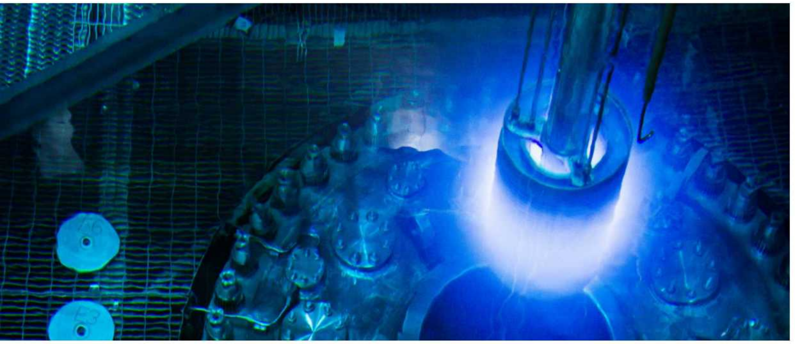
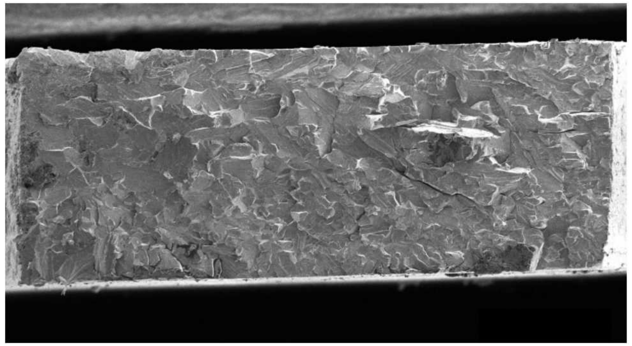
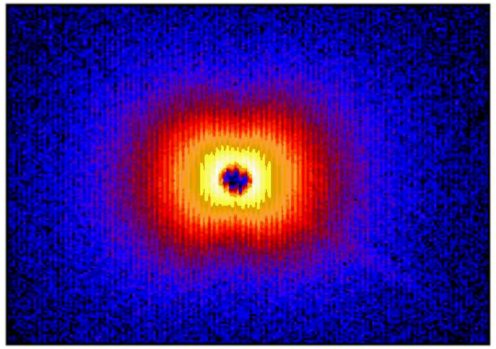
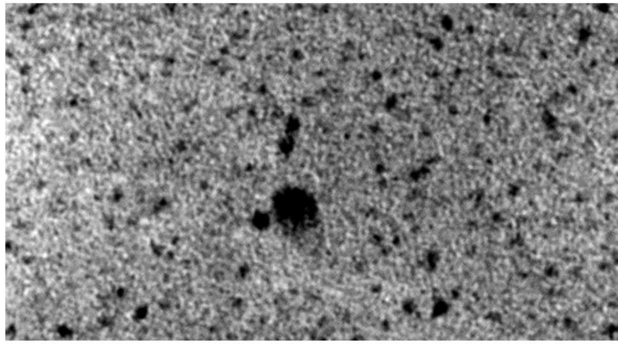
SAND2018-1398PE

Correlative microscopy of neutron-irradiated FeCrAl alloys

Presented by:

Samuel A. Briggs

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- This research was performed, in part, using instrumentation (FEI Talos F200X TEM) provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program, and the Nuclear Science User Facilities.

Oregon State University (2007-2011)
Dr. Todd Allen
Dr. Kumar Sridharan
University of Wisconsin – Madison (2011-2016)
Oak Ridge National Laboratory (2015-2016)
Sandia National Laboratories (2017-Present)
Dr. Khalid Hattar
Dr. Kevin Field
PNNL
INL
THE UNITED STATES
PHYSICAL
LAMBERT CONFORMAL CONIC PROJECTION

INL CAES
• FEI Quanta FIB
• Tecnai TF30
• Cameca LEAP 4000X HR
SNL I³TEM
• JEOL 2100
U. Wisconsin
• Zeiss Auriga FIB
• Tecnai TF30
• FEI Titan (S)TEM
ANL IVEM-Tandem
• Hitachi-9000
ORNL LAMDA
• FEI Quanta/Versa FIB
• JEOL 2100F
• FEI Talos F200X
INL
AURIGA
The United States
Physical
Lambert Conformal Conic Projection

Motivation: Accident Tolerant Fuel Forms

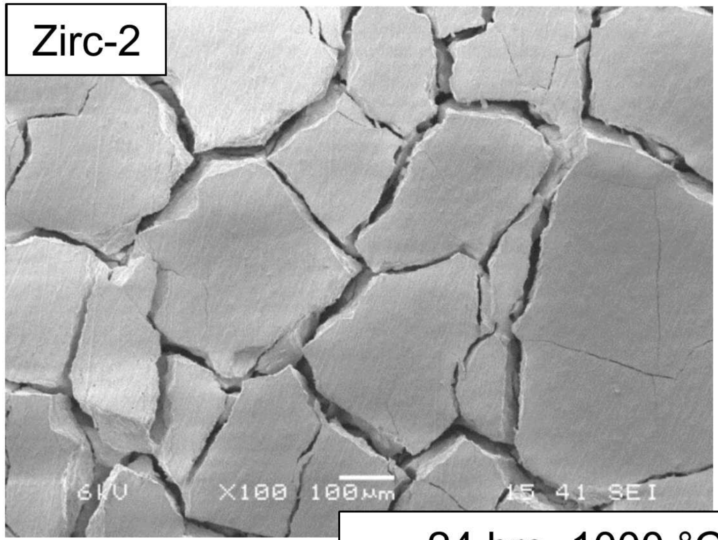
- Fukushima accident has demonstrated that Zircaloy cladding is detrimental in Loss of Coolant Accident (LOCA) scenarios
  - Exothermic oxidation reaction with H_2O produces H_2 gas

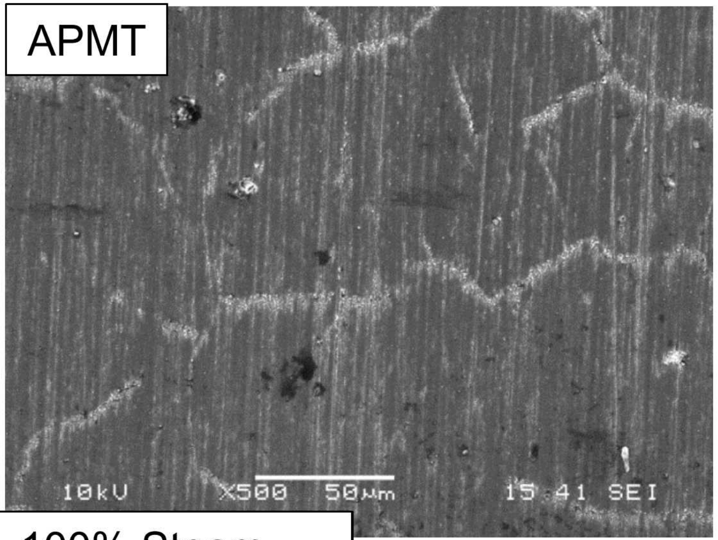
- DOE has funded development of accident-tolerant fuel (ATF) and fuel claddings
  - **Fe-Cr-Al Claddings**
  - SiC/SiC Composite Claddings
  - SiC/Cr/MAX-phase Coatings for Zr
  - High-density/high-conductivity fuels (UN, U_3Si_2)

$$Zr + 2H_2O \rightarrow 2H_2 + ZrO_2 + Heat$$

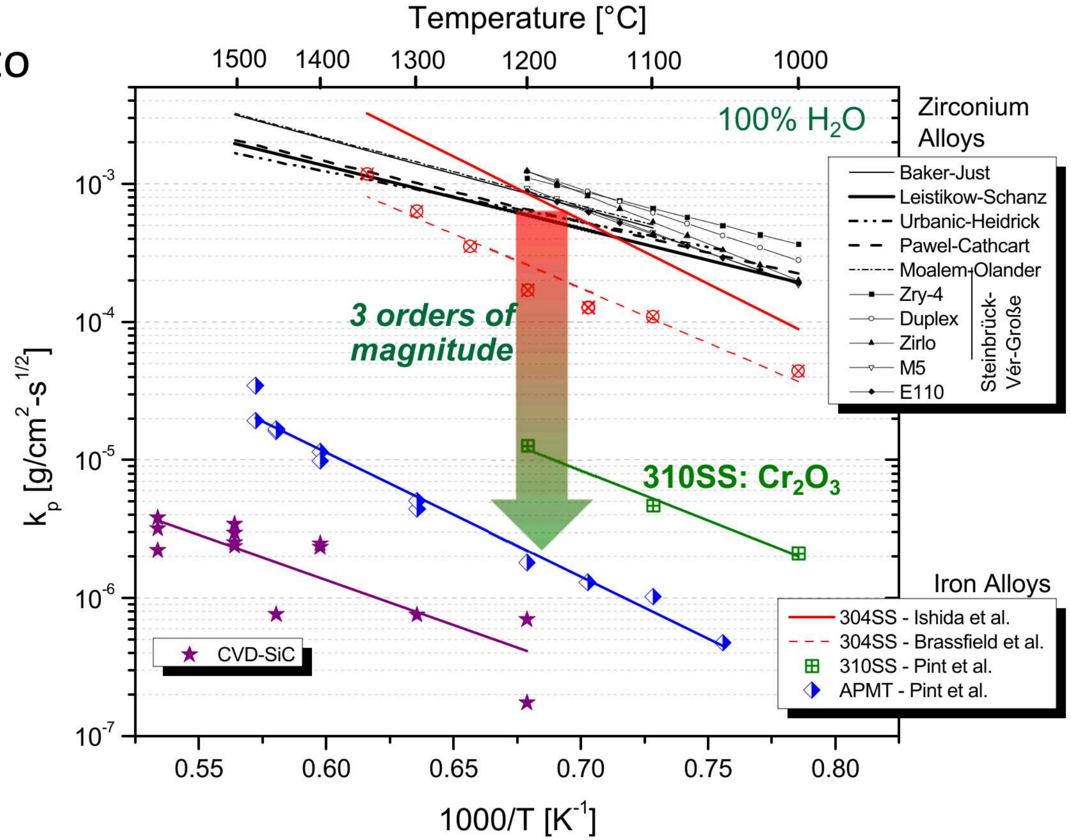
Fe-Cr-Al Alloys for Nuclear Systems

- Why is Fe-Cr-Al attractive as a LWR cladding material?
  - Exceptional high temperature oxidation resistance due to formation of passivating Al_2O_3 (up to 1200-1475 °C)
  - High strength, with potential for oxide-dispersion strengthened variants
  - Low swelling rates in irradiation environments
  - Potential for near-term deployment



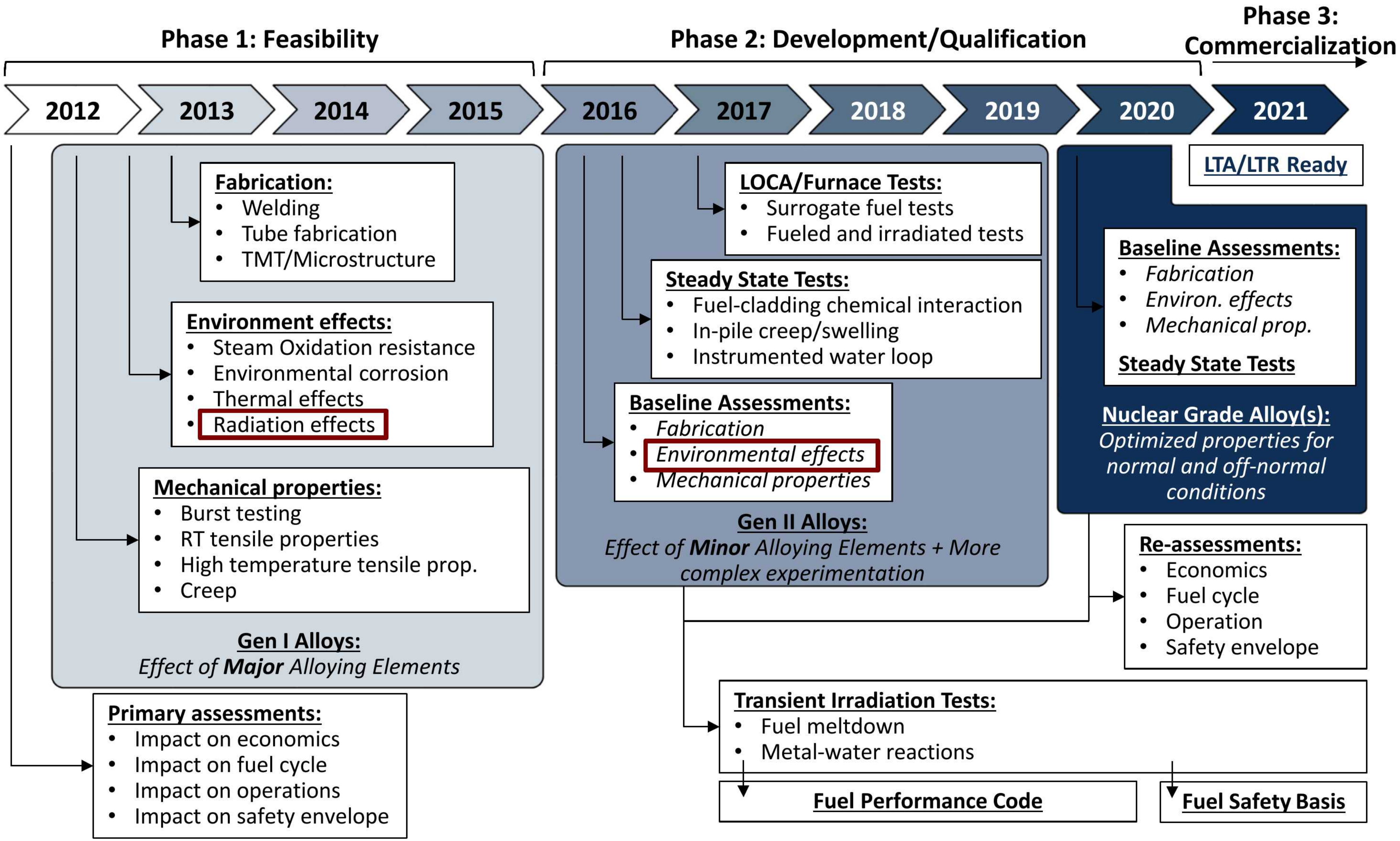


24 hrs, 1000 °C, 100% Steam

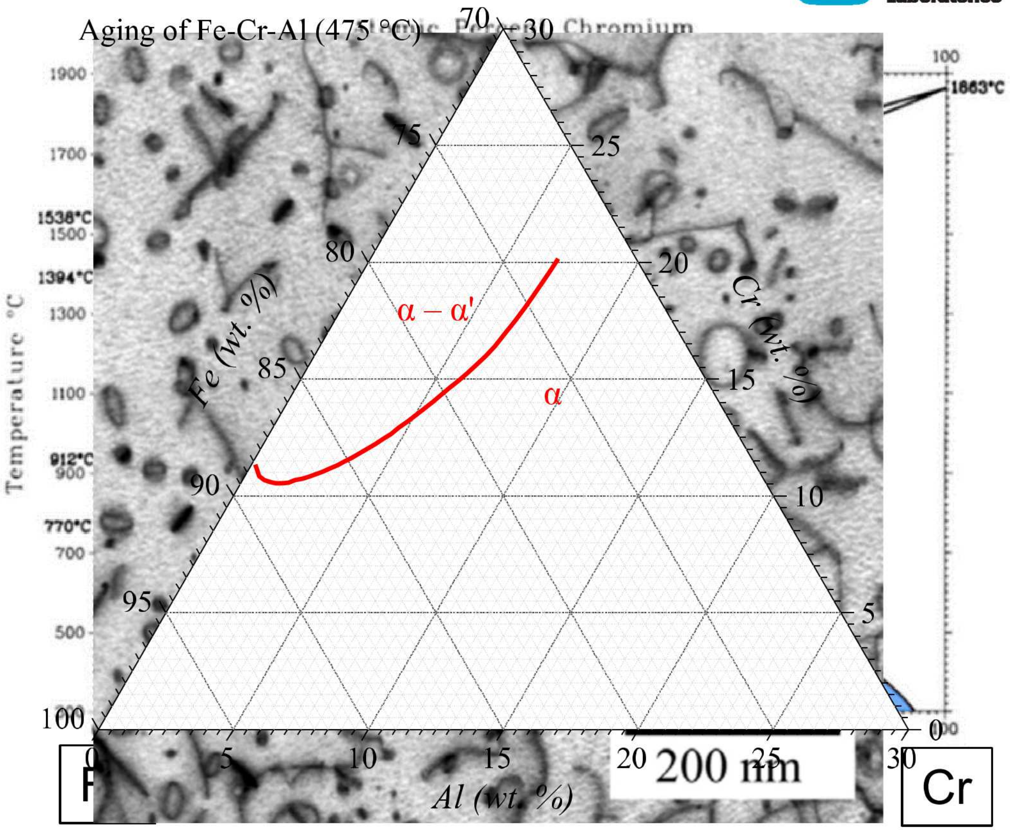


Fe-Cr-Al Cladding Design Campaign

- Multidisciplinary design problem, numerous performance metrics
- Primarily involved in assessing radiation tolerance
  - Gen. I model ternary alloys
  - Gen. II ODS variants



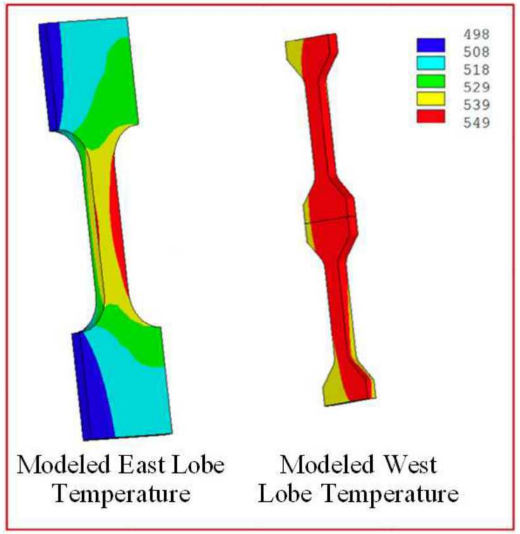
Radiation Damage in High-Cr Ferritics



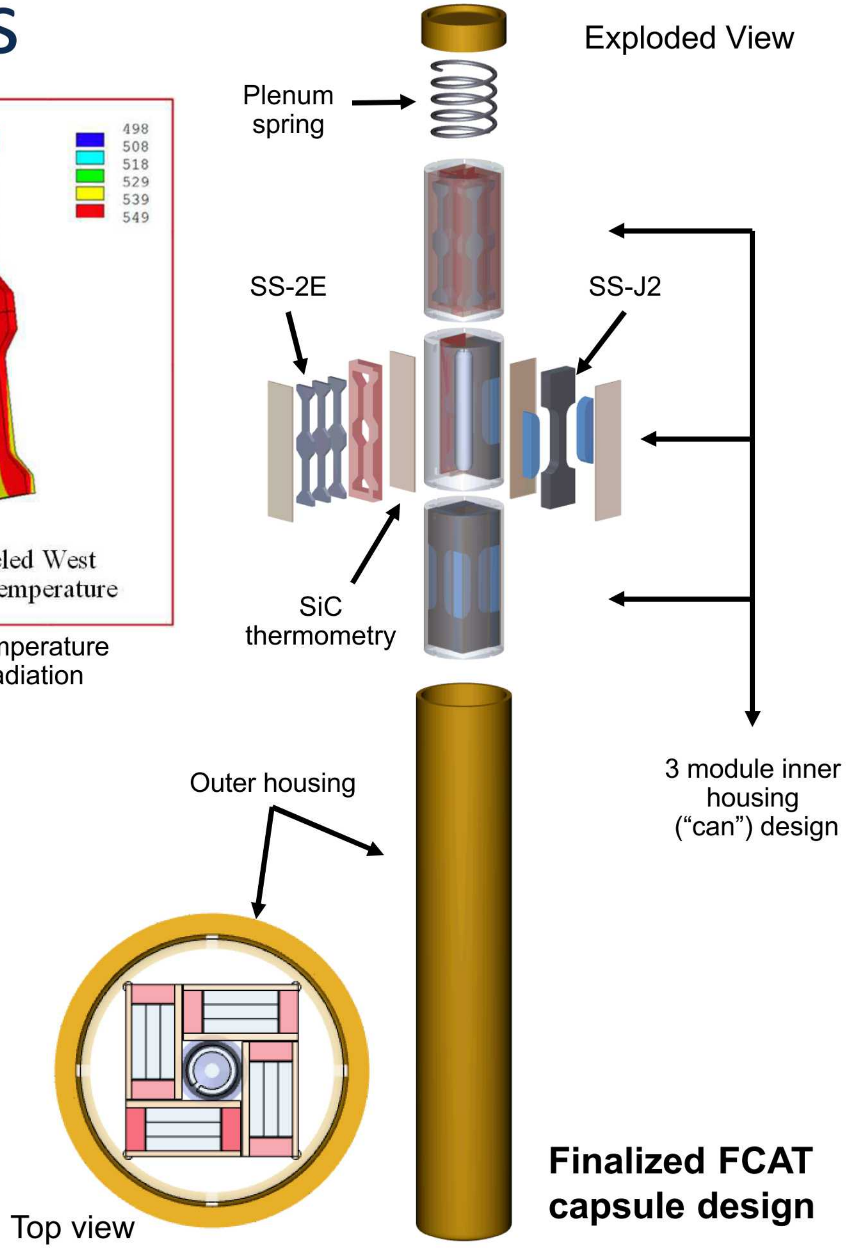
- While ferritic alloys are known to possess excellent swelling resistance, they have a perceived susceptibility to irradiation-induced hardening and embrittlement
- For low Cr alloys, hardening is primarily due to the formation of dislocation loops
- Above 8-9 wt.% Cr, radiation-enhanced precipitation of Cr-rich α′ dominates the radiation-induced hardening and embrittlement response
  - α′ phase is stable at temperatures below ~475-500 °C
  - Irradiation-enhanced diffusion effects allow the phase to form at LWR-relevant temperatures (300-350 °C) where diffusion kinetics are typically slow

HFIR Irradiation: FCAY and FCAT Rabbits

- Alloys studied:
  1. Model alloys (M): F1C5AY, B125Y, B154Y-2, B183Y-2
  2. Engineering grade alloys (E): C06M, C35M, C36M, C37M, C35MN, C35M10TC
  3. Commercial alloys (C): Kanthal APMT™, and Alkrothal 720
  4. ODS Alloys (O): 125YF
- SS-J2 and SS-2E flat sheet tensile specimen geometries
- Design temperatures of 200-550 °C
  - Temperature monitored passively using SiC thermometry

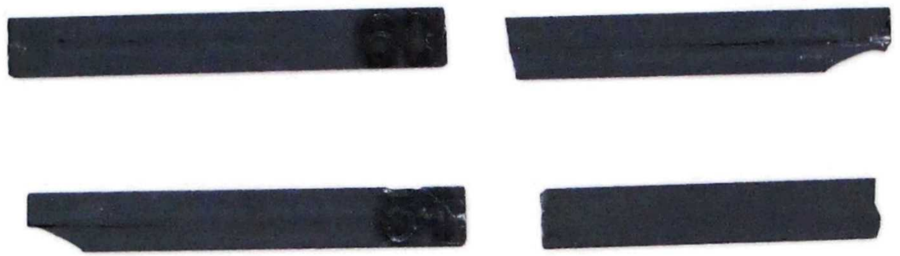


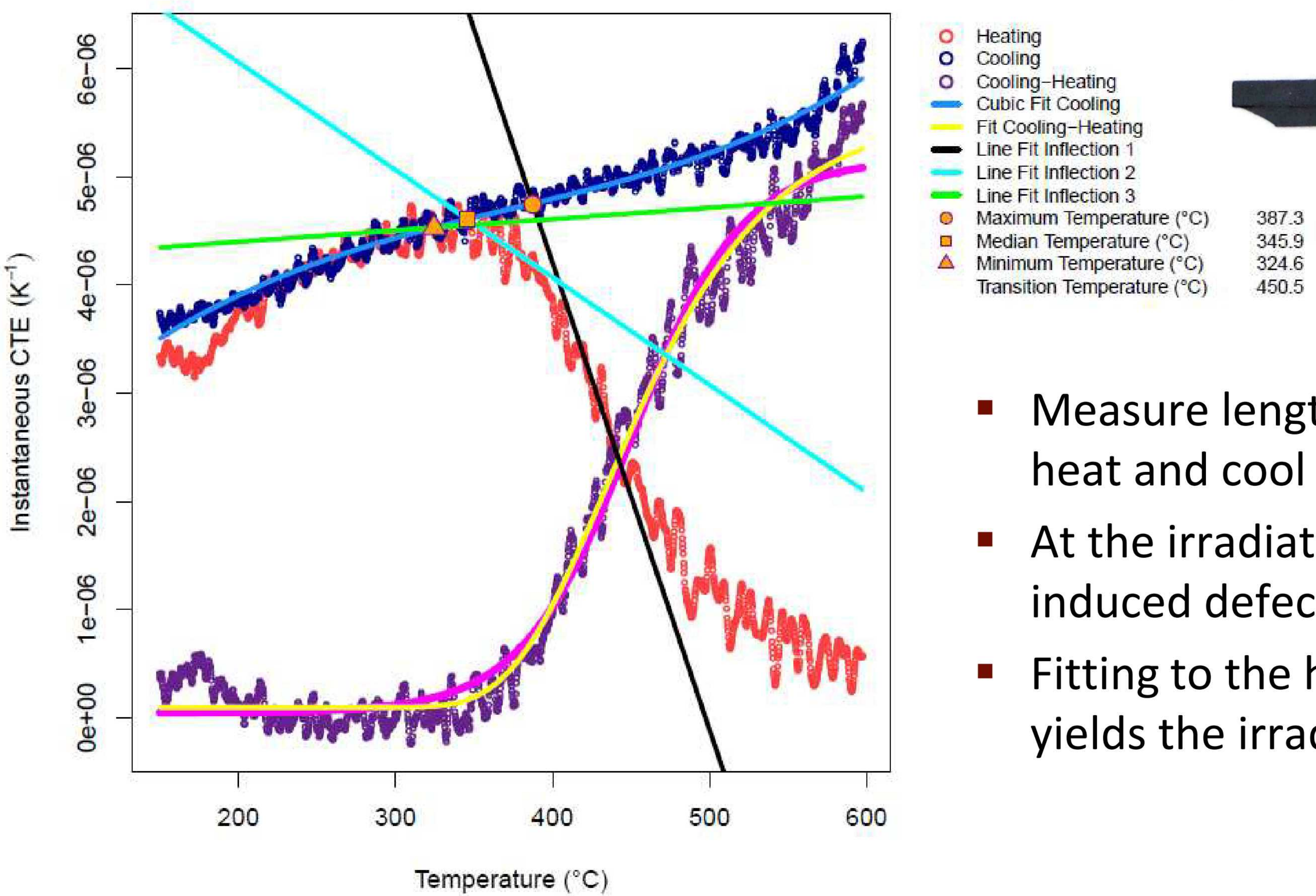
Example of specimen temperature gradients for 550°C irradiation



Capsule ID	Alloys	Exposure Time (hrs)	Neutron Fluence (n/cm^2) E > 0.1 MeV	Dose Rate (dpa/s)	Dose (dpa)	Irradiation Temperature (°C)
FCAY-01	M+C	120	3.69×10^{20}	7.7×10^{-7}	0.3	334.5 ± 0.6
FCAY-02	M+C	301	9.25×10^{20}	7.7×10^{-7}	0.8	355.1 ± 3.4
FCAY-03	M+C	614	1.95×10^{21}	8.1×10^{-7}	1.8	381.9 ± 5.4
FCAY-04	M+C	2456	7.73×10^{21}	7.9×10^{-7}	7.0	319.9 ± 10.2
FCAY-05	M+C	4914	1.55×10^{22}	7.8×10^{-7}	13.8	340.5 ± 25.7
FCAT-01	E+O	548	2.17×10^{21}	9.6×10^{-7}	1.9	194.5 ± 37.9
FCAT-02	E+O	548	2.05×10^{21}	9.1×10^{-7}	1.8	362.7 ± 21.2
FCAT-03	E+O	548	2.17×10^{21}	9.6×10^{-7}	1.9	559.4 ± 28.1

SiC Thermometry

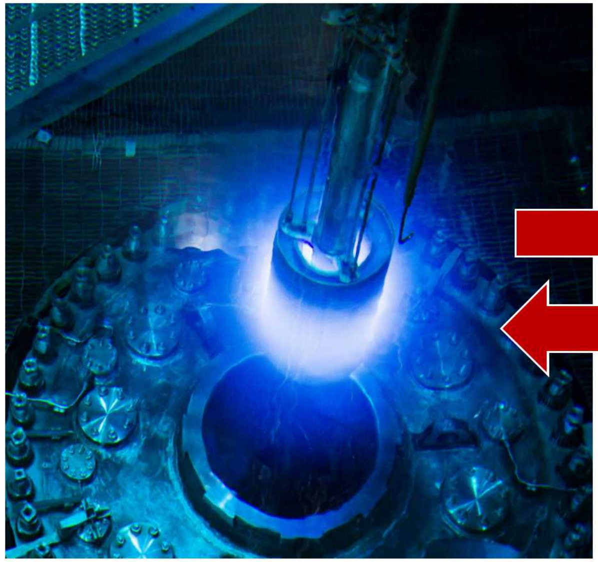




- Measure length change of specimens as you heat and cool the material (dilatometry)
- At the irradiation temperature, radiation-induced defects begin to anneal out
- Fitting to the heating and cooling curves yields the irradiation temp

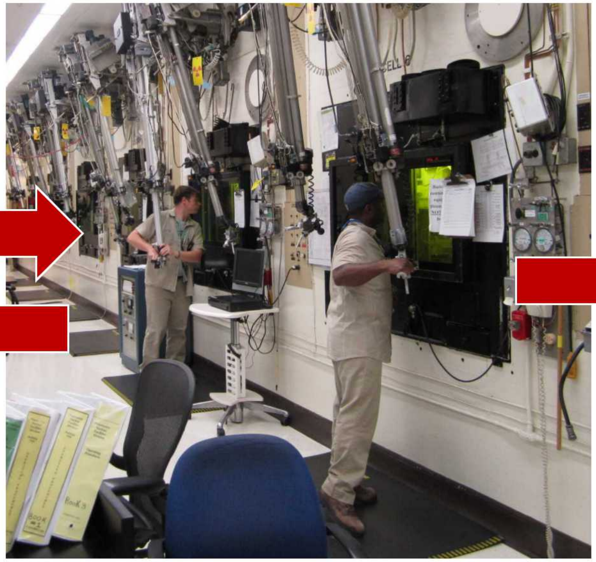
Sample Handling Logistics

- Neutron-irradiated samples pose a significant radiological hazard
- Optimized workflow maximizes scientific yield while minimizing personnel exposure



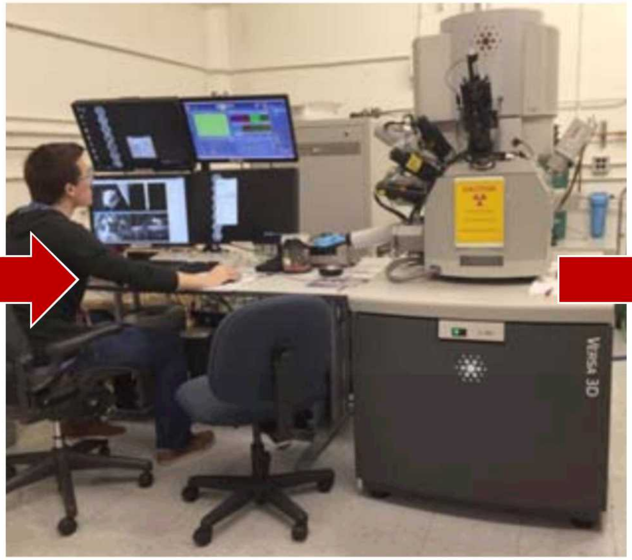
HFIR

- Sample Irradiation
- SANS



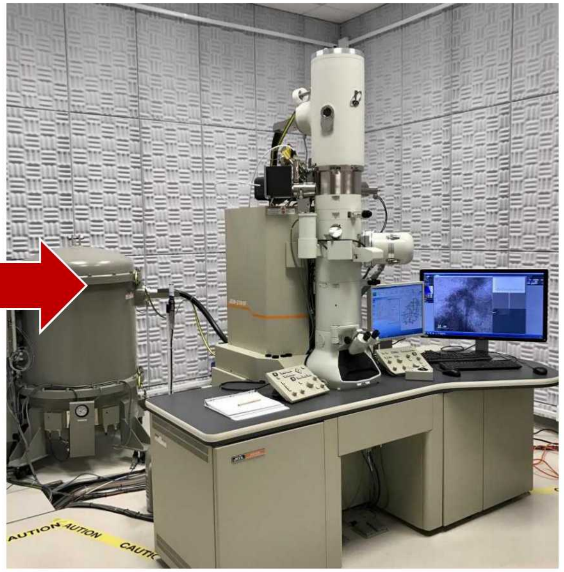
IMET Hot Cells

- Tensile Testing
- Sectioning



LAMDA Laboratory

- Metallography
- FIB Sample Prep



Microscopy & Analysis

- TEM/STEM
- APT

Characterization techniques for nanoparticles

	Advantages	Disadvantages
Analytical TEM (STEM/EDS & EFTEM)	• Reveals microstructural heterogeneities • Quick/easy to perform • Direct microstructure observation	• Poor signal to noise ratio; can limit resolution • Moderate volume analyzed • Dependent on sample quality • Limited composition information
Small Angle Neutron Scattering (SANS)	• Large sampling volume; excellent counting statistics • Limited to no sample prep • Quick/easy to perform • Composition can be inferred (magnetic SANS only)	• Indirect microstructure observation • No microstructural relationships (i.e. assumes homogenous distributions) • Requires bulk sample; increased radioactivity
Atom Probe Tomography (APT)	• Composition information readily available • Excellent spatial resolution • Direct microstructure observation	• Small sample volume analyzed • Dependent on sample quality • Data interpretation can be convoluted; aberration effects • Time intensive

Characterization techniques for nanoparticles

Complementary Techniques

	Advantages	Disadvantages
Analytical TEM (STEM/EDS & EFTEM)	• Reveals microstructural heterogeneities • Quick/easy to perform • Direct microstructure observation	• Poor signal to noise ratio; can limit resolution • Moderate volume analyzed • Dependent on sample quality • Limited composition information
Small Angle Neutron Scattering (SANS)	• Large sampling volume; excellent counting statistics • Limited to no sample prep • Quick/easy to perform • Composition can be inferred (magnetic SANS only)	• Indirect microstructure observation • No microstructural relationships (i.e. assumes homogenous distributions) • Requires bulk sample; increased radioactivity
Atom Probe Tomography (APT)	• Composition information readily available • Excellent spatial resolution • Direct microstructure observation	• Small sample volume analyzed • Dependent on sample quality • Data interpretation can be convoluted; aberration effects • Time intensive

α′ Precipitation in Gen. I Fe-Cr-Al Model Alloys

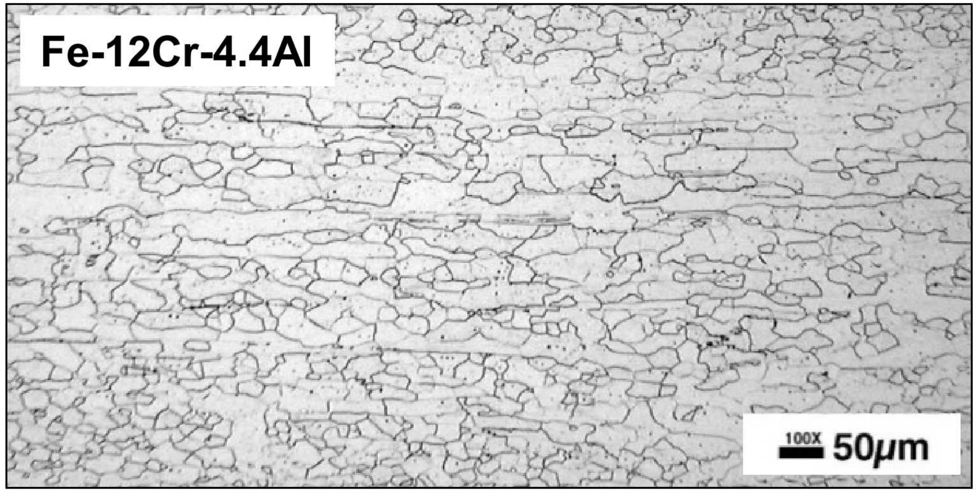
Experimental Design

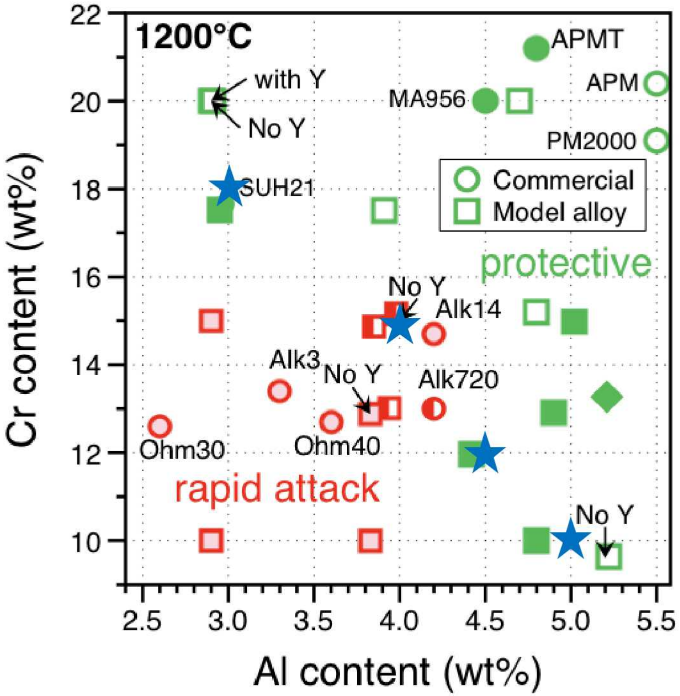
- Four Fe-(10-18)Cr-(5.8-9.3)Al+Y (at.%) model alloys have been selected for initial investigation
  - Y is added to enhance adhesion of Al_2O_3 scale

ID	Composition, at.%							
	Fe	**Cr**	**Al**	**Y**	C	S	O	N
Fe-10Cr-9.3Al	**80.46**	**10.15**	**9.34**	**0.023**	0.022	0.0016	0.0043	0.0011
Fe-12Cr-8.7Al	**79.13**	**12.16**	**8.66**	**0.016**	0.022	0.0021	0.0056	0.0034
Fe-15Cr-7.7Al	**76.92**	**15.33**	**7.70**	**0.021**	0.022	0.0007	0.0083	0.0026
Fe-18Cr-5.8Al	**76.15**	**18.00**	**5.81**	**0.010**	0.022	0.0010	0.0050	0.0042

- Model alloys were fabricated by arc-melting pure element feed stocks and pre-alloyed Al-Y specimens. After arc-melting the model alloys were hot forged/rolled and heat treated to control the grain size to 20-50 µm.[1]

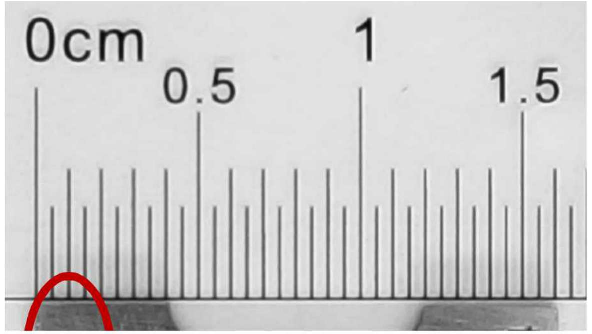
- Warm rolling with a 10% thickness reduction was used to flatten the model alloy sheet samples prior to machining.





High temperature oxidation of model Fe-Cr-Al alloys exposed to steam at 1200 °C (source: B. Pint, ORNL)

LEAP Data Collection

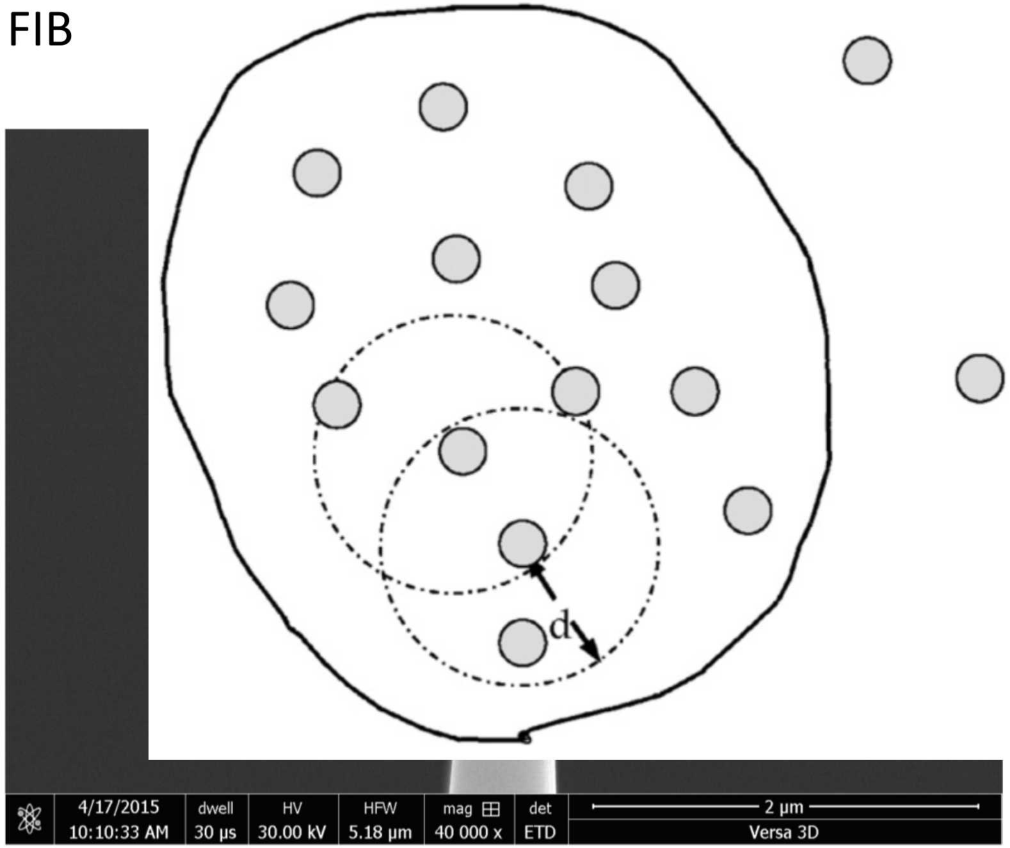


- Data collected on Cameca LEAP 4000X HR at the Center for Advanced Energy Studies (CAES) at INL and at the Center for Nanophase Materials Sciences (CNMS) at ORNL

- APT samples prepared from broken half-tensile heads using FIB
  - Prepared from regions away from strained neck

- Operated in laser mode, specimen temp of 50K, pulse repetition rate of 200 kHz and laser energy of 50 pJ

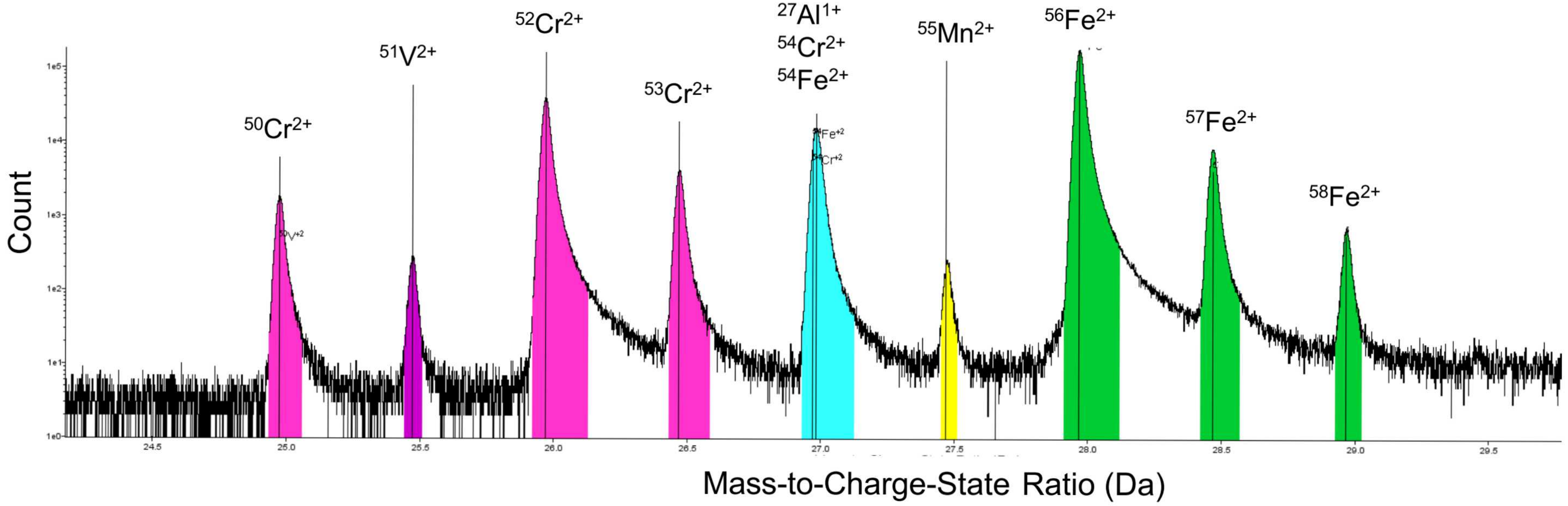
- Clusters were indexed using the maximum separation method
  - d_{max} – max. separation distance between clustered atoms
  - N_{min} – minimum number of atoms required to define a cluster



[1] Vaumousse, D., Cerezo, A., & Warren, P. J. (2003). A procedure for quantification of precipitate microstructures from three-dimensional atom probe data. Ultramicroscopy, 95(SUPPL.), 215–221.

Challenges for APT Analysis – Peak Deconvolution

- Overlapping peaks in the time-of-flight (TOF) spectrum need to be separated
  - Peak deconvolution is built into IVAS – based on natural isotopic abundances
  - Adjusted isotopic abundances generated using ORIGEN-2.2 Isotope Generation & Depletion software package[1]
  - Manually deconvolution can be performed on raw count info using calculated isotopic abundances following irradiation



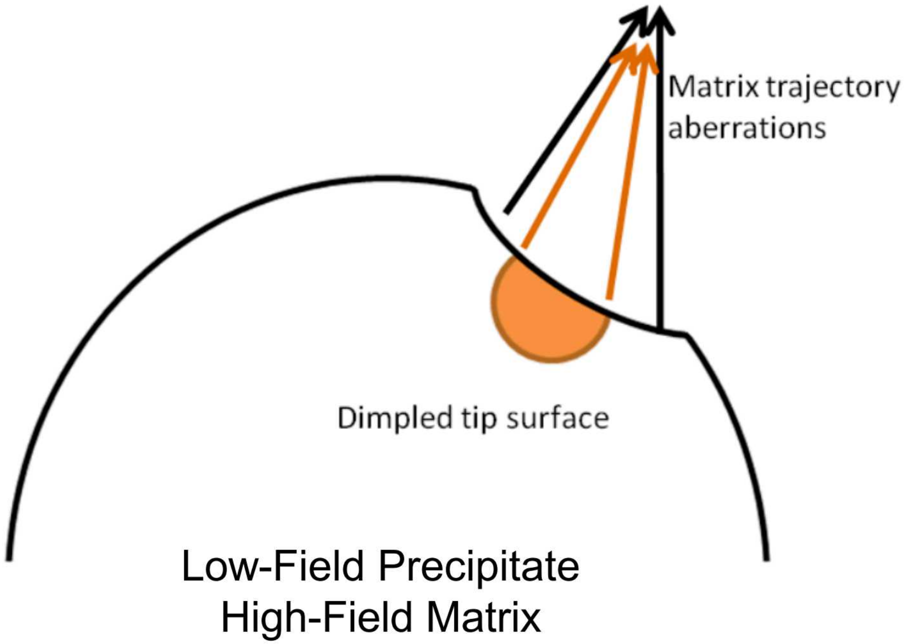
Adjusted isotopic abundances Generated by ORIGEN-2.2

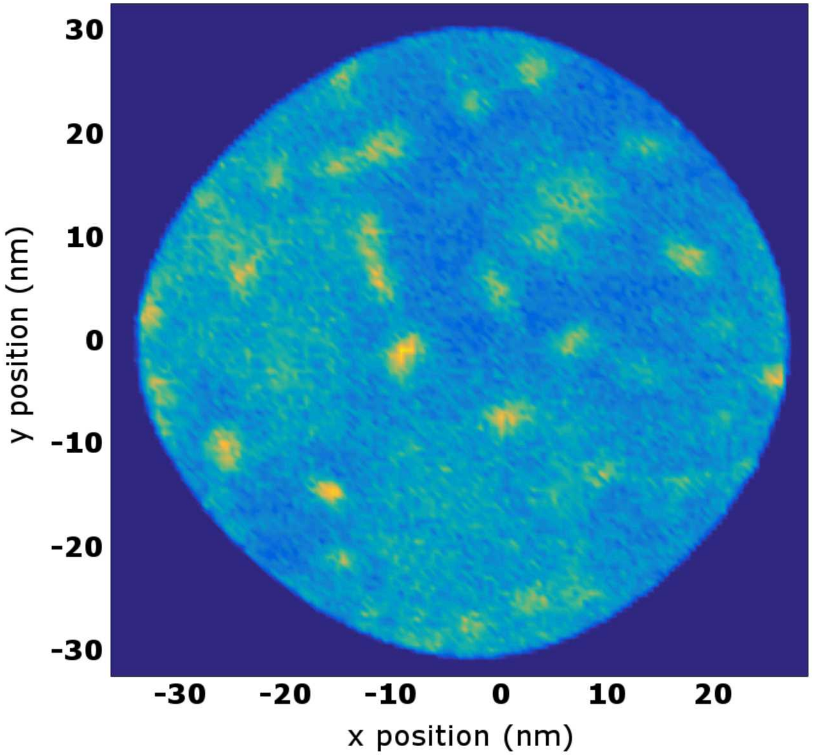
Isotope	Nat. Abun.	Mod. Abun.
^{50}Cr	4.34%	3.69%
^{52}Cr	83.79%	83.68%
^{53}Cr	9.50%	8.52%
^{54}Cr	2.37%	4.11%
^{54}Fe	5.85%	5.71%
^{56}Fe	91.75%	89.32%
^{57}Fe	2.12%	4.52%
^{58}Fe	0.28%	0.36%
^{27}Al	100%	100%

[1] A.G. Croff, (2002). ORIGEN-2.2 [Computer software]. Retrieved from https://www.oecd-nea.org/tools/abstract/detail/ccc-0371

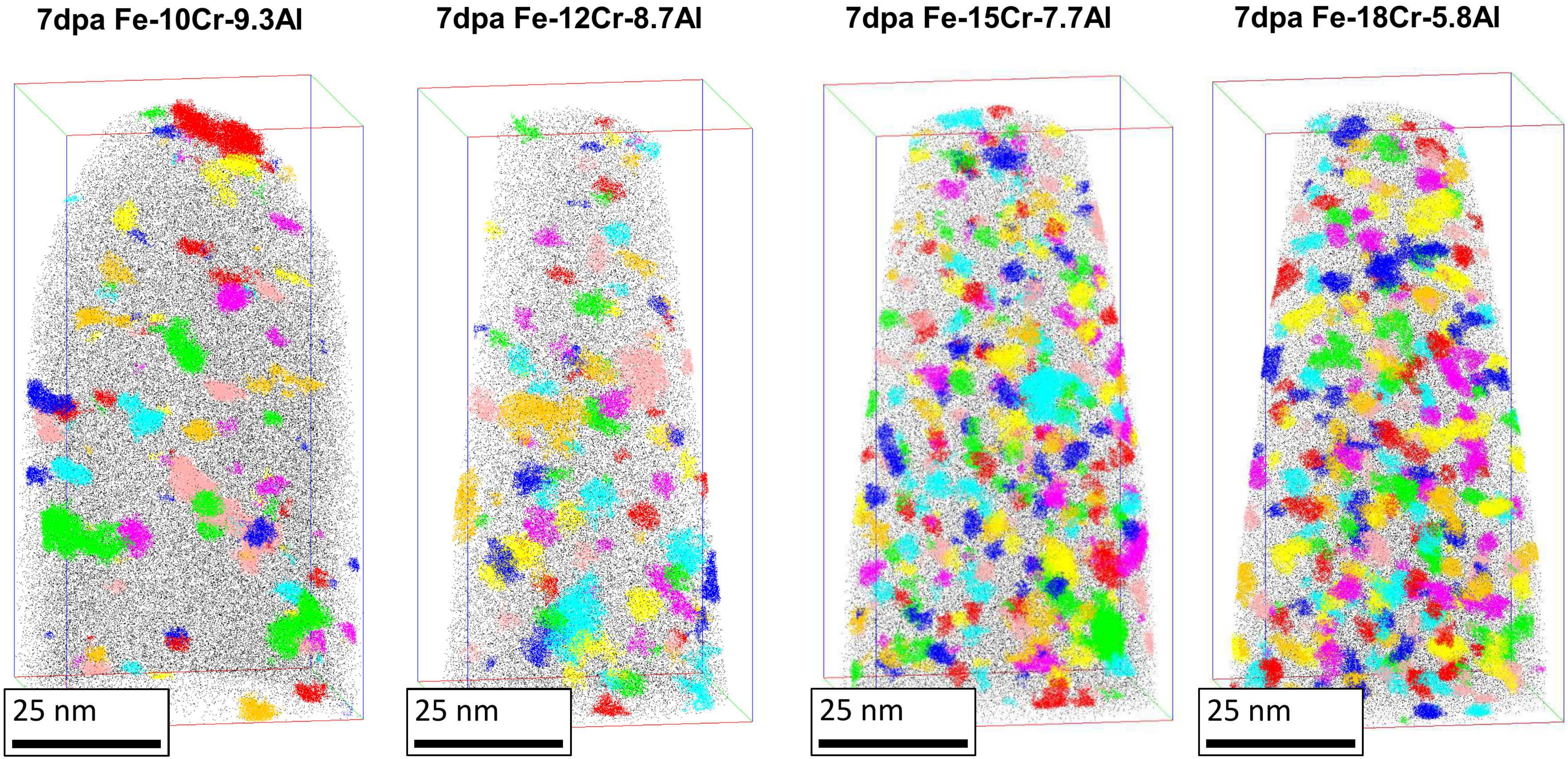
Challenges for APT Analysis – Aberration Artifacts

- Trajectory aberration effects are observed as regions of increased atomic density
  - Results in an artificial enrichment of Fe in the detected precipitate volume
  - Quantifying the magnitude of density variation allows for additional composition correction based on deviation from the expected atomic density





Increasing Cr, Decreasing Al



Total Volume Analyzed: 1.01×10^6 nm^3

Total Volume Analyzed: 4.08×10^6 nm^3

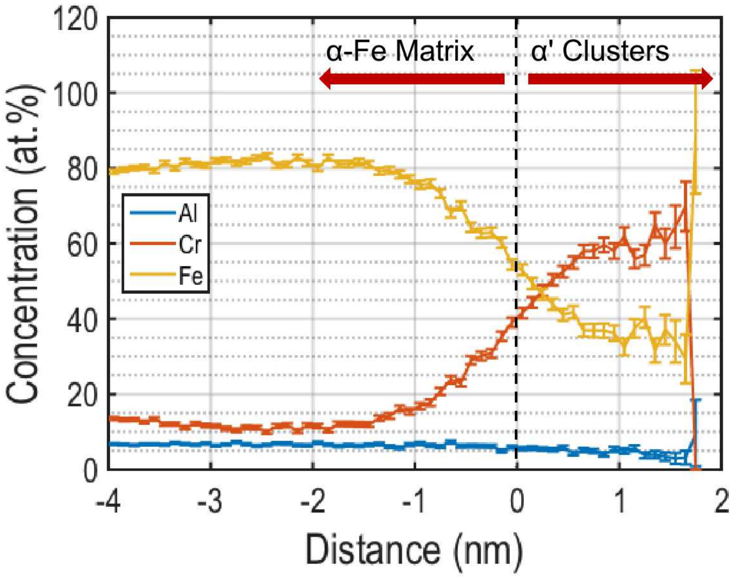
Total Volume Analyzed: 1.37×10^6 nm^3

Total Volume Analyzed: 7.53×10^5 nm^3

Reconstructions cropped to 50x50x100 nm

Summarized APT Results for Fe-Cr-Al Alloys

			Matrix Composition (at. %)			Average Cluster Composition (at. %)			Number Density	Volume Fraction	Average Radius
Alloy	**Irradiation Dose (dpa)**	**Irradiation Temp. (°C)**	Fe	Cr	Al	Fe	Cr	Al	($\times 10^{24}$ m^{-3})	(%)	(nm)
Fe-10Cr-9.3Al	7.0	320 ± 12.7	80.99	9.26	9.54	30.59 ± 8.50	65.55 ± 9.67	3.73 ± 2.50	0.51	1.75	1.48 ± 0.89
Fe-12Cr-8.7Al	7.0	320 ± 12.7	80.69	10.61	8.57	32.85 ± 6.85	62.86 ± 7.30	4.13 ± 1.60	0.69	2.93	1.77 ± 0.81
Fe-15Cr-7.7Al	7.0	320 ± 12.7	80.30	11.91	7.60	20.64 ± 7.90	75.93 ± 8.36	3.30 ± 1.66	2.24	5.46	1.55 ± 0.61
Fe-18Cr-5.8Al	0.8	355 ± 3.4	79.11	14.90	5.90	25.02 ± 6.38	72.62 ± 6.65	2.29 ± 1.06	3.14	5.29	1.47 ± 0.40
	1.8	382 ± 5.4	80.61	13.21	6.07	16.51 ± 7.00	81.37 ± 7.37	2.06 ± 1.08	2.93	6.99	1.62 ± 0.52
	7.0	320 ± 12.7	80.61	13.13	6.02	9.46 ± 6.93	88.20 ± 7.31	2.23 ± 1.28	1.92	6.56	1.79 ± 0.67

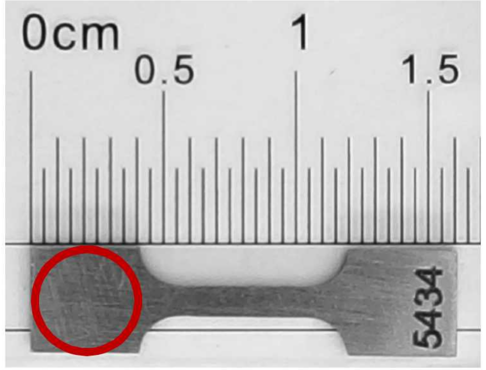


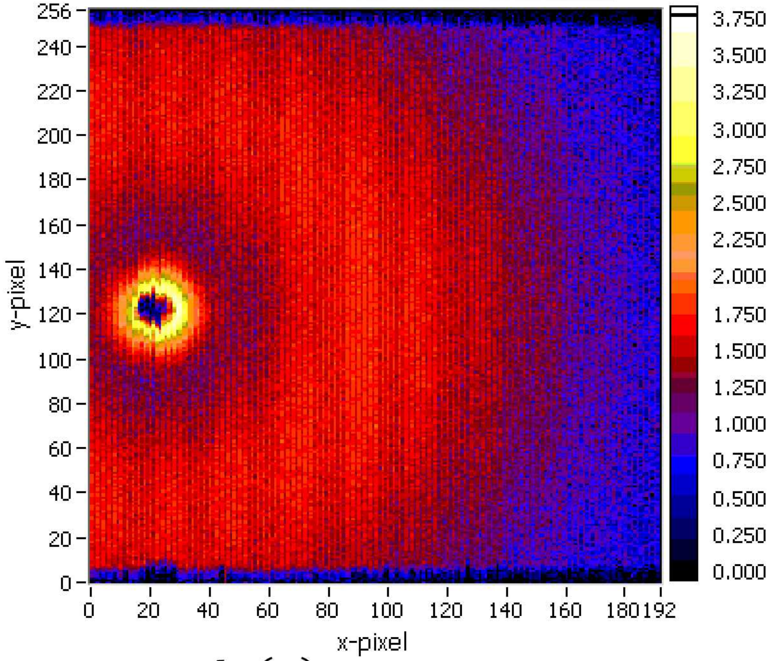
- ↑ dpa leads to ↑ avg. cluster size, ↓ cluster number density
  - Volume fraction saturates early, clusters continue to coarsen
- ↑ Cr generally leads to ↑ cluster number density, ↑ volume fraction
- α′ precipitate Cr content decreases with increasing alloy Al content
  - Al is also seen to be rejected from the precipitates volume

P.D. Edmondson, *et al.*, (2016). Irradiation-Enhanced α′ Precipitation in Model FeCrAl Alloys. *Scripta Materialia* **116** (2016) 112-116.
S.A. Briggs, *et al.*, (2017). A combined APT and SANS investigation of α′ phase precipitation in neutron-irradiated model FeCrAl alloys. *Acta Materialia* **129** (2017) 217-228.

Standard SANS Analysis Methodology

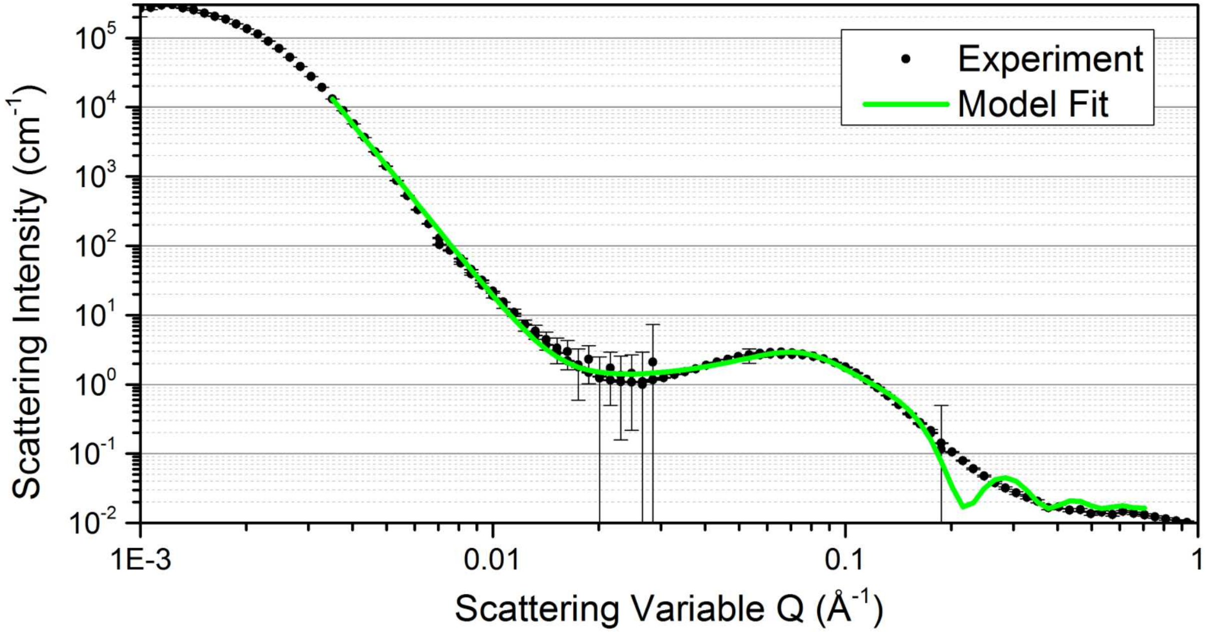
- All measurements performed at room temperature on broken half-tensile specimens at CG-2 general purpose SANS beamline at HFIR
- Final curves combine data from three detector configurations
  - Spans a greater momentum transfer (Q) range: $0.01 < Q < 10\ nm^{-1}$
- Fits assume monodisperse distribution of spherical precipitates interacting with an exclusion volume – not physical but should provide an adequate description of the precipitate microstructure





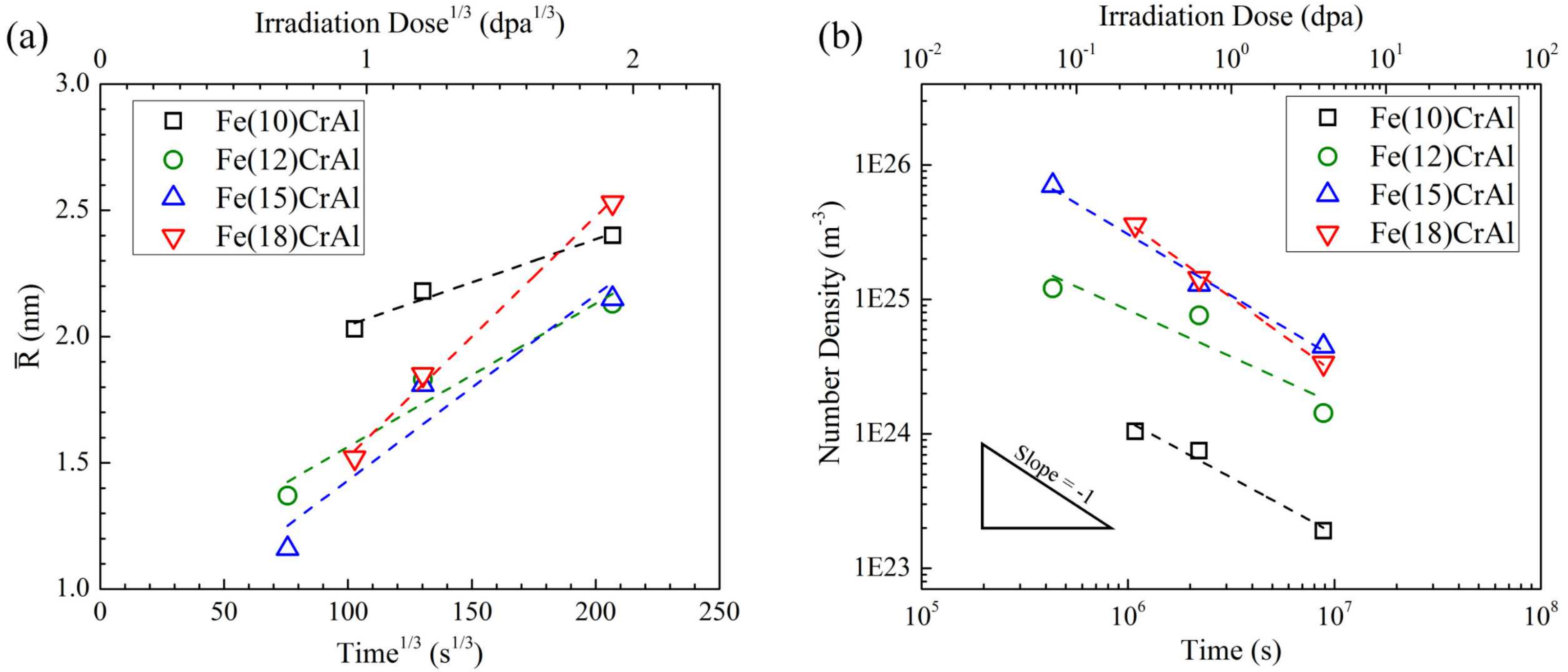
Convert 2D to 1D

Fit Model to Data



$$\frac{d\sigma(q)}{d\Omega} = n\Delta\rho^2 V^2 P(q,r)S(q) = I_0 P(q,r)S(q)$$

Discussion – LSW/UOKV Models for Precipitate Evolution

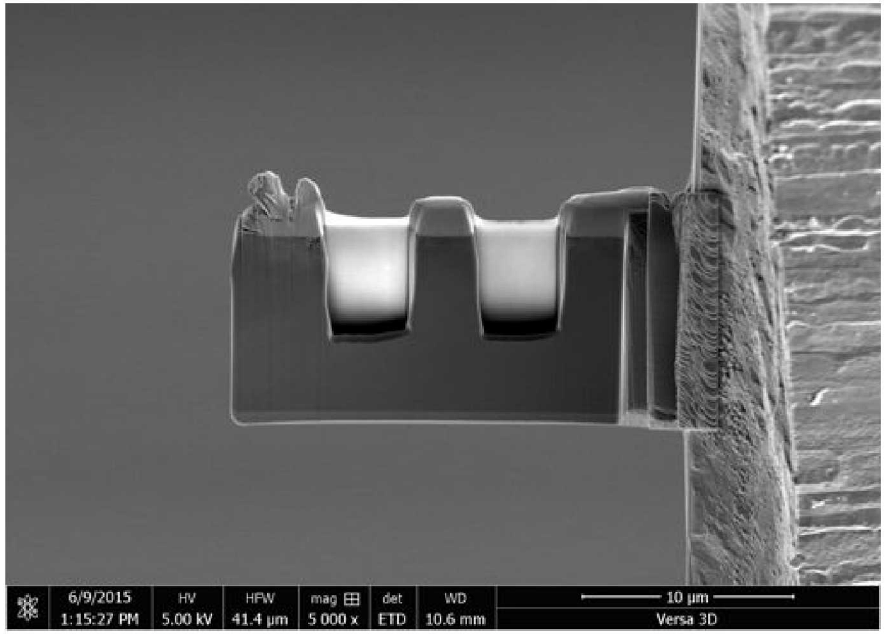


$$\overline{R}_{\alpha'}(t) = K_R t^{1/3} \qquad N_{\alpha'}(t) = K_N t^{-1}$$

- Suggests a similar mechanism for precipitation in irradiated Fe-Cr-Al as in thermally aged systems and that α′ precipitation is a diffusion-limited phenomenon
- Susceptibility for α′ precipitation in irradiated materials can likely be screened using thermal aging experiments

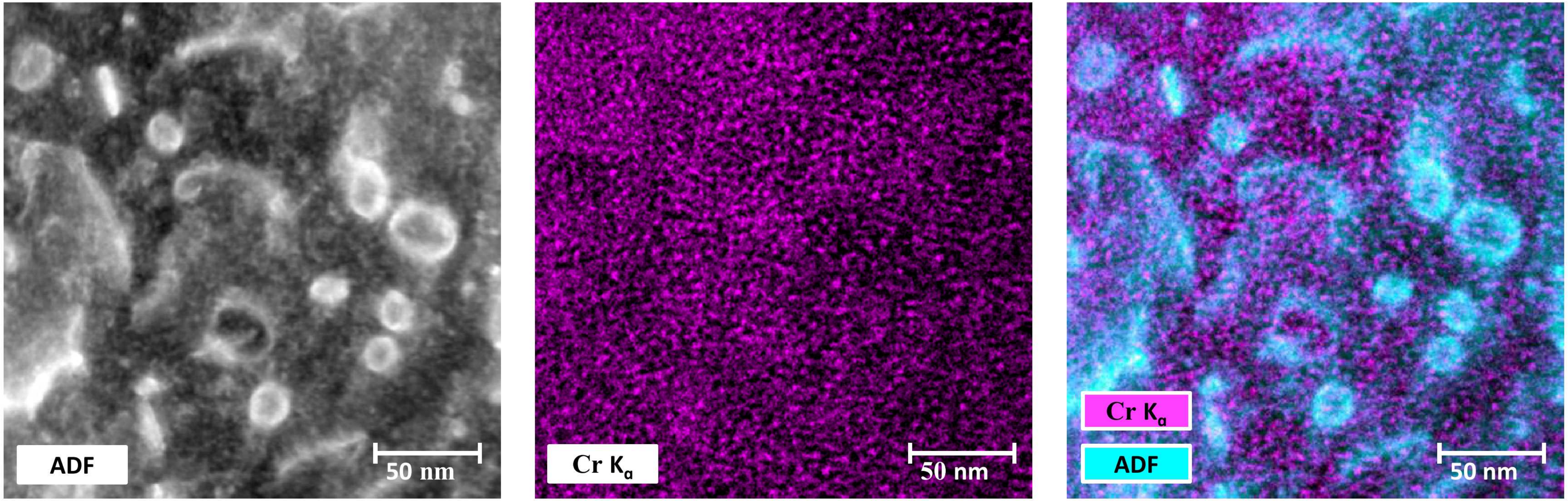
TEM/STEM Investigation

- Precipitates characterized using STEM/EDS on FEI Talos 200X at ORNL Low-Activation Materials Development & Analysis (LAMDA) Laboratory
- Samples prepared using FIB lift-out method
- Data collection with 2 nA beam on [110] zone axis allows for simultaneous imaging of precipitates (STEM/EDS) and dislocation loops (BF STEM)



STEM/EDS Results

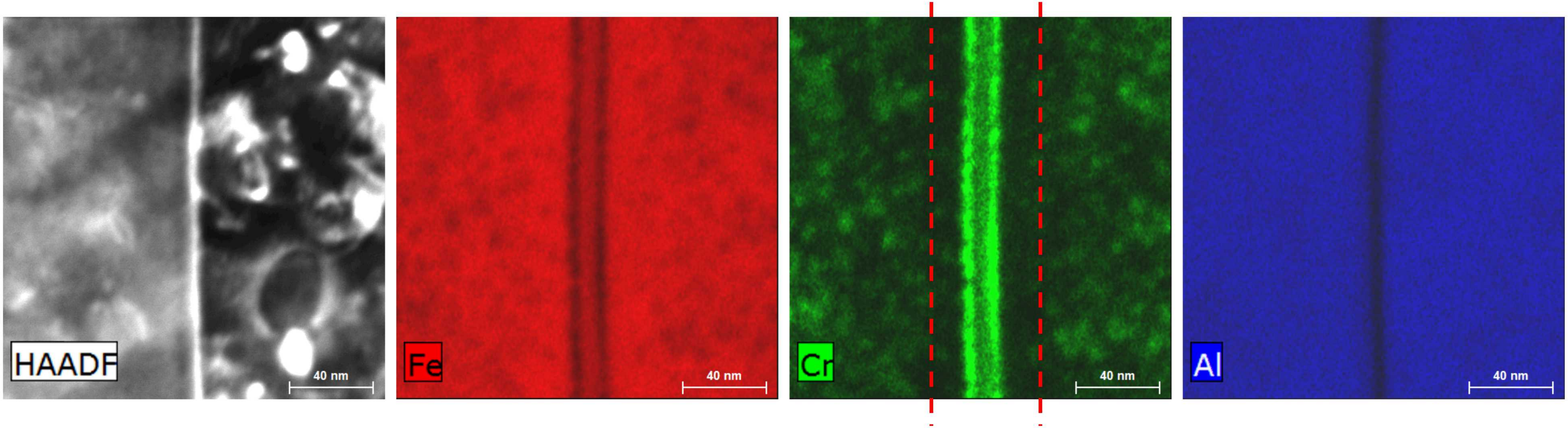
Fe-18Cr-5.8Al, 7.0 dpa, 320 °C



- Correlation of precipitates with dislocation loops can be studied by overlaying a [100] on-zone STEM image with STEM/EDS map for Cr-K_α x-rays
- α′ precipitates appears to nucleate homogeneously in the Fe-Cr-Al matrix and is not preferentially co-located with loops (supported by APT data)

STEM/EDS Results

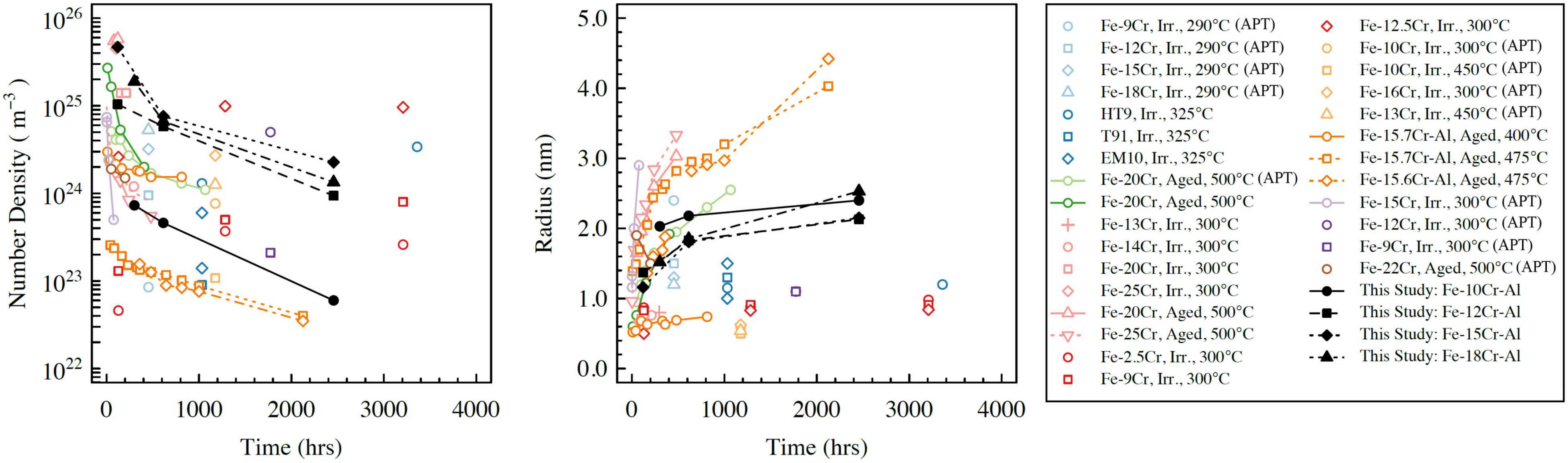
Fe-12Cr-8.7Al, 7.0 dpa, 320 °C



- Exception is observed at grain boundaries where precipitate denudation is observed
- Suggests that α′ precipitation might be mitigated using either a nanocrystalline material or by engineering a high density of defect sinks (i.e., ODS variants)

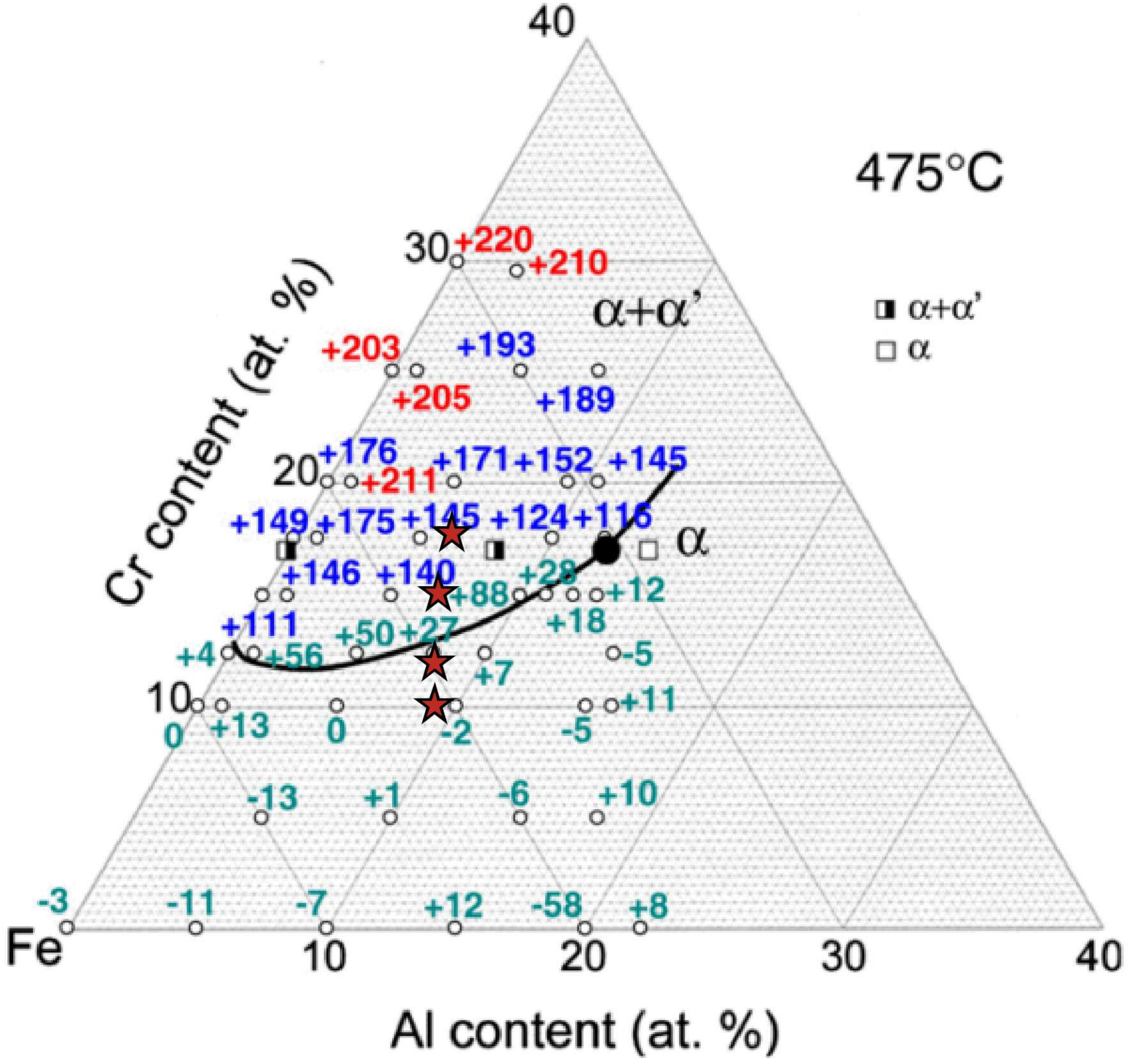
Observed Trends and Their Significance

- A high density of small precipitates form at low doses, coarsening over time with increasing dose
- Increasing Cr results in higher number densities and volume fractions of precipitates
- These general trends agree with past studies on aged and irradiated binary Fe-Cr and high-Cr ferritic alloys
- Large spread in reported data reinforces the importance of systematic studies of α′ precipitates



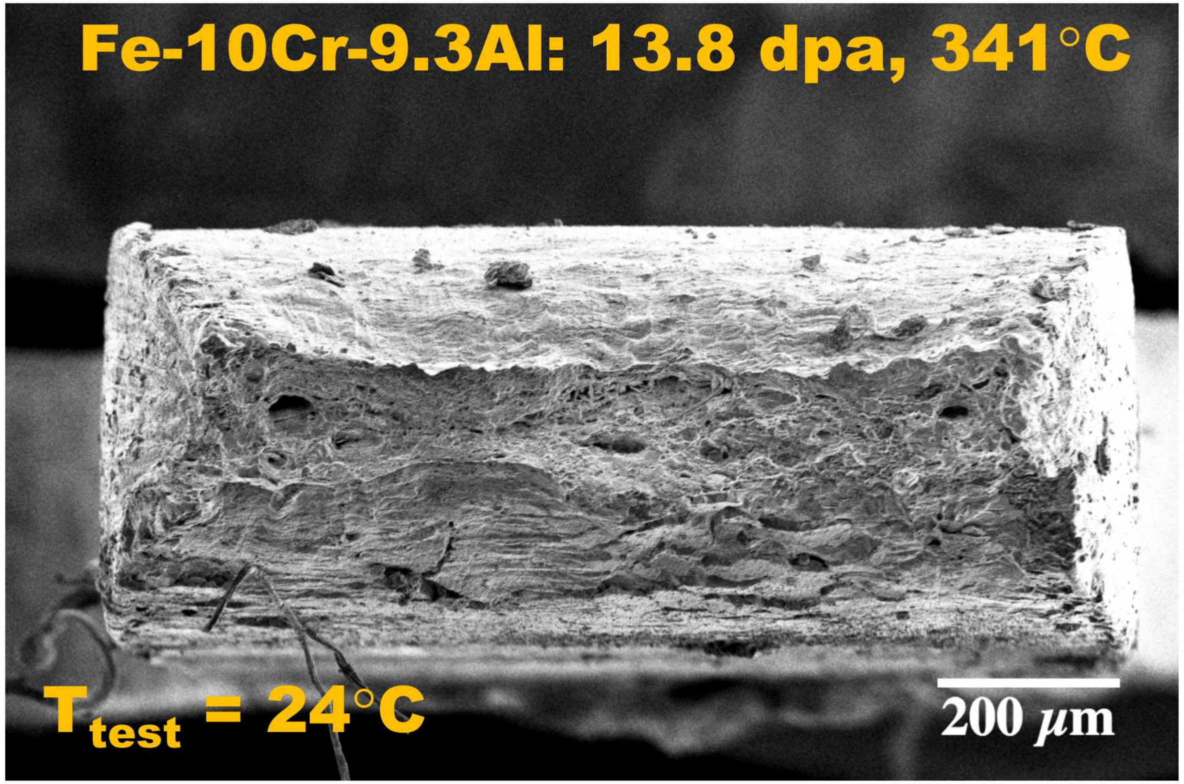
Observed Trends and Their Significance

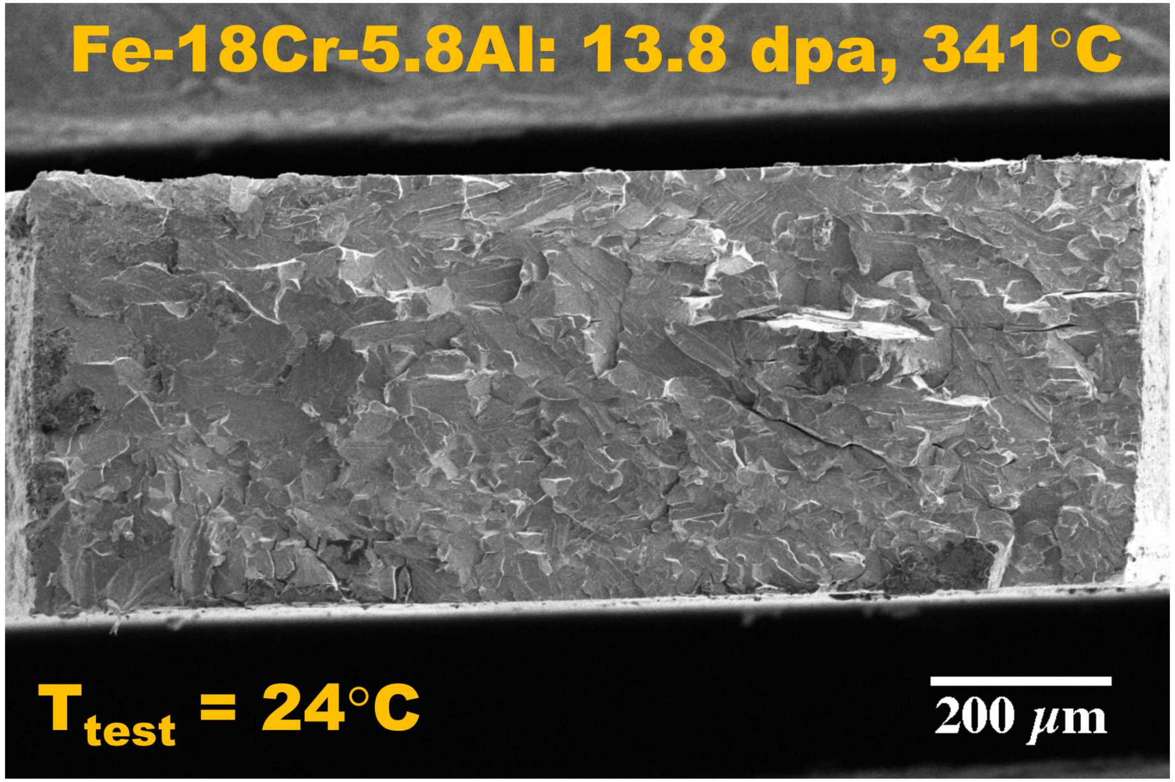
- Precipitation observed in all compositions, contrary to expectations based on phase boundary proposed by Kobayashi et al.
- This boundary is based on hardness measurements – suggests that not all precipitation is application limiting
- Phase boundary is for 475 °C, irradiations performed at ~320 °C – less Cr solubility expected at lower temperatures



Kobayashi, S., & Takasugi, T. (2010). Mapping of 475C embrittlement in ferritic Fe-Cr-Al alloys. *Scripta Materialia*, 63(11), 1104–1107.

Observed Trends and Their Significance



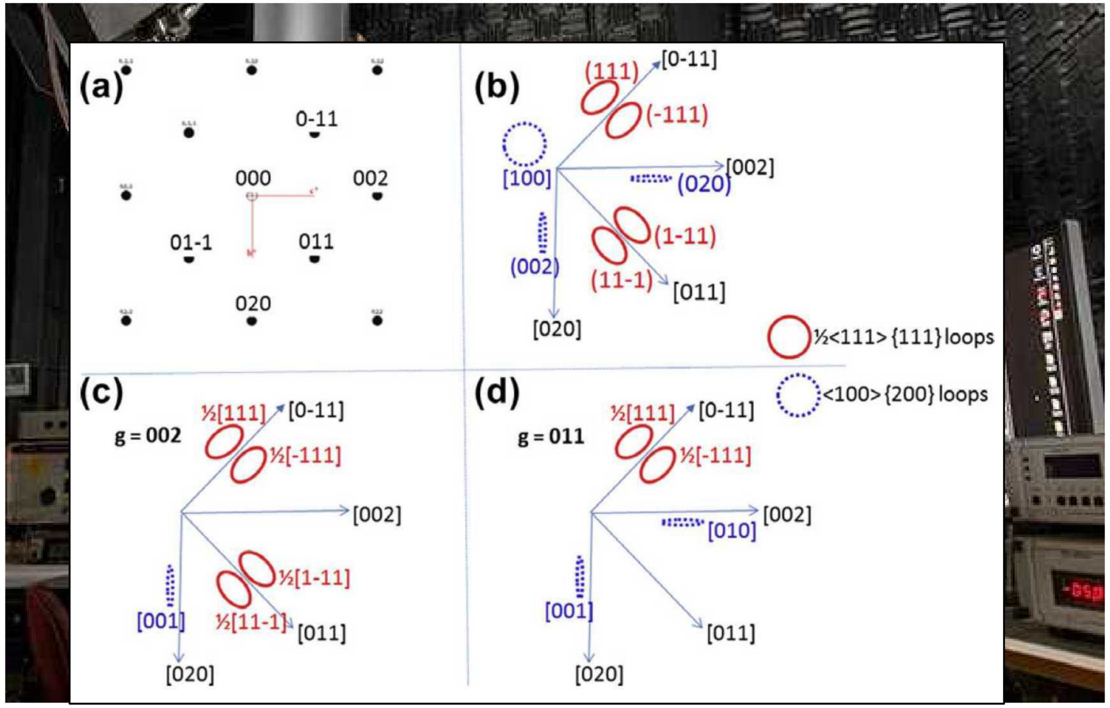


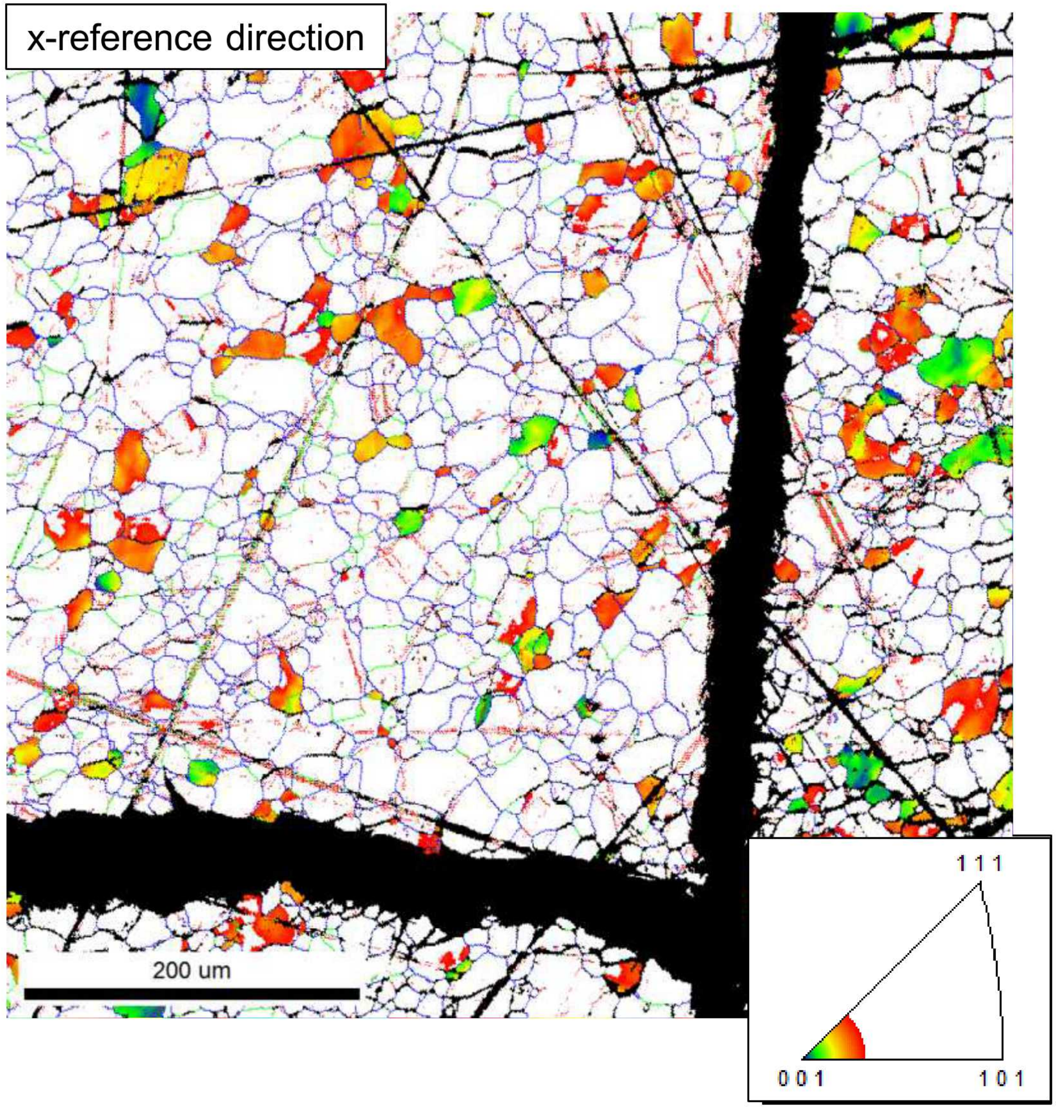
- α′ precipitation needs to be mitigated in these materials for nuclear applications
  - Minimize Cr content, maximize Al content while maintaining adequate mechanical/oxidation performance
  - Microstructural engineering may have some effect at reducing or retarding precipitation response

K.G. Field, S.A. Briggs, K. Sridharan, R.H. Howard, Y. Yamamoto. *Mechanical properties of neutron-irradiated model and commercial FeCrAl alloys.* Journal of Nuclear Materials **489** (2017) 118-128.

Additional Microscopy of Irradiated FeCrAl Alloys

In-Situ TEM Irradiation Experiments



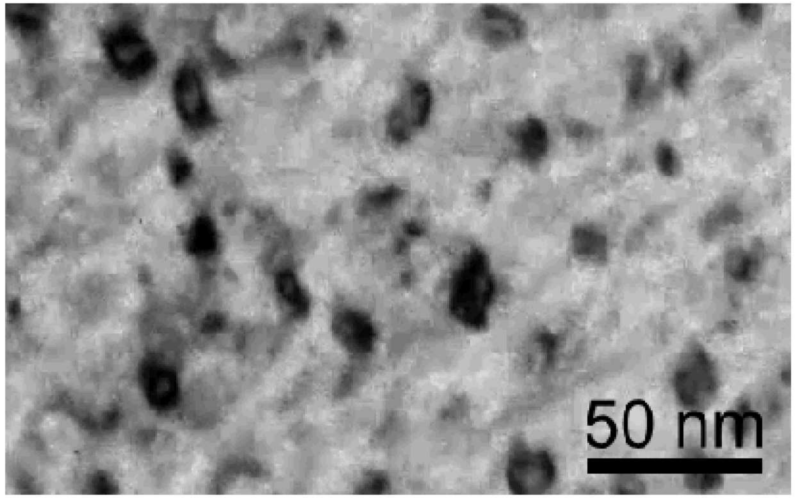


- Dislocation loops also contribute to hardening & embrittlement in irradiated Fe-Cr-based alloys and are of interest for determining alloy viability and radiation tolerance
- Site-specific FIB lift-outs guarantee orientation required for two-beam imaging is contained within specimens

In-Situ TEM Irradiation Experiments

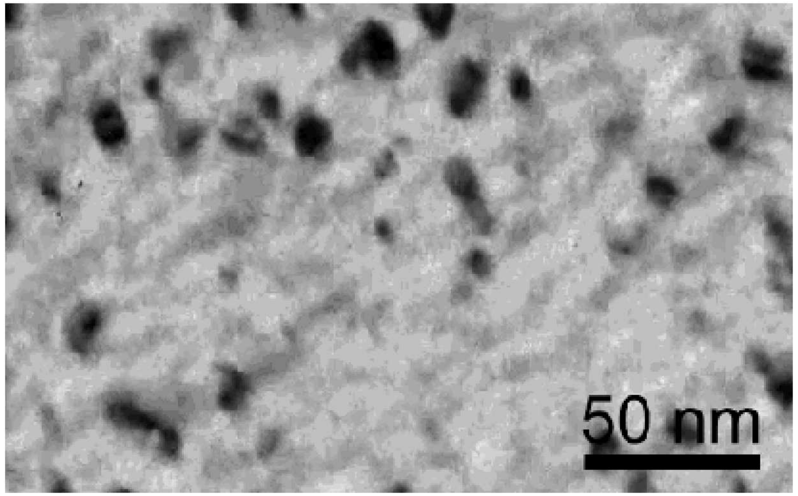
Fe-10Cr-4.8Al, Speed 25x

$Near\ [001]\ zone\ axis, g = 011$



Defect Hopping:

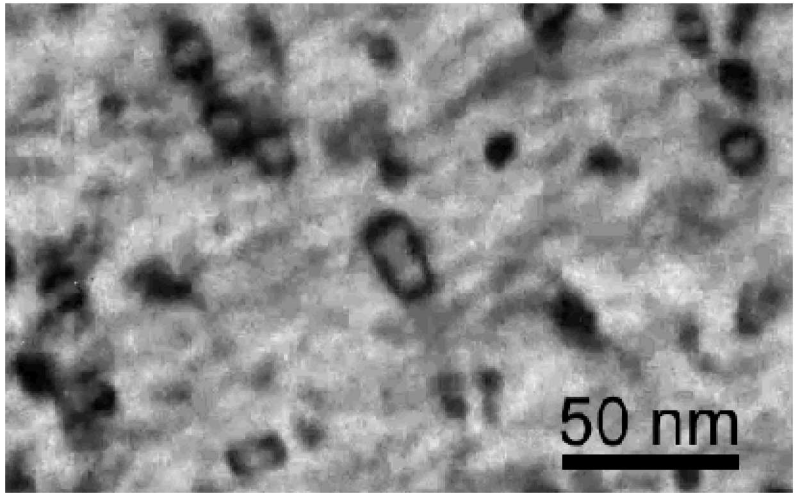
$Near\ [001]\ zone\ axis, g = 011$



Defect loss/Defect shrinking:

Fe-15Cr-3.9Al, Speed 25x

$Near\ [001]\ zone\ axis, g = 011$



Defect-Defect Interaction/Defect growth:

- Ion irradiation in-situ with TEM provides insight regarding dislocation loop evolution with dose

- Additionally allows for dynamic observation of loop microstructural evolution and defect interactions

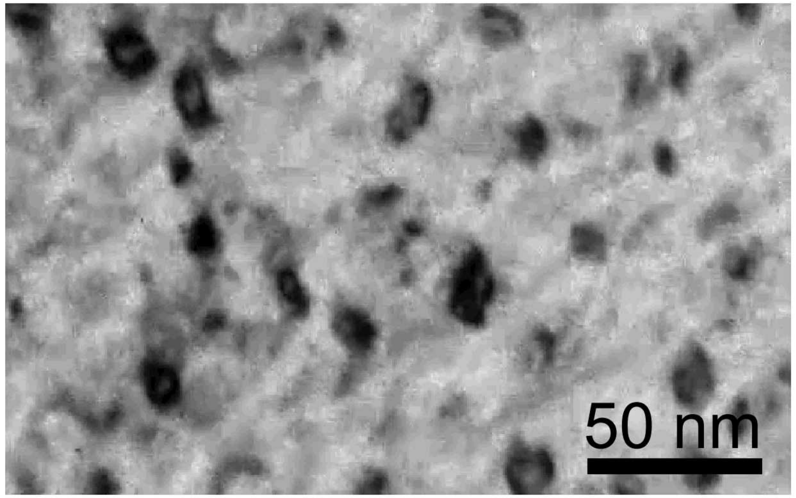
In-Situ TEM Irradiation Experiments

Sandia National Laboratories

Fe-10Cr-4.8Al, Speed 25x

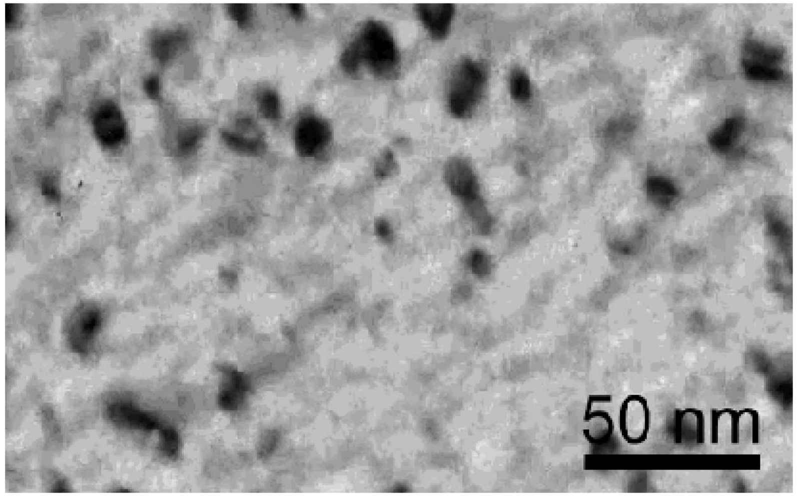
Fe-15Cr-3.9Al, Speed 25x

$Near\ [001]\ zone\ axis, g = 011$



Defect Hopping:
Infrequent Observation

$Near\ [001]\ zone\ axis, g = 011$



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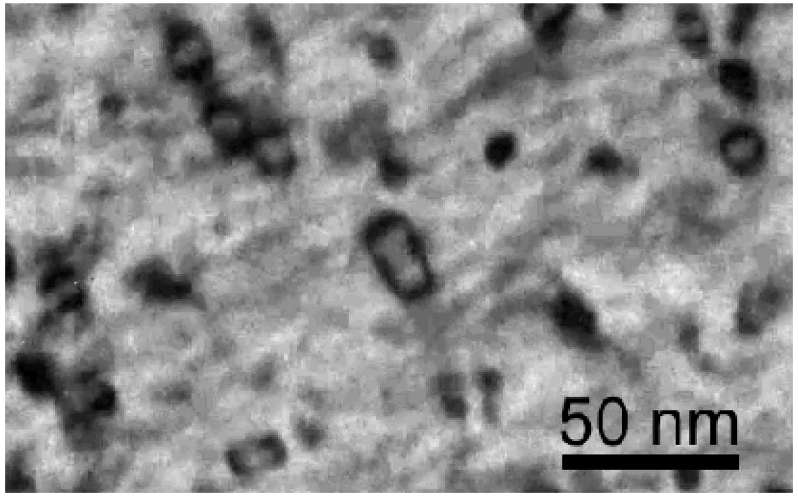
$Near\ [001]\ zone\ axis, g = 011$



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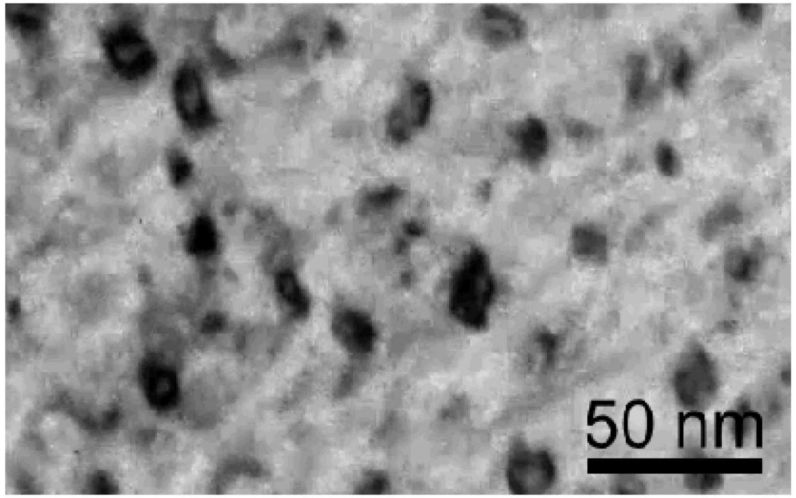
J.C. Haley, et al. Dislocation loop evolution during in-situ irradiation of model FeCrAl alloys. *Acta Materialia* **136** (2017) 390-401.

In-Situ TEM Irradiation Experiments

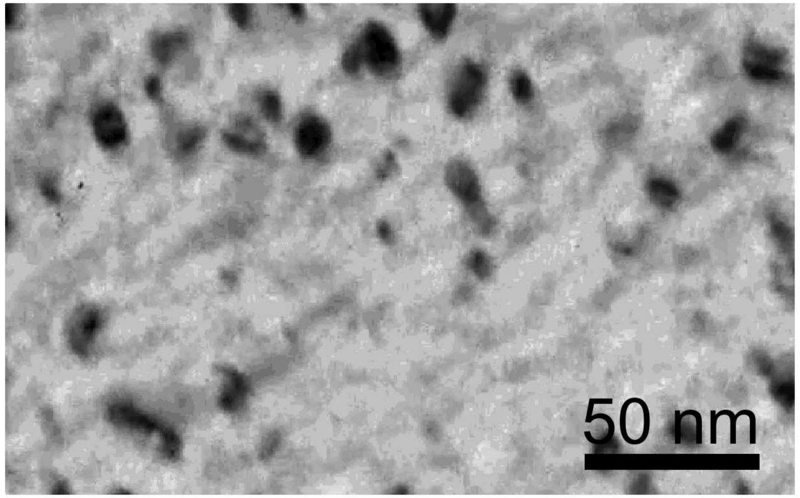
Fe-10Cr-4.8Al, Speed 25x

$Near\ [001]\ zone\ axis, g = 011$



Defect Hopping:
Infrequent Observation

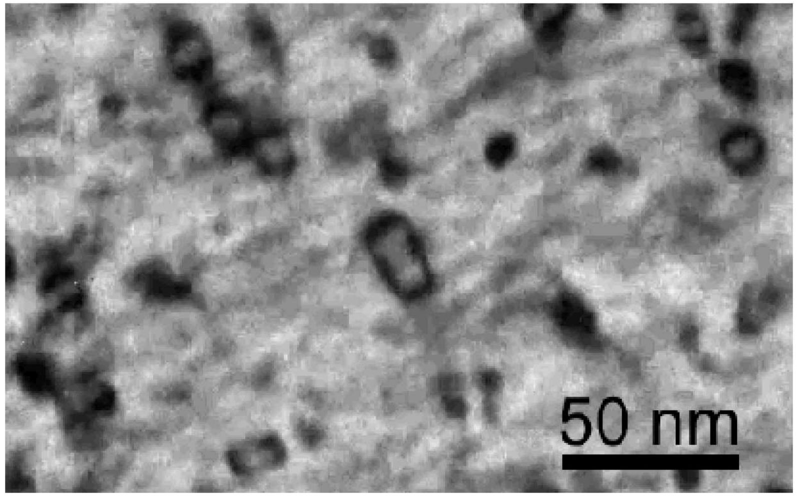
$Near\ [001]\ zone\ axis, g = 011$



Defect loss/Defect shrinking:
Frequent Observation

Fe-15Cr-3.9Al, Speed 25x

$Near\ [001]\ zone\ axis, g = 011$



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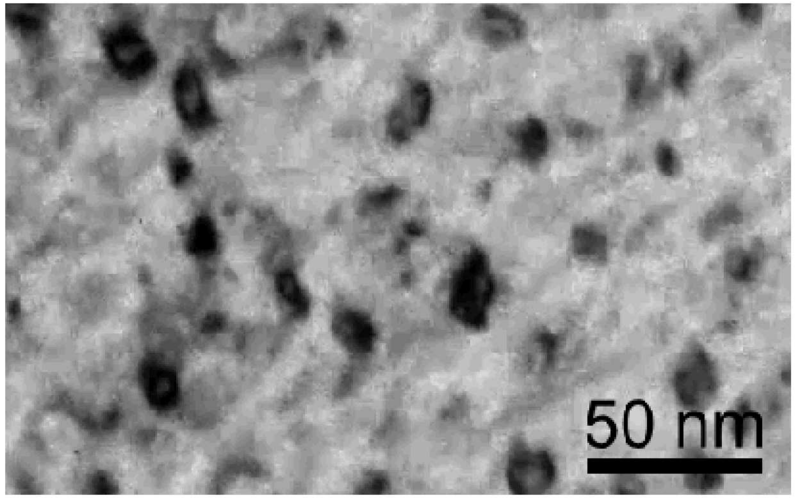
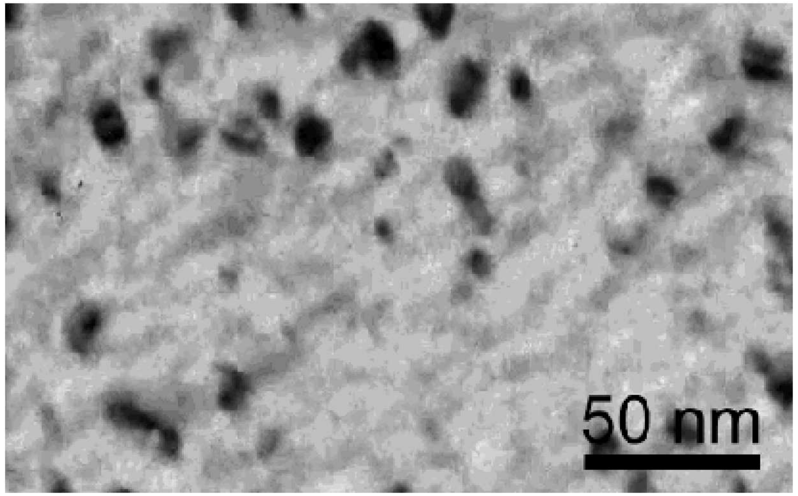


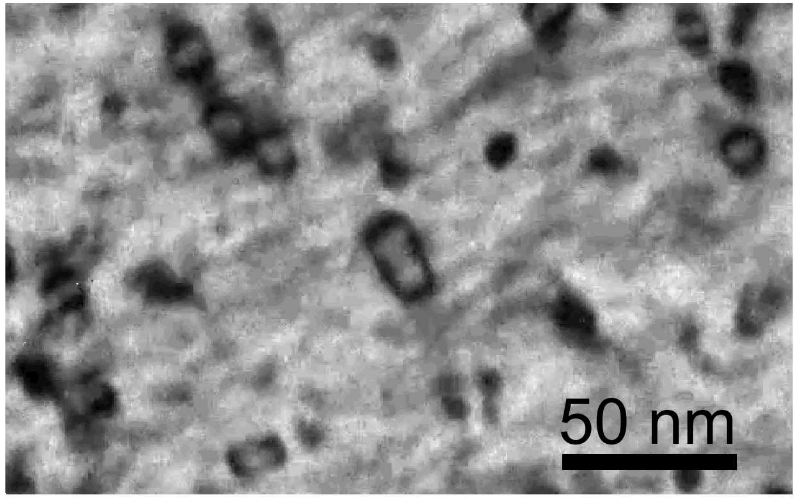
Defect Hopping:
Infrequent Observation

$Near\ [001]\ zone\ axis, g = 011$



Defect loss/Defect shrinking:
Frequent Observation

$Near\ [001]\ zone\ axis, g = 011$



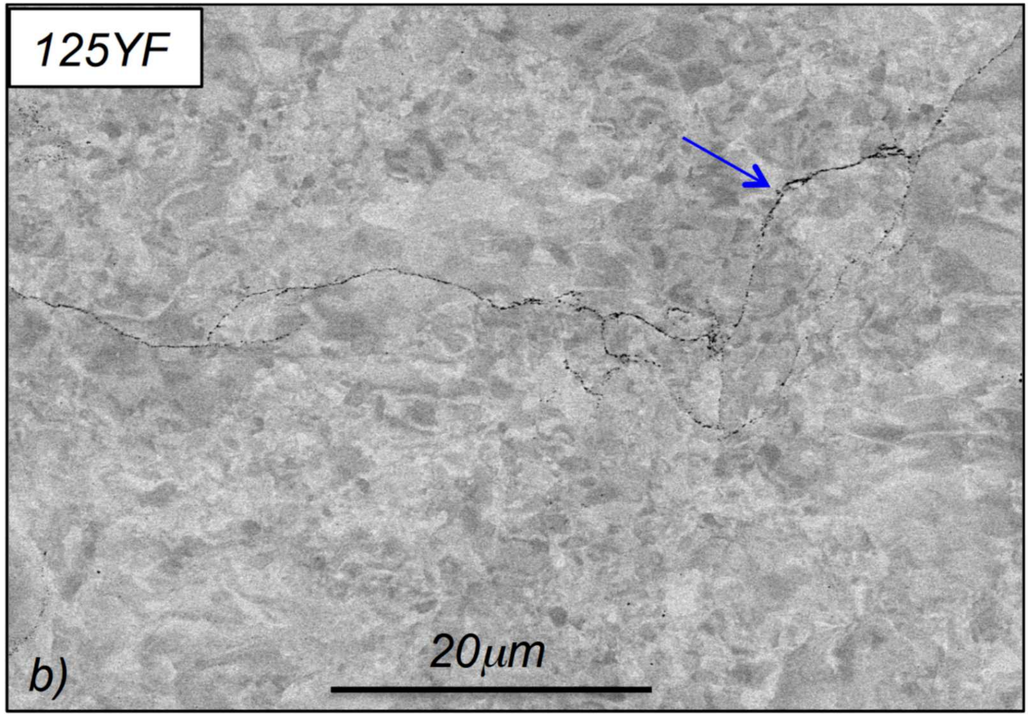
Defect-Defect Interaction/Defect growth:
Moderately Frequent Observation

- Ion irradiation in-situ with TEM provides insight regarding dislocation loop evolution with dose
- Additionally allows for dynamic observation of loop microstructural evolution and defect interactions

J.C. Haley, et al. Dislocation loop evolution during in-situ irradiation of model FeCrAl alloys. *Acta Materialia* **136** (2017) 390-401.

ODS FeCrAl Variants

- One Fe-12Cr-5Al+Y_2O_3 (wt.%) powder metallurgy FeCrAl variant selected for study
- Gas atomized Fe-12Cr-5Al power was ball milled with Y_2O_3 powder in Ar for 40 hrs, degassed for 24 hrs at 300 °C, and extruded at 950 °C.[1]
- 100-300 nm grain sizes, with some alumina stringers apparent



ID	Composition, wt.%								
	Fe	**Cr**	**Al**	**Y**	Si	C	S	O	N
125YF	**82.99**	**11.67**	**4.73**	**0.19**	0.010	0.020	0.0030	0.192	0.0202

Capsule ID	Exposure Time (hrs)	Neutron Flux (n/cm^2s) E > 0.1 MeV	Neutron Fluence (n/cm^2) E > 0.1 MeV	Dose Rate (dpa/s)	Dose (dpa)	Irradiation Temperature (°C)
FCAT-01	590	1.10×10^{15}	2.17×10^{21}	9.8×10^{-7}	1.9	194.5 ± 37.9
FCAT-02	590	1.04×10^{15}	2.17×10^{21}	9.3×10^{-7}	1.8	363.6 ± 23.1
FCAT-03	590	1.10×10^{15}	2.17×10^{21}	9.8×10^{-7}	1.9	559.4 ± 28.1

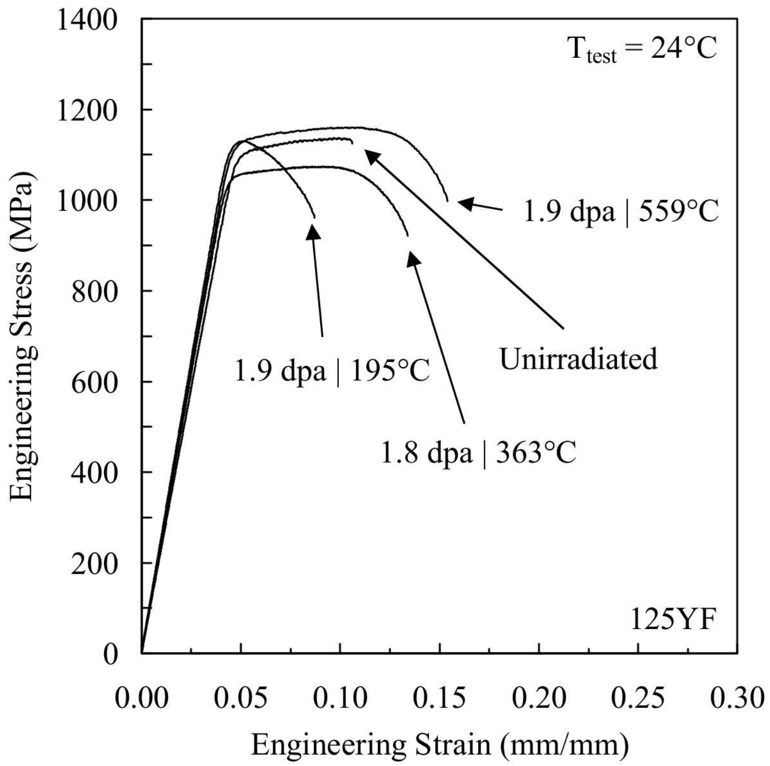
[1] Dryepondt, S., *et al.* (2015). Oak Ridge National Laboratory Development of ODS FeCrAl Alloys for Accident-Tolerant Fuel Cladding. ORNL/TM-2015/539.

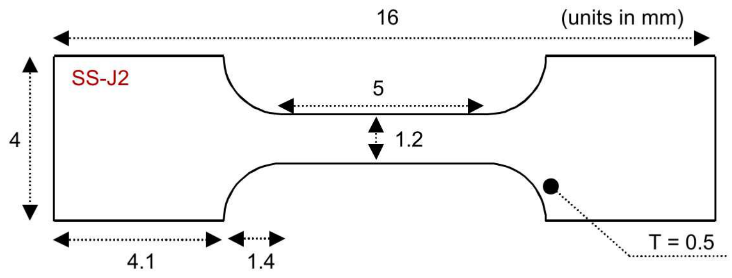
ODS FeCrAl Mechanical Properties at ~2 dpa

- Tensile tests performed in ambient air
- Medium to elevated temperature irradiations show little change in mechanical properties

Specimen	Irradaition Temperature (°C)	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Uniform Elongation (%)	Tensile Elongation (%)
OD34	-	1085	1137	4.8	5.8
OD01	195	1108	1130	0.8	5.0
OD03	363	1037	1074	5.0	9.7
OD06	559	1104	1160	6.2	11.2

- Low temperature irradiation showed embrittlement
  - *Due to cluster stability even at low dose?*

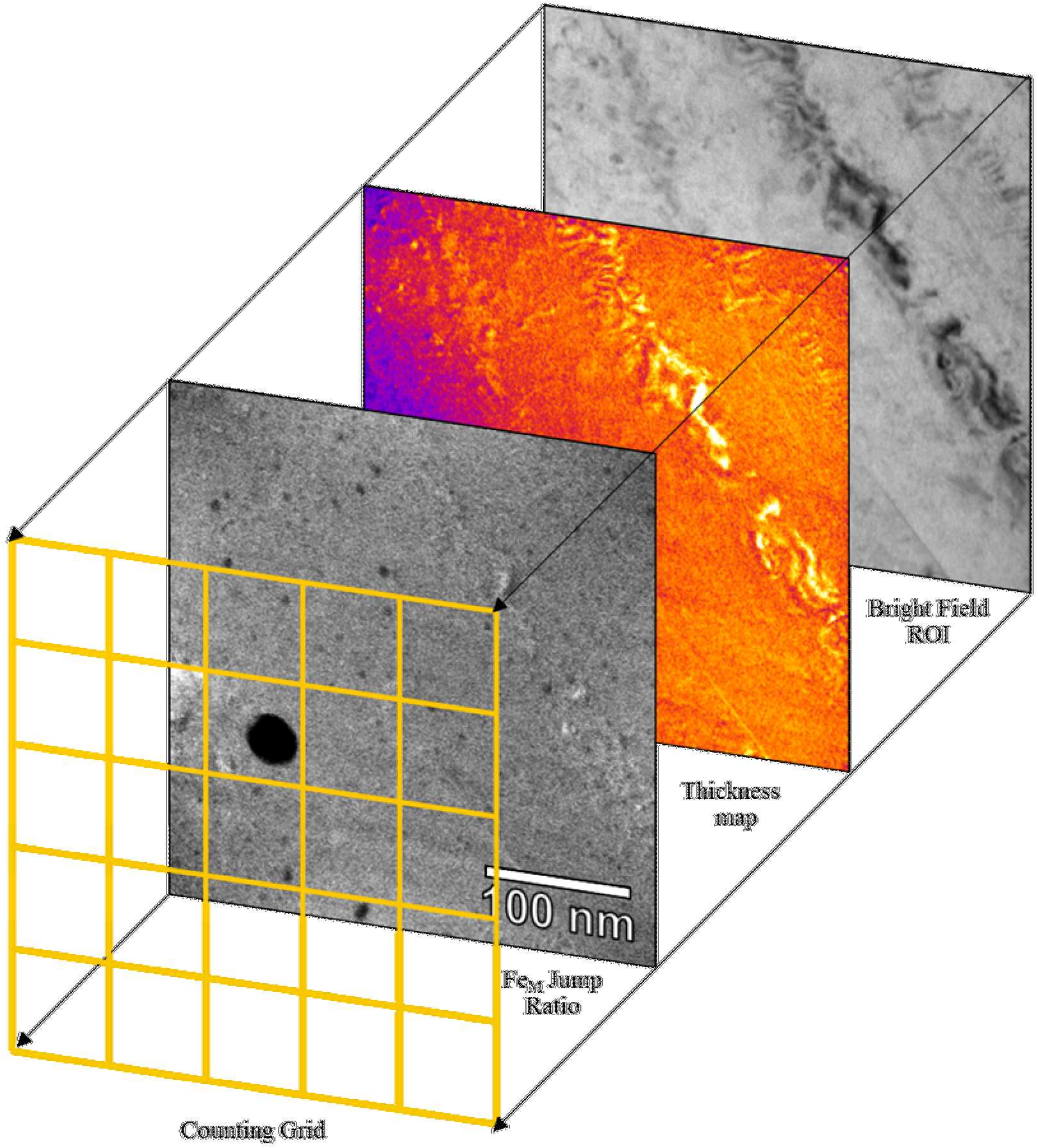




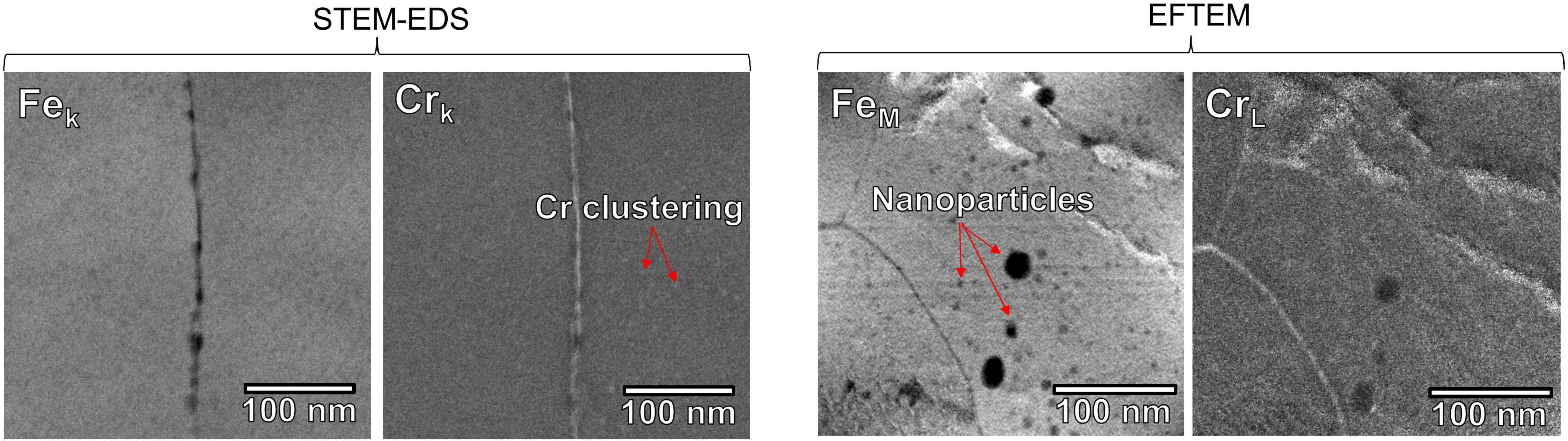
EFTEM Data Configuration and Analysis

- EFTEM Configuration:
  - JEOL 2100F in LAMDA at ORNL
  - Fe_M jump-ratio map & thickness map per RO
    - 10 eV slits
    - Manual drift correction

- EFTEM analysis:
  - Subdivided into 25 area bins
  - B/C Correction + Mean Image Filter
  - Manually counted precipitates using ImageJ
  - Volume calculated using avg. thickness in each bin



Radiation-enhanced precipitation (α′)

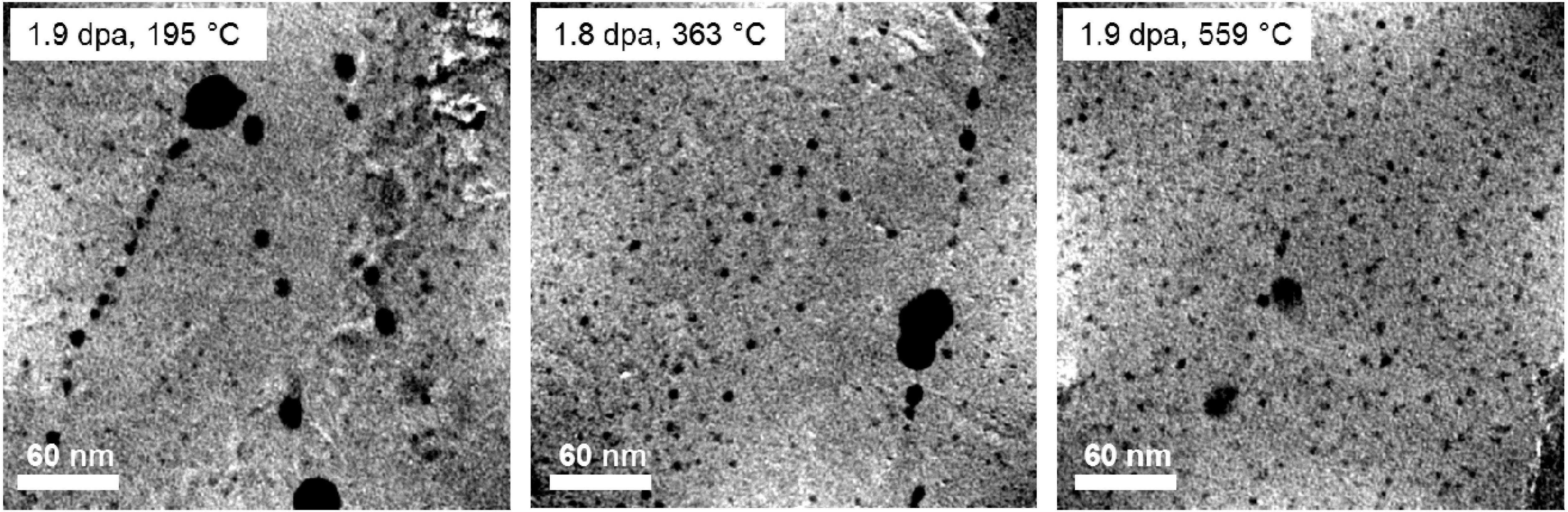


- FeCrAl alloys have been shown to be susceptible to Cr-rich α′ precipitation under neutron irradiation[1]
- STEM-EDS reveals possible Cr-clustering but most likely weak composition variance to matrix
- EFTEM insensitive to detection of Cr-cluster found in STEM-EDS

[1]Briggs et al. Acta Mat. 129, 2017, 217-228

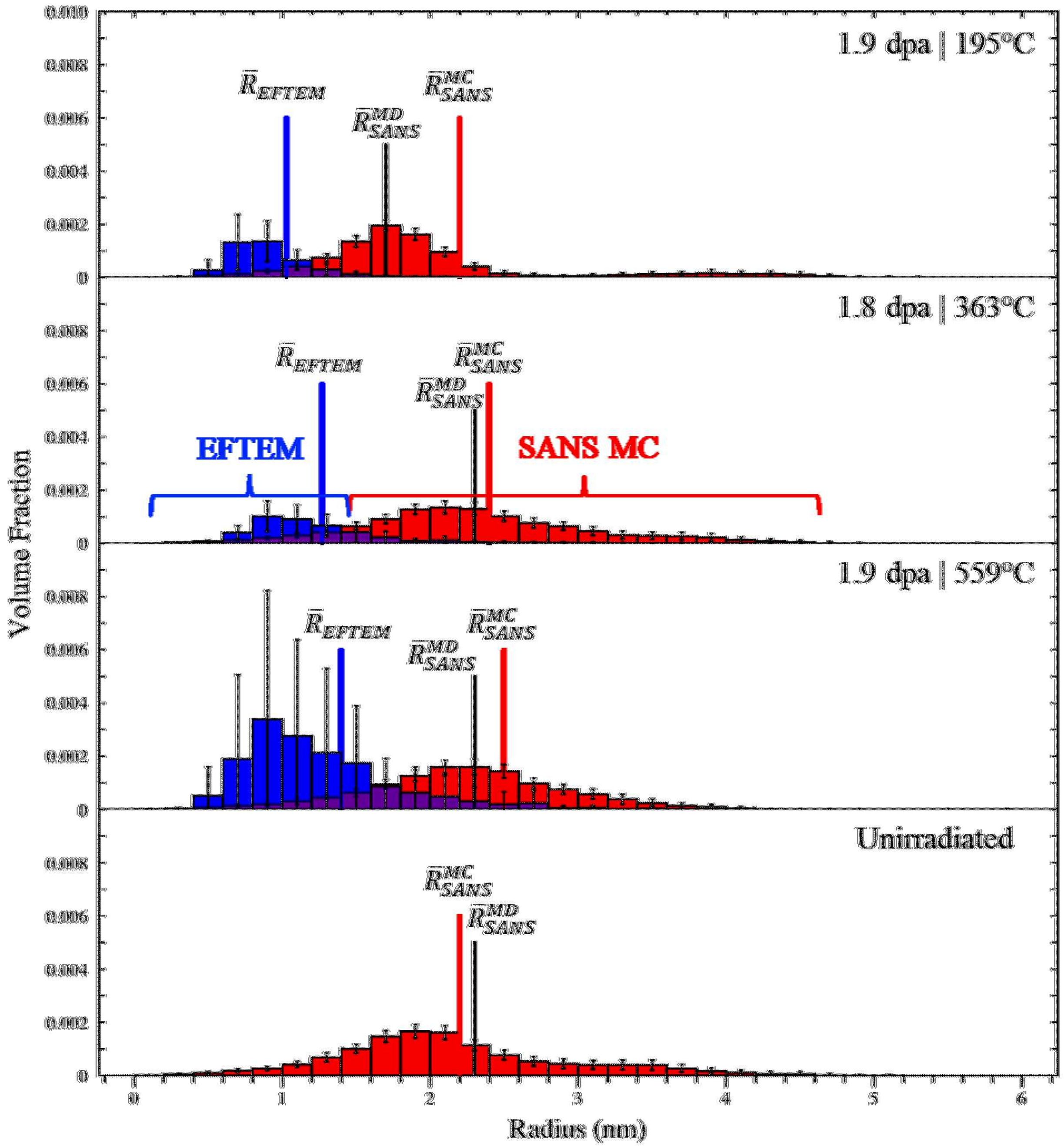
EFTEM Qualitative Observations

- Bimodal size distribution apparent
  - Larger precipitates decorate grain boundaries (likely $Y_3Al_5O_{12}$ (YAG) and alumina phases)
  - Finer precipitate dispersion throughout bulk material
- Heterogeneous distributions – large grain-to-grain variation



Size Distributions

- Peak shifts and distribution broadening/tailing towards larger sizes suggest:
  - 1.9 dpa | 195° C: NP instability
  - 1.8 dpa | 363° C: NP stability
  - 1.9 dpa | 559° C: NP coarsening
- Difference in size distributions between SANS and EFTEM due to varying resolution limits
- Large error in EFTEM results are indicative of technique errors and grain-to-grain heterogeneity
- Reasonable agreement between the monodispersed (MD) approximation and ”brute-force” Monte Carlo (MC) model mean size suggests monodispersed model is a reasonable first-order analysis



A-ratio determination (composition + structure)

Particle	ρ (g/cm^3)	$\Delta\rho^2_{nuclear}$ (×10^{-12} Å)	$\Delta\rho^2_{magnetic}$ (×10^{-12} Å)	Calculated A-ratio
YAG - $Y_3Al_5O_{12}$	4.56	2.73	0.16	6.68
YAP – $YAlO_3$	5.35	1.26	0.16	13.30
YAM – $Y_4Al_2O_9$	4.56	5.18	0.16	3.99
Al_2O_3	3.95	1.16	0.16	14.40
AlN	3.26	37.5	0.16	42.34
Y_2O_3	5.01	5.52	0.16	3.81
α'	7.20	0.11	0.16	2.44

Specimen ID	Irradiation Temp. (°C)	A-ratio (unitless)	
		SANS MD	SANS Monte Carlo
OD34	-	1.75±0.05	2.75±0.54
OD01	195	1.31±0.08	2.06±0.37
OD03	363	1.63±0.05	2.51±0.48
OD06	559	1.96±0.11	2.32±0.40

Contrast (ρ^2) independant (SANS Monte Carlo)

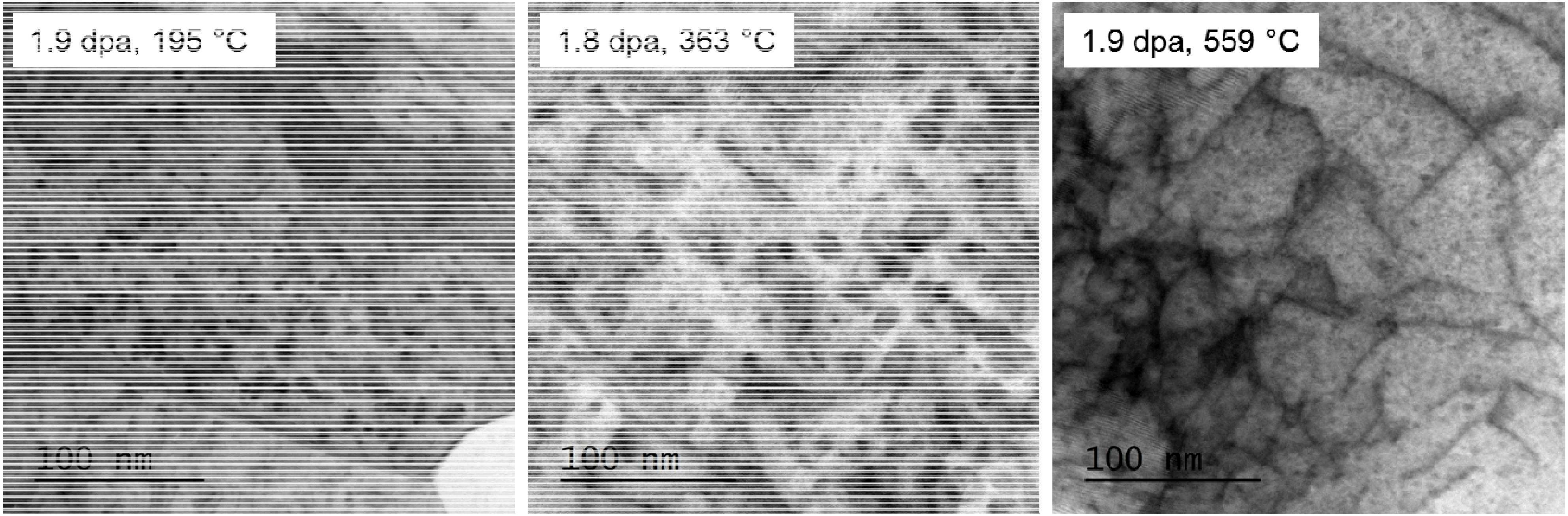
Contrast (ρ^2) used as a fitting parameter (SANS MD)

Reduction after low temperature irradiation -> instability?

- Highly dependent on stoichiometry, chemical composition, and structure (density)
- A-ratio of 1.75-2.75 in the as-received condition suggests far-from perfect particle phases (amorphization, Fe/Cr substitution, etc.)
- Reduction after irradiation could be due to particles changing over the course of irradiation or the addition of the Cr-rich α' phase in OD01 and OD03

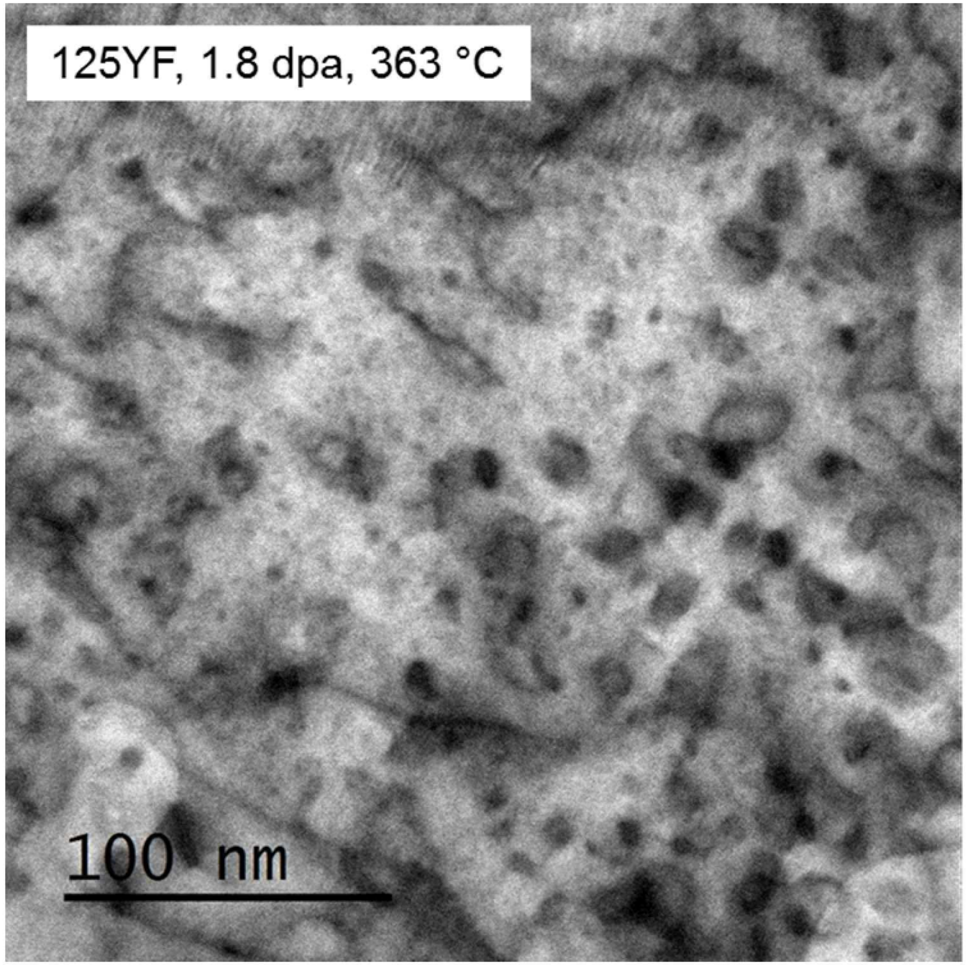
125YF Dislocation Loop Microstructures

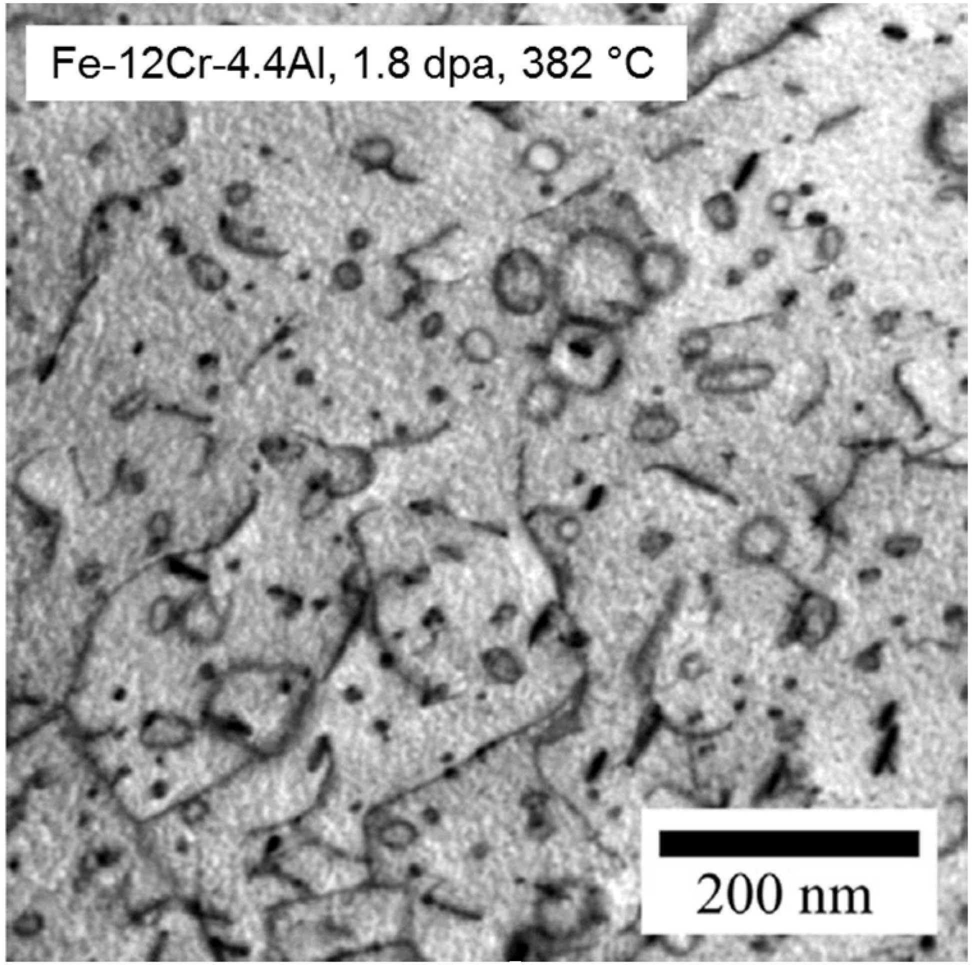
- Low temp irradiation resulted in high density of small, mostly black-dot loop defects
- Medium temp irradiation yielded lower density of larger, more well defined loop structures
- No loop structures observed in high temp irradiation



Comparison to non-ODS Alloys

- Higher density of smaller loops observed in ODS variant
- Smaller grain size may also contribute to observed effect





[1] Field, K. G., *et al*. (2015). Radiation tolerance of neutron-irradiated model Fe-Cr-Al alloys. *Journal of Nuclear Materials*. 465, 746-755.

Studies at Sandia's I^3TEM Facility

Sandia's I^3TEM Facility

- Direct real time observation
  tion, ion
  , or both with
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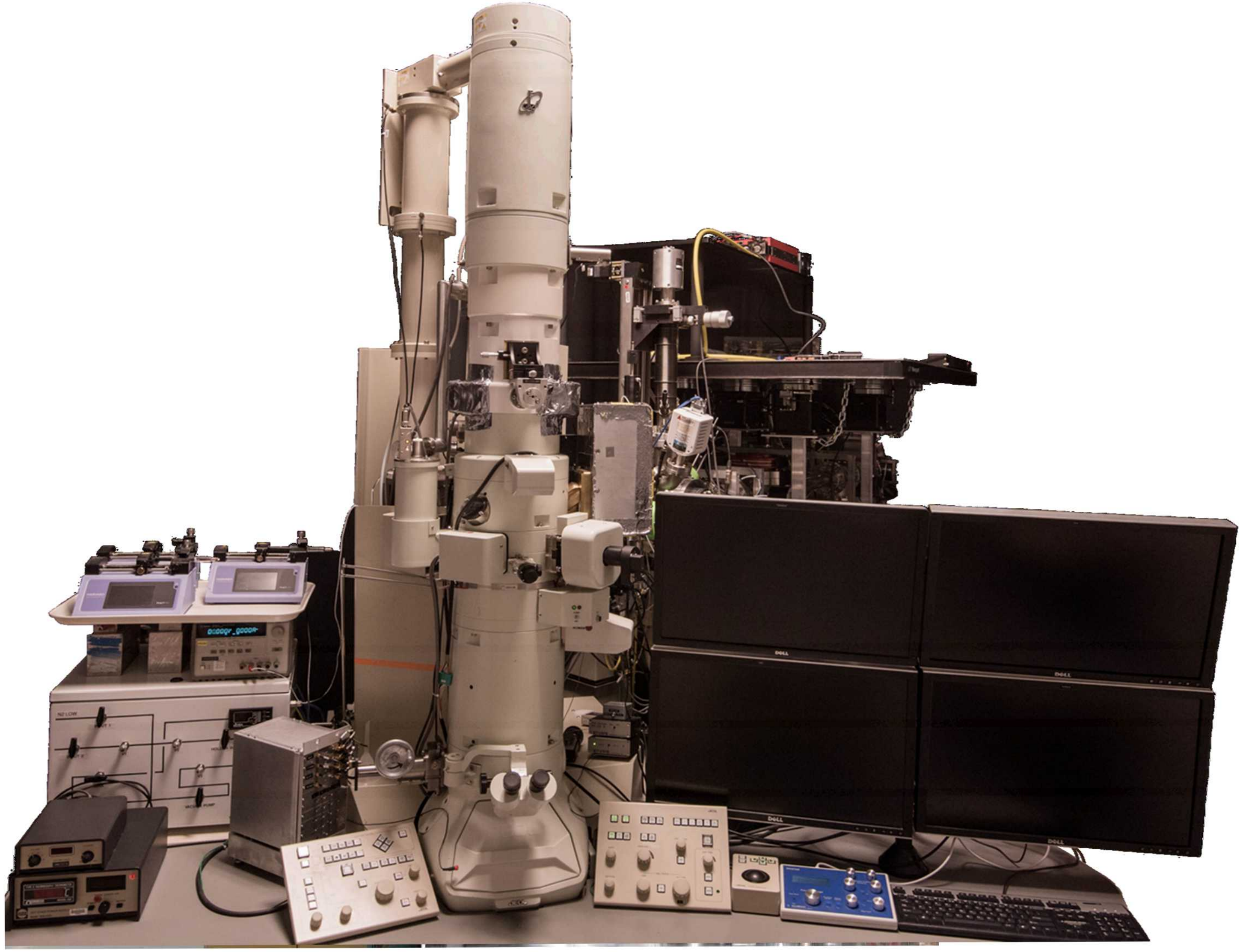
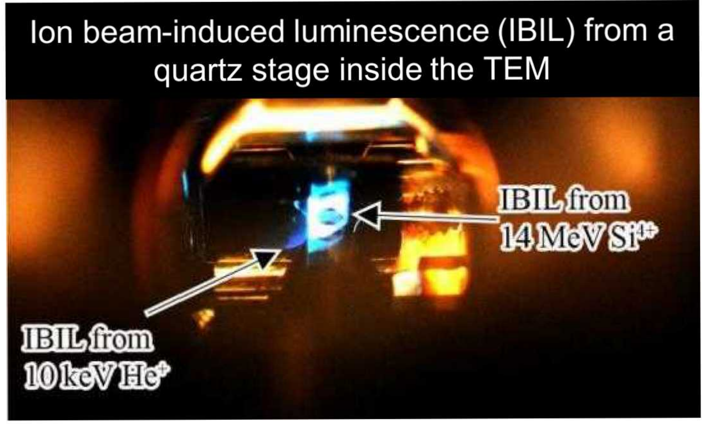
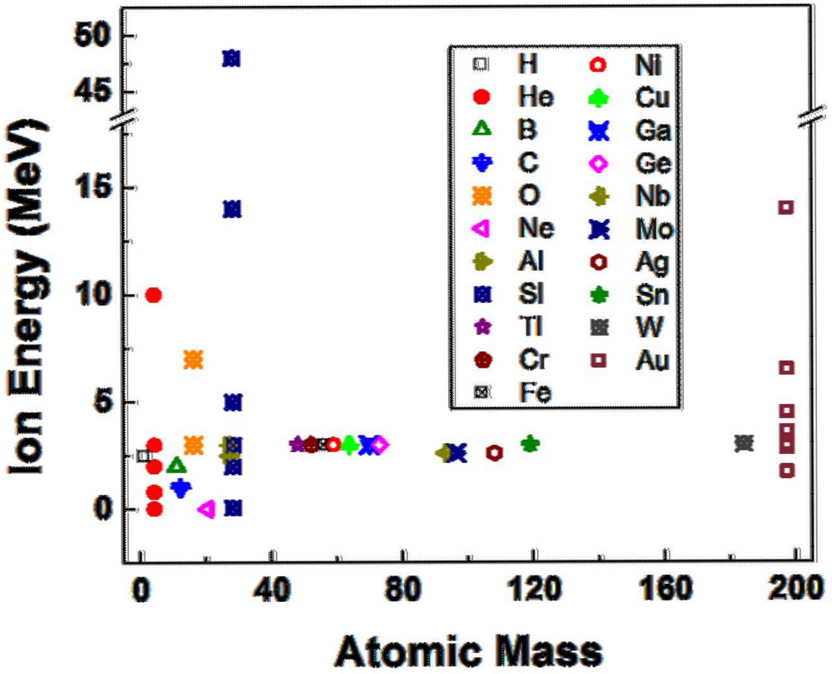




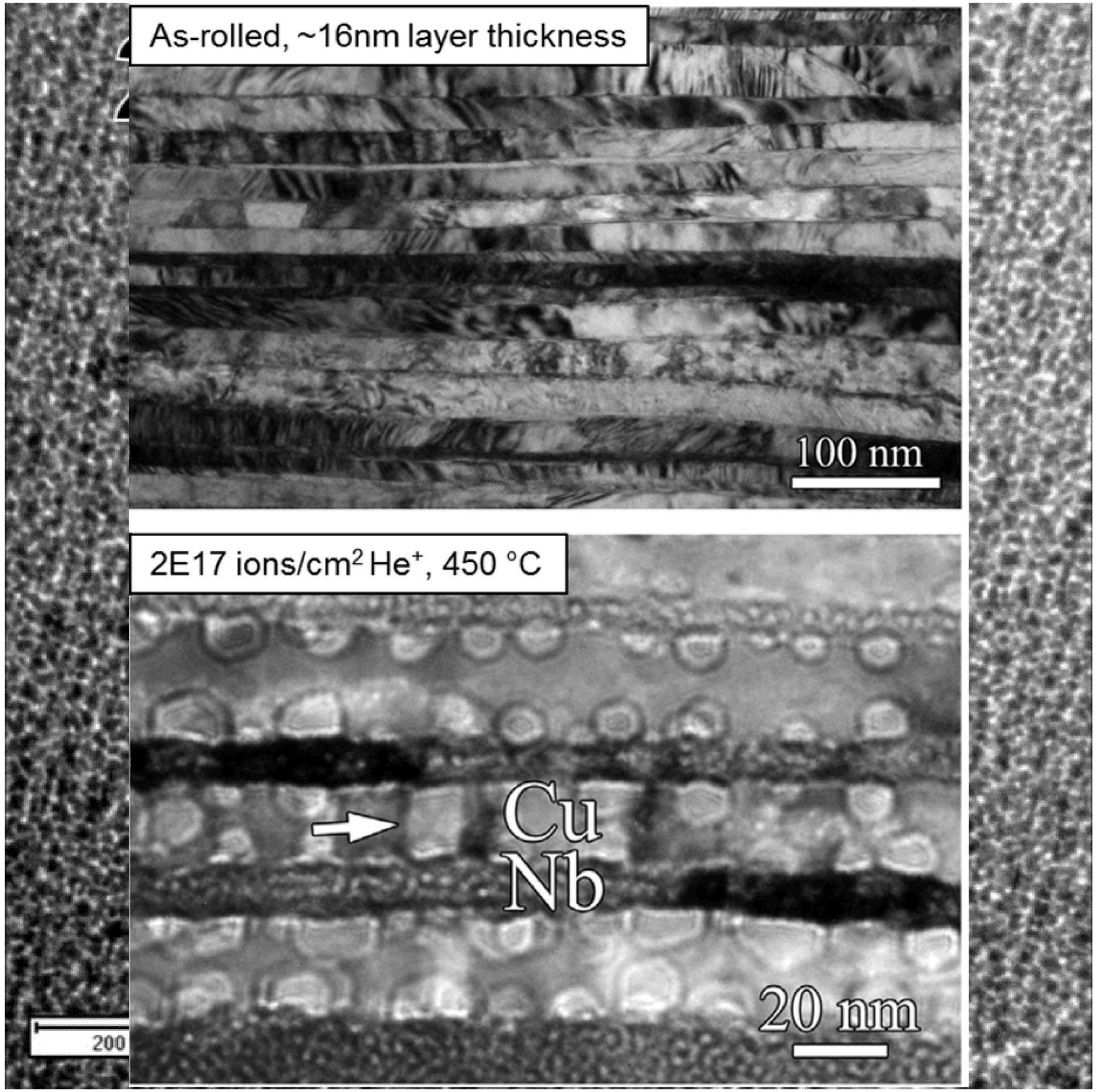


Nanodispersed CuNb for Enhanced Radiation Tolerance

- Lots of previous work on nanolaminates
- Working on developing nanodispersed CuNb thin films as model systems for nanofeatured alloys

- 50/50 Cu/Nb on Si_3N_4 grid
- Held at 700 °C for 20 mins
- Ramped to and held at 750, 800 °C for 5 to 10 mins

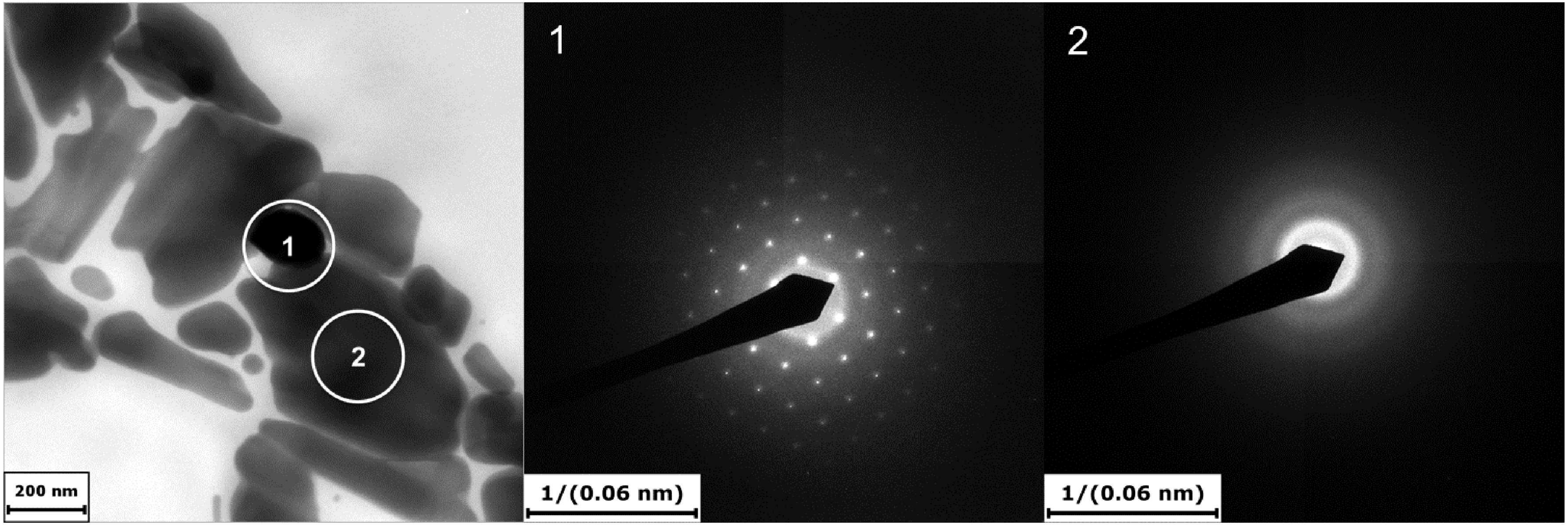
- Cu phase precipitates start to grow at ~120 °C, coarsening at ~200 °C
- Recrystallization of smaller Nb grains after holding at 700 °C
- Faster kinetics at higher temperatures



Synthesis and Characterization of d-UO_2 Nanoparticles

- Nanoparticles prepared by PAD ($UO_2(NO_3)_2 \cdot 6H_2O$, EDTA, PEI) followed by sintering at 1000 °C under varied atmospheric conditions

- Air-sintered show some crystalline phase, but mostly amorphous
- Ar-sintered show smaller nanoparticles that appear to be $UO_{2\pm x}$ phase



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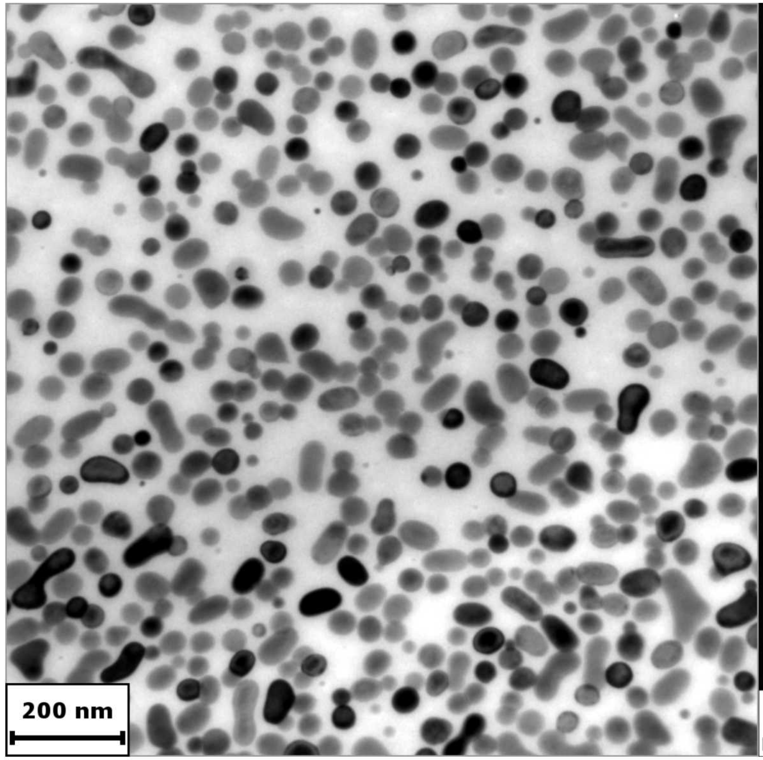
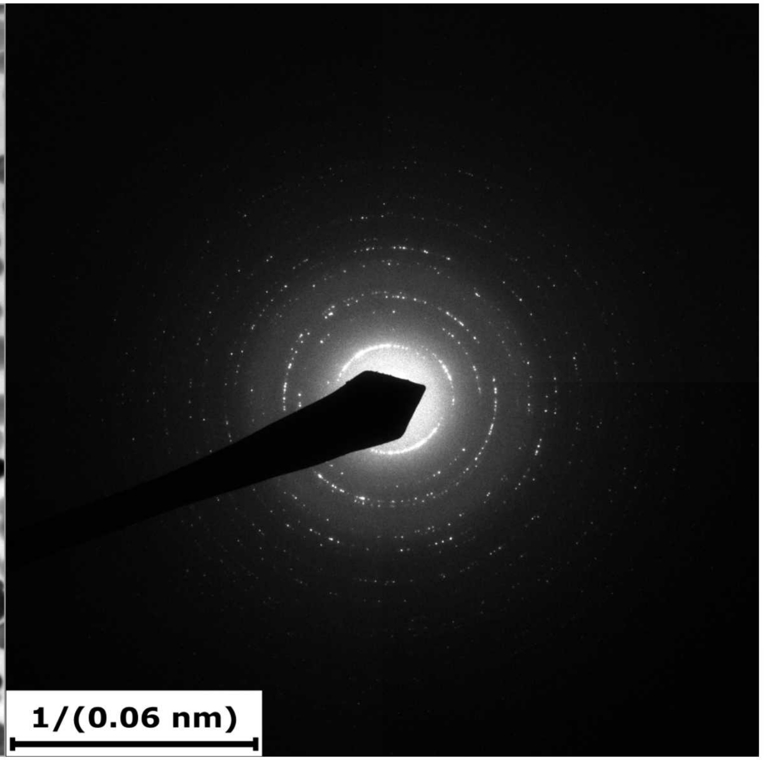
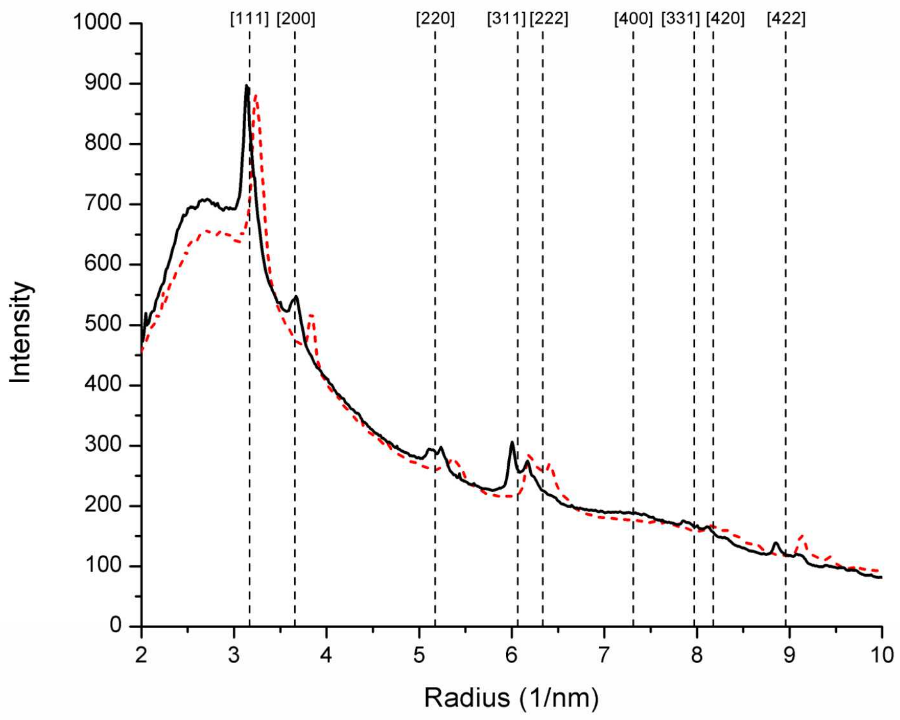
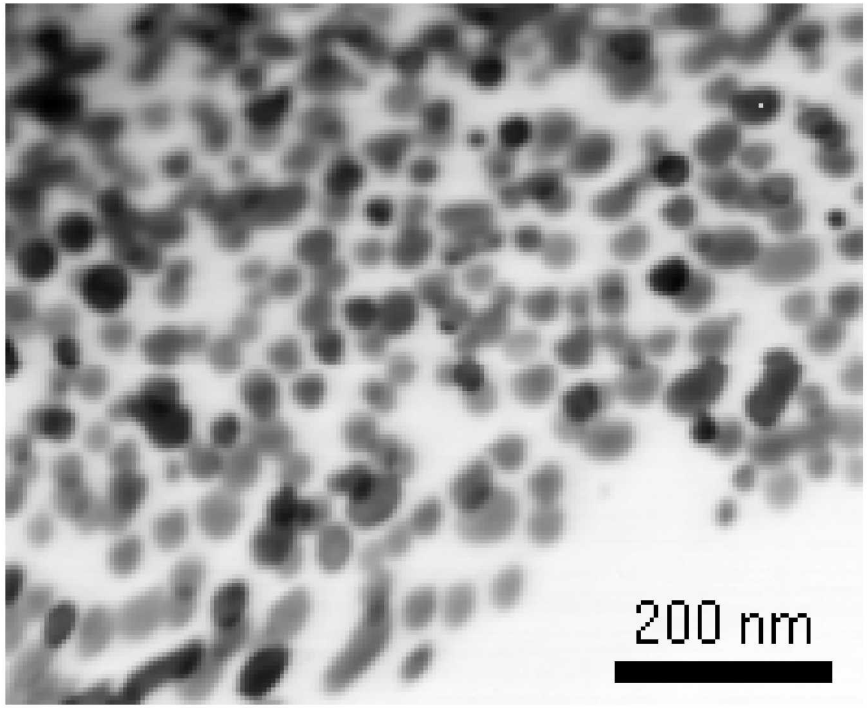


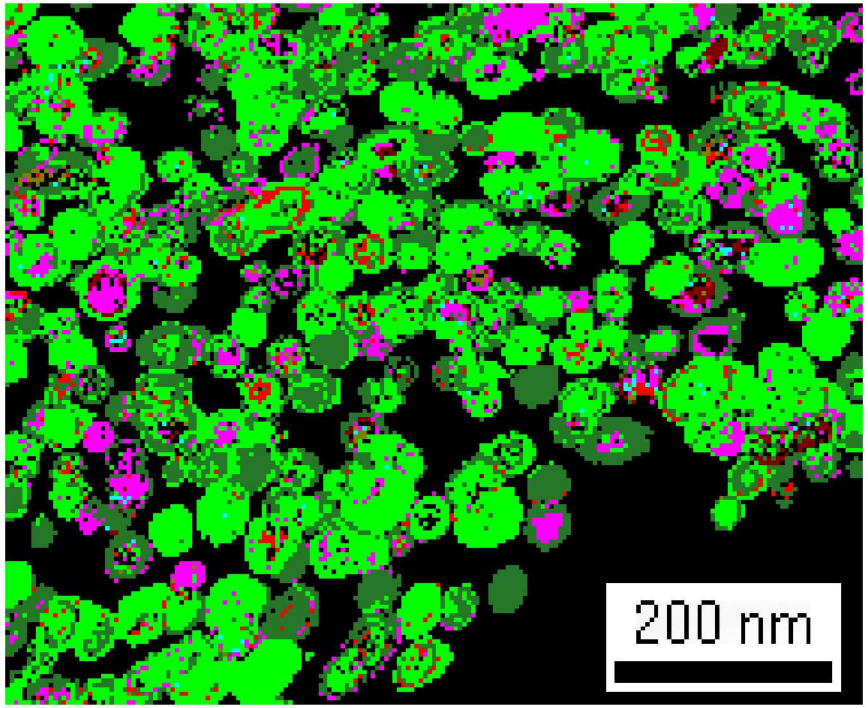




Synthesis and Characterization of d-UO_2 Nanoparticles

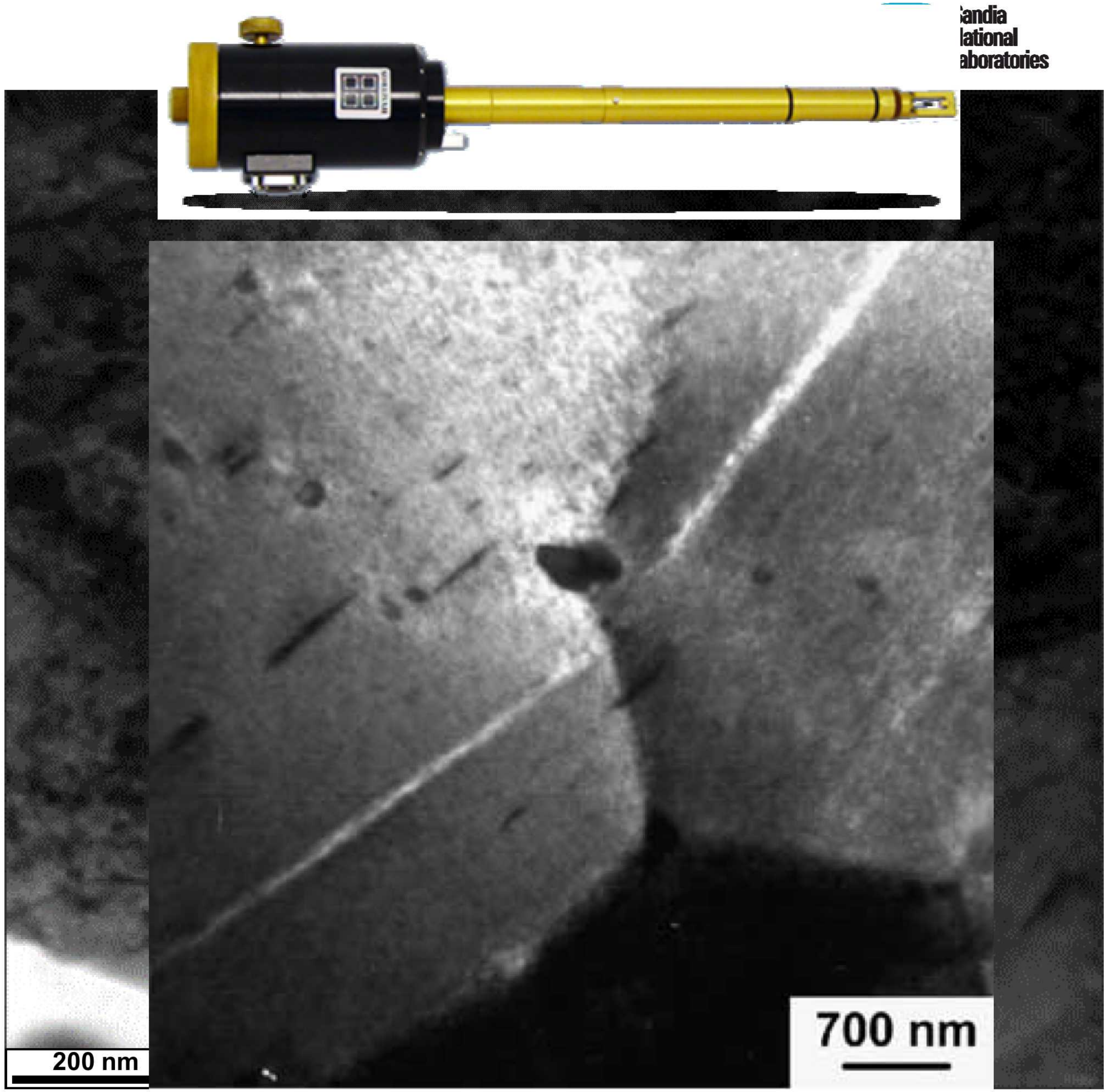
- PED analysis not useful for determining exact phase stoichiometry
- Does appear to confirm that phase is indeed $UO_{2\pm x}$ as opposed to a more O-rich phase





Irradiated Zirlo-b In-situ Indentation

- Irradiated with Zr ions to 4 dpa at 400 °C
- Interested in observing dislocation channel formation during straining using Hysitron/Bruker PI-95 picoindenter
- Dislocation activity/plastic dislocation observed, but no channeling
    - Maybe not enough dose, maybe thin film effects



Onimus, F, et al. (2004). A statistical TEM investigation of dislocation channeling mechanism in neutron irradiated zirconium alloys. *JNM*, 328, 165–179.

Summary

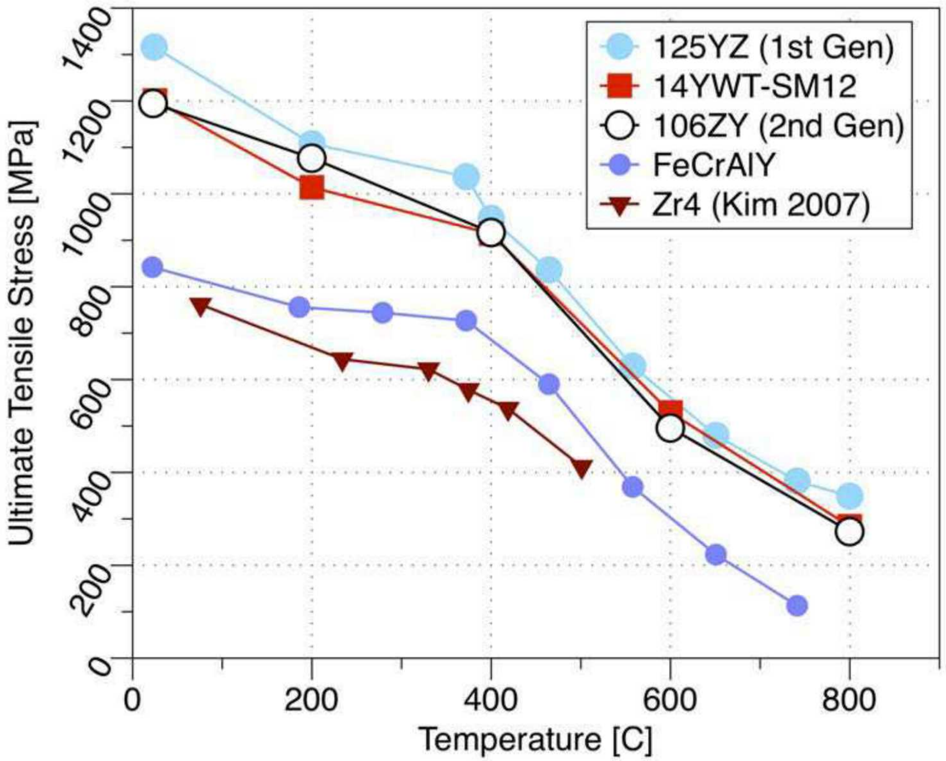
- **Results Summary**
  - Al additions lower α′ phase Cr content in FeCrAl
  - Precipitate coarsening mechanism is similar to the thermally-aged system
  - Precipitates appear to nucleate homogeneously except for at boundaries
  - Precipitates dissolve rapidly at temperatures above the phase boundary
  - Oxide nanoclusters show signs of instability during low temperature irradiation
  - Dislocation loop microstructure is strongly affected by temperature and the presence of nanoclusters

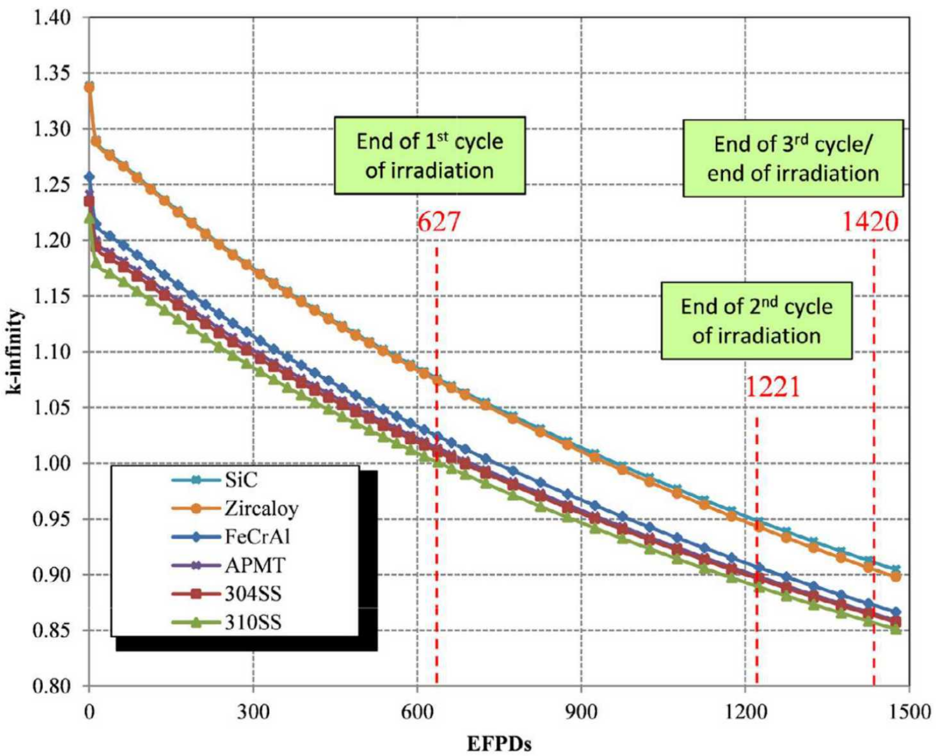
- **TEM and Relevant Microscopy Skills**
  - CTEM
  - STEM
  - STEM/EDS
  - EFTEM
  - PED
  - In-situ Heating
  - In-situ Irradiation
  - In-situ Indentation
  - APT
  - SANS
  - XRD
  - SEM
  - FIB
  - EBSD/TKD
  - Metallography
  - Jet/Electropolishing
  - Tensile Testing

- **Colleagues & Collaborators**
  - Kevin Field (ORNL)
  - Khalid Hattar (SNL)
  - Kumar Sridharan (UW)
  - Phil Edmondson (ORNL)
  - Chad Parish (ORNL)
  - Ken Littrell (ORNL)
  - Kurt Terrani (ORNL)
  - Dane Morgan (UW)
  - Remi Dingreville (SNL)
  - Julie Tucker (OSU)
  - David Hoelzer (ORNL)
  - Todd Allen (UW)

Extra Slides

ODS FeCrAl Alloy Development





- Exhibit high strength at elevated temperatures, excellent oxidation and corrosion resistance, high thermal conductivity, low thermal expansion and good void swelling resistance
- Nanoparticles could lead to high irradiation resistance due to a higher density of defect sinks compared to wrought FeCrAl alloys
- Improved strength allows for thinner cladding wall thickness, improved neutron economy

N.M. George, et al. "Neutronic analysis of candidate accident-tolerant cladding condepts in pressurized water reactors." Ann. Nucl. Energy **75** (2015) 703-712.

Summary & Conclusions

- **Gen. I Fe-Cr-Al Model Alloys**
  - Al additions result in a lower α′ phase Cr content than in binary Fe-Cr systems
  - Precipitate coarsening behavior has a similar mechanism to the thermally-aged system
  - Precipitates appear to nucleate homogeneously except for at grain boundaries where segregation and local denudation is observed
  - Precipitates dissolve rapidly at temperatures above the phase boundary
  - Dislocation loop density decreases with Cr content and <100> loops appear to grow faster than ½<111> loops

Summary & Conclusions

- **Gen. II Fe-Cr-Al ODS Variants Alloys**
  - Nanoclusters appear stable during medium- and high-temperature irradiation
  - Some signs of cluster instability during low temperature irradiation – additional work require to determine exact mechanism
  - Dislocation loop microstructure has strong temperature dependence and is greatly affected by ODS inclusions and/or small grain sizes and internal stresses

Colleagues & Collaborators

Special thanks to:

- Kevin Field (ORNL)
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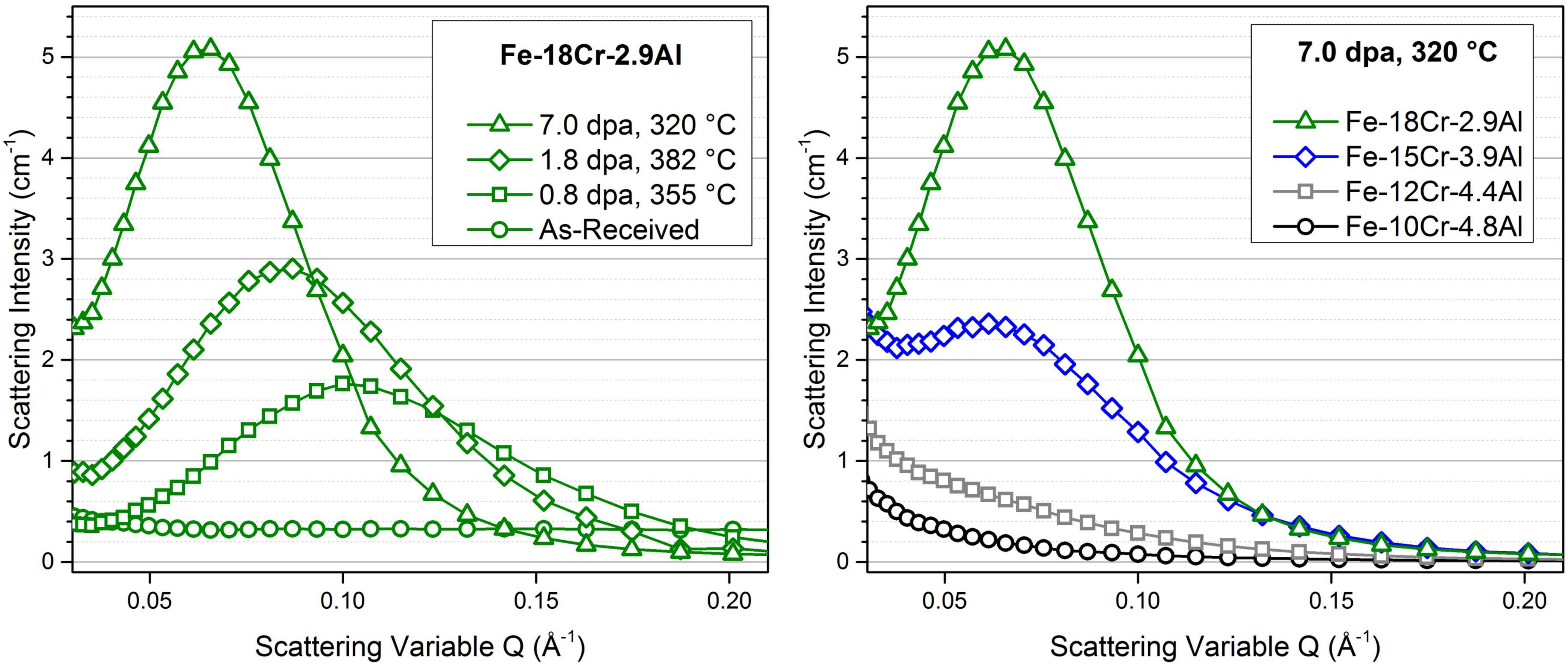
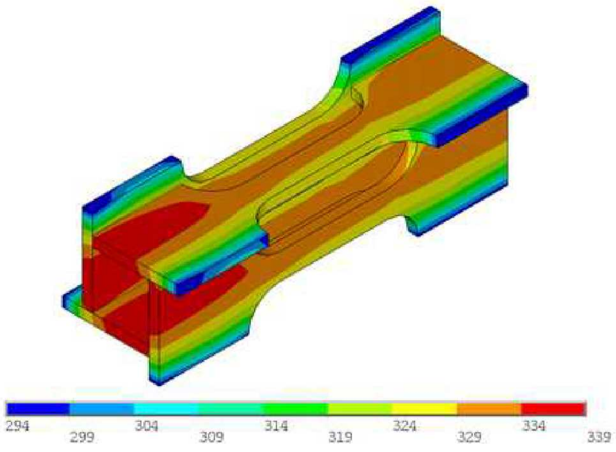
- Caleb Massey (ORNL)
- David Hoelzer (ORNL)
- Remi Dingreville (SNL)
- Ryan Hess (SNL)

Comparison of SANS Scattering Intensities

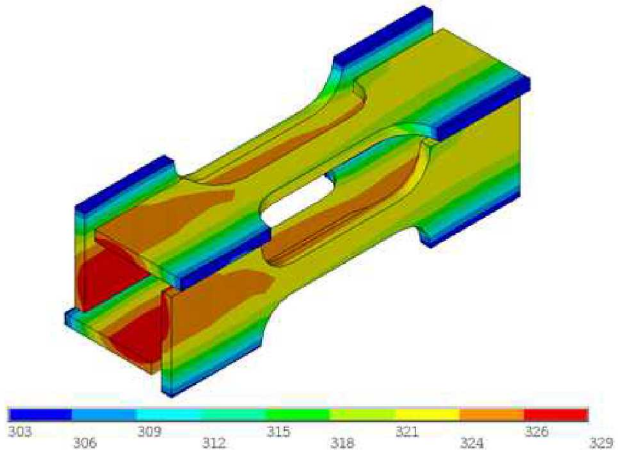


Irradiation Temperature Analysis

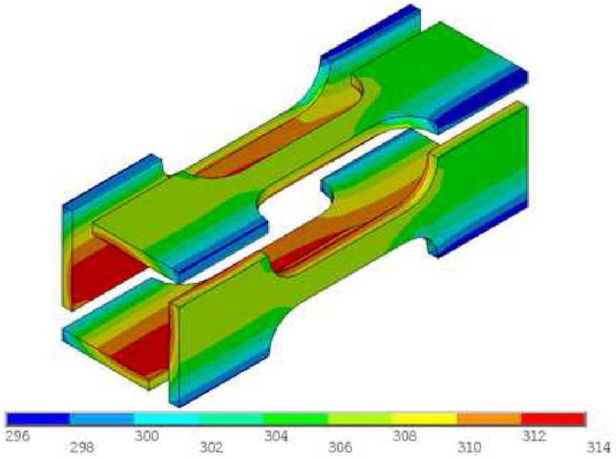
Inner Tensile



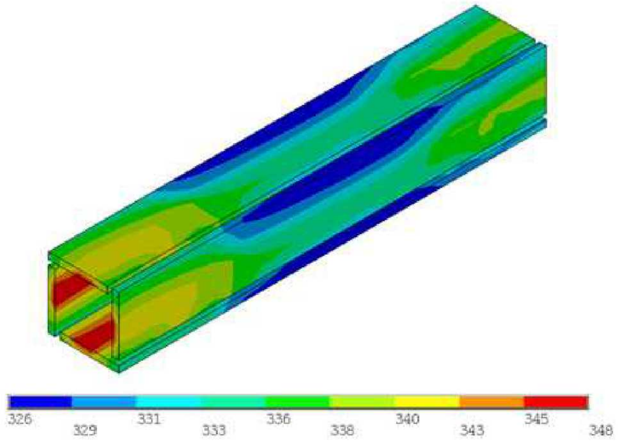
Middle Tensile



Outer Tensile



Sic Thermometry Bar

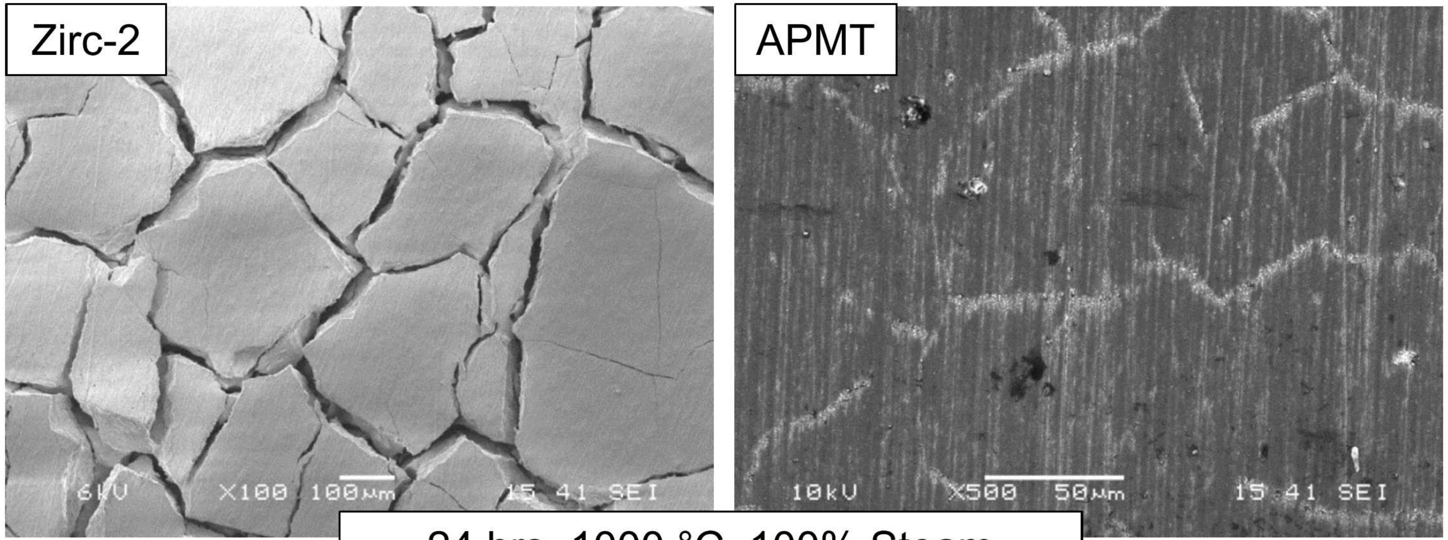


- Some thermal gradient expected in uninstrumented neutron-irradiation experiments
- Finite element analysis performed using ANSYS Workbench software using known HFIR heat generation rate and convection parameters
- Average temperatures within ~20 °C

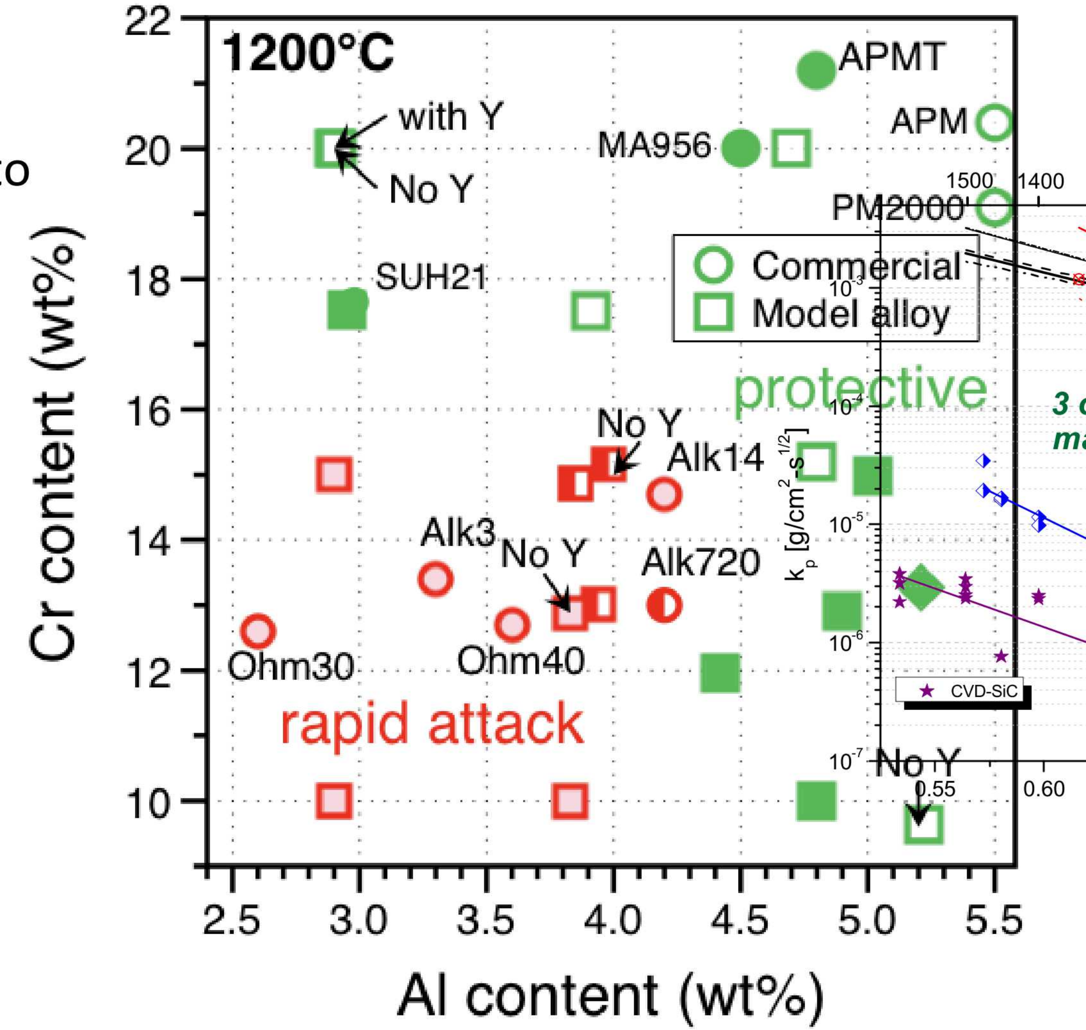
Specimen	Specimen Temp (°C) Average (Min-Max)
Inner Tensile	328 (294-339)
Middle Tensile	321 (303-329)
Outer Tensile	307 (296-314)
SiC Thermometry	336 (328-344)

Fe-Cr-Al Alloys for Nuclear Systems

- Why is Fe-Cr-Al attractive as a LWR cladding material?
  - Exceptional high temperature oxidation resistance due to formation of passivating Al_2O_3 (up to 1200-1475 °C)
  - High strength, with potential for oxide-dispersion strengthened variants
  - Low swelling rates in irradiation environments
  - Potential for near-term deployment



24 hrs, 1000 °C, 100% Steam



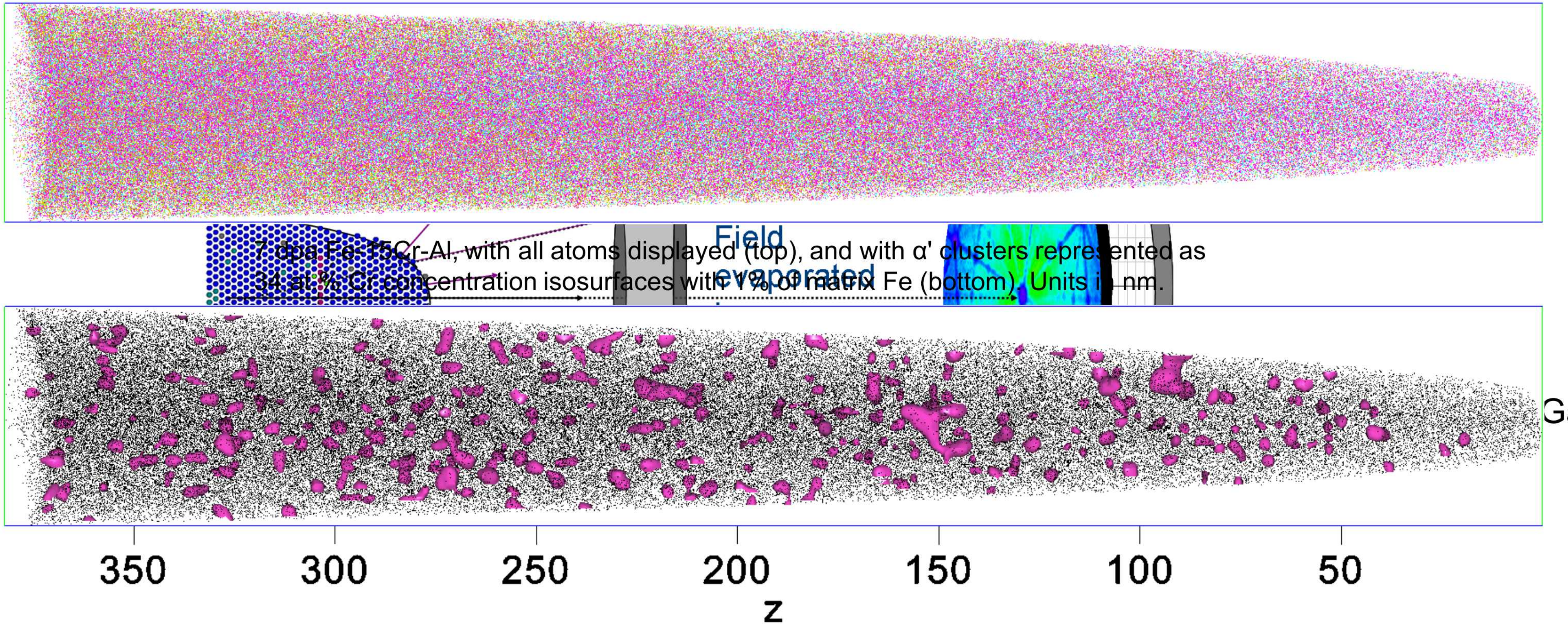
High temperature oxidation of model Fe-Cr-Al alloys exposed to steam at 1200 °C [1]

Images courtesy of Raul Rebak, GE Global Research

[1] Pint, B. A., Unocic, K. A., & Terrani, K. A. (2015). Effect of steam on high temperature oxidation behaviour of alumina-forming alloys. *Materials at High Temperatures*, *32*(1-2), 28–35.

Atom Probe Tomography

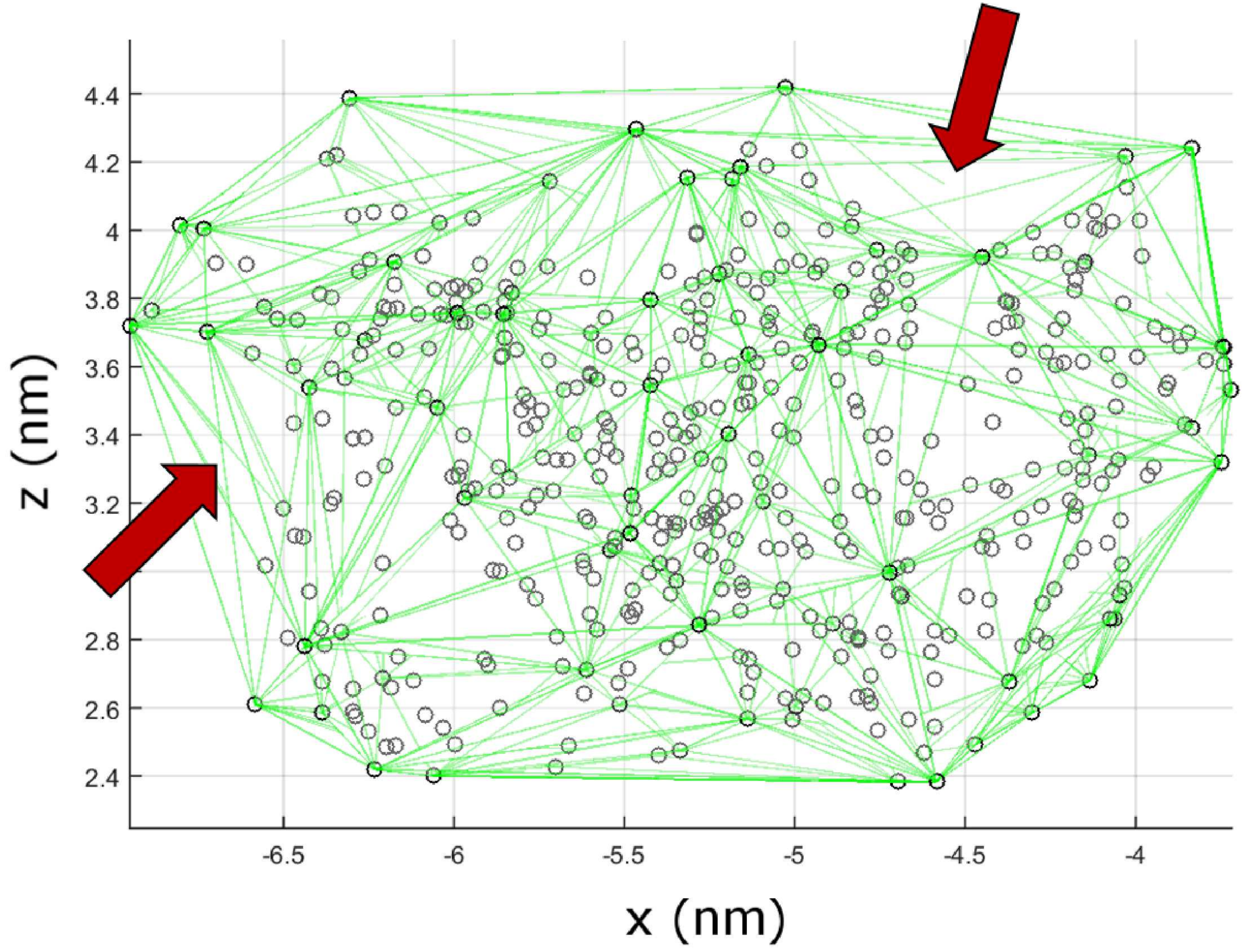
- Destructive analysis – field evaporates atoms from cryo-cooled, sharp needle specimen using localized high voltage pulses coupled with focused laser pules
- Can reconstruct specimen geometry in 3D using ion time-of-flight (TOF) and position-sensitive detector – allows for detailed elemental analysis
- Most comprehensive α′ analysis method – yields data regarding phase morphology, distribution and composition



7 dpa Fe-15Cr-Al, with all atoms displayed (top), and with α' clusters represented as 34 at.% Cr concentration isosurfaces with 1% of matrix Fe (bottom). Units in nm.

Gault

Application of Delaunay Triangulation Methods

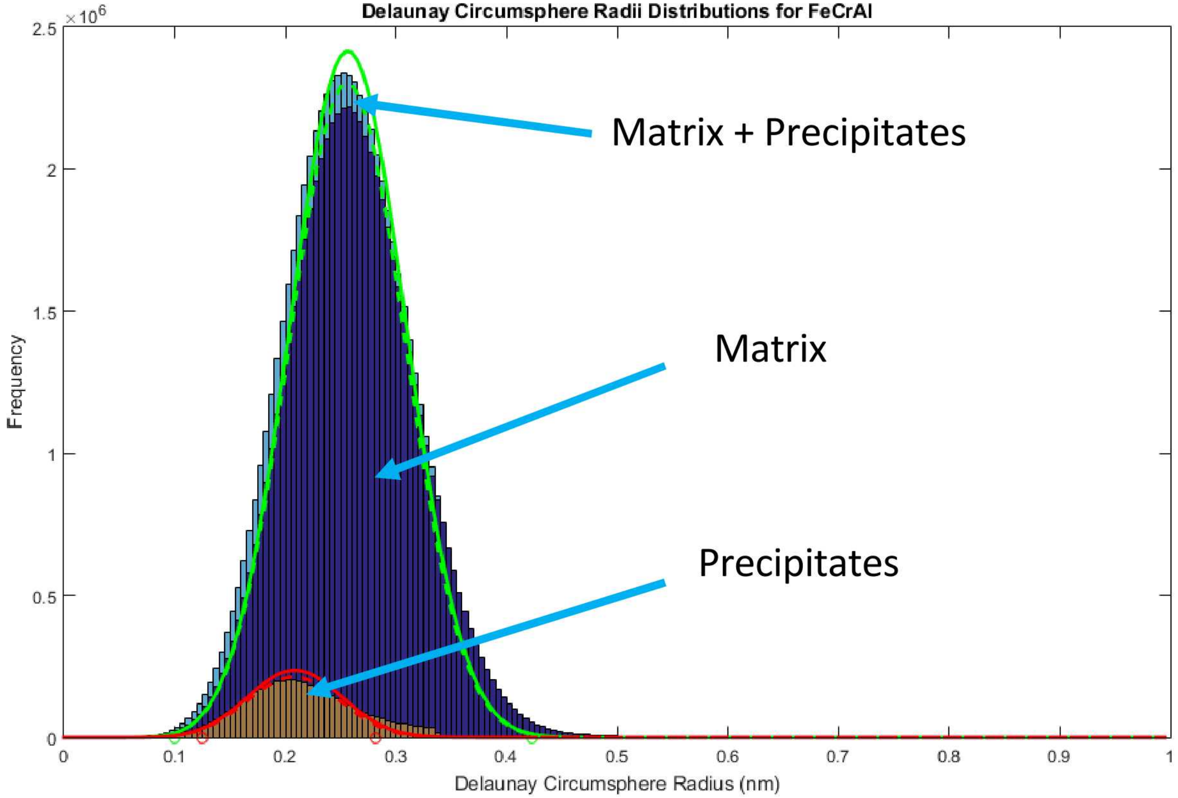


- Mesh cells "bridge" concave surfaces
- Overestimate cluster volume, underestimates cluster density, lower measured density ratio
- Correct by either:
  - Thresholding based on cell volume or Delaunay radius
  - Fitting to theoretical distribution

Application of Delaunay Triangulation Methods

- There exists a theoretical distribution for Delaunay circumsphere radii for a Delaunay triangulation of data resulting from a Poisson process (top right)
- Though randomness isn't a perfect assumption (lattice distances preserved), i is counter-balanced by imperfect spatial resolution of LEAP
- Reasonable fits are achieved to present data
- Density is able to be extracted analytically

$$f(R_C) = \frac{32\pi^3\rho^3}{9} {R_C}^8 e^{-(4\pi\rho/3)R_c^3}$$



Lefebvre, W., Philippe, T., & Vurpillot, F. (2011). Application of Delaunay tessellation for the characterization of solute-rich clusters in atom probe tomography. *Ultramicroscopy*, *111*(3), 200–206. http://doi.org/10.1016/j.ultramic.2010.11.034

Summarized SANS Results for Fe-Cr-Al Alloys

Alloy	Irradiation Dose (dpa)	Irradiation Temp. (°C)	Number Density ($\times 10^{24}$ m^{-3})	Volume Fraction (%)	Average Radius (nm)
Fe-10Cr-9.3Al	0.8	355 ± 3.4	0.73	2.55	2.03
	1.8	382 ± 5.4	0.46	2.01	2.18
	7.0	320 ± 12.7	0.06	0.57	2.40
Fe-12Cr-8.7Al	0.3	334.5 ± 0.6	10.44	11.25	1.37
	1.8	382 ± 5.4	5.81	14.91	1.83
	7.0	320 ± 12.7	0.94	3.81	2.13
Fe-15Cr-7.7Al	0.3	334.5 ± 0.6	46.81	30.61	1.16
	1.8	382 ± 5.4	7.57	18.81	1.81
	7.0	320 ± 12.7	2.27	9.39	2.15
Fe-18Cr-5.8Al	0.8	355 ± 3.4	18.89	27.79	1.52
	1.8	382 ± 5.4	6.64	17.61	1.85
	7.0	320 ± 12.7	1.34	9.08	2.53

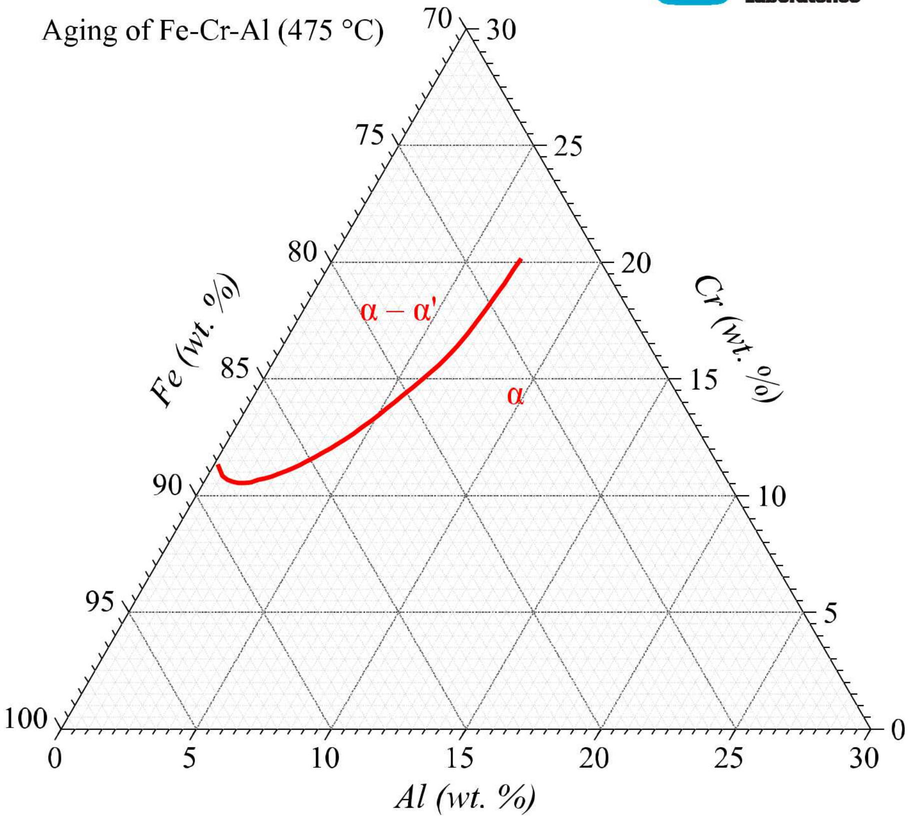
- Scattering contrast for specimens not analyzed by APT determined via extrapolation
- Trends from APT mostly preserved

Full SANS/EFTEM Comparison

Specimen ID	Irradiation Temp. (°C)	Number Density ($x10^{23}$ #/m^3)			Volume Fraction (%)			A-ratio (unitless)		Mean Radius (nm)		
		SANS MD	SANS Monte Carlo	EFTEM	SANS MD	SANS Monte Carlo	EFTEM	SANS MD	SANS Monte Carlo	SANS MD	SANS Monte Carlo	EFTEM
OD34	-	2.14±0.82	2.78±0.87	-	1.07±0.40	1.24±0.35	-	1.75±0.05	2.75±0.54	2.3±0.1	2.2±0.1 (unimodal)	-
OD01	195	5.02±2.80	1.54±0.54	1.04±0.24	0.96±0.45	1.01±0.33	0.43±0.28	1.31±0.08	2.06±0.37	1.7±0.2	2.5±0.1 (bimodal)	1.03±0.87
OD03	363	2.09±0.68	1.97±0.60	0.94±0.14	1.12±0.36	1.14±0.32	0.43±0.26	1.63±0.03	2.51±0.48	2.3±0.1	2.4±0.1 (unimodal)	1.27±0.90
OD06	559	1.39±0.80	1.89±0.61	0.49±0.34	0.72±0.41	1.24±0.37	1.56±1.93	1.96±0.11	2.32±0.40	2.3±0.1	2.5±0.1 (unimodal)	1.40±1.61

Experimental Goals

- Assess severity of α′ precipitation in neutron-irradiated model Fe-Cr-Al alloys using a correlative microscopy approach
  - Investigate how precipitation behavior varies with composition
  - Study evolution of precipitate morphology with dose
  - Determine effect of Al additions compared to binary Fe-Cr systems
  - Assist in developing structure/property relationships for radiation-induced hardening and embrittlement



Ternary Fe-Cr-Al phase diagram showing destabilization of α' phase by bulk Al additions[1]

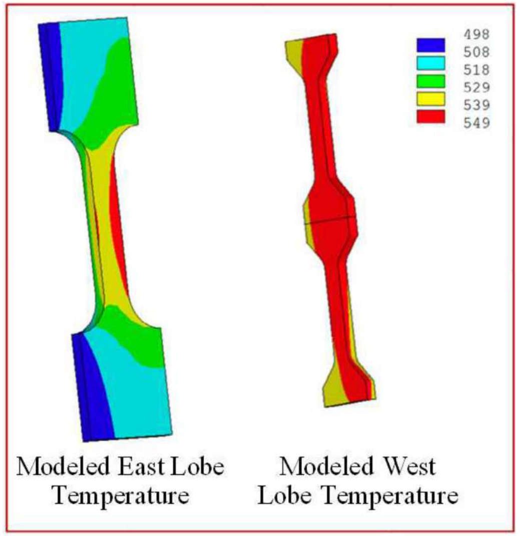
- **Develop a mechanistic understanding of the factors that influence precipitation in this alloy system in order to make informed design decisions regarding Fe-Cr-Al for accident-tolerant fuel cladding applications**

FCAY and FCAT Rabbits

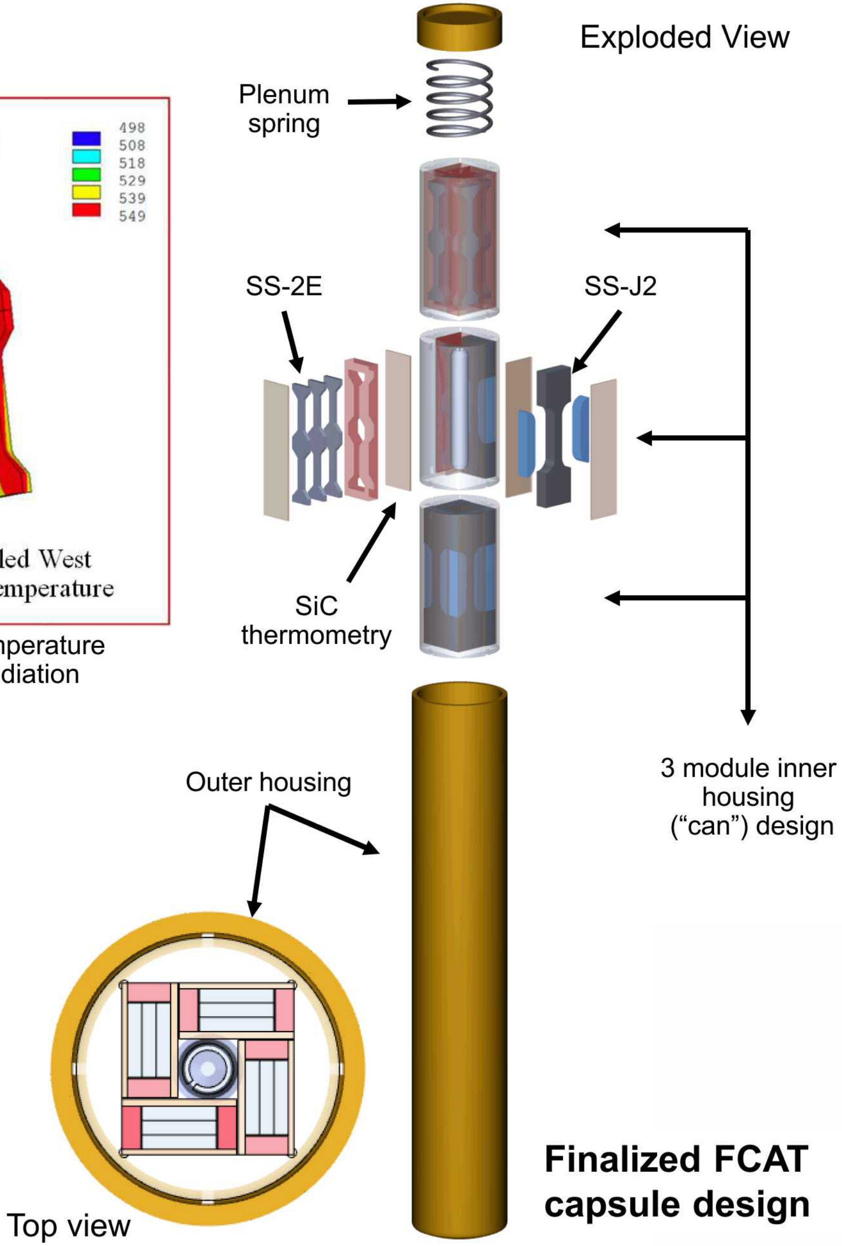
<u>PURPOSE</u>: rapid screening of alloy irradiated tensile properties and microstructure

Specifications:

- SS-J2 and SS-2E flat sheet tensile specimen geometries
- Design temperatures of 200-550° C
    - Temperature monitored passively using SiC thermometry
- Modular; can accept any ratio of SS-J2 to SS-2E specimen configurations
- Robust, proven design over the past 4+ years



Example of specimen temperature gradients for 550°C irradiation



FCAY and FCAT Rabbits

- Alloys studied:
  1. Model alloys (M): F1C5AY, B125Y, B154Y-2, B183Y-2
  2. Engineering grade alloys (E): C06M, C35M, C36M, C37M, C35MN, C35M10TC
  3. Commercial alloys (C): Kanthal APMT™, and Alkrothal 720
  4. ODS Alloys (O): 125YF

Capsule ID	Number Samples	Alloys	Exposure Time (hrs)	Neutron Flux (n/cm^2s) E > 0.1 MeV	Neutron Fluence (n/cm^2) E > 0.1 MeV	Dose Rate (dpa/s)	Dose (dpa)	Irradiation Temperature (°C)
FCAY-01	36	M+C	120	8.54×10^{14}	3.69×10^{20}	7.7×10^{-7}	0.3	334.5 ± 0.6
FCAY-02	36	M+C	301	8.54×10^{14}	9.25×10^{20}	7.7×10^{-7}	0.8	355.1 ± 3.4
FCAY-03	36	M+C	614	8.84×10^{14}	1.95×10^{21}	8.1×10^{-7}	1.8	381.9 ± 5.4
FCAY-04	36	M+C	2456	8.74×10^{14}	7.73×10^{21}	7.9×10^{-7}	7.0	319.9 ± 10.2
FCAY-05	36	M+C	4914	8.74×10^{14}	1.55×10^{22}	7.8×10^{-7}	13.8	340.5 ± 25.7
FCAT-01	45	E+O	548	1.10×10^{15}	2.17×10^{21}	9.6×10^{-7}	1.9	194.5 ± 37.9
FCAT-02	45	E+O	548	1.04×10^{15}	2.05×10^{21}	9.1×10^{-7}	1.8	362.7 ± 21.2
FCAT-03	45	E+O	548	1.10×10^{15}	2.17×10^{21}	9.6×10^{-7}	1.9	559.4 ± 28.1
FCAT-04	45	E+O	1754	1.10×10^{15}	9.32×10^{21}	9.6×10^{-7}	8.3	200*
FCAT-05	45	E+O	1754	1.04×10^{15}	8.81×10^{21}	9.1×10^{-7}	7.9	330*
FCAT-06	45	E+O	1754	1.10×10^{15}	9.32×10^{21}	9.6×10^{-7}	8.3	550*
FCAT-07	45	E+O	4032	1.10×10^{15}	1.82×10^{22}*	9.6×10^{-7}	16.3*	200*
FCAT-08	45	E+O	4032	1.04×10^{15}	1.73×10^{22}*	9.1×10^{-7}	15.4*	330*
FCAT-09	45	E+O	4032	1.10×10^{15}	1.82×10^{22}*	9.6×10^{-7}	16.3*	550*

*Target values

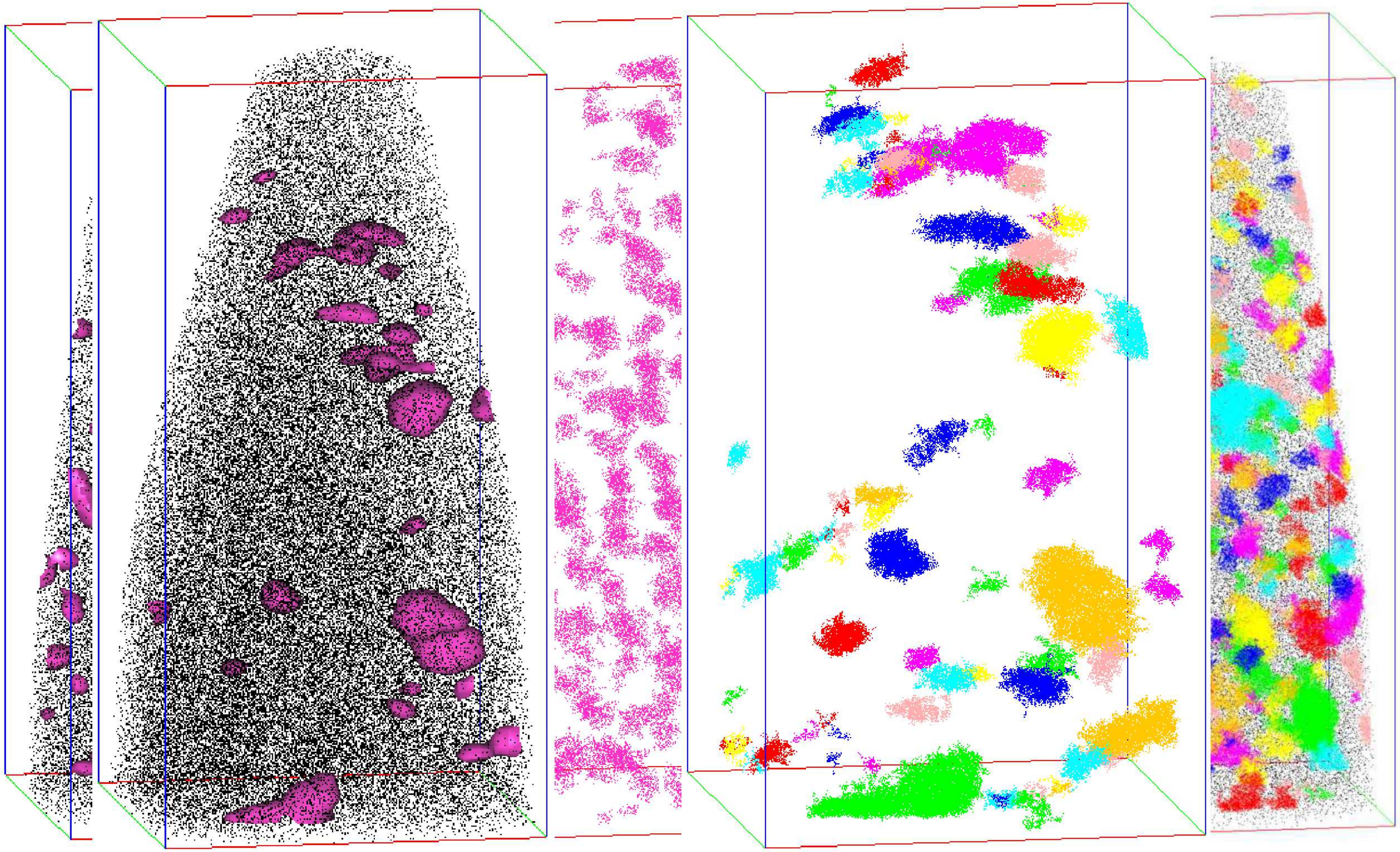
Note on Representation of APT Data

Left: 30 at.% Cr Concentration Isosurfaces

Center: Clusters from Maximum Separation Method

Right: Indexed Clusters from Max. Separation Method, 2 at.% Fe Matrix

- Variation in precipitate composition makes concentration isosurfaces not representative of measured cluster properties between conditions
- Indexed cluster diagrams allow for quantified precipitates to be easily distinguished

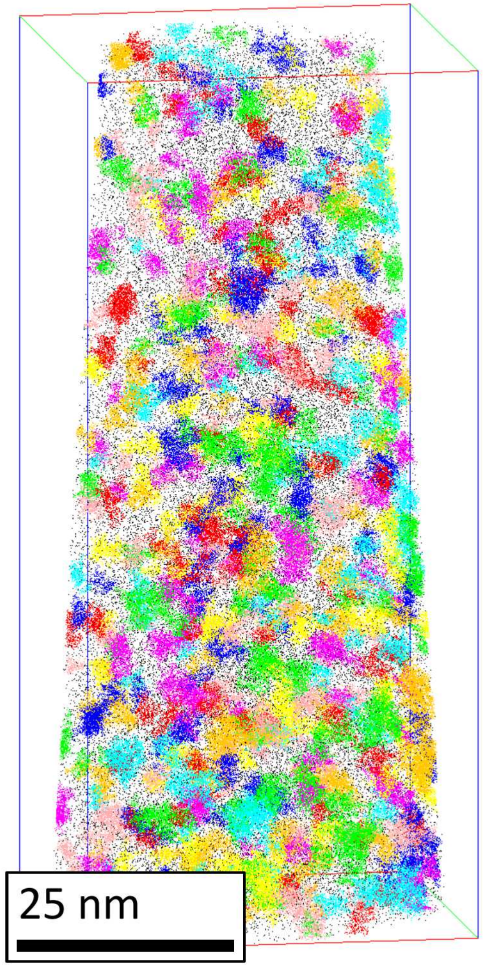


Fe-18Cr-5.8Al, 7 dpa, 320°C

Increasing Dose

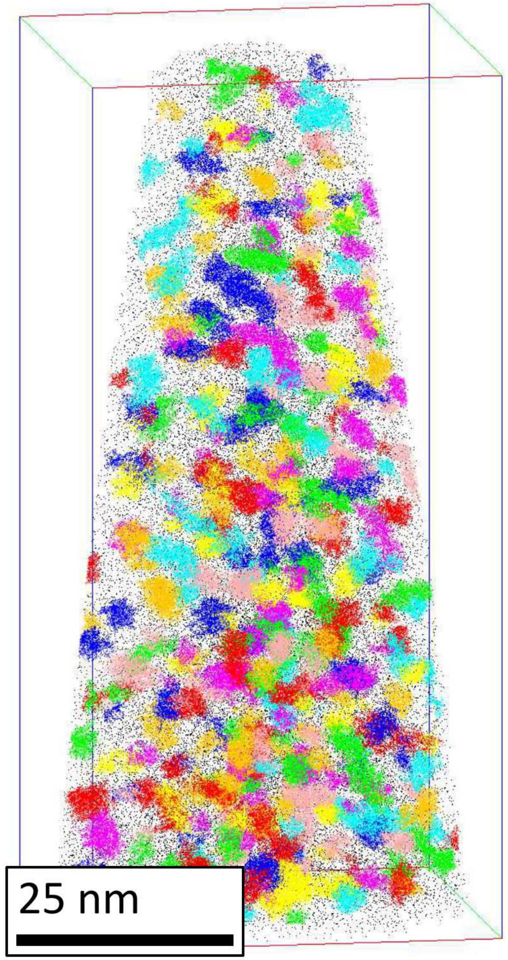
Fe-18Cr-5.8Al

0.8 dpa, 355ºC



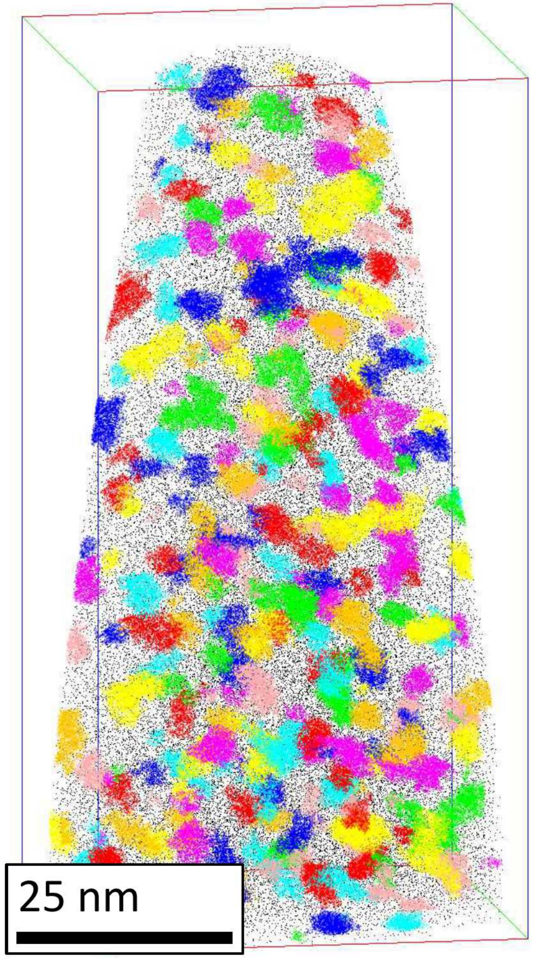
Total Volume Analyzed:
1.68×10^6 nm^3

1.8 dpa, 382ºC



Total Volume Analyzed:
1.16×10^6 nm^3

7 dpa, 320ºC



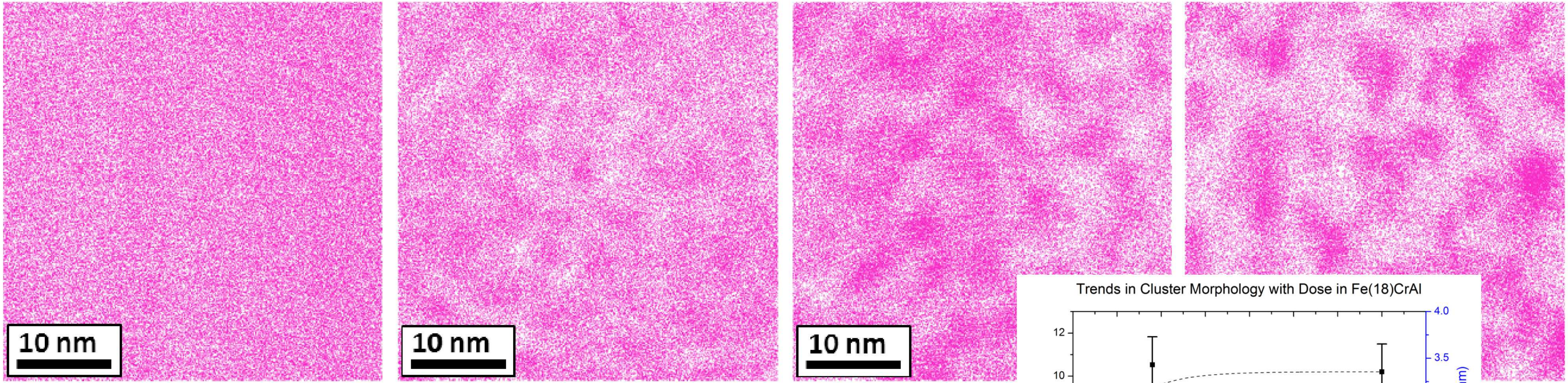
Total Volume Analyzed:
7.53×10^5 nm^3

Reconstructions cropped to 50x50x100 nm

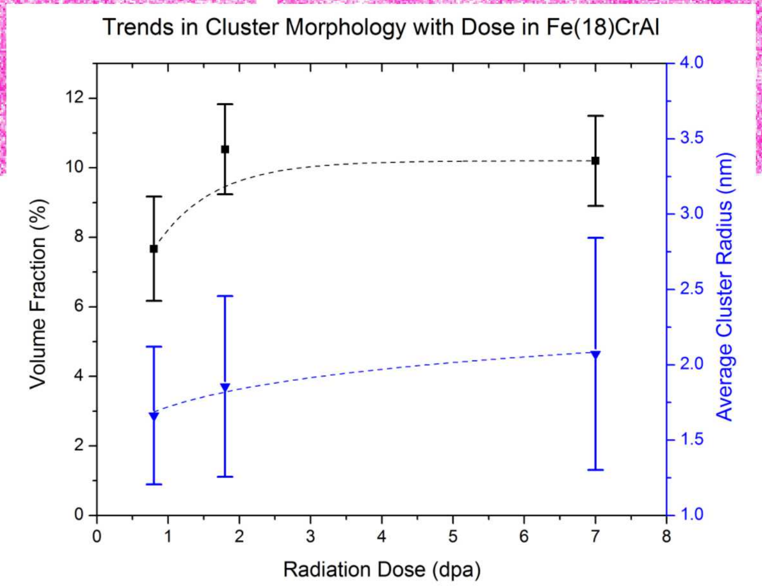
Increasing Dose

Cr Atom Maps (40nm × 40nm × 20nm)

As-Received | **0.8 dpa, 355ºC** | **1.8 dpa, 382ºC** | **7 dpa, 320ºC**



Fe-18Cr-5.8Al



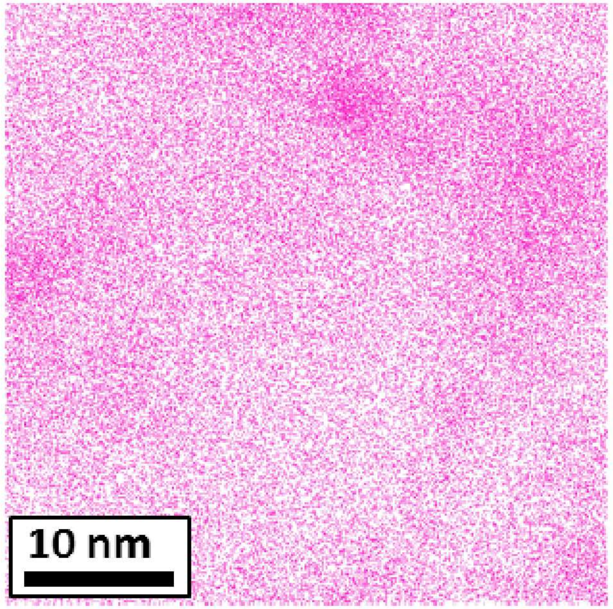
Key observations of dose evolution

- Precipitation observed in all irradiated specimens
- ↑ dpa leads to ↑ avg. cluster size, ↓ cluster number density
- Volume fraction saturates early, clusters continue to coarsen

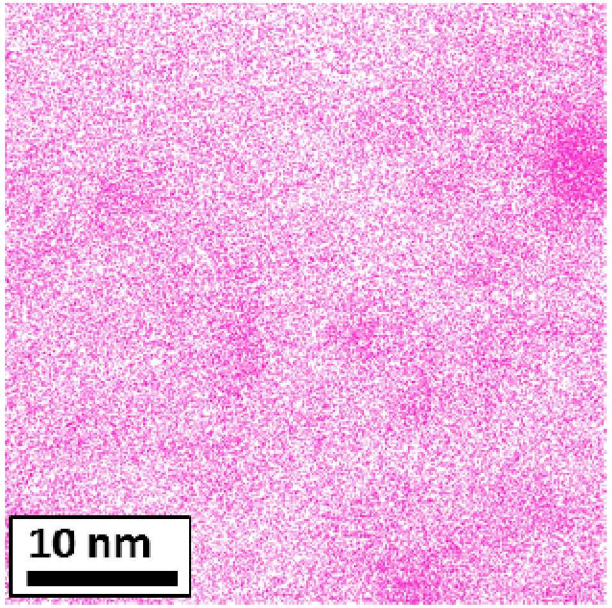
Increasing Cr, Decreasing Al

Cr Atom Maps (40nm × 40nm × 20nm)

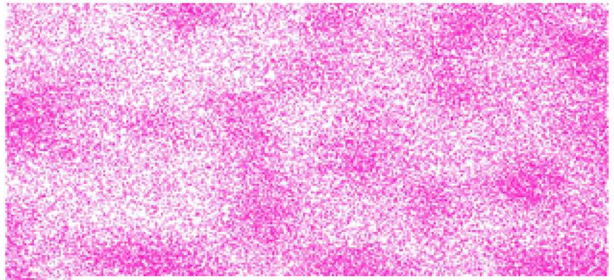
7dpa Fe-10Cr-9.3Al



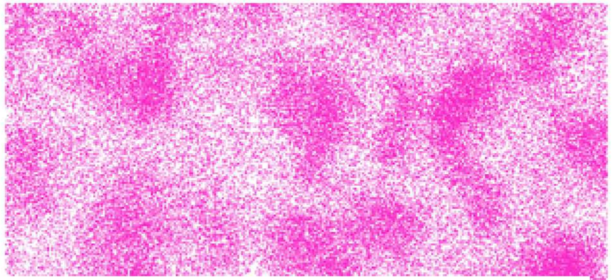
7dpa Fe-12Cr-8.7Al

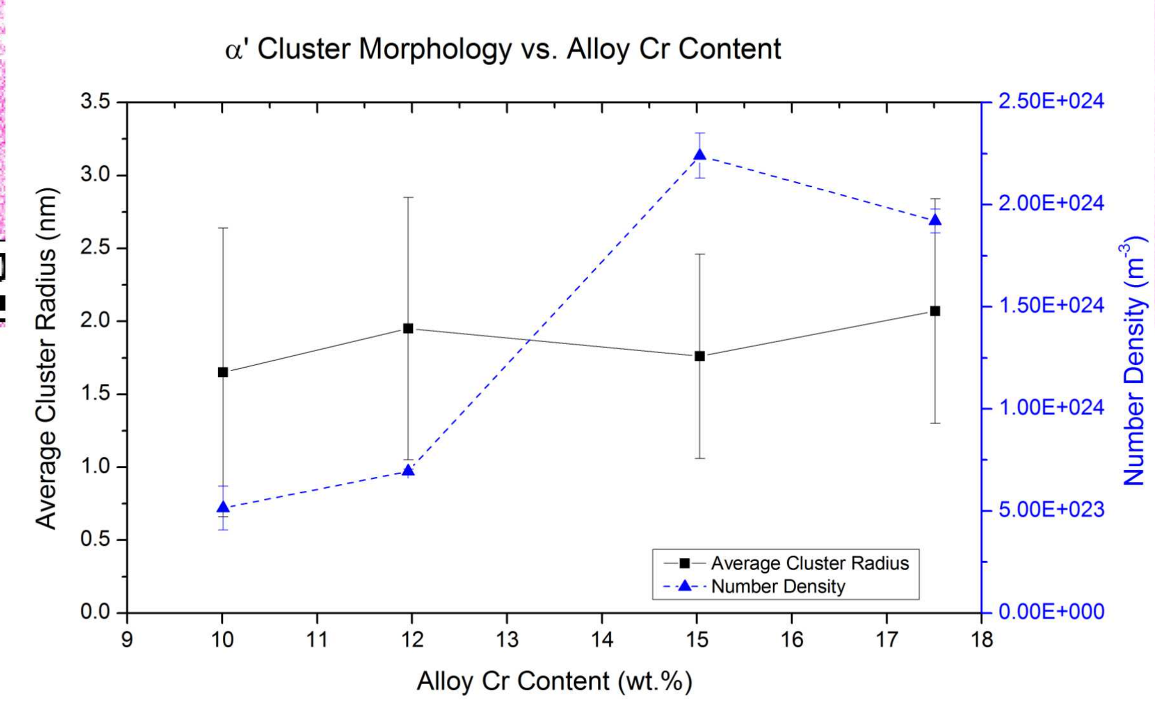


7dpa Fe-15Cr-7.7Al



7dpa Fe-18Cr-5.8Al

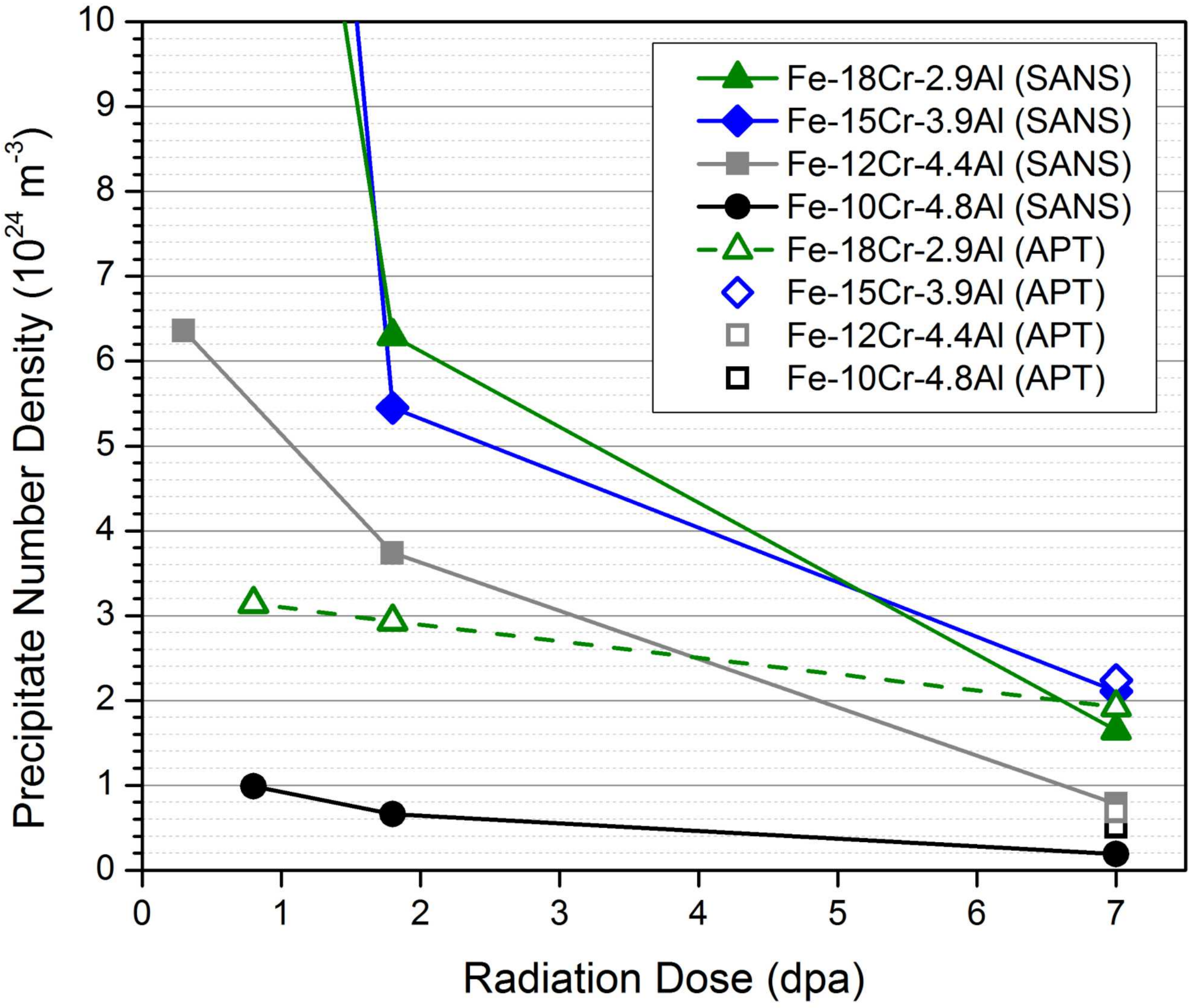




Key observations of composition dependence

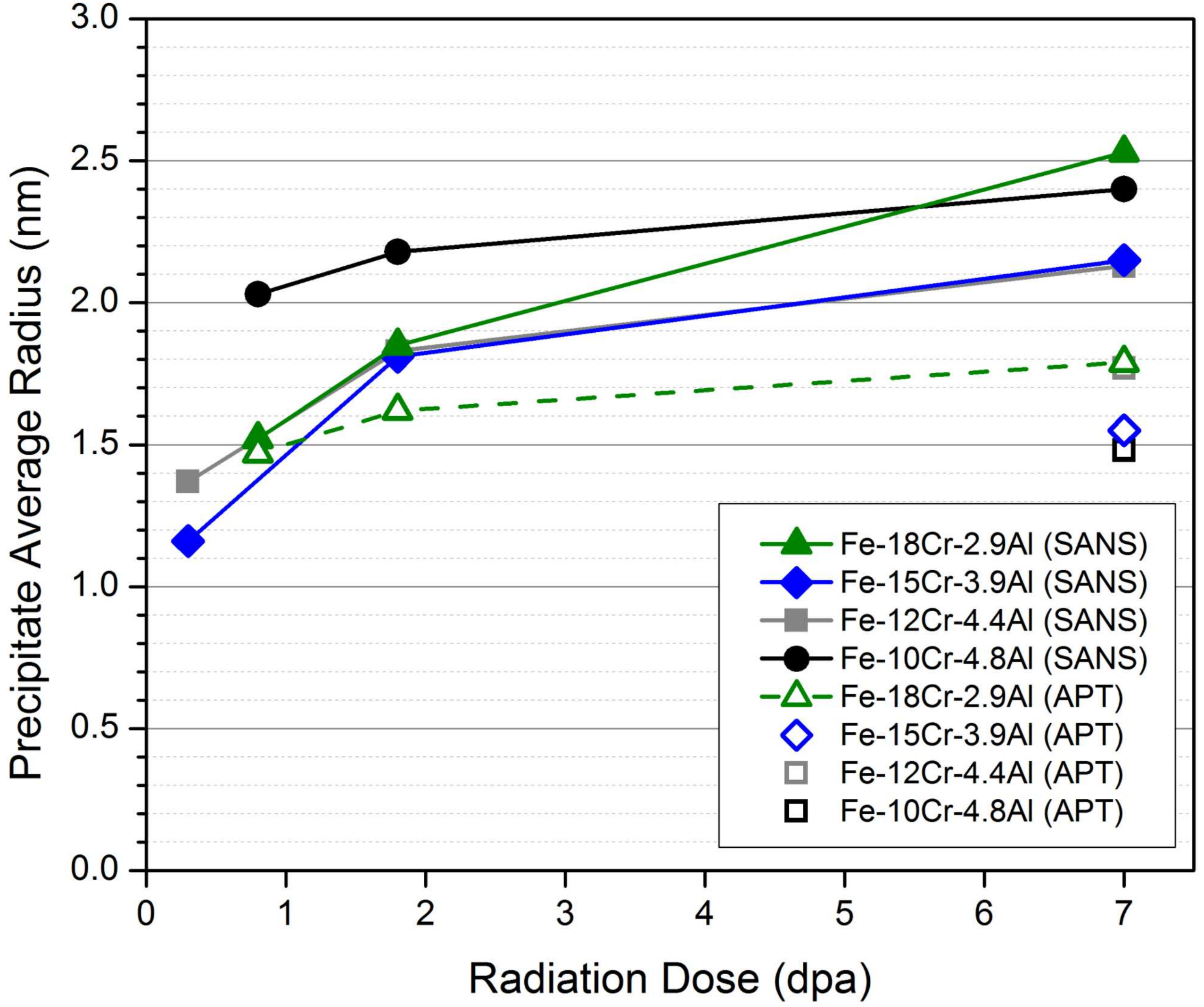
- Precipitation in all compositions studied
- Volume fraction increases with increasing Cr
- ↑ Cr generally leads to ↑ cluster number density
- Large distribution of cluster sizes
- Al additions reduce Cr concentration of precipitates

Comparing APT & SANS



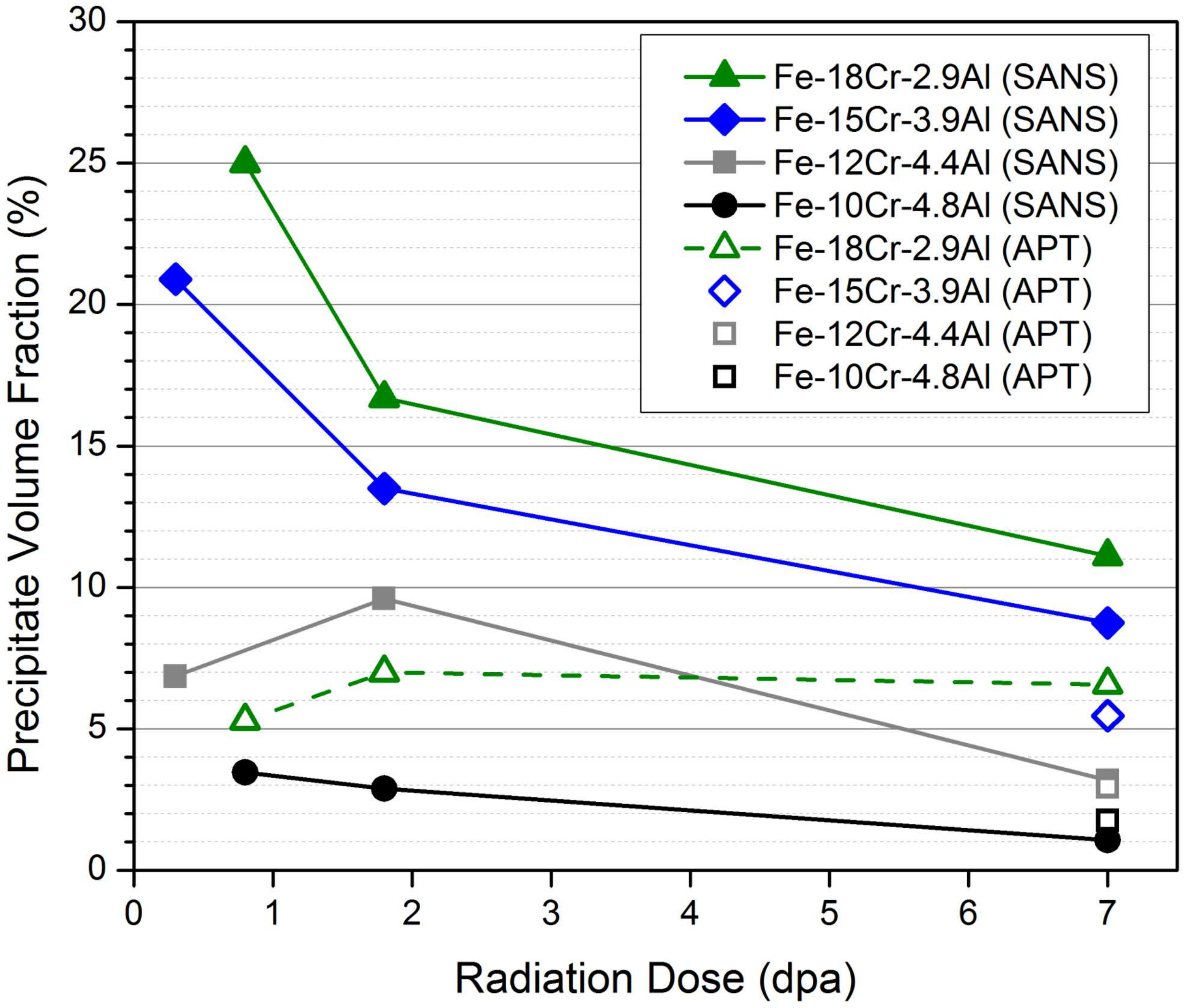
- Scattering contrast for specimens not analyzed by APT determined via extrapolation
- Trends from APT mostly preserved
  - Number density decreases with dose
  - Higher Cr content results in increased number density

Comparing APT & SANS



- Scattering contrast for specimens not analyzed by APT determined via extrapolation
- Trends from APT mostly preserved
  - Radius increases with dose as precipitates coarsen

Comparing APT & SANS



- Scattering contrast for specimens not analyzed by APT determined via extrapolation
- Trends from APT mostly preserved
  - Expect volume fraction to increase to saturation (APT data), not to decrease with dose
  - Trends with Cr content match
  - Attempting to reconcile by including polydispersity in the SANS model

Discussion – APT & SANS Correlation

- Despite significant effort, discrepancies remain in SANS & APT results arising from a variety of potential sources of error:
  - Different physical resolution limits
  - Artifacts in data due to aberrations (APT) or magnetic scattering effects (SANS)
  - Uncertainty in compositions/scattering length densities
  - Potentially oversimplifying assumptions in models used to fit SANS data

Discussion – LSW/UOKV Models for Precipitate Evolution

- Lifshitz, Slyozov, and Wagner (LSW) developed seminal model for diffusion-limited coarsening in binary alloys
- Umantsev, Olson, Kuehmann, and Voorhees (UOKV) extended this model to ternary systems
- Ultimately describes precipitate coarsening with aging time using a series of power laws:

$$\overline{R}_{\alpha'}(t) = K_R t^{1/3}$$

$$N_{\alpha'}(t) = K_N t^{-1}$$

$$\Delta C(t) = K_C t^{-1/3}$$

- Assumes:
  - spherical precipitates and constant volume fraction
  - terminal phase states are dilute solutions
  - stress-free matrix
  - negligible interparticle interactions

- Due to uncertainty in instantaneous and equilibrium phase compositions, we will focus on the first two relationships using the SANS data