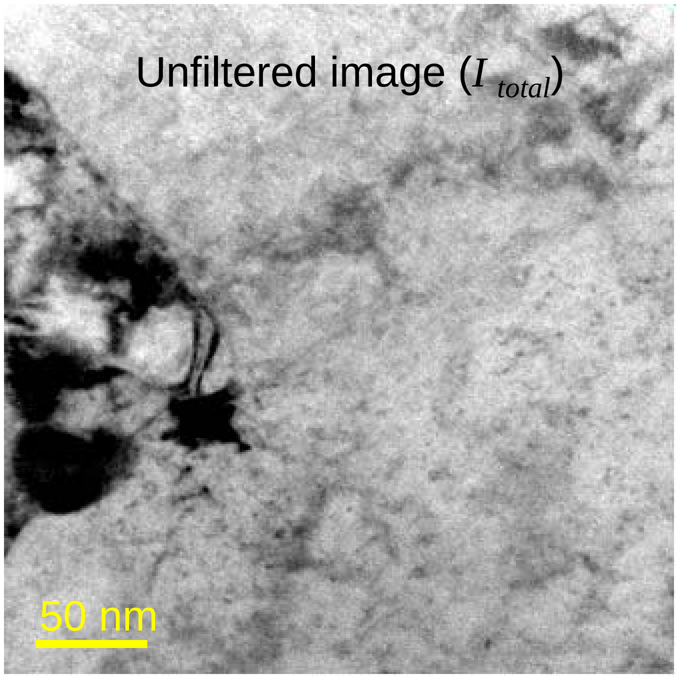
APT – data analysis

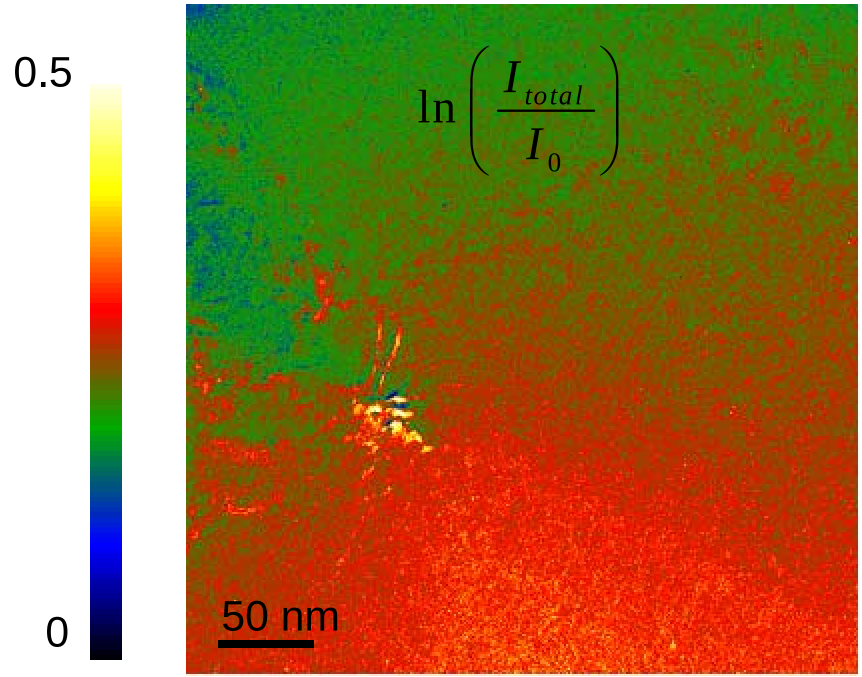
- 100 dpa, -75 °C sample – nanoclusters missing
- Supports EFTEM results
- Cluster finding algorithms indicate Y, Ti, and O in randomly distributed solid solution
- More data collection and analysis to come….



100 dpa, -75 °C

EFTEM
Thickness map





$$t = \lambda \ln\left(\frac{I_{total}}{I_0}\right)$$

t – thickness

λ – electron mean free path

I_{total} – total intensity

I_0 – zero loss intensity (not shown)

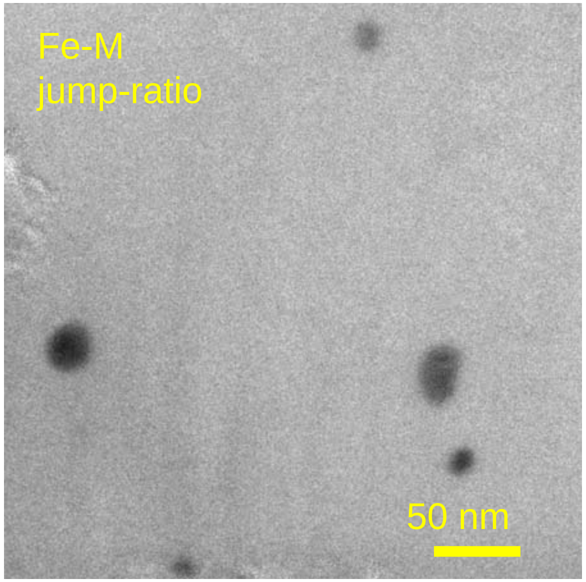
Mean free path ~ 140 nm

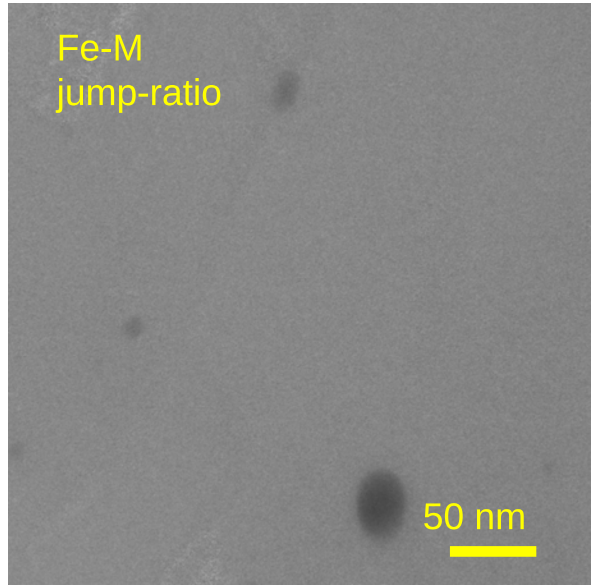
red area ~ 40 nm

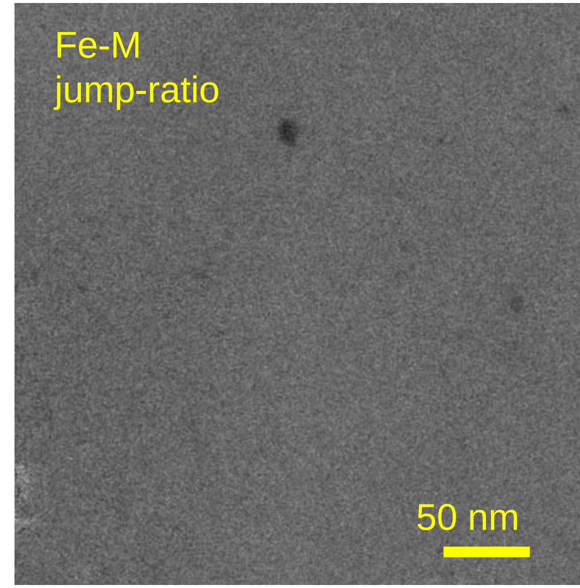
green area ~ 30 nm

Used for number density calculation

EFTEM – 50 dpa, -75 ºC irradiated 14YWT







Average cluster size – 7.3 nm (1σ = 8.0 nm)
Number density – 2×10^3 clusters/μm^3 (1σ = 1×10^3 clusters/μm^3)*
Total volume analyzed – 0.065 μm^3
Total clusters analyzed – 129

*Number density standard deviation calculated from variation in 300 nm x 300 nm x 10 – 40 nm volume measurements (i.e. each image)