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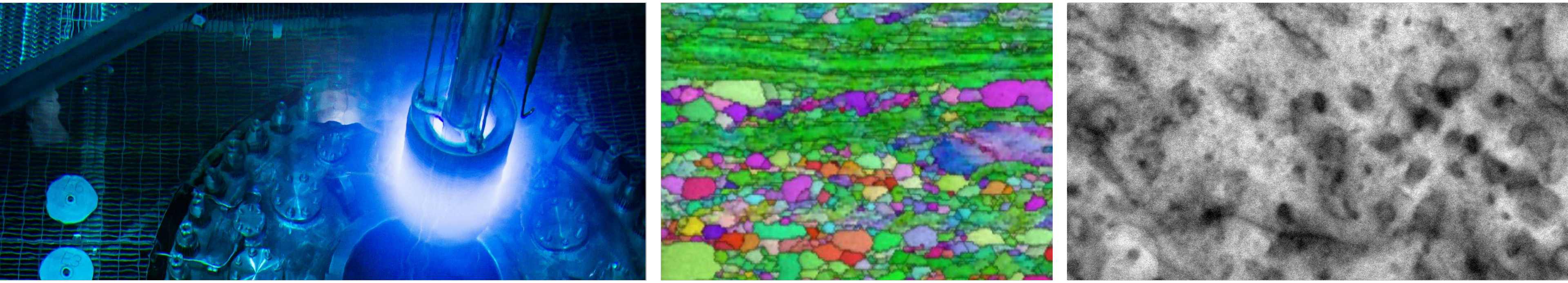

Post-Irradiation Examination of Candidate FeCrAl alloys for Accident Tolerant Fuel Cladding Applications

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Sandia National Laboratories & University of Wisconsin - Madison

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Acknowledgements

- Multi-institutional research effort involving collaboration between UW, ORNL, SNL and NSUF staff and facilities

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Motivation: Accident Tolerant Fuel Forms

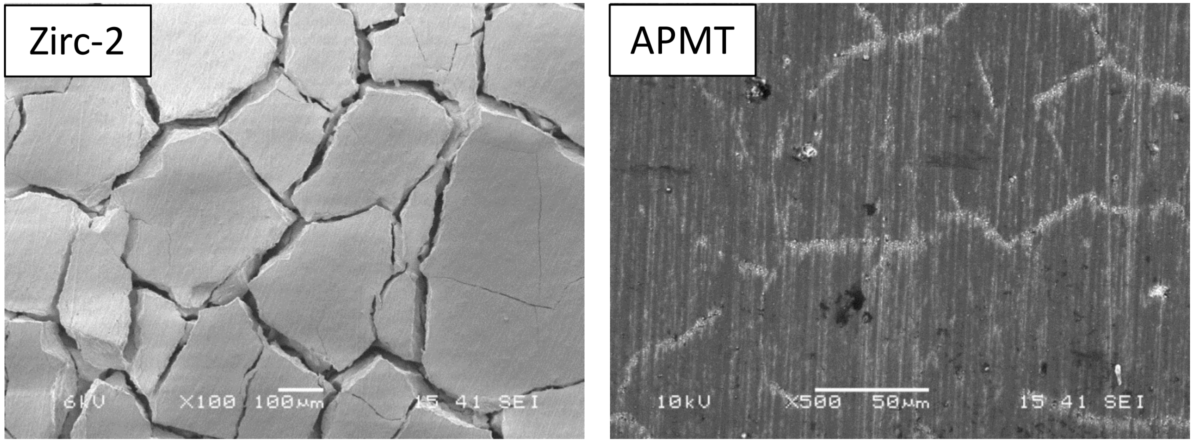
- Fukushima accident has demonstrated that Zircaloy cladding is detrimental in Loss of Coolant Accident (LOCA) scenarios
  - Exothermic oxidation reaction with H2O produces H2 gas

- 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, U3Si2)

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

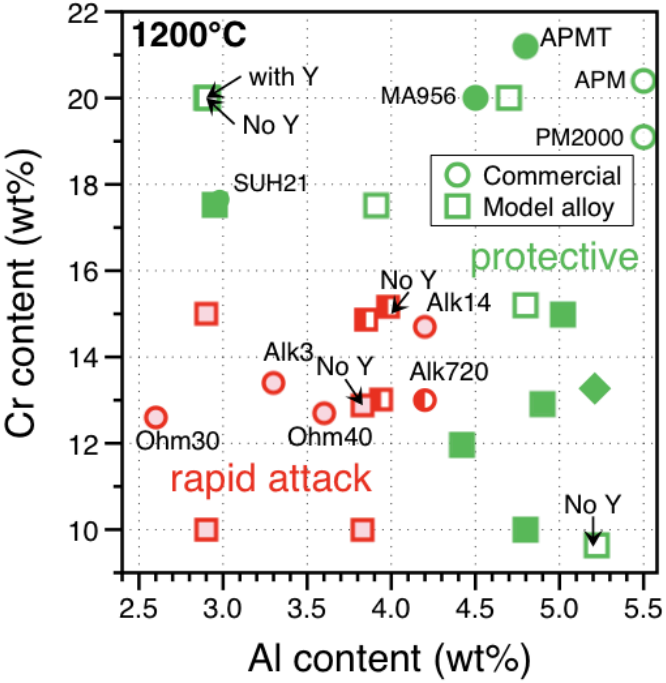
Fe-Cr-Al alloys for Nuclear Systems

- 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

Images courtesy of Raul Rebak, GE Global Research



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

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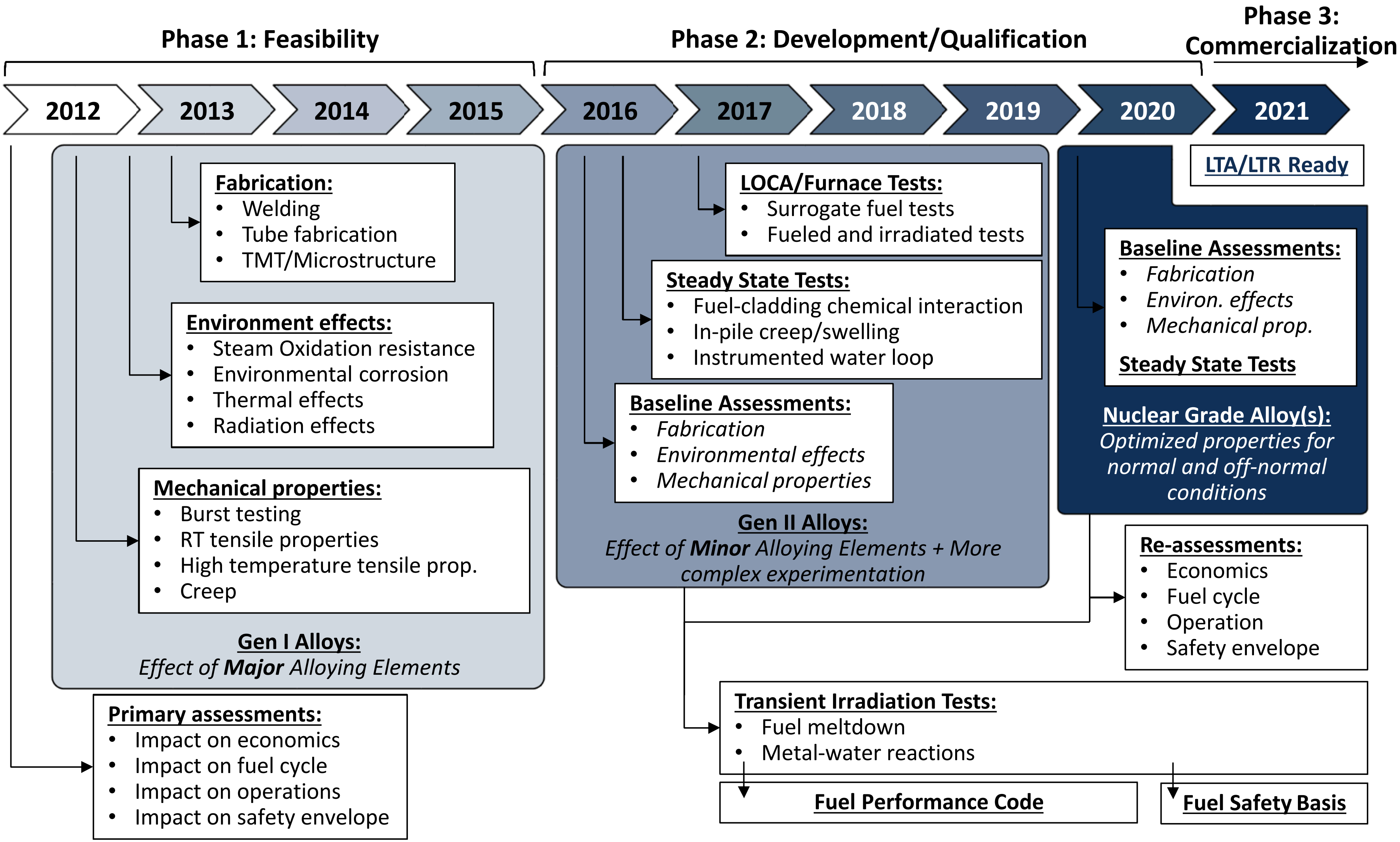
[1] Pint, B. A., Unocic, K. A., & Terrani, K. A. (2015). Effect of steam on high temperature oxidation behaviour of alumina-forming alloys. *Materials at High Temperatures*, *32*(1-2), 28–35.

Fe-Cr-Al Alloy Development Campaign

Sandia National Laboratories



Phase 1: Feasibility

Phase 2: Development/Qualification

Phase 3: Commercialization

2012 · 2013 · 2014 · 2015 · 2016 · 2017 · 2018 · 2019 · 2020 · 2021

Fabrication:
- Welding
- Tube fabrication
- TMT/Microstructure

Environment effects:
- Steam Oxidation resistance
- Environmental corrosion
- Thermal effects
- Radiation effects

Mechanical properties:
- Burst testing
- RT tensile properties
- High temperature tensile prop.
- Creep

Gen I Alloys:
*Effect of **Major** Alloying Elements*

Primary assessments:
- Impact on economics
- Impact on fuel cycle
- Impact on operations
- Impact on safety envelope

LOCA/Furnace Tests:
- Surrogate fuel tests
- Fueled and irradiated tests

Steady State Tests:
- Fuel-cladding chemical interaction
- In-pile creep/swelling
- Instrumented water loop

Baseline Assessments:
- *Fabrication*
- *Environmental effects*
- *Mechanical properties*

Gen II Alloys:
*Effect of **Minor** Alloying Elements + More complex experimentation*

LTA/LTR Ready

Baseline Assessments:
- *Fabrication*
- *Environ. effects*
- *Mechanical prop.*

Steady State Tests

Nuclear Grade Alloy(s):
Optimized properties for normal and off-normal conditions

Re-assessments:
- Economics
- Fuel cycle
- Operation
- Safety envelope

Transient Irradiation Tests:
- Fuel meltdown
- Metal-water reactions

Fuel Performance Code

Fuel Safety Basis

NSUF-Supported Research Efforts

- Characterization of α′ precipitation in irradiated 1st Gen. FeCrAl model alloys
    - FIB & APT at MaCS (CAES)

- Characterization of α′ precipitation in irradiated 2nd Gen. FeCrAl alloys and weldments
    - FIB & APT at MaCS (CAES)

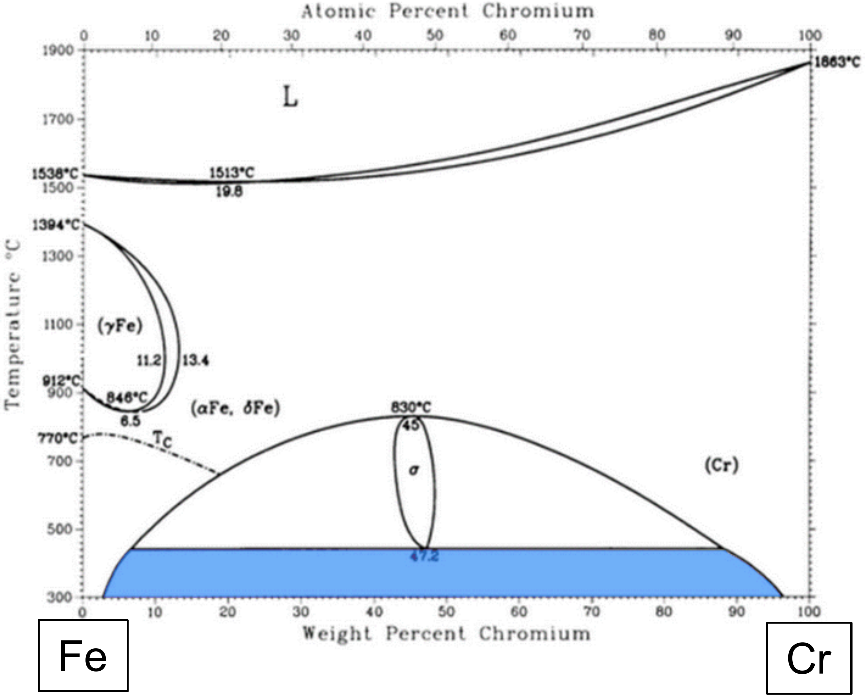
- Study of radiation damage effects and precipitate stability in ODS FeCrAl alloys
    - FIB & TEM at LAMDA (ORNL)

APT of 1st Generation FeCrAl Alloys

α′ Precipitation & Embrittlement

- While ferritic alloys are known to possess excellent swelling resistance, they have a perceived susceptibility to irradiation-induced hardening and embrittlement

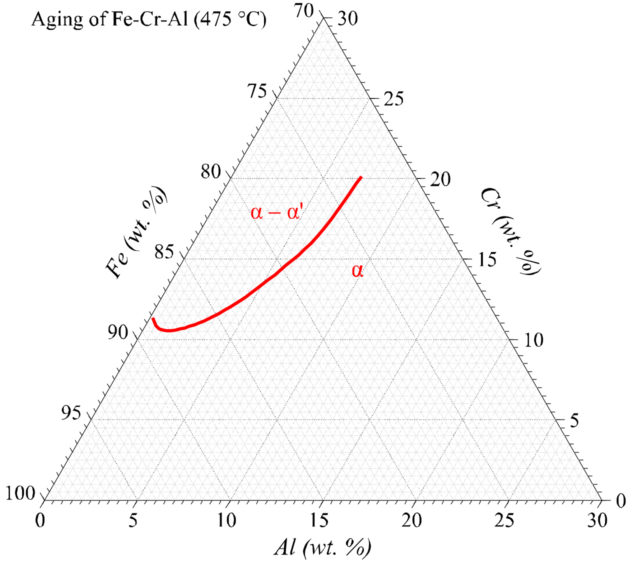
- For low Cr alloys, hardening is primarily due to the formation of dislocation loops



- 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

Experimental Goals

- Assess severity of α′ precipitation in neutron-irradiated model Fe-Cr-Al alloys using a correlative microscopy approach (APT + SANS)
    - 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

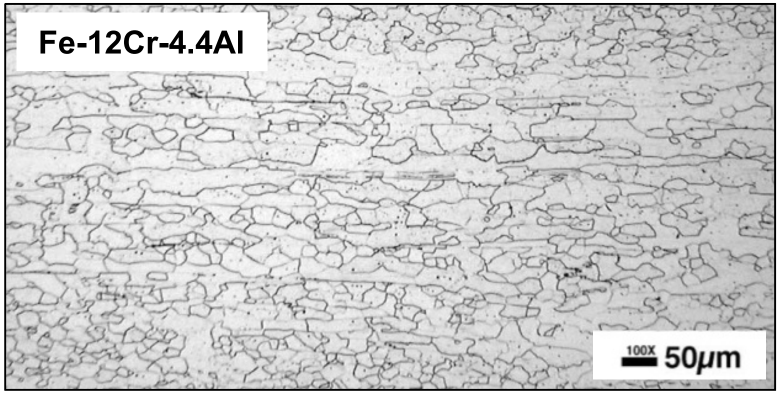


Ternary Fe-Cr-Al phase diagram showing destabilization of α' phase by bulk Al additions[1]

- **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**

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

Experimental Design

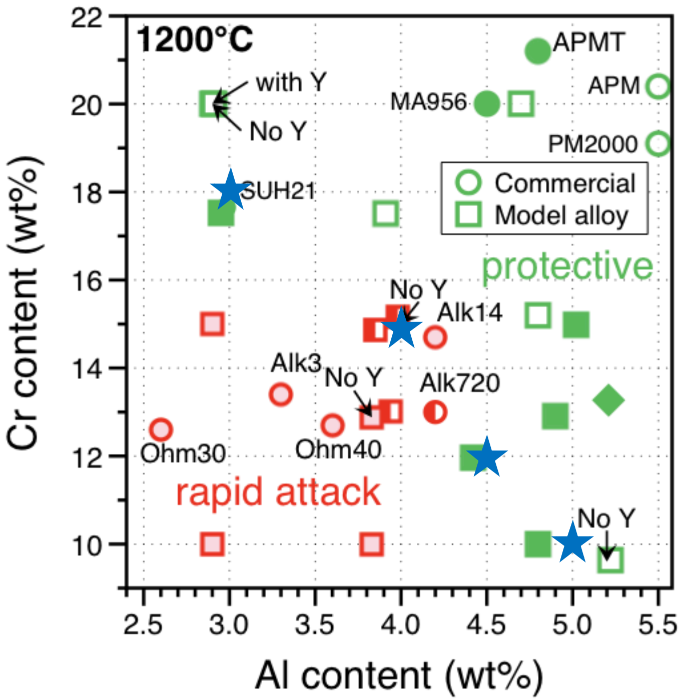


- Four Fe-(10-18)Cr-(5.8-9.3)Al+Y (at.%) model alloys have been selected for initial investigation
  - Y is added to enhance adhesion of Al_2O_3 scale

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)

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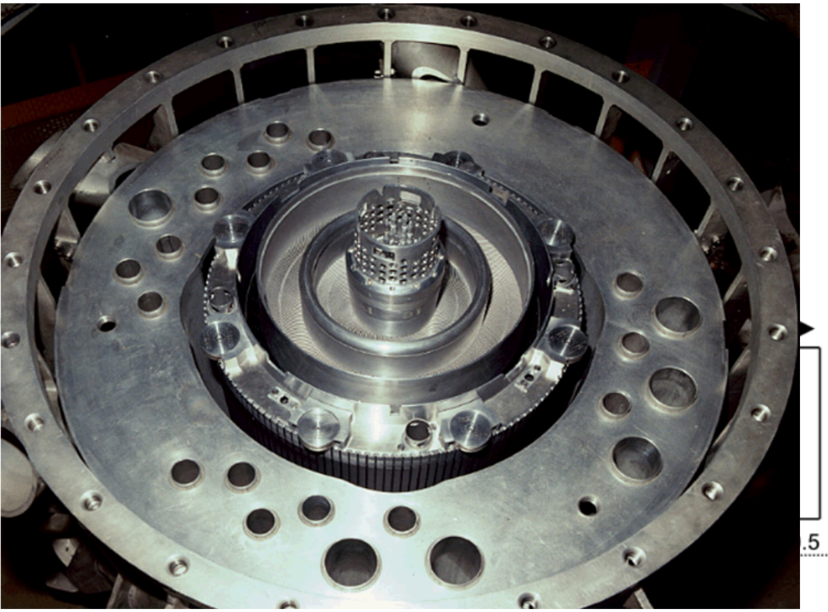
[1] Yamamoto, Y., Pint, B. A., Terrani, K. A., Field, K. G., Yang, Y., & Snead, L. L. (2015). Development and property evaluation of nuclear grade wrought FeCrAl fuel cladding for light water reactors. *Journal of Nuclear Materials*, *467*, 703–716.

Summary of FeCrAl Irradiation Campaign



Capsule ID	Exposure Time (hrs)	Neutron Flux (n/cm²s) E > 0.1 MeV	Neutron Fluence (n/cm²) E > 0.1 MeV	Dose Rate (dpa/s)	Dose (dpa)	Irradiation Temperature (°C)
FCAY-01	120	8.54×10^{14}	3.69×10^{20}	7.7×10^{-7}	0.3	334.5 ± 0.6
FCAY-02	301	8.54×10^{14}	9.25×10^{20}	7.7×10^{-7}	0.8	355.1 ± 3.4
FCAY-03	614	8.84×10^{14}	1.95×10^{21}	8.1×10^{-7}	1.8	381.9 ± 5.4
FCAY-04	2456	8.74×10^{14}	7.73×10^{21}	7.9×10^{-7}	7.0	319.9 ± 10.2
FCAY-05	4914	8.74×10^{14}	1.55×10^{22}	7.8×10^{-7}	13.8	340.5 ± 25.7

[1] Campbell, A. A., Porter, W. D., Katoh, Y., & Snead, L. L. (2016). Method for analyzing passive SiC thermometry with a continuous dilatometer to determine irradiation temperature. *Nuclear Instruments and Methods in Physics Research B*, *370*, 49–58.

1st Gen. APT Sample Matrix

- APT investigations included all compositions in the 7 dpa condition, Fe-18Cr-5.8Al for all irradiation conditions

Alloy	Irradiation Dose (dpa)	Irradiation Temp. (°C)
Fe-10Cr-9.3Al	7.0	320 ± 12.7
Fe-12Cr-8.7Al	7.0	320 ± 12.7
Fe-15Cr-7.7Al	7.0	320 ± 12.7
Fe-18Cr-5.8Al	7.0	320 ± 12.7

Composition Dependence

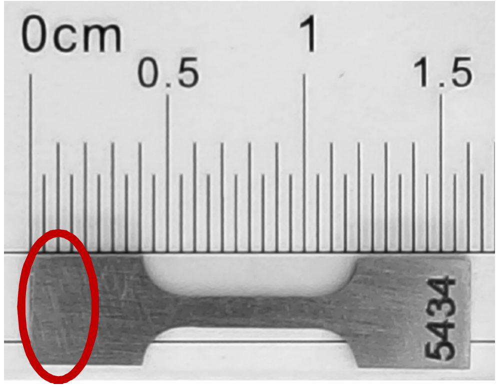
Alloy	Irradiation Dose (dpa)	Irradiation Temp. (°C)
Fe-18Cr-5.8Al	As-Rec’d	N/A
	0.8	355 ± 3.4
	1.8	382 ± 5.4
	7.0	320 ± 12.7

Dose Dependence

- APT findings are ratified through SANS measurements, performed at the GP-SANS beamline at HFIR

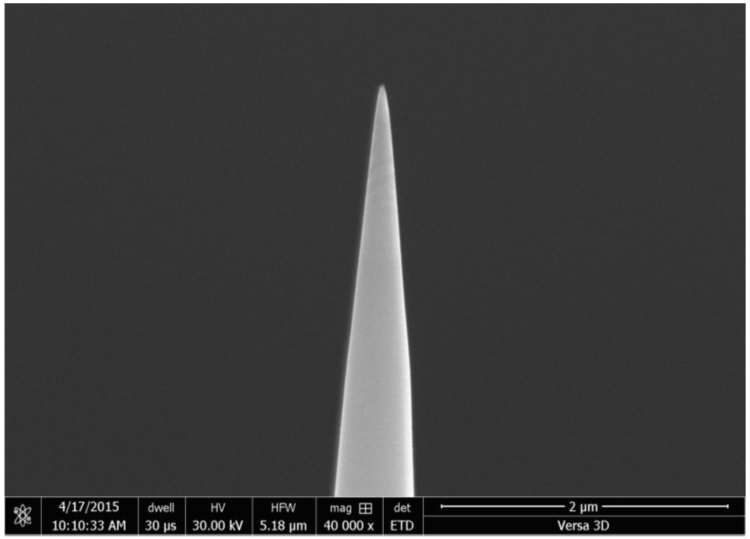
LEAP Data Collection

- 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

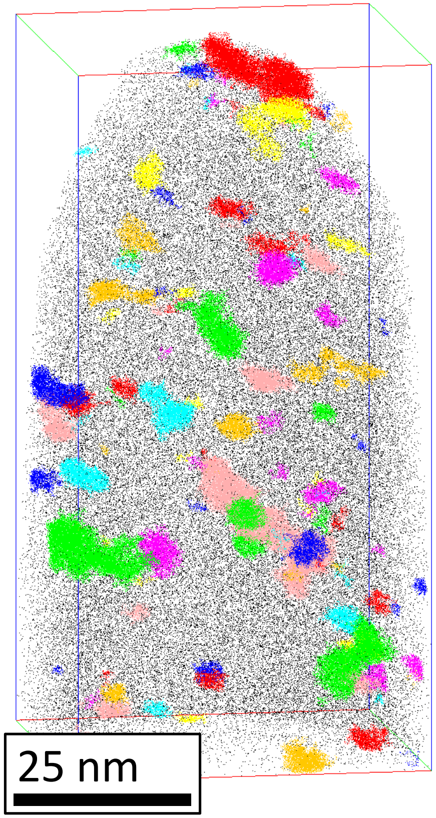


- Precipitates were indexed using the maximum separation method
  - Standard method for cluster analysis

Precipitation Composition Dependence

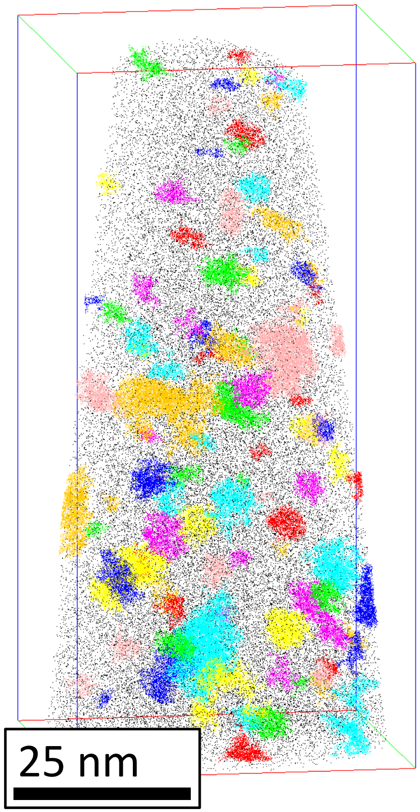
Increasing Cr, Decreasing Al

7dpa Fe-10Cr-9.3Al



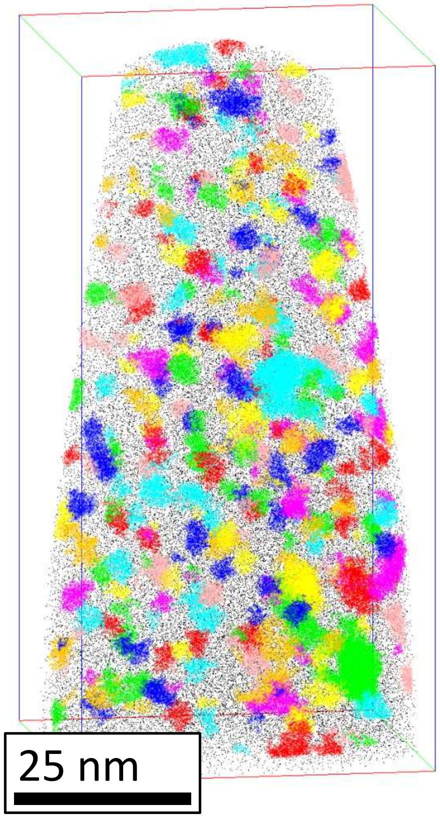
Total Volume Analyzed:
1.01×10^6 nm^3

7dpa Fe-12Cr-8.7Al



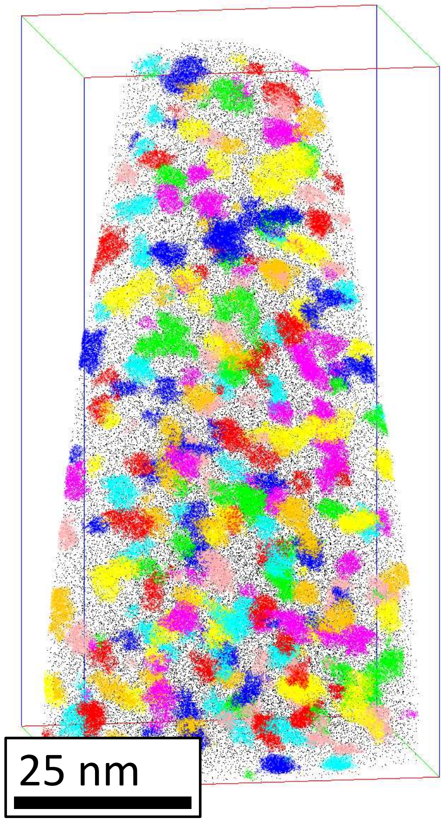
Total Volume Analyzed:
4.08×10^6 nm^3

7dpa Fe-15Cr-7.7Al



Total Volume Analyzed:
1.37×10^6 nm^3

7dpa Fe-18Cr-5.8Al



Total Volume Analyzed:
7.53×10^5 nm^3

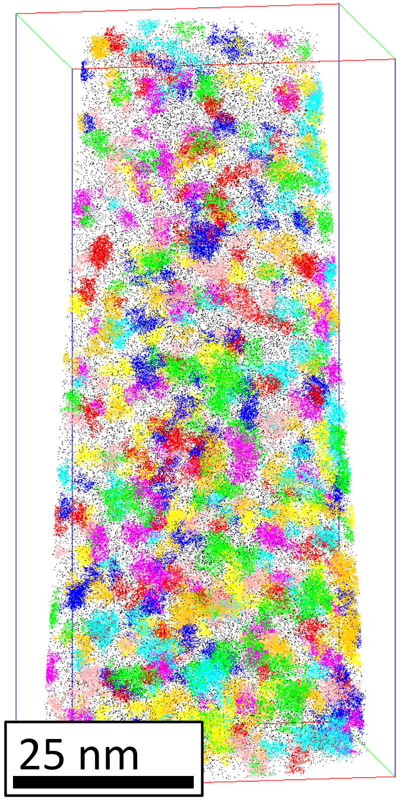
Reconstructions cropped to 50 × 50 × 100 nm

Precipitation Dose Dependence

Increasing Dose

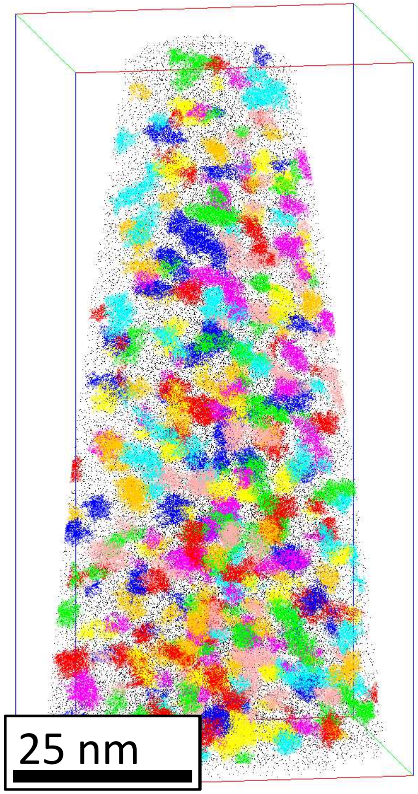
Fe-18Cr-5.8Al

0.8 dpa, 355 °C



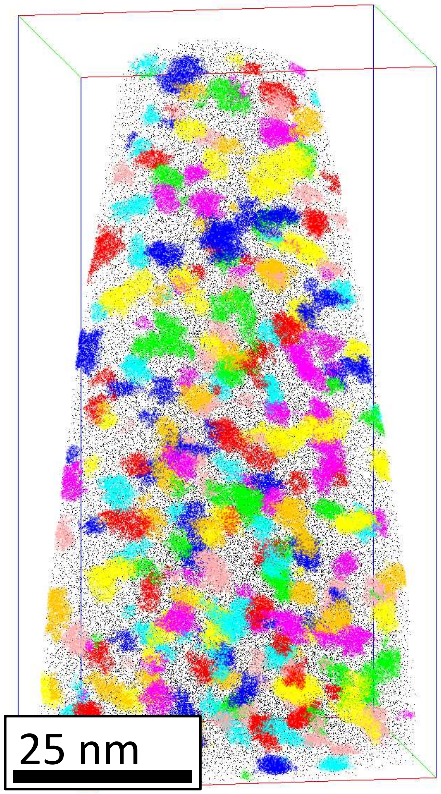
Total Volume Analyzed:
1.68×10^6 nm^3

1.8 dpa, 382 °C



Total Volume Analyzed:
1.16×10^6 nm^3

7 dpa, 320 °C



Total Volume Analyzed:
7.53×10^5 nm^3

Reconstructions cropped to 50 × 50 × 100 nm

1st Gen. FeCrAl APT Summary

		Matrix Composition (at. %)			**Average Cluster Composition** (at. %)			**Number Density**	**Volume Fraction**	**Average Radius**
Alloy	**Irradiation Dose (dpa)**	Fe	Cr	Al	Fe	Cr	Al	(×10^{24} m^{-3})	(%)	(nm)
Fe-10Cr-9.3Al	7.0	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	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	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	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	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	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

α-Fe Matrix ← | → α' Clusters

α′ precipitate Cr content decreases with increasing alloy Al content

- Compare to binary systems – typical reported cluster composition of ~85 at.% Cr
- Suggests that Al additions are shifting the phase boundary
- Al is also seen to be rejected from the precipitates volume

➡ **Less Cr-rich clusters may have implications on precipitate hardening/embrittlement contribution**

[1] P.D. Edmondson, *et al.,* (2016). Irradiation-Enhanced α′ Precipitation in Model FeCrAl Alloys. *Scripta Materialia*. http://doi.org/10.1016/j.scriptamat.2016.02.002.

[2] S.A. Briggs, *et al.*, (2017). A combined APT and SANS investigation of α′ phase precipitation in neutron-irradiated model FeCrAl alloys. *Acta Materialia*. https://doi.org/10.1016/j.actamat.2017.02.077

APT of 2nd Generation FeCrAl Alloys

Experimental Goals

- Assess α′ precipitation response in down-selected, neutron-irradiated model FeCrAl alloys with minor alloying additions
    - Study how minor alloying additions affect precipitation
    - Investigate temperature dependence of precipitation response
    - Compare precipitation in recrystallized weldments to bulk material[1]

- Investigate potential mechanisms for embrittlement of weldments in irradiated FeCrAl

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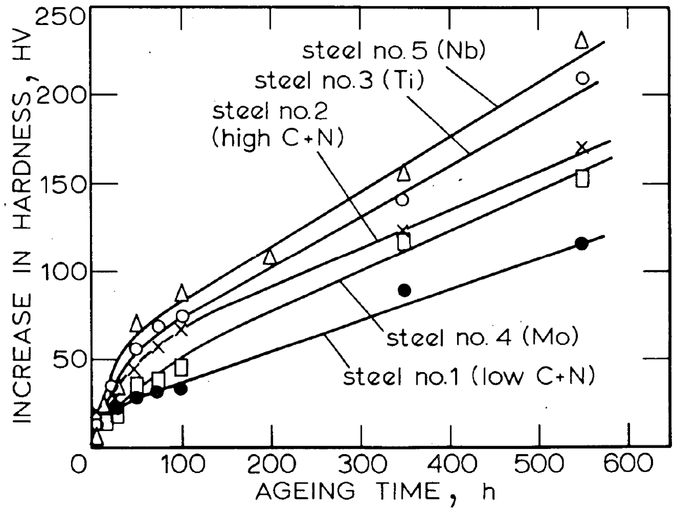
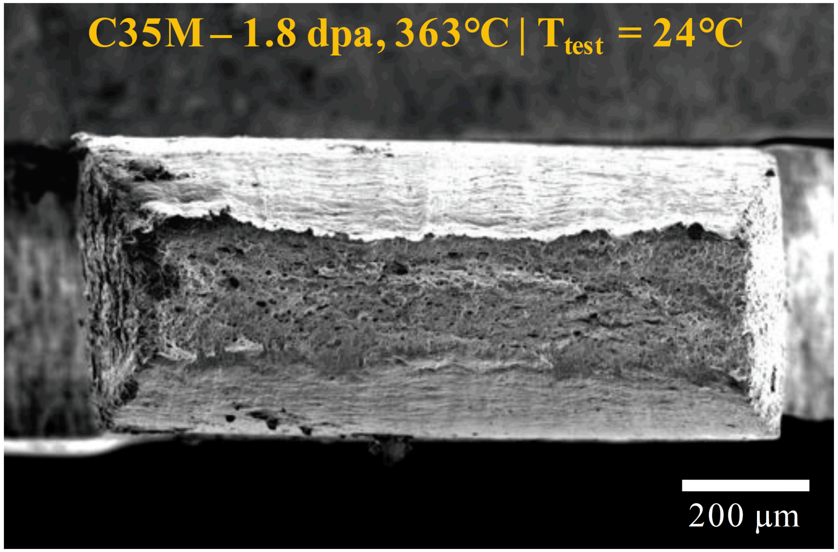
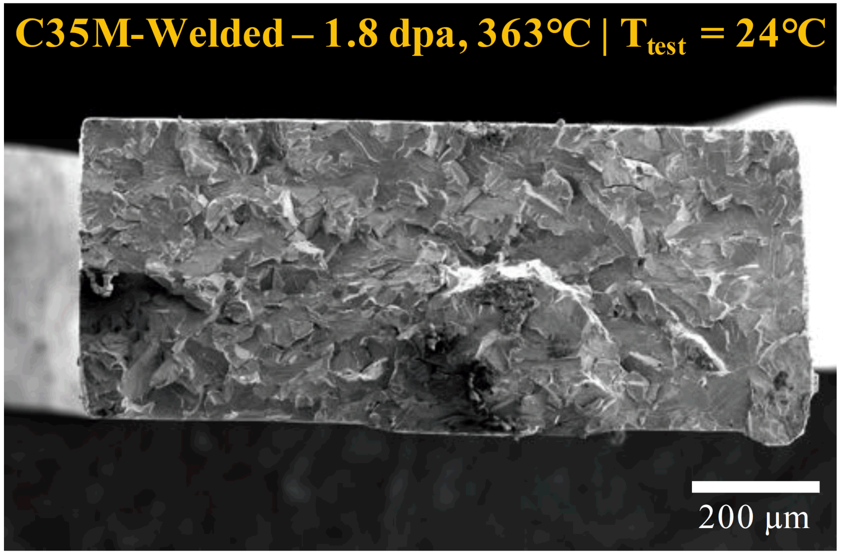
[1] Capdevila, C, *et al*. (2012). Influence of recrystallization on phase separation kinetics of oxide dispersion strengthened Fe-Cr-Al alloy. *Scripta Materialia*, 66(5), 254-257.

Alloying & Welding Effects

- Solute additions tend to enhance α′ precipitation response[1]
- Embrittlement due to welding is potentially application-limiting for ATF cladding tube deployment[2]




C35M – 1.8 dpa, 363°C | T_{test} = 24°C


C35M-Welded – 1.8 dpa, 363°C | T_{test} = 24°C

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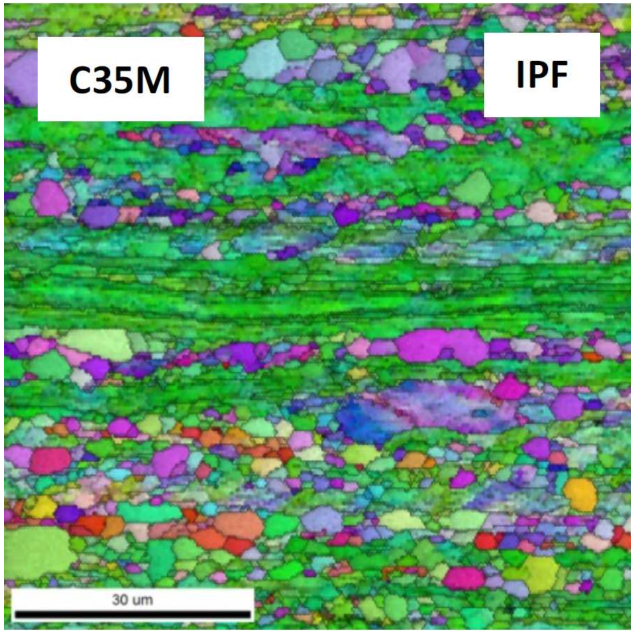
[1] Courtnall, M. and Pickering, F. B. (1976). The effect of alloying on 485C embrittlement. *Metal Science*, 10(8), 273-276.

[2] Gussev, M. N., *et al.* (2016). Preliminary Analysis of the General Performance and Mechanical Behavior of Irradiated FeCrAl Base Alloys and Weldments. ORNL/TM-2016/552.

Experimental Design

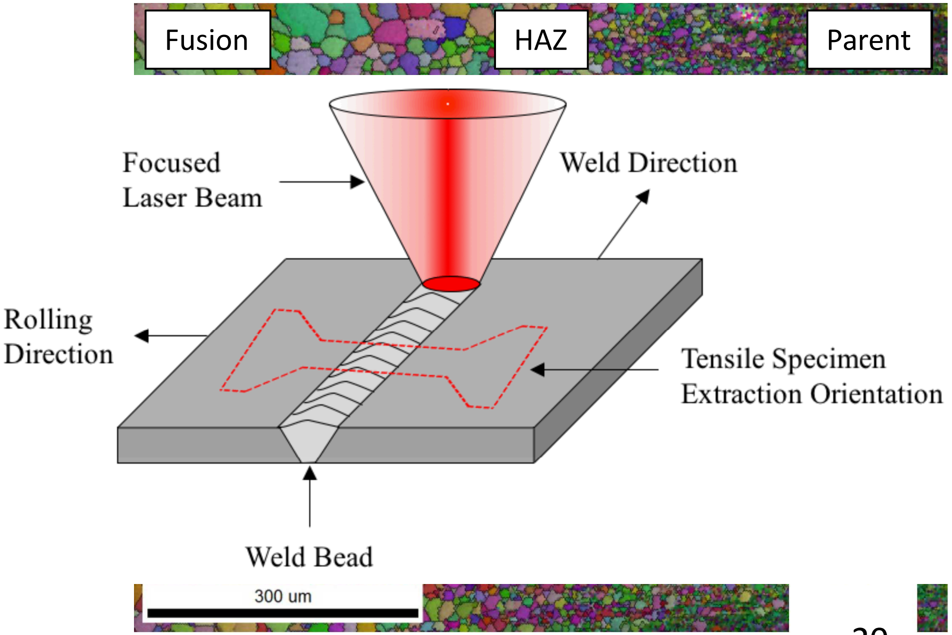
- Two Fe-Cr-Al-Mo+Y 2nd generation model alloys have been selected for APT investigation

ID	Composition, at.%									
	Fe	**Cr**	**Al**	**Mo**	**Y**	Si	C	S	O	N
C35M	**74.99**	**13.24**	**10.38**	**1.10**	**0.031**	0.244	0.004	<0.0005	0.0040	0.0011
C37M	**71.74**	**12.94**	**13.83**	**1.07**	**0.047**	0.350	0.004	<0.0005	0.0084	0.0007



- Alloys were fabricated by vacuum induction melting, hot forged and rolled, and annealed at 650 °C, resulting in micron-sized grains.[1]

- Welded specimens were fabricated by autogeneous, pulsed laser welding
  - Welding direction perpendicular to gauge length and rolling direction



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[1] Field, K. G., *et al.* (2016). Second Annual Progress Report on Radiation Tolerance of Controlled Fusion Welds in High Temperature Oxidation Resistant FeCrAl Alloys. ORNL/TM-2017/770.

2nd Gen. APT Sample Matrix

- Six total specimens
- Efforts sought to probe composition and temperature dependencies and welding effects

Alloy	ROI	Irradiation Dose (dpa)	Irradiation Temp. (°C)
C35M	Bulk	1.9	194.5 ± 37.9
C35M	Bulk	1.8	363.6 ± 23.1
C35M	Bulk	1.9	559.4 ± 28.1
C35M	HAZ	1.8	363.6 ± 23.1
C35M	Fusion	1.8	363.6 ± 23.1
C37M	Bulk	1.8	363.6 ± 23.1

Composition Dependence

- Sample matrix to be completed September 2017

Alloy	ROI	Irradiation Dose (dpa)	Irradiation Temp. (°C)
C35M	Bulk	1.9	194.5 ± 37.9
		1.8	363.6 ± 23.1
		1.9	559.4 ± 28.1

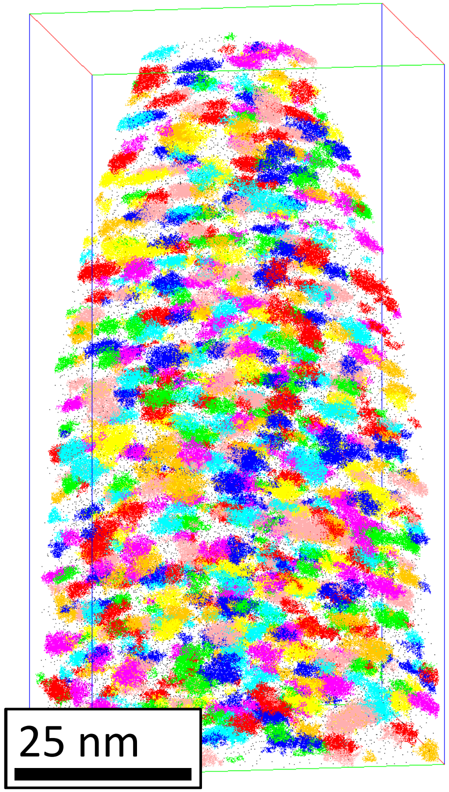
Temperature Dependence

Capsule ID	Exposure Time (hrs)	Neutron Flux (n/cm²s) E > 0.1 MeV	Neutron Fluence (n/cm²) 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

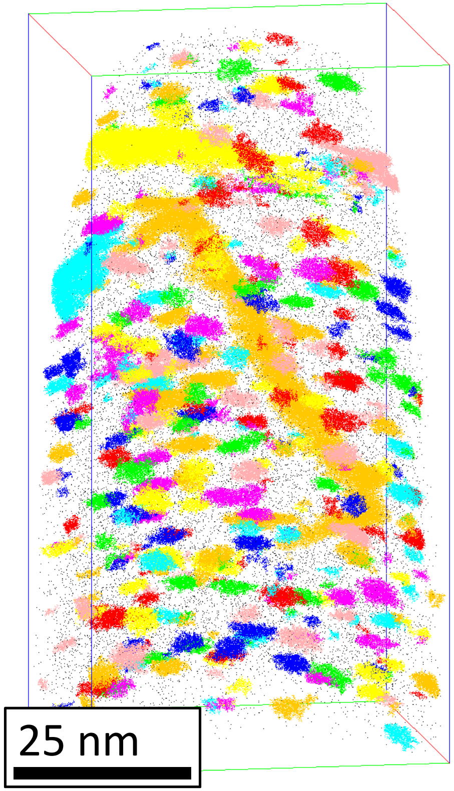
Preliminary 2nd Gen. APT Data

- α′ precipitates still present in 2nd Gen alloys
- Lower density of precipitates apparent in recrystallized HAZ grains

C35M, 1.8 dpa, 330°C, Bulk



C35M, 1.8 dpa, 330°C, HAZ



TEM of ODS FeCrAl Variants

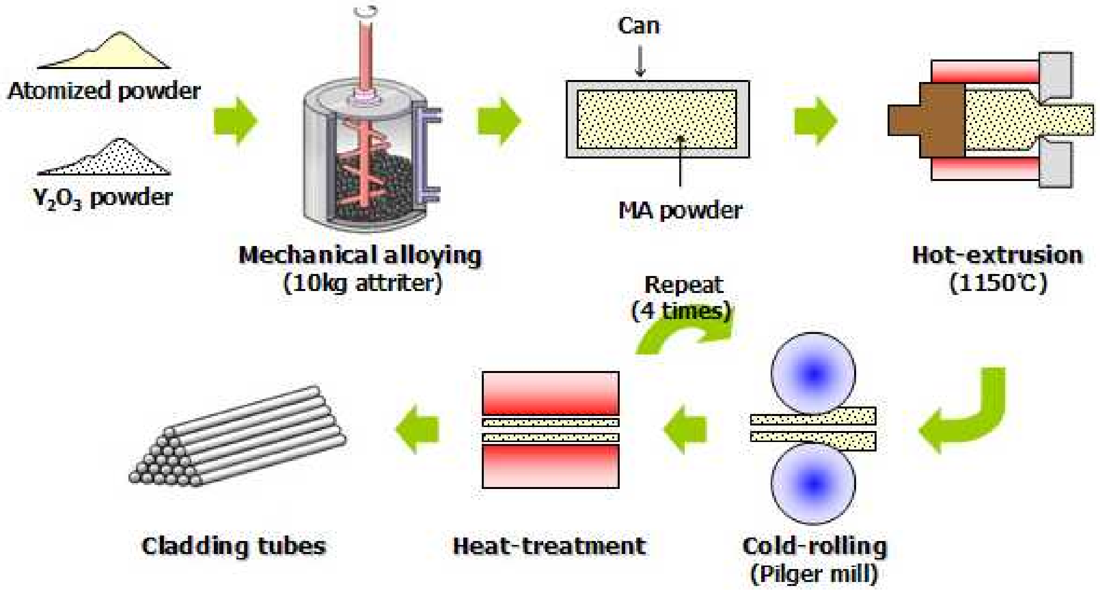
Experimental Goals

- Investigate effect of ODS particles on radiation tolerance of model FeCrAl alloys using TEM
    - Study dislocation loop microstructure
    - Investigate oxide nanoparticle stability under irradiation
    - Use subsequent *in situ* ion irradiation to probe nanoparticle stability dose rate dependence

- Complements additional planned work for APT and SANS studies of ODS and α′ precipitates

ODS FeCrAl Motivation

- Oxide dispersion-strengthened FeCrAl variants seek to increase alloy strength and creep resistance
- Have the added benefit of introducing a high density of interfaces that serve as sinks for point defects
  - Results in enhanced radiation tolerance

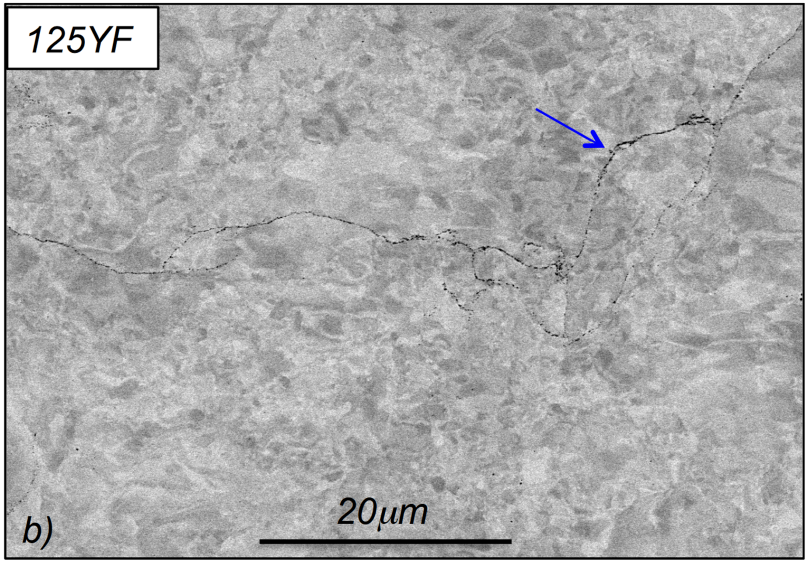


[1] Development of Oxide Dispersion Strengthened Ferritic Steel Claddings for Sodium-Cooled Fast Breeder Reactor. *JAEA News Release.* http://www.jaea.go.jp/english/news/p06101302/.

Experimental Design

- One Fe-12Cr-5Al+Y_2O_3 (wt.%) powder metallurgy FeCrAl variant selected for study

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



- 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]

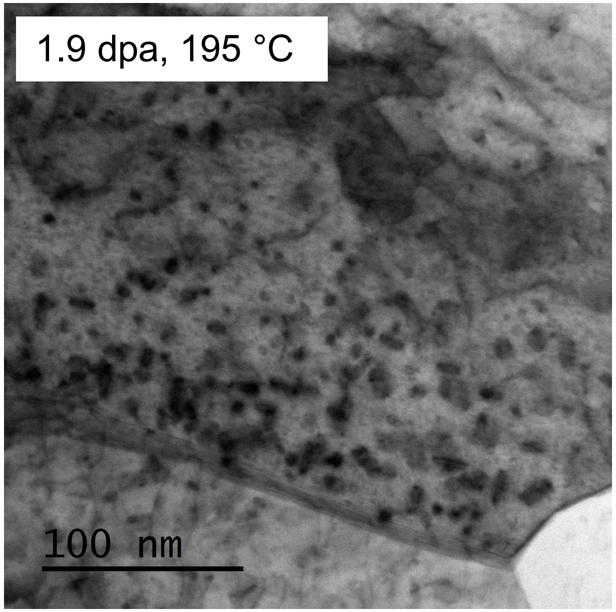
- 100-300 nm grain sizes, with some alumina stringers apparent

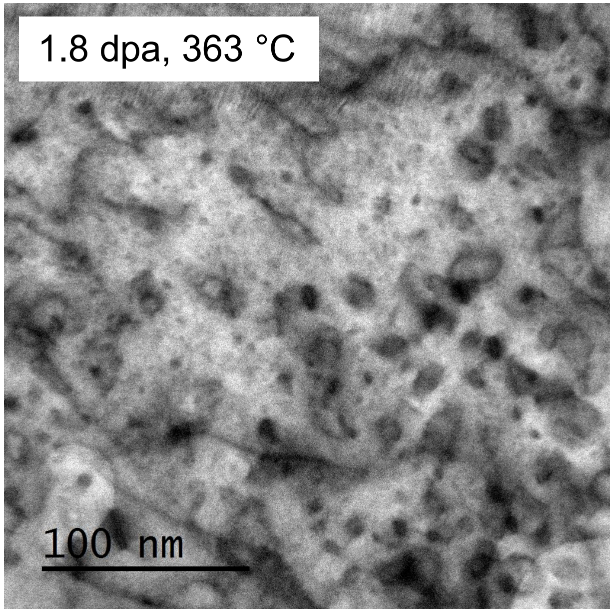
Capsule ID	Exposure Time (hrs)	Neutron Flux (n/cm^2s) E > 0.1 MeV	Neutron Fluence (n/cm^2) E > 0.1 MeV	Dose Rate (dpa/s)	Dose (dpa)	Irradiation Temperature (°C)
FCAT-01	590	1.10×10^{15}	2.17×10^{21}	9.8×10^{-7}	1.9	194.5 ± 37.9
FCAT-02	590	1.04×10^{15}	2.17×10^{21}	9.3×10^{-7}	1.8	363.6 ± 23.1
FCAT-03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

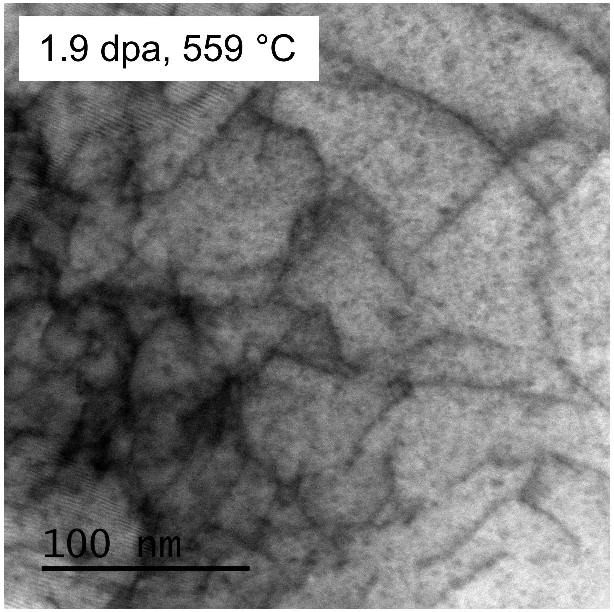
[1] Dryepondt, S., *et al*. (2015). Oak Ridge National Laboratory Development of ODS FeCrAl Alloys for Accident-Tolerant Fuel Cladding. ORNL/TM-2015/539.

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

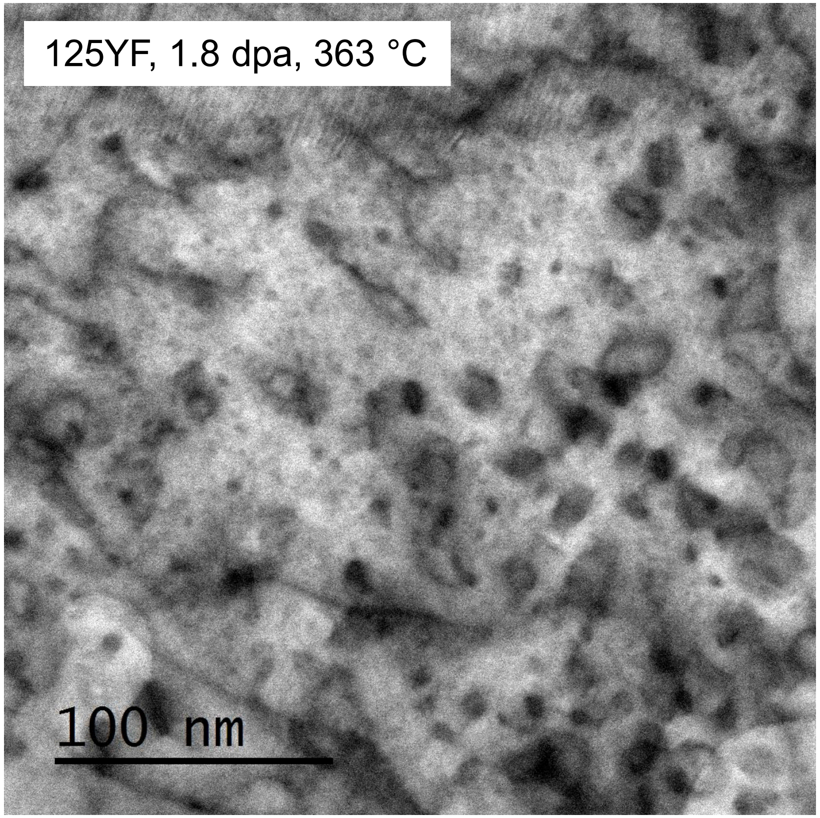

1.9 dpa, 195 °C

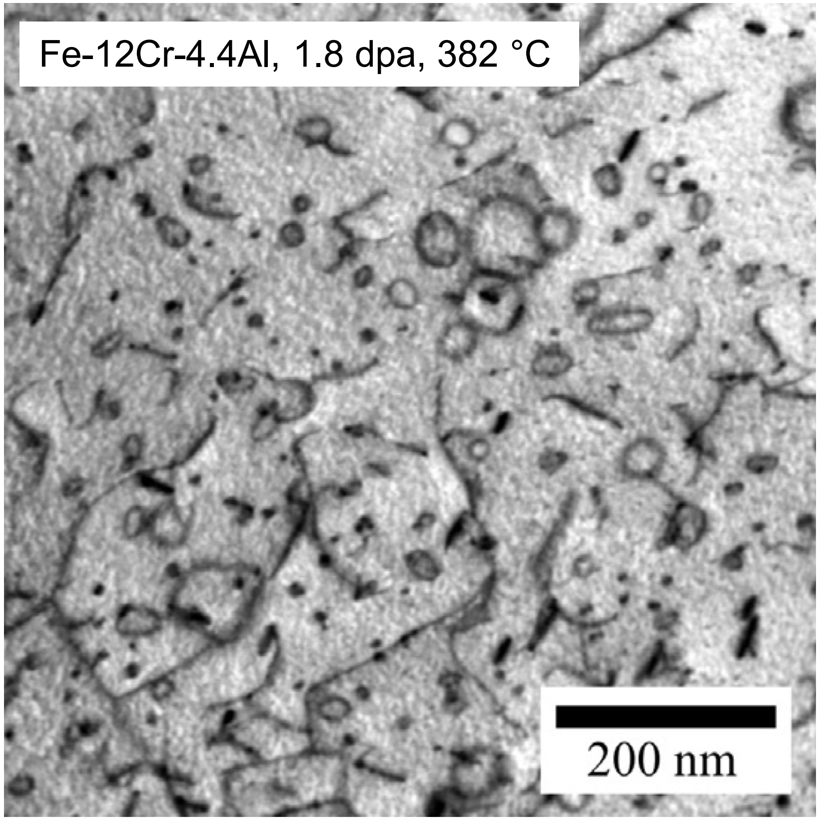

1.8 dpa, 363 °C


1.9 dpa, 559 °C

Comparison to non-ODS Alloys

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

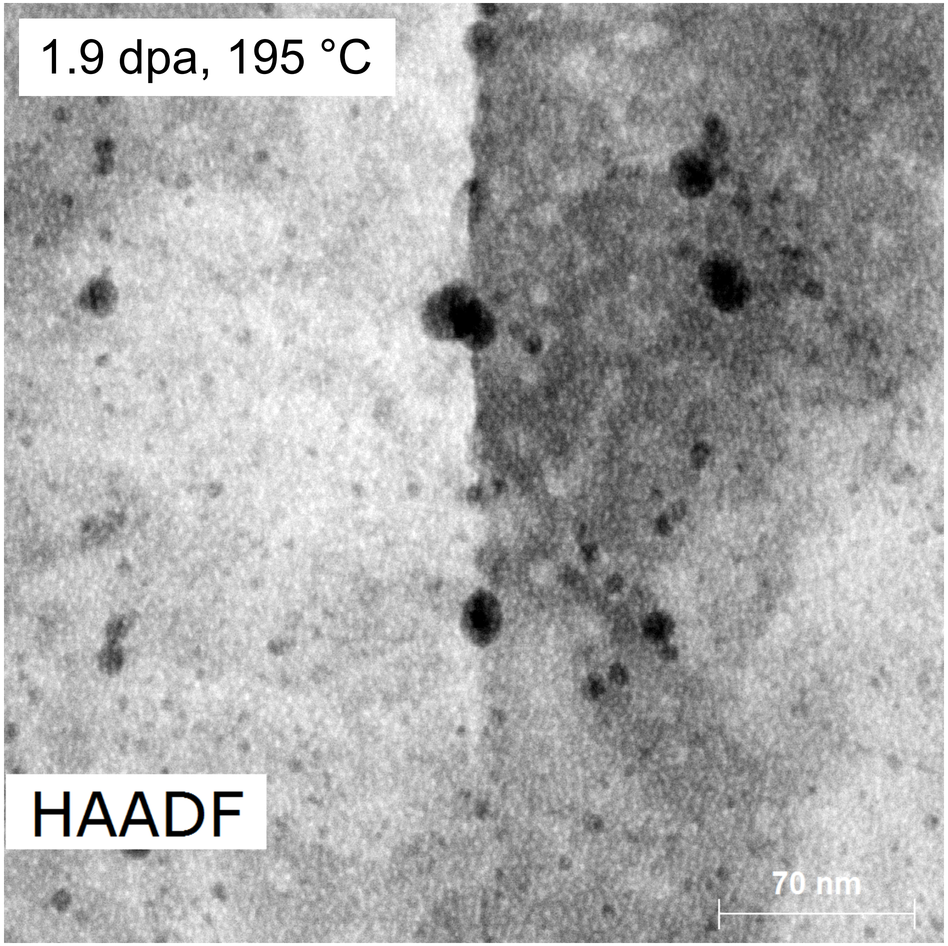

125YF, 1.8 dpa, 363 °C

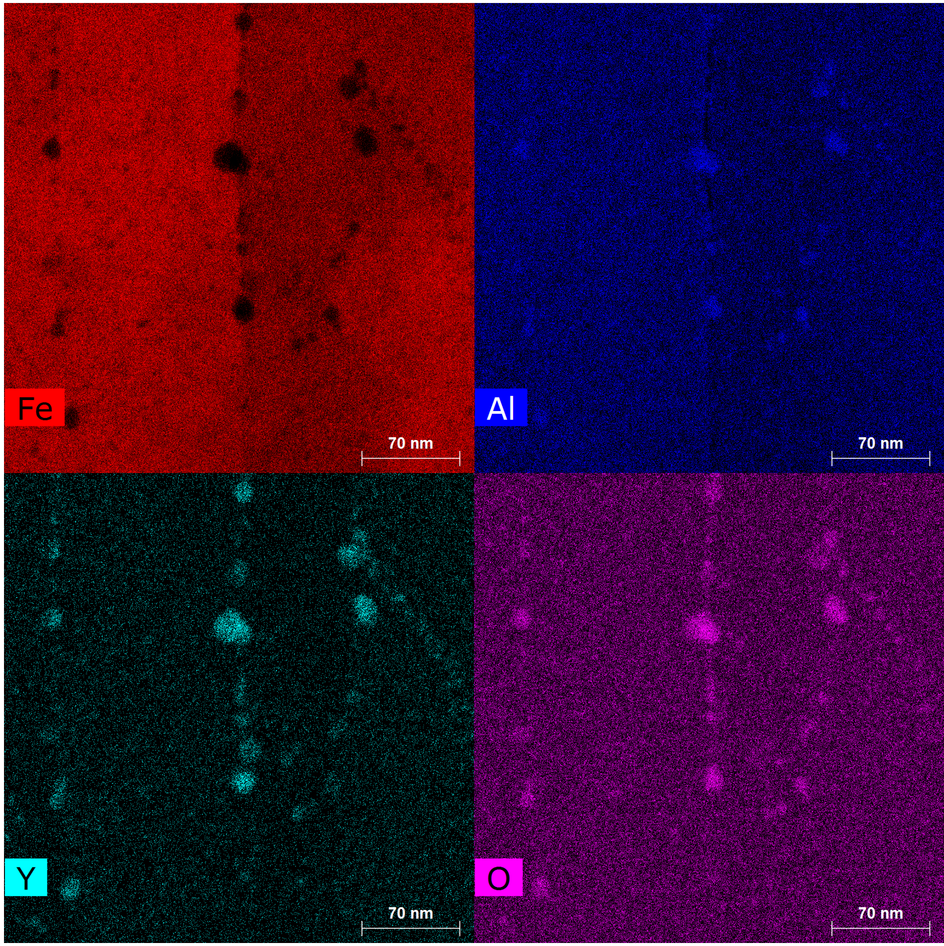

Fe-12Cr-4.4Al, 1.8 dpa, 382 °C

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

125YF Oxide Microstructures

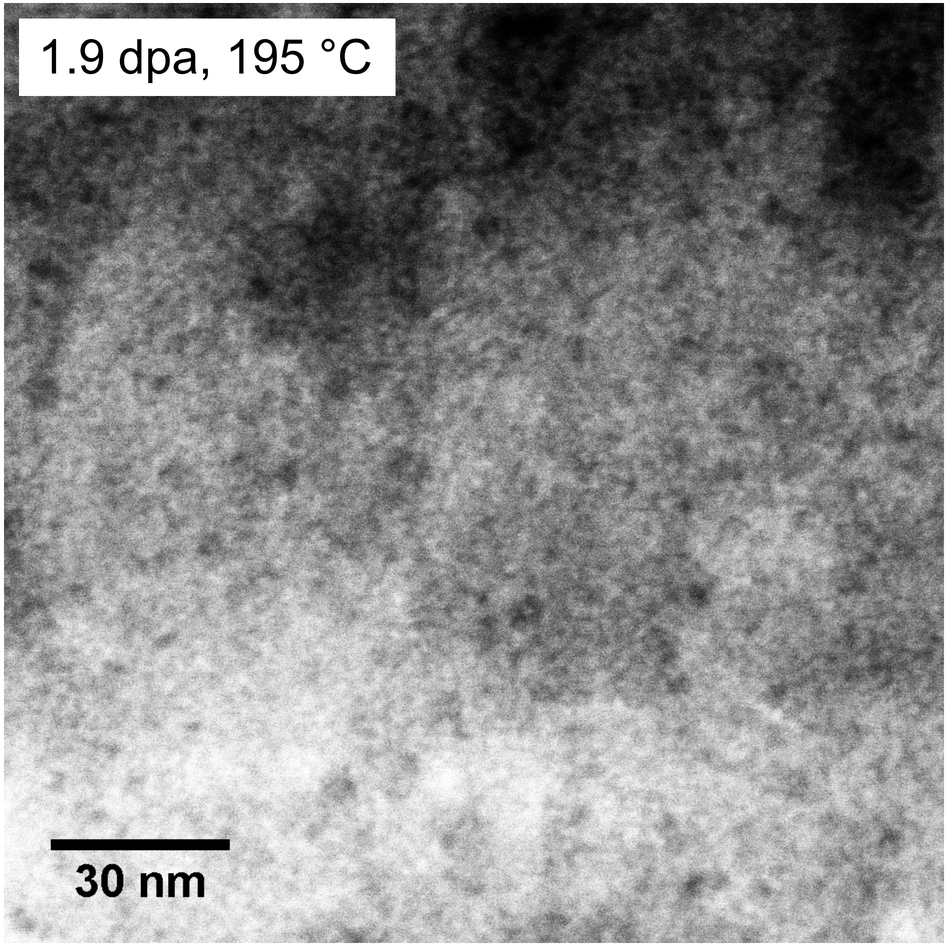
- Yttria/alumina precipitates decorating some GBs, some larger precipitates in the matrix



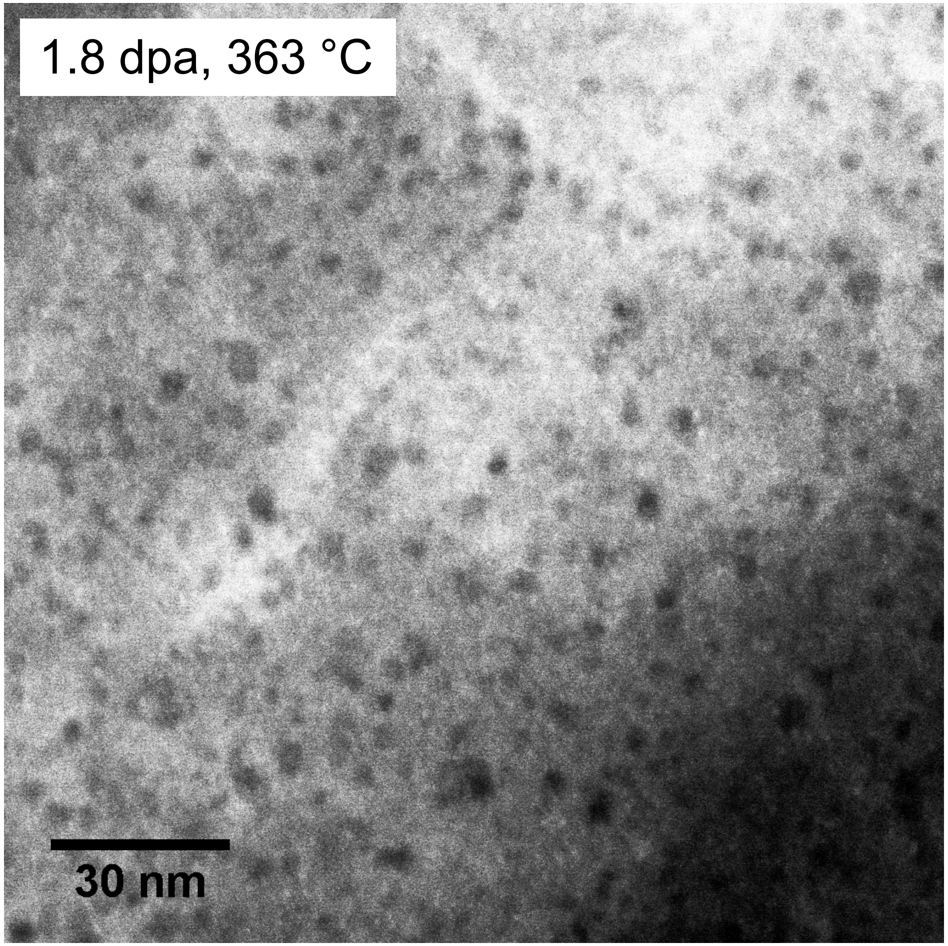


125YF Oxide Microstructures

- Yttria/alumina precipitates decorating some GBs, some larger precipitates in the matrix



1.9 dpa, 195 °C



1.8 dpa, 363 °C

Conclusions

- Completed investigations of 1st Gen. FeCrAl have shown that:
  - Al additions result in a lower α′ phase Cr content than in binary Fe-Cr systems
  - Al rejected from clusters
  - Nucleation regime progresses quickly – completed by 1.8 dpa
  - Severity of precipitation response increases with increasing Cr
  - Precipitate coarsening behavior has a similar mechanism to the thermally aged system
- Preliminary data on 2nd Gen. & ODS FeCrAl demonstrates:
  - 2nd Gen. materials are still susceptible to α′ precipitation
  - Recrystallized grains in welded HAZ show lower densities of precipitates
  - Loops in ODS FeCrAl are much smaller than conventional alloys
  - Strong temperature dependence for loop size and densities
  - Oxide particles appear stable under neutron irradiation at all temperatures

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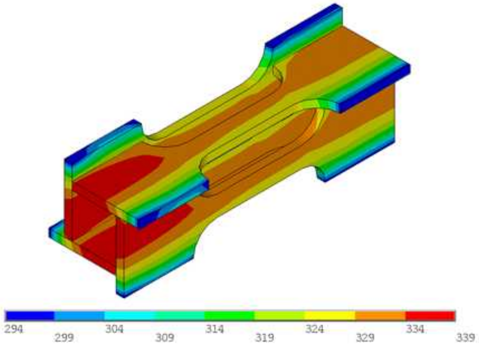
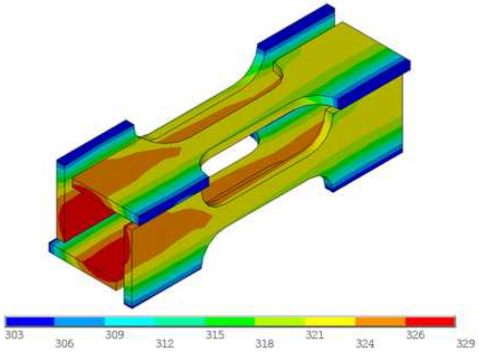
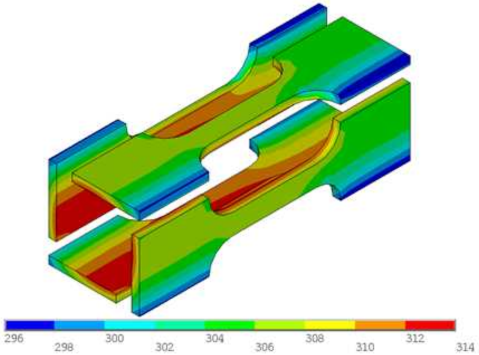
- This research was performed, in part, using instrumentation (FEI Talos F200X TEM) provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program, and the Nuclear Science User Facilities.

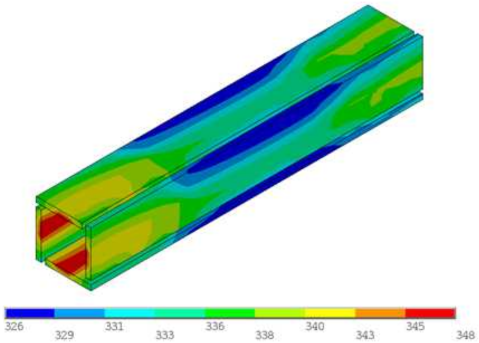
Thank you for your attention.
Questions?

Irradiation Temperature Analysis


Inner Tensile


Middle Tensile

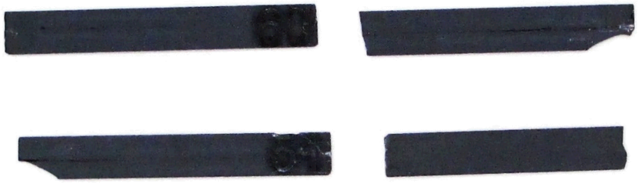

Outer Tensile

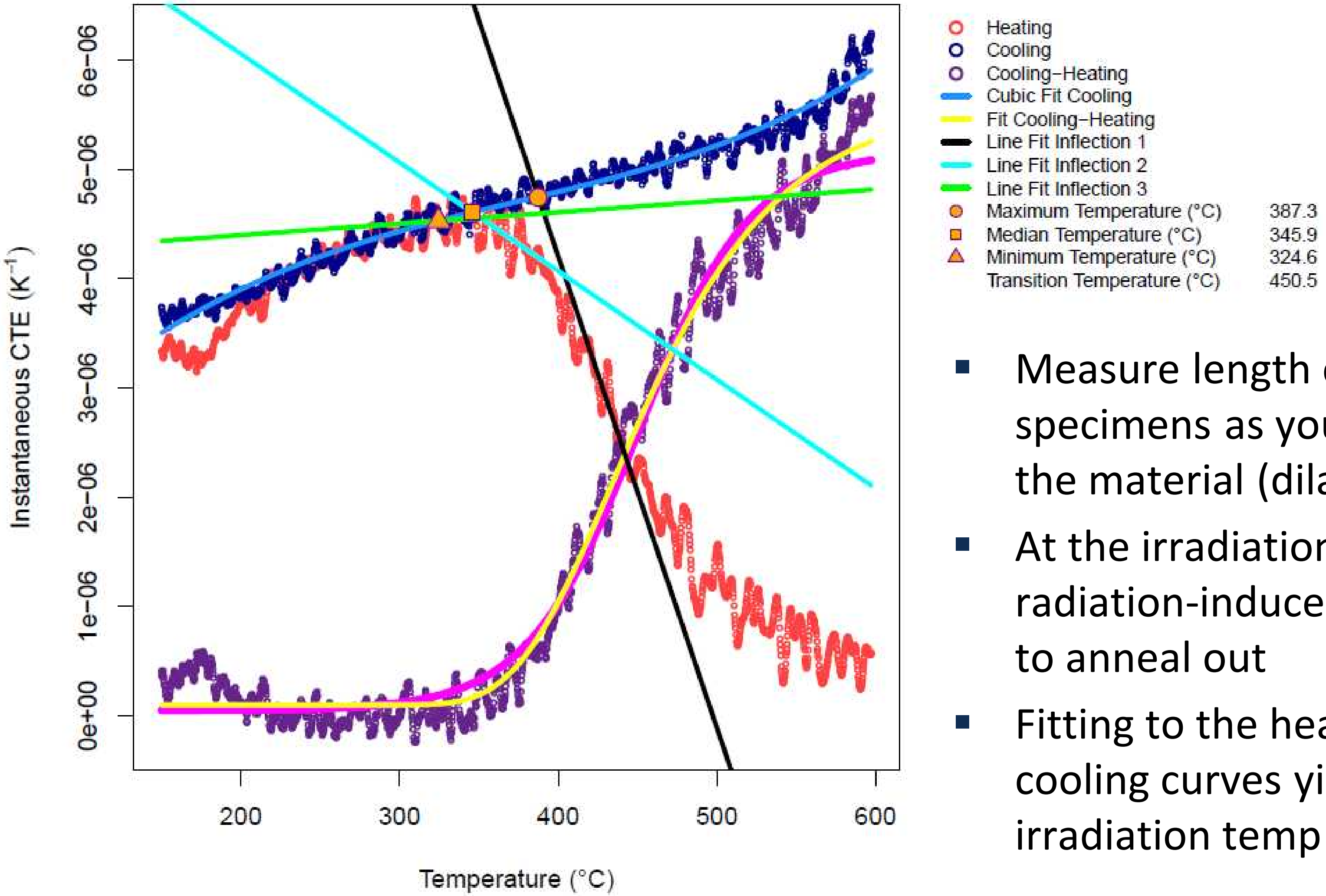

Sic Thermometry Bar

- 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)

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