Advanced Methods for Manufacturing

DEC 2 – 3, 2020

Enhancing irradiation tolerance of steels via nanostructuring by innovative manufacturing techniques

Award Number: DE-NE0008524 (Project number 16-10537)

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Introduction

- **Why nanostructuring?**

Strengthening mechanisms:

A. Work hardening: dislocation-dislocation interaction

B. Solid solution strengthening: solute-dislocation interaction

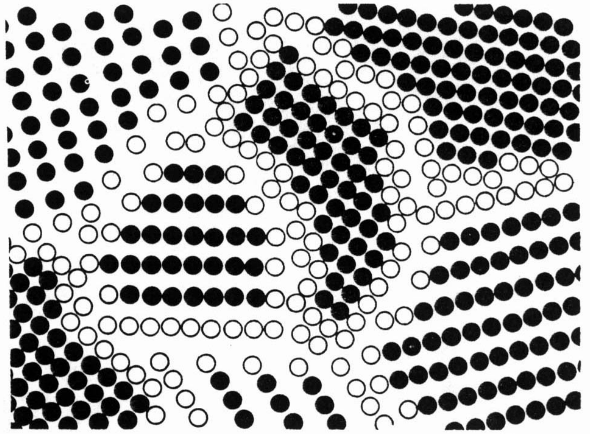
C. Particle strengthening: dislocation-particle interaction
Including precipitate strengthening and dispersion strengthening

D. Grain boundary strengthening: dislocation-grain boundary interaction

Hall-Petch relationship:

$\sigma_y = \sigma_0 + k_y \cdot d^{-1/2}$

σ_0, k_y : material constants



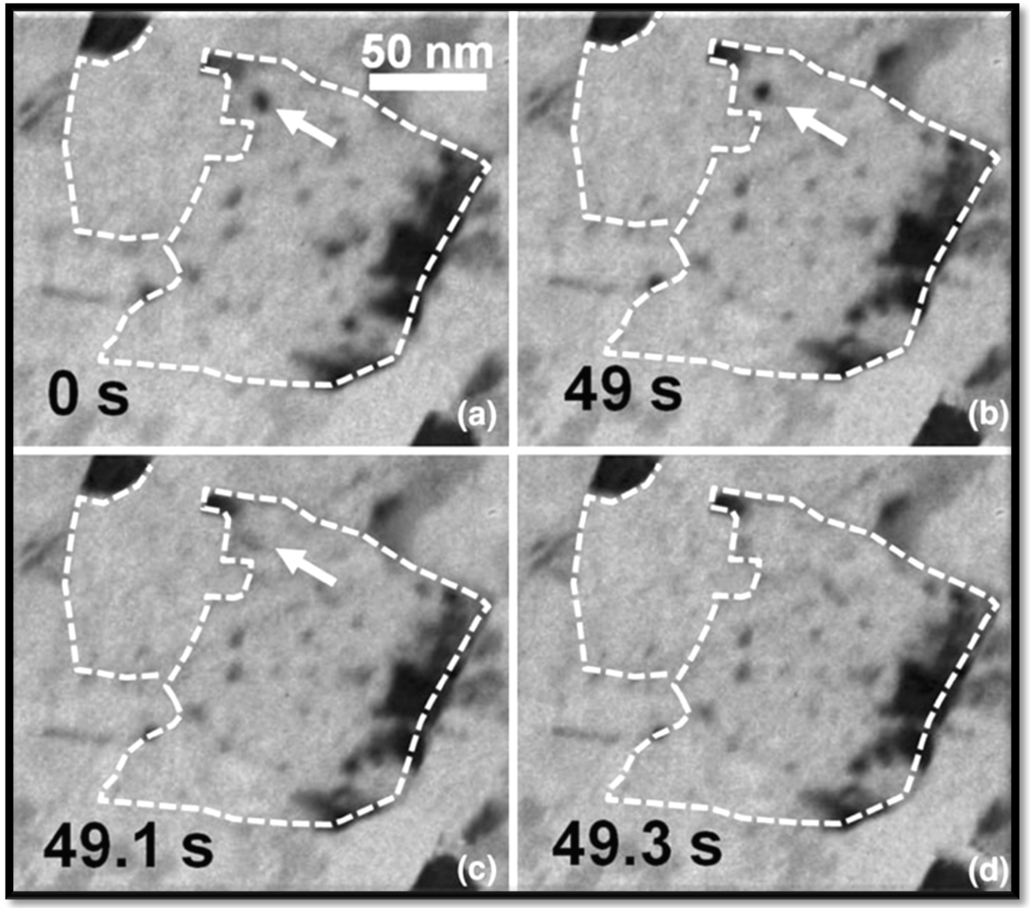
D=5 nm, fraction of GBs=50%

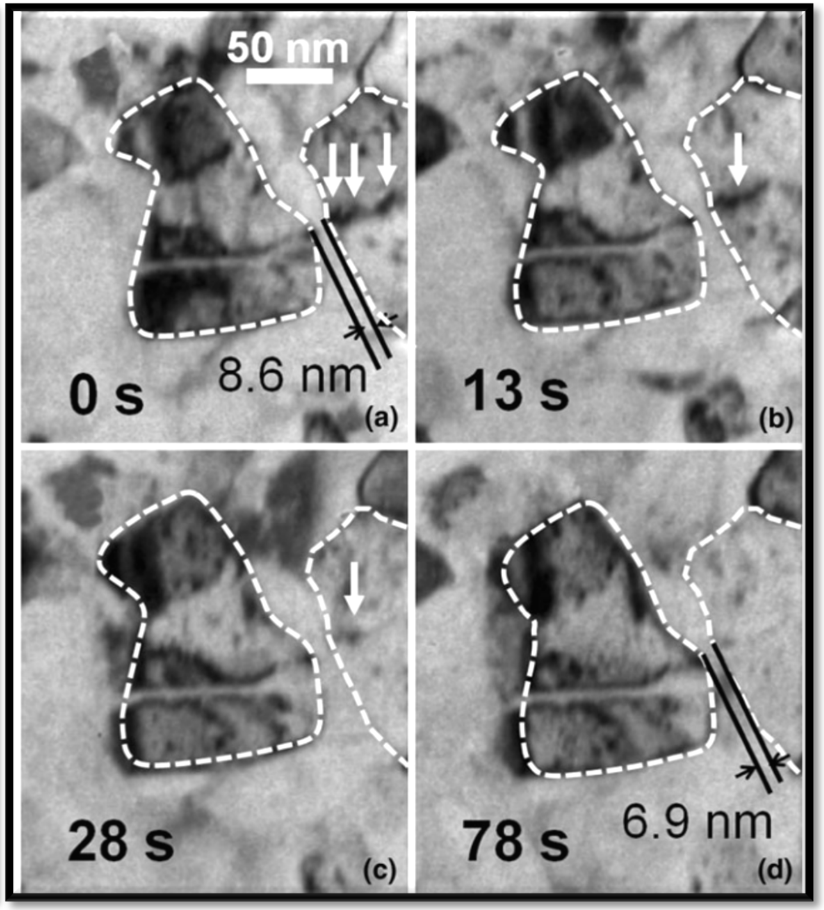
- Nanocrystalline materials: single or multiple-phase polycrystals with structural features (typically grains) smaller than 100 nm
- D=100 nm~1 μm, ultrafine grained materials; D=1~10μm, fine grained materials; D>10 μm, coarse grained conventional materials

-H. Gleiter, in Proceedings of the second Risϕ International Symposium on Metallurgy and Materials Science,1981, Denmark: Risϕ National Laboratory, Roskilde

Introduction

- **GBs as Sinks for Irradiation Defects**





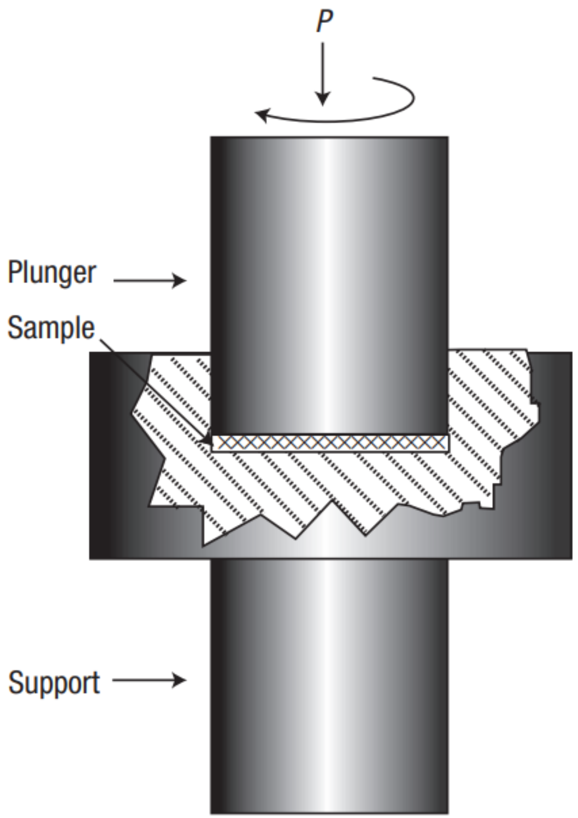
-Sun C, et al., Metall Mater Trans A 44 (2013) 1966

- In-situ TEM imaging during ion irradiation of NC Ni films
- Grain boundaries as sinks for irradiation-induced dislocation loops and segments

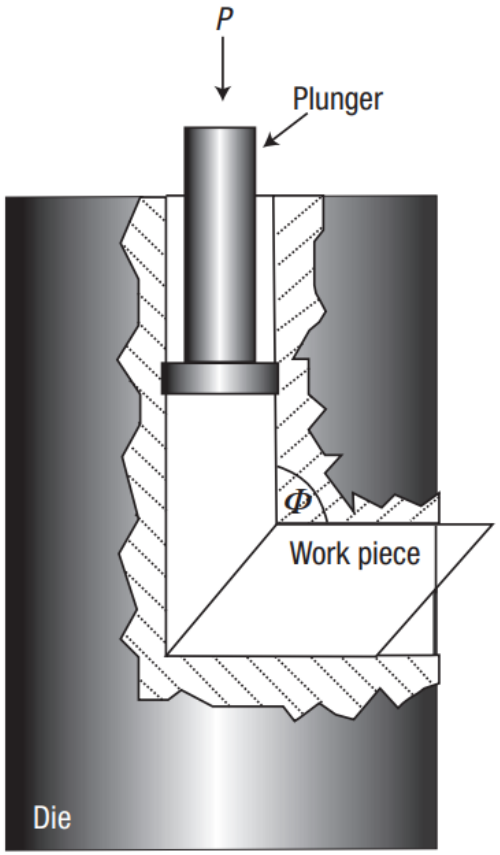
Introduction

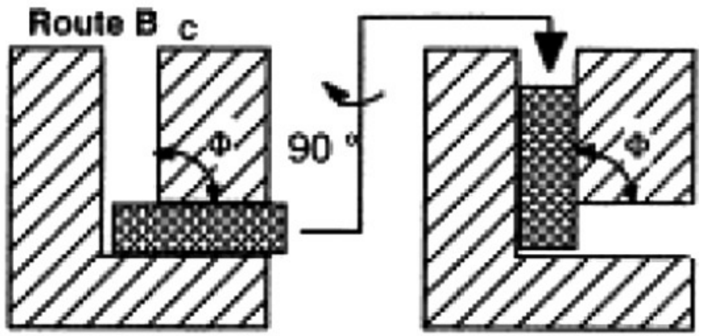
- **Nanostructuring through severe plastic deformation (SPD)**

High pressure torsion (HPT)

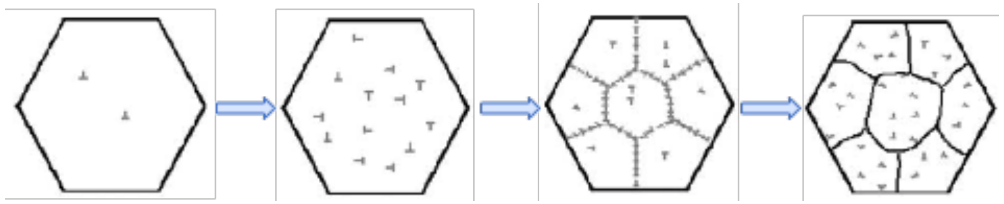


Equal Channel Angular Pressing (ECAP)





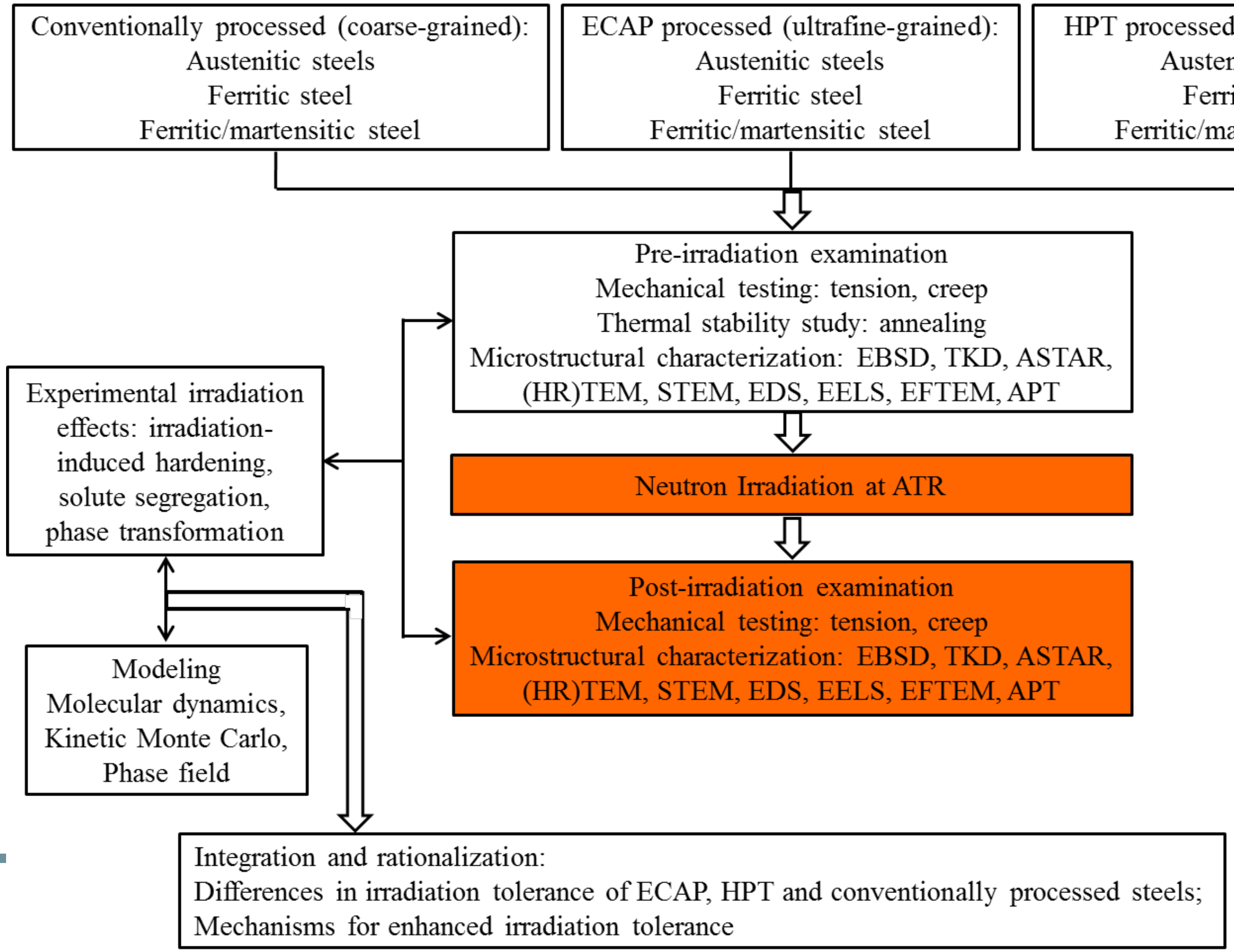
Grain refinement process



-Valiev, Ruslan. "Nanostructuring of metals by severe plastic deformation for advanced properties." *Nature materials* 3, no. 8 (2004): 511-516.

Project Objectives

- Establish/enhance our fundamental understanding of irradiation effects in ultrafine-grained or nanocrystalline steels produced by ECAP or HPT.
- Assess the potential applications of ECAP and HPT in fabricating materials for applications in current and advanced reactors



<u>Sample set 1:</u> Conventionally processed (coarse-grained) austenitic 316 steel

<u>Sample set 2:</u> ECAP processed (ultra-fine grained) austenitic 316 steel

<u>Sample set 3:</u> HPT processed (nanocrystalline) austenitic 316 steel

<u>Sample set 4:</u> Conventionally processed (coarse-grained) austenitic 304 steel

<u>Sample set 5:</u> ECAP processed (ultra-fine grained) austenitic 304 steel

<u>Sample set 6:</u> HPT processed (nanocrystalline) austenitic 304 steel

<u>Sample set 7:</u> Conventionally processed (coarse-grained) F/M Grade 91 steel

<u>Sample set 8:</u> ECAP processed (ultra-fine grained) F/M Grade 91 steel

<u>Sample set 9:</u> HPT processed (nanocrystalline) F/M Grade 91 steel

<u>Sample set 10:</u> Conventionally processed (coarse-grained) ferritic Kanthal-D

<u>Sample set 11:</u> ECAP processed (ultra-fine grained) ferritic Kanthal-D

<u>Sample set 12:</u> HPT processed (nanocrystalline) ferritic Kanthal-D

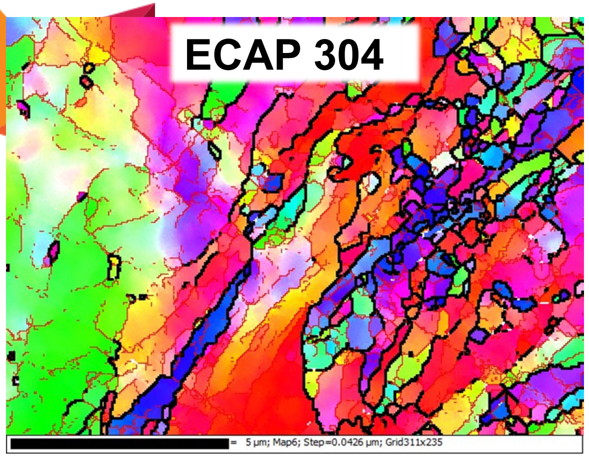
Advanced manufacturing using severe plastic deformation

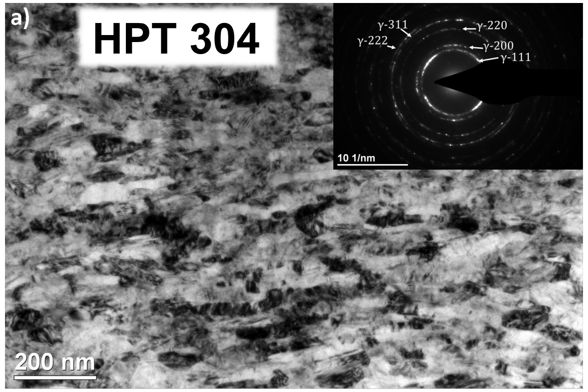
Element	SS304	SS316	G91	Kanthal-D
Fe	Balance	Balance	Balance	Balance
Cr	17.22	16.18	8.38	20.57
Ni	9.56	12.24	0.17	0.26
C	0.03	0.02	0.11	0.026
Mo	0.12	2.47	0.9	-
Al	-	-	-	4.79
V	0.04	0.04	0.2	0.03
Ti	0.26	0.32	-	0.02
Cu	0.16	0.23	0.17	0.02
Si	0.24	0.37	0.46	0.24
W	0.04	0.04	-	-
P	0.03	0.03	0.01	-
Mn	-	-	0.43	0.18
Nb	-	-	0.06	-

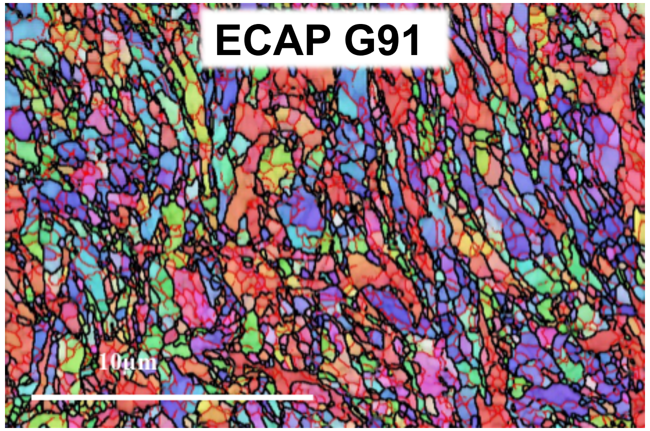
Material	Technique	Temp (°C)	# of passes/turns
SS 304	HPT	300	10
SS 316	HPT	300	10
Grade 91	HPT	300	10
Kanthal D	HPT	300	10
SS 304	ECAP	450	6
SS 316	ECAP	380	6
Grade 91	ECAP	300	6
Kanthal D	ECAP	520	6

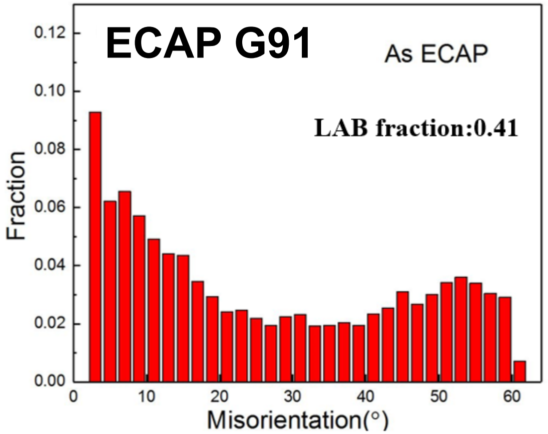
- HPT was performed at 300 °C for all the alloys.
- ECAP manufacturing temperature is material specific to prevent cracking.
- Deformation at elevated temperatures suppressed deformation induced martensitic transformation: 304 and 316 fully austenitic after SPD

Microstructures obtained by SPD

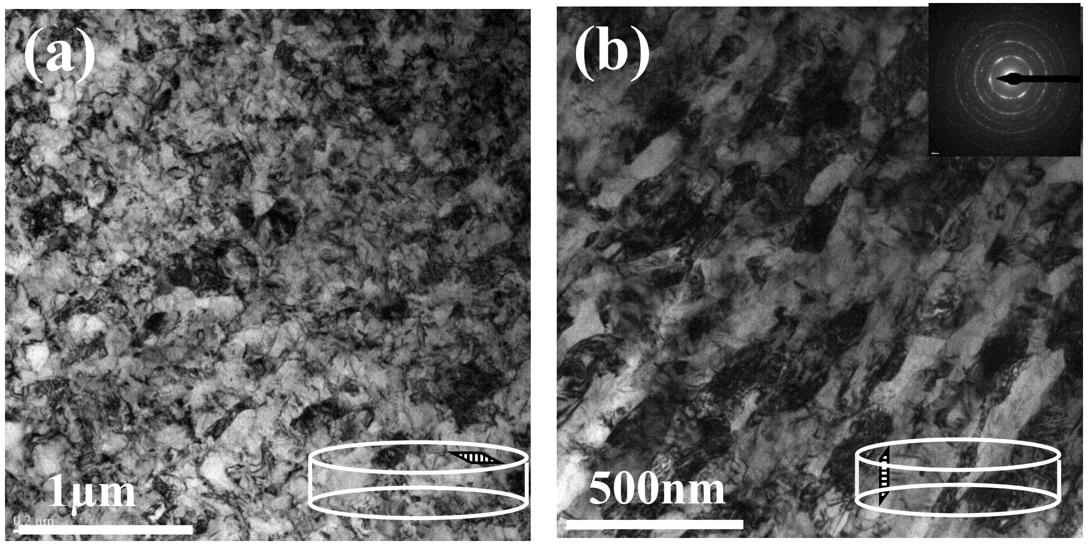


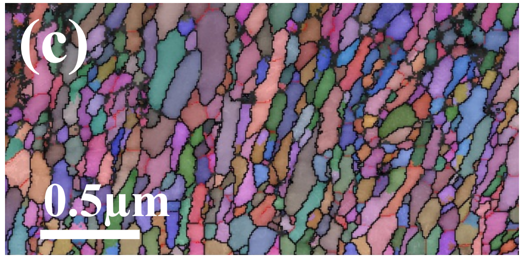


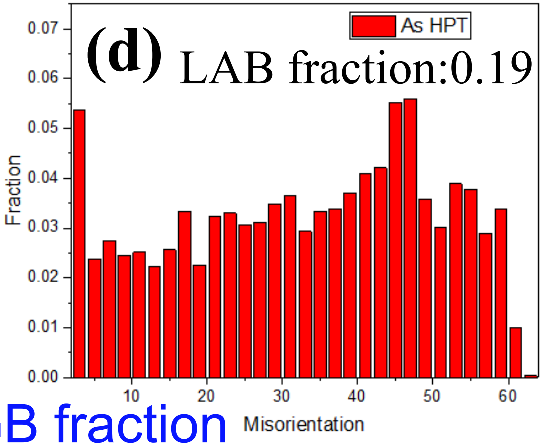


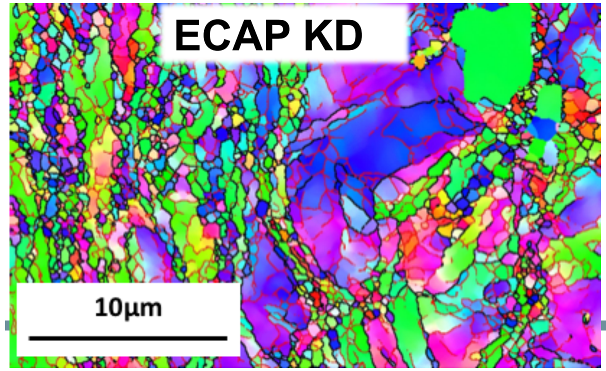


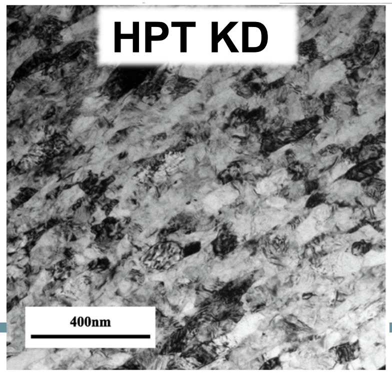
HPT G91







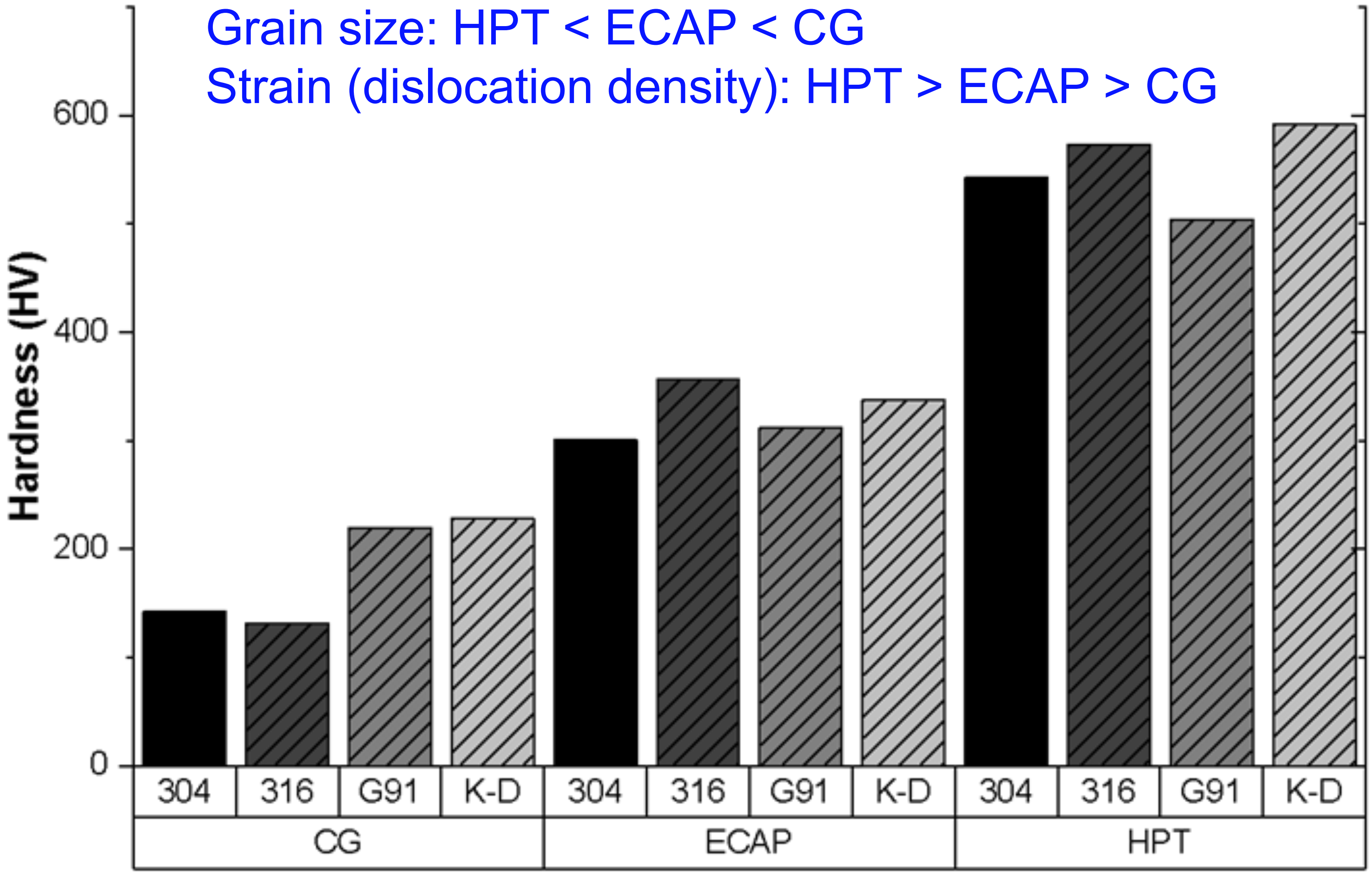


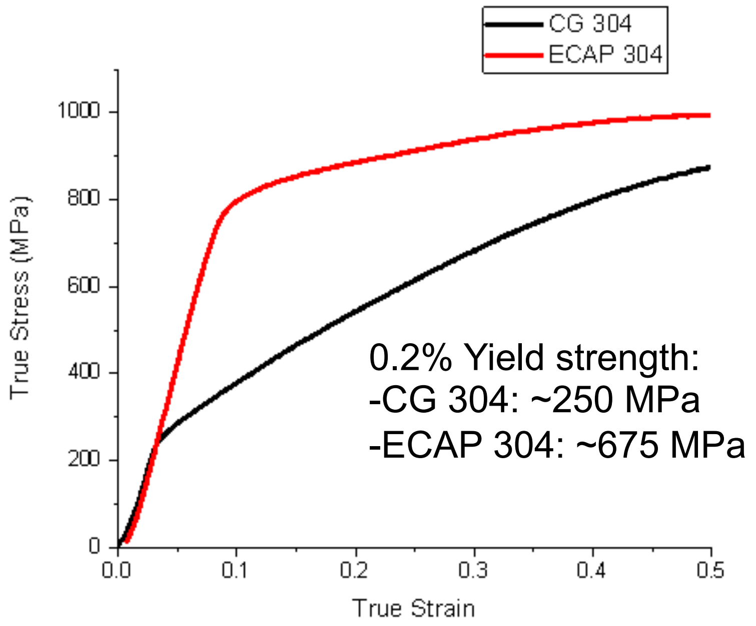


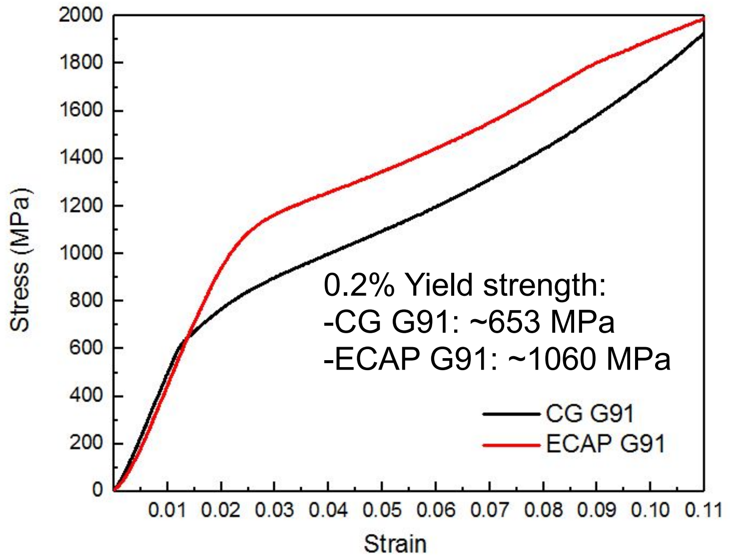
- HPT: ~100 nm average grain size, homogeneous microstructure, low LAGB fraction
- ECAP: ~400 nm average grain size, inhomogeneous microstructure, significant LAGB fraction.
- HPT + ECAP: high dislocation density

Mechanical Properties of Nanostructured Steels

Vickers Hardness: HPT > ECAP > CG
Grain size: HPT < ECAP < CG
Strain (dislocation density): HPT > ECAP > CG





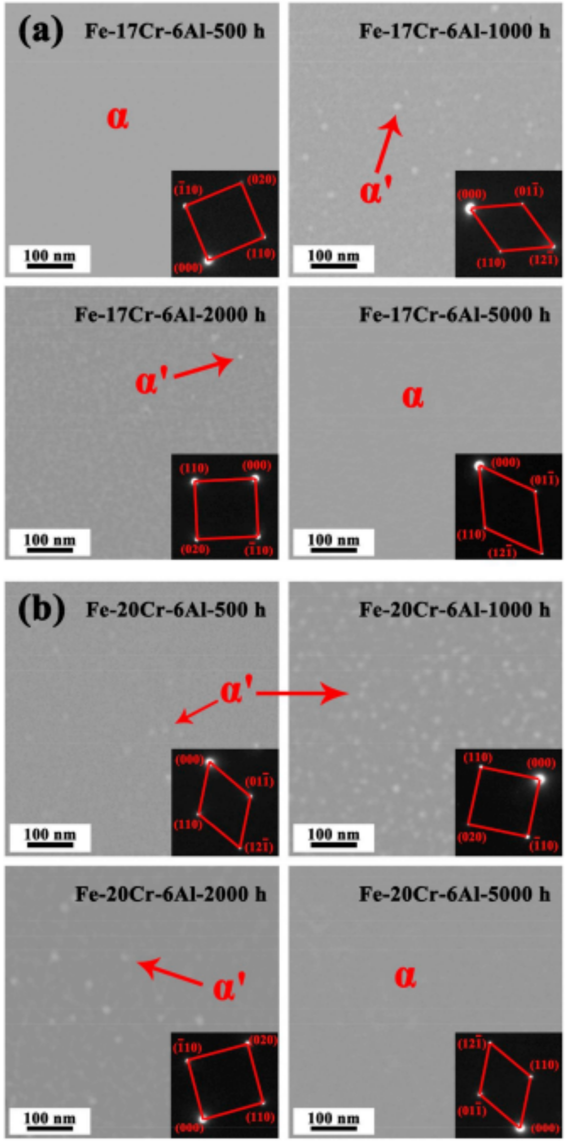


Technical Progress/Accomplishments

α’ Cr precipitation on isothermal aging in high-Cr ferritic alloys

- FeCrAl alloys have high ductile to brittle transition (DBTT) temperature of 119 °C to 318 °C (results in cracking during tube forming).
- FeCrAl alloys suffer from embrittlement after aging at ~475 °C due to α’ Cr precipitation increasing the DBTT.
- Grain refinement by advanced manufacturing may reduce the DBTT and enhance ductility.
- Grain size may influence α’ Cr precipitation in FeCrAl.

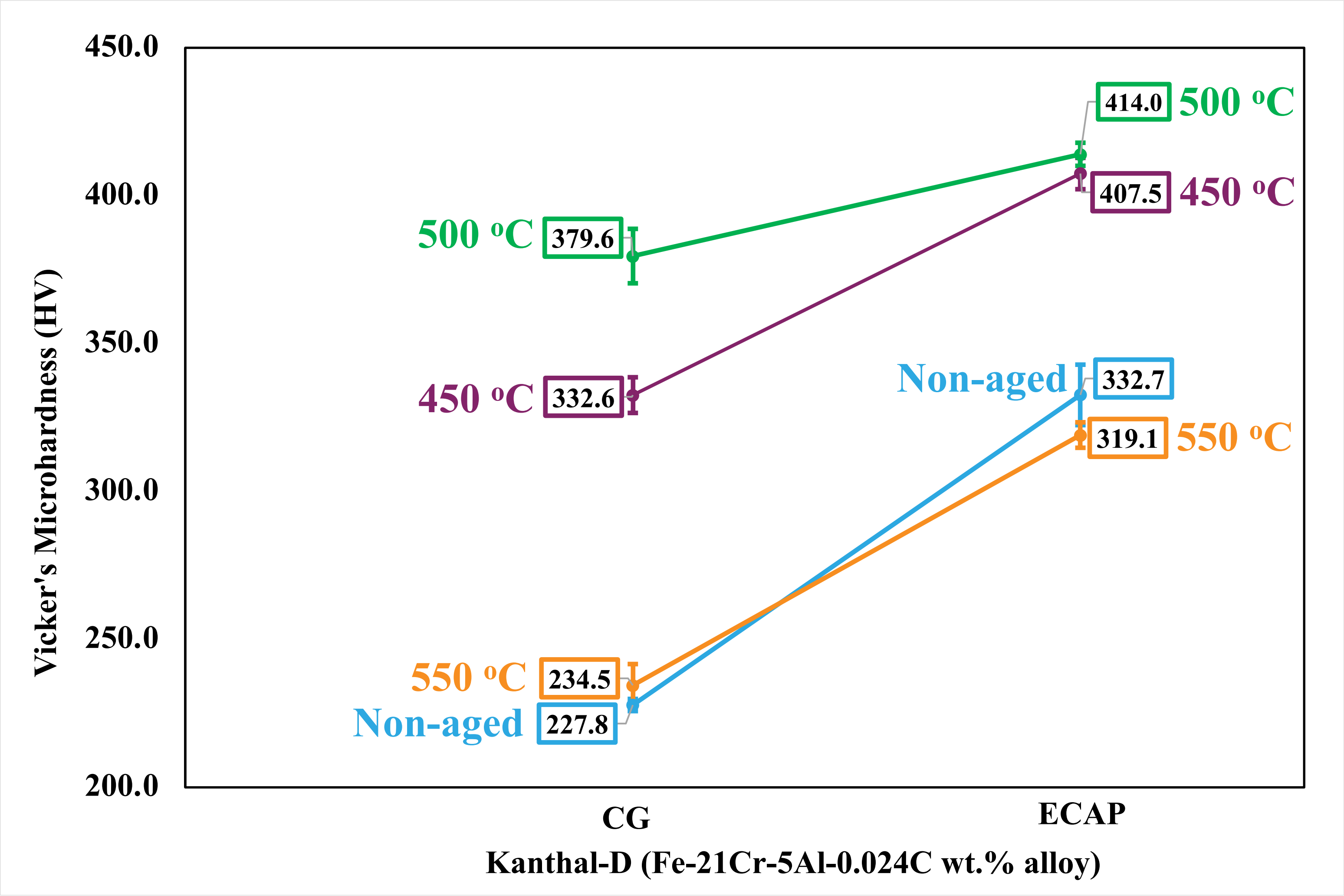
-Sun, Zhiqian, Yukinori Yamamoto, and Xiang Chen. "Impact toughness of commercial and model FeCrAl alloys." Materials Science and Engineering: A 734 (2018): 93-101.
-Field, Kevin G., Mary A. Snead, Yukinori Yamamoto, and Kurt A. Terrani. Handbook on the Material Properties of FeCrAl Alloys for Nuclear Power Production Applications (FY18 Version: Revision 1). No. ORNL/SPR-2018/905. Oak Ridge National Lab.(ORNL), Oak Ridge, TN (United States), 2018.
-Yang, Z., Z. X. Wang, C. H. Xia, M. H. Ouyang, J. C. Peng, H. W. Zhang, and X. S. Xiao. "Aluminum suppression of α′ precipitate in model Fe–Cr–Al alloys during long-term aging at 475° C." Materials Science and Engineering: A 772 (2020): 138714.



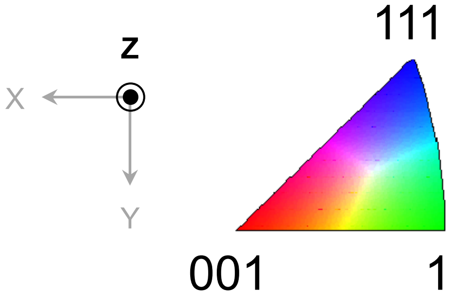
SAED patterns and STEM images of (a) the Fe-17Cr-6Al alloy and (b) the Fe-20Cr-6Al alloy aged at 475 °C for various times

Isothermal aging of coarse grained (CG) and equal channel angular pressed (ECAP) Kanthal-D (Fe-21Cr-5Al-0.026C alloy)

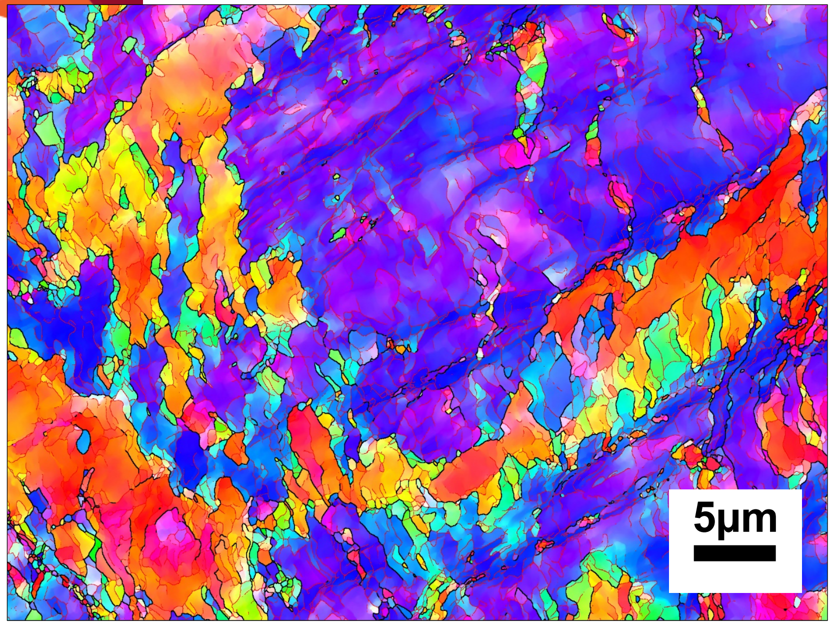
- Aging of CG and ECAP Kanthal-D was done at 450 ºC, 500 ºC and 550 ºC for 500h
- The **increase in hardness of CG is higher than that of ECAP** after aging at 450 and 500 ºC
- There is a further increase in hardness of CG after aging at 500 ºC but not in ECAP
- There is no change in hardness after aging at 550 ºC suggesting that the miscibility gap is between 500 ºC and 550 ºC

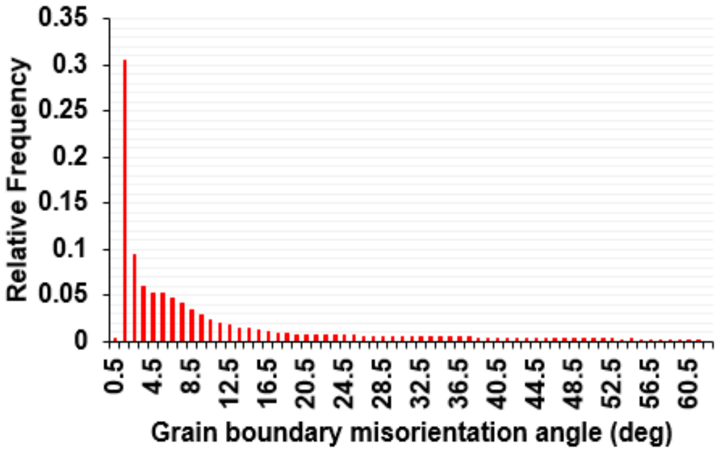


Aged ECAP Kanthal-D microstructure

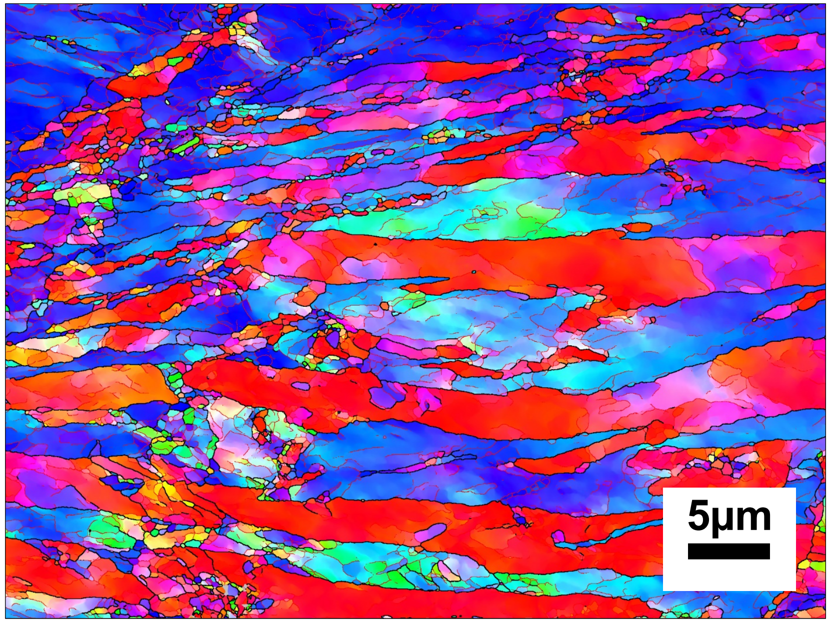


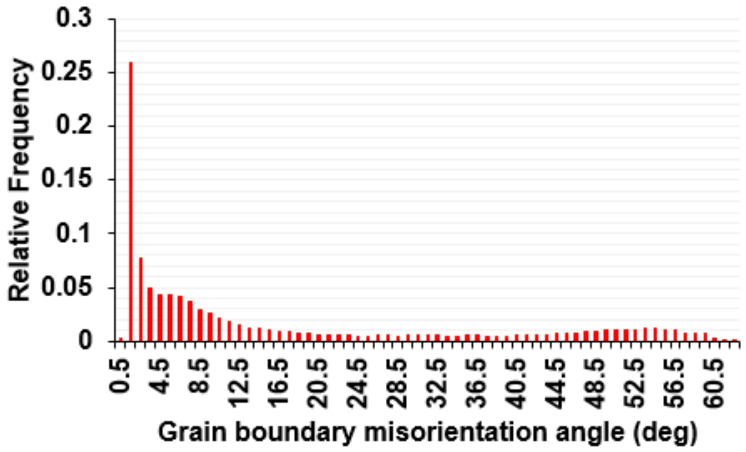
450°C





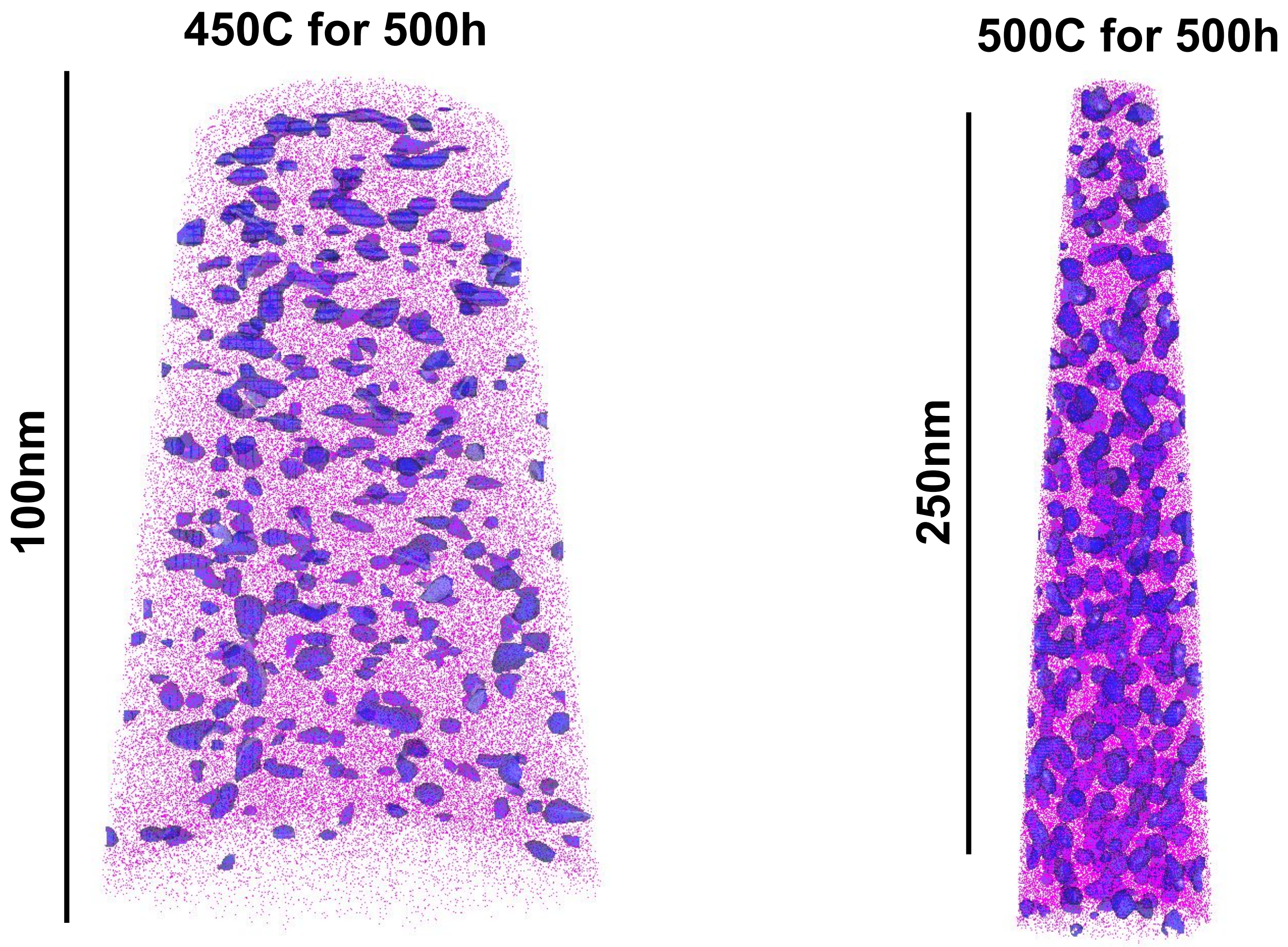
500°C





- The microstructure resembles the as-ECAP'd microstructure
- Area fraction of LAGBs,
  - 450 ^{o}C = 71.8%
  - 500 ^{o}C = 57.4%
- There is an increase in HAGBs with increase in aging temperature
- There is no sign of recrystallization

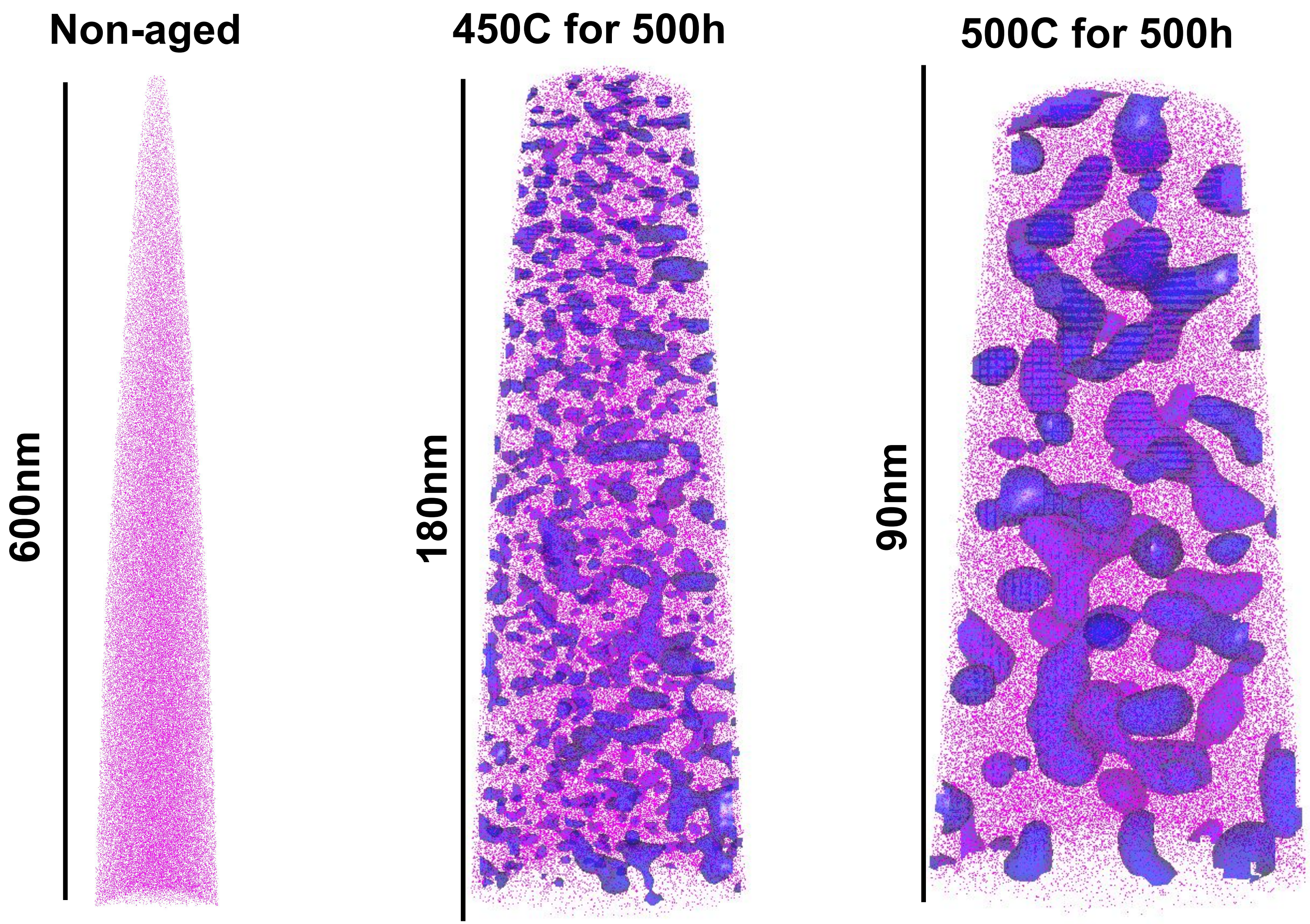
APT analysis of isothermally aged CG Kanthal-D



Fe atoms (pink) with 35 at.% Cr iso-concentration surface (blue)

- α' Cr precipitation is found in both 450 °C and 500 °C aged CG Kanthal-D.
- The hardness increase is attributed to α' Cr precipitation

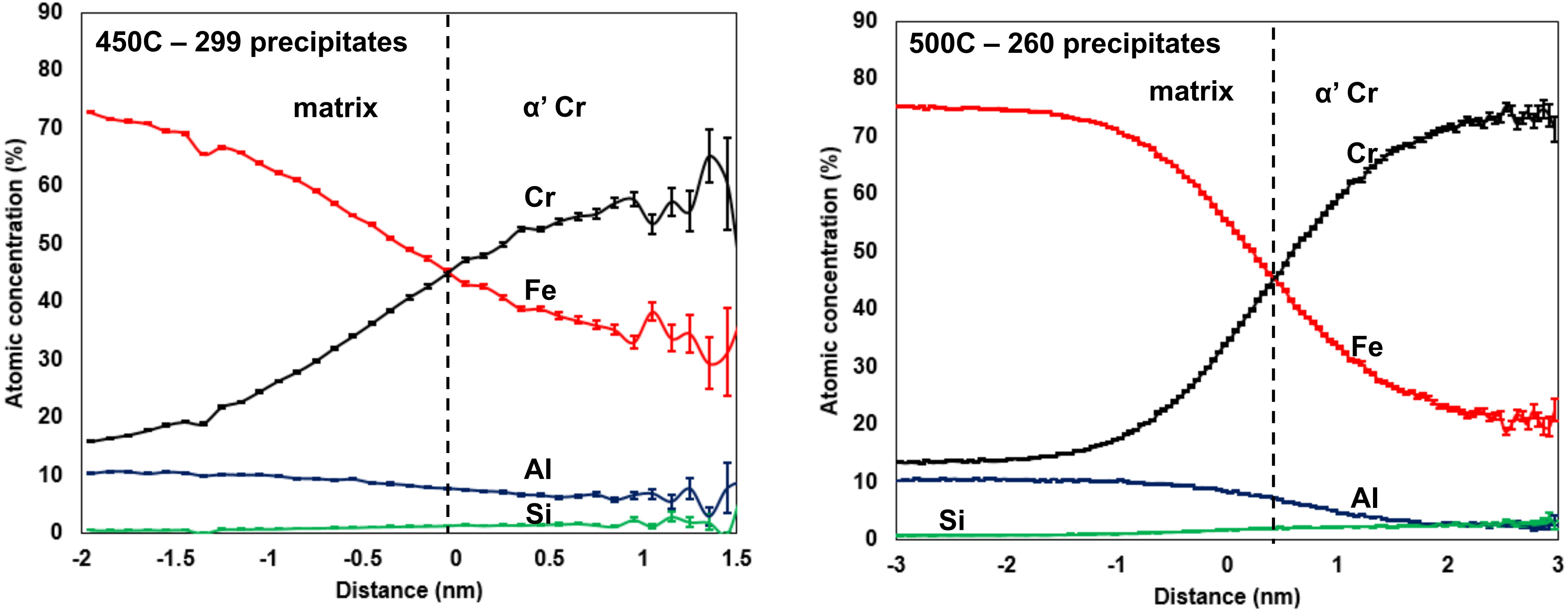
APT analysis of isothermally aged ECAP Kanthal-D



Fe atoms (pink) with 35 at.% Cr iso-concentration surface (blue)

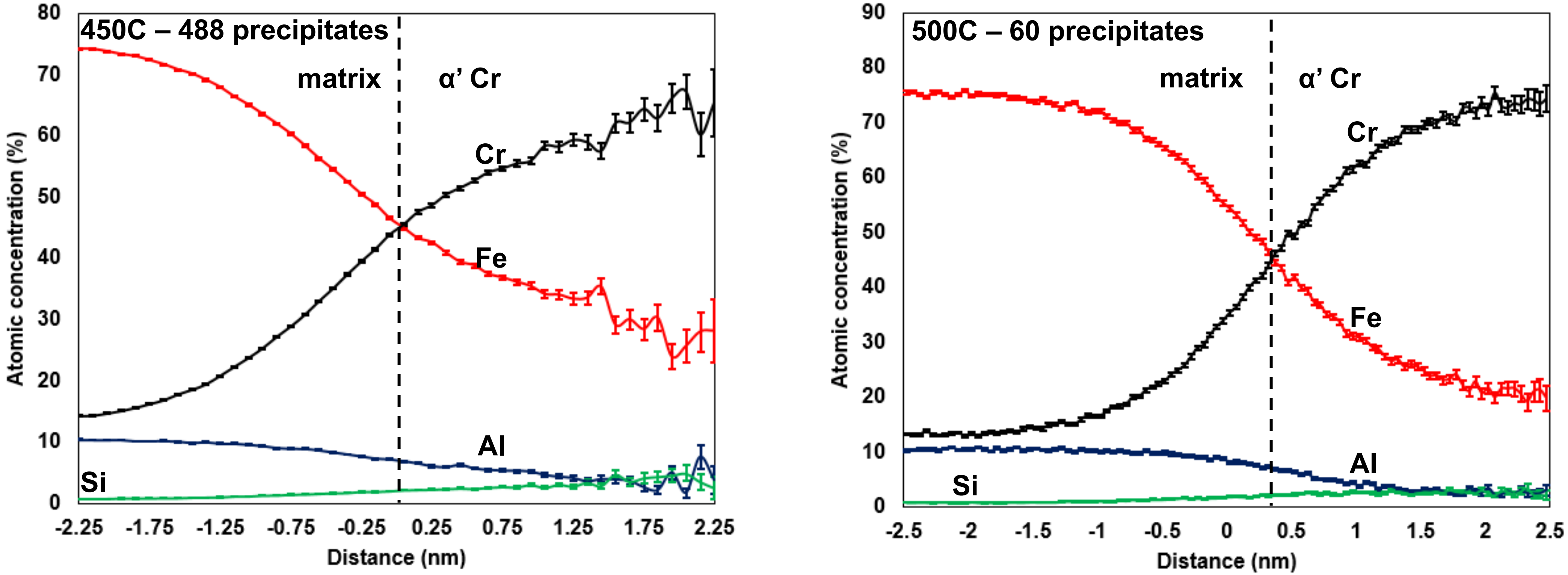
- SPD does not lead to α' Cr precipitation
- α' Cr precipitation is found in both 450 ^{o}C and 500 ^{o}C aged ECAP Kanthal-D.
- Similar to CG Kanthal-D, the hardening is attributed to α' Cr precipitation

Concentration profiles of Cr precipitates in 450C and 500C aged CG Kanthal-D



- Statistical proxigrams based on 35 at.% Cr isoconcentration surface
- Average concentration of Cr in the α’ Cr phase is higher in the 500C aged CG.
- Fe and Al are depleted, whereas Si is enriched in the α‘ Cr phase

Concentration profiles of Cr precipitates in 450C and 500C aged ECAP Kanthal-D



- Similar phenomenon of Cr concentration variation in α' Cr phase is observed in ECAP
- Increase in temperature below the miscibility gap leads to increase in Cr concentration in α' Cr
- Fe and Al are depleted, whereas Si is enriched in the α' Cr phase

Quantitative analysis – α' Cr precipitation in 450 °C aged Kanthal-D

Quantitative analysis based on cluster analysis in IVAS 3.8.4

Sample	***CG*** **Kanthal-D 450C 500h**		***ECAP*** **Kanthal-D 450C 500h**	
APT analysis volume	Volume 1	Volume 2	Volume 1	Volume 2
Average radius (nm)	2.81	2.76	4.21	4.17
Number density ($x10^{23}$ /m^3)	7.17	7.45	4.78	5.11

- Precipitate size is larger in ECAP compared to that in CG
- Number density is found to be lower in ECAP
- This explains the smaller aging-induced hardness increase in ECAP compared to that in CG
- This suggests that there is an **influence of grain size on α' Cr precipitation**

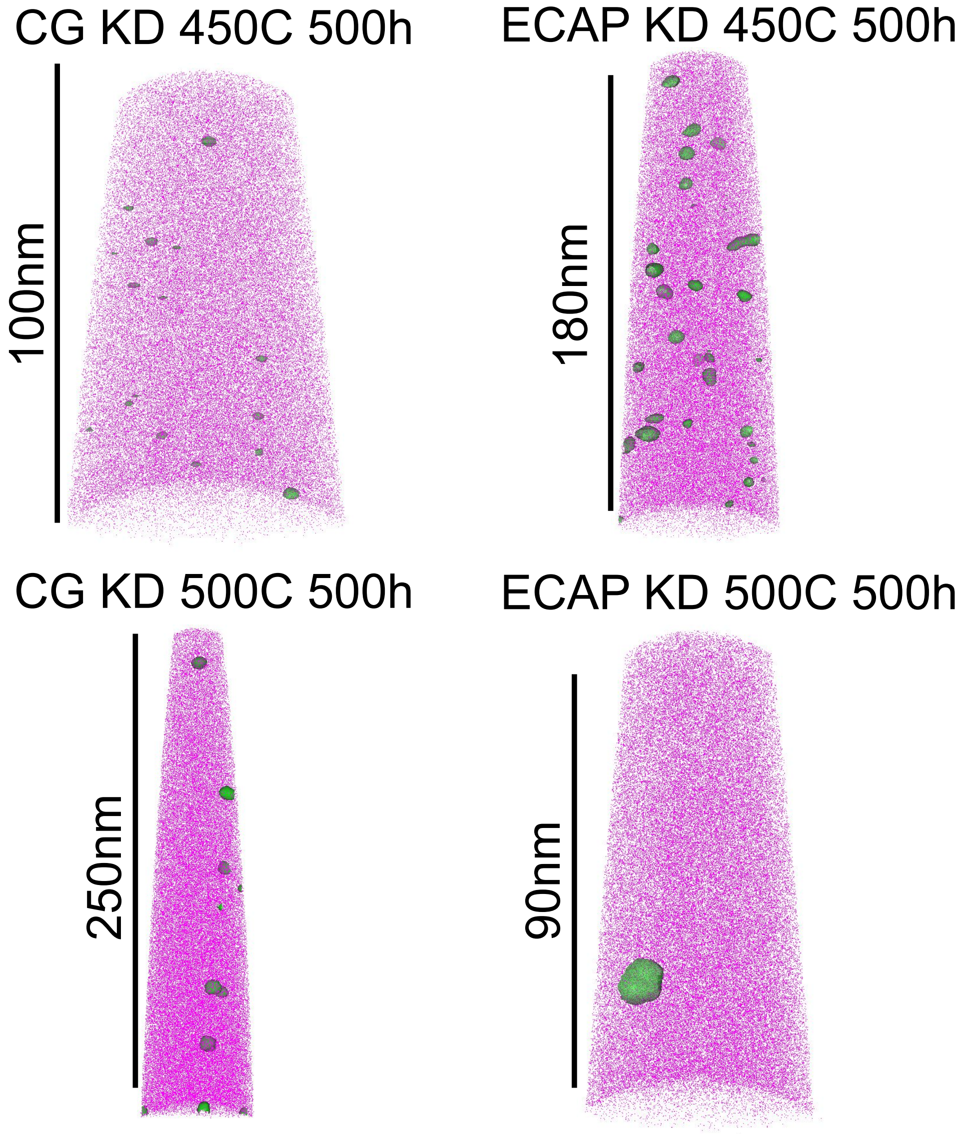
Quantitative analysis – α’ Cr precipitation in 500 °C aged Kanthal-D

Quantitative analysis based on cluster analysis in IVAS 3.8.4

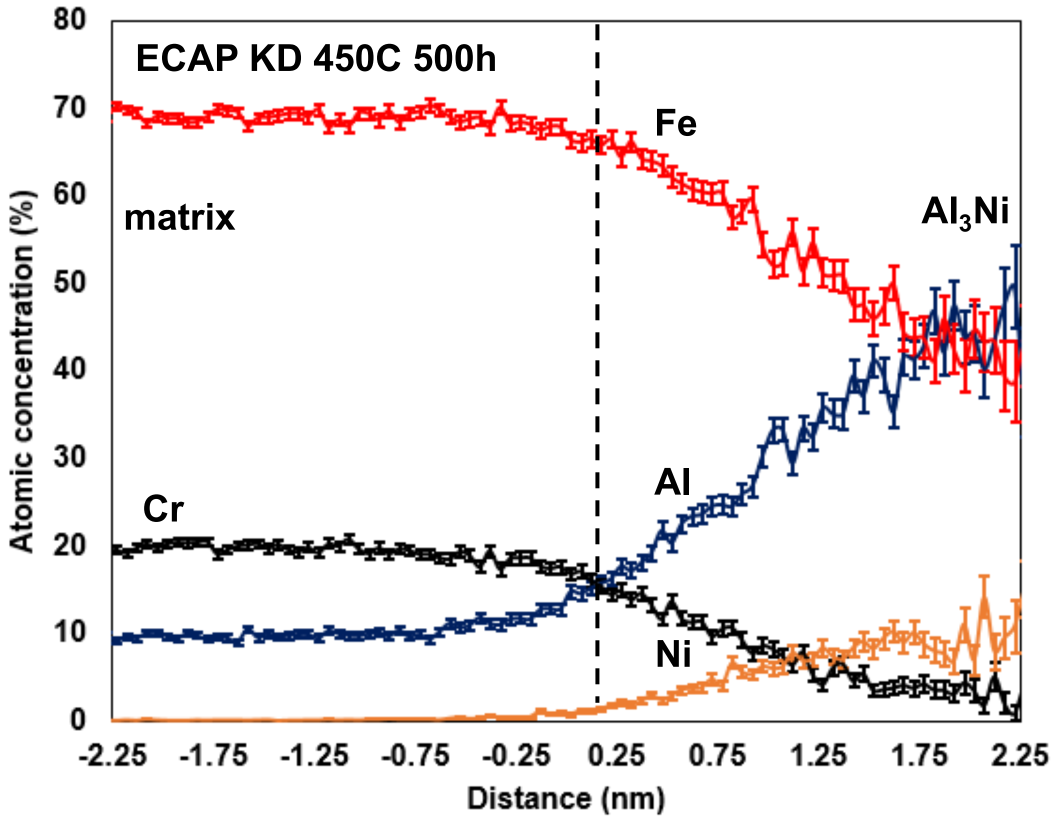
Sample	***CG*** **Kanthal-D 500C 500h**		***ECAP*** **Kanthal-D 500C 500h**	
APT analysis volume	Volume 1	Volume 2	Volume 1	Volume 2
Average radius (nm)	3.12	3.19	4.61	4.54
Number density ($x10^{23}$ $1/nm^3$)	8.21	8.60	4.29	4.34

- Precipitate size is larger in ECAP compared to that in CG
- Number density is found to be lower in ECAP
- **α’ Cr precipitate size and density in 500 °C aged ECAP KD are comparable to those in 450 °C aged ECAP KD**
- **α’ Cr precipitate size and density in 500 °C aged CG KD are larger than those in 450 °C aged CG KD**

Al_3Ni precipitation in aged Kanthal-D



Fe atoms (pink) with 2 at.% Ni iso-concentration surface (green)



Statistical proxigram based on 2 at.% Ni isosurface (34 precipitates)

- Al_3Ni (orthorhombic) precipitation is found after aging of CG and ECAP KD.

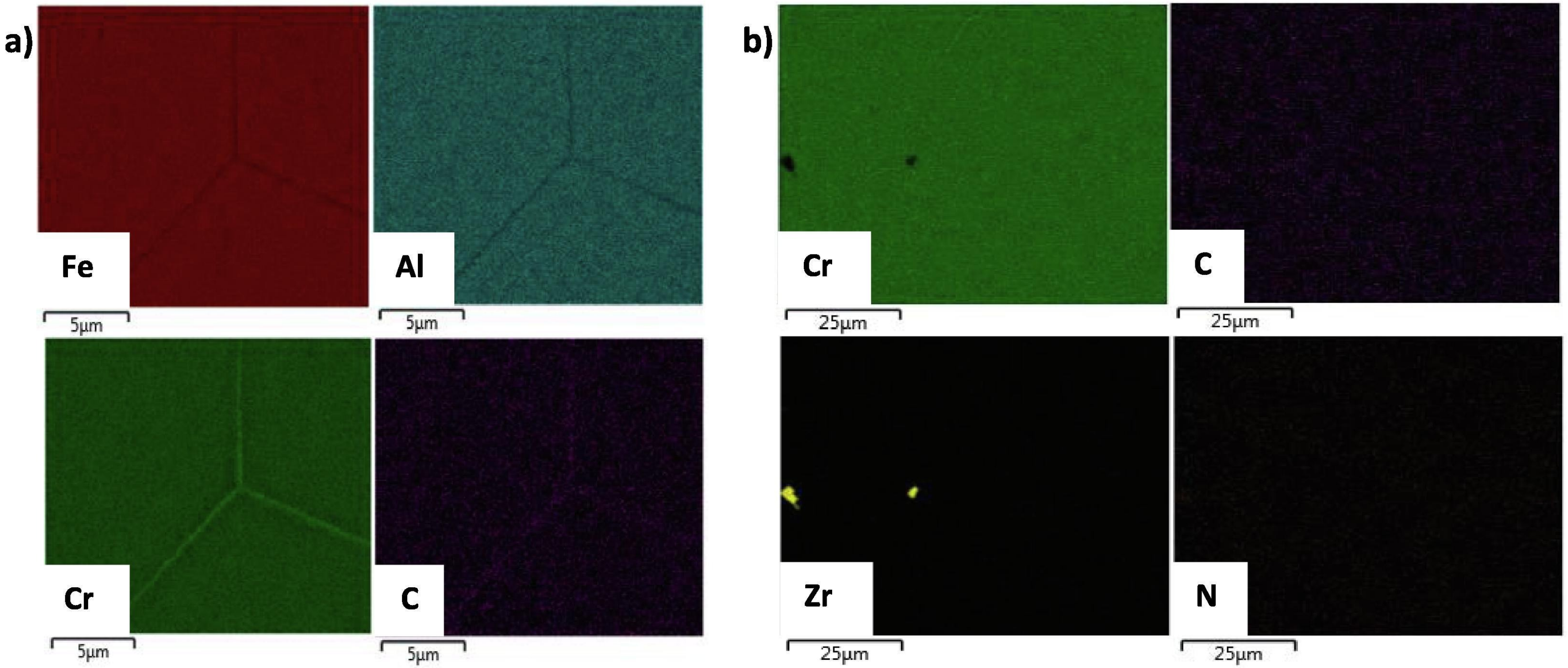
Ion irradiation of coarse grained (CG) and nanocrystalline (NC) Kanthal-D (Fe-21Cr-5Al-0.026C alloy)

- Funded by Nuclear Science User Facilities (NSUF) Rapid Turnaround Experiment (RTE) program (RTE 19-1761).
- Project title: "Alleviating irradiation-induced precipitation in a Fe-21Cr-5Al alloy via nanostructuring"
- Samples irradiated:
  - CG Kanthal-D (grain size range = 100 – 500 μm)
  - NC Kanthal-D (average grain size = 75 ± 40 nm)
- Irradiation experiments:
  - 3.5 MeV Fe^{2+} ion with dose rate being < 10^{-4} dpa/s (in order to reduce ballistic mixing)
  - Peak dpa region was found at a depth of 0.8 - 1μm from SRIM calculations

Room Temperature	500 C
5 DPA	5 DPA
50 DPA	50 DPA

Grain boundary segregation of Cr and C in CG Kanthal-D after thermal annealing

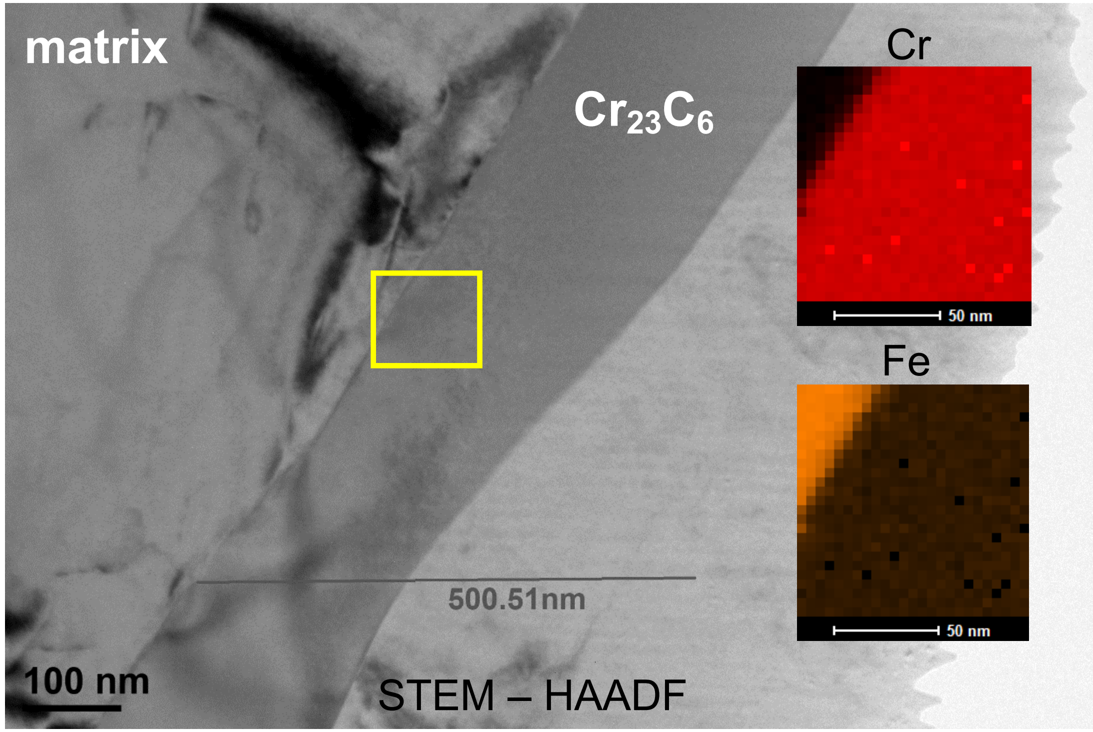
- CG Kanthal-D did not show precipitation of $Cr_{23}C_6$ even after annealing at 520 ^{o}C for 6h.
- Cr and C were found to segregate along grain boundaries (GBs) after annealing at 520 ^{o}C for 6h



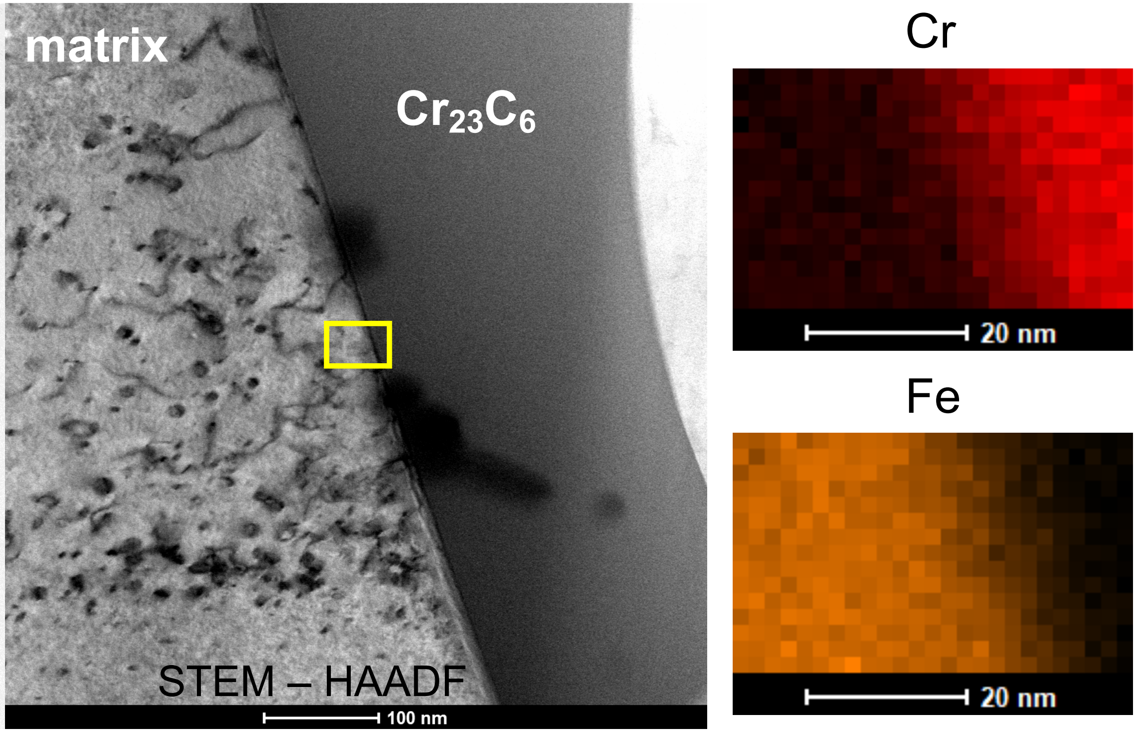
SEM-EDS elemental maps from two different locations in CG Kanthal-D after annealing at 520^{o}C

$Cr_{23}C_6$ precipitation in CG Kanthal-D after room temperature irradiation

CG 5 dpa RT

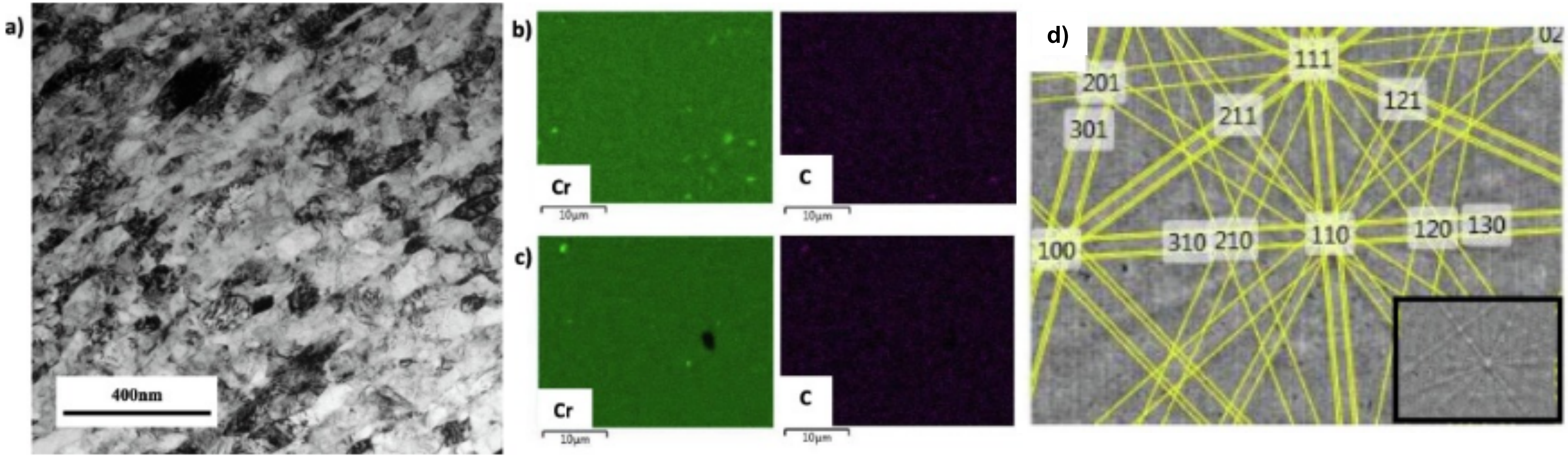


CG 50 dpa RT



- $Cr_{23}C_6$ precipitates are found along GBs.
- Irradiation-induced $Cr_{23}C_6$ precipitation in CG Kanthal D at RT.

$Cr_{23}C_6$ precipitation in Unirradiated HPT Kanthal-D



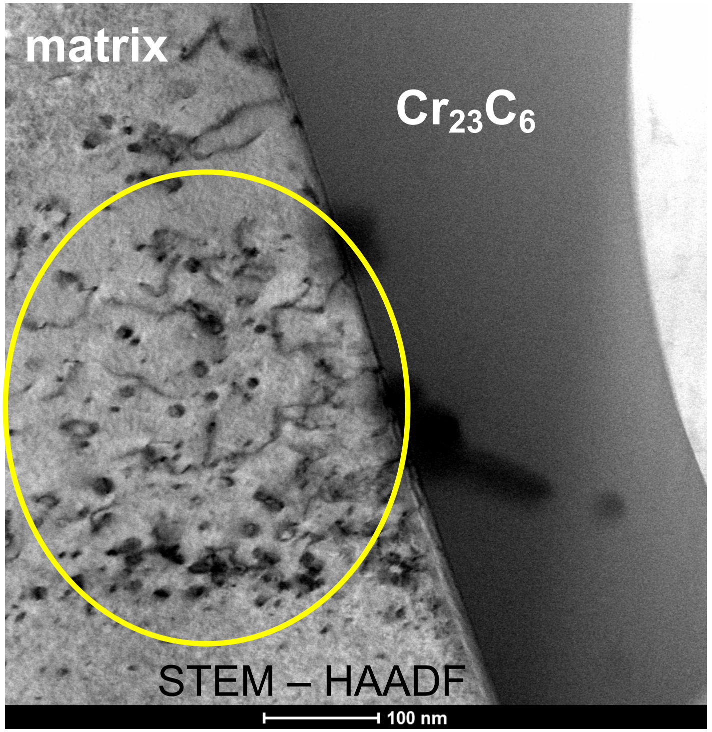
a) TEM Bright field (BF) image of HPT KD. b) and c) shows the Cr and C elemental maps from two different locations in HPT-KD, using SEM-EDS. d) Indexed Kikuchi diffraction pattern of $Cr_{23}C_6$ with inset showing unindexed pattern

- It appears that there was no further precipitation of $Cr_{23}C_6$ in HPT KD during irradiation as opposed to CG KD.
- Consequently, **irradiation induced precipitation accompanied by hardening/embrittlement may be reduced**.

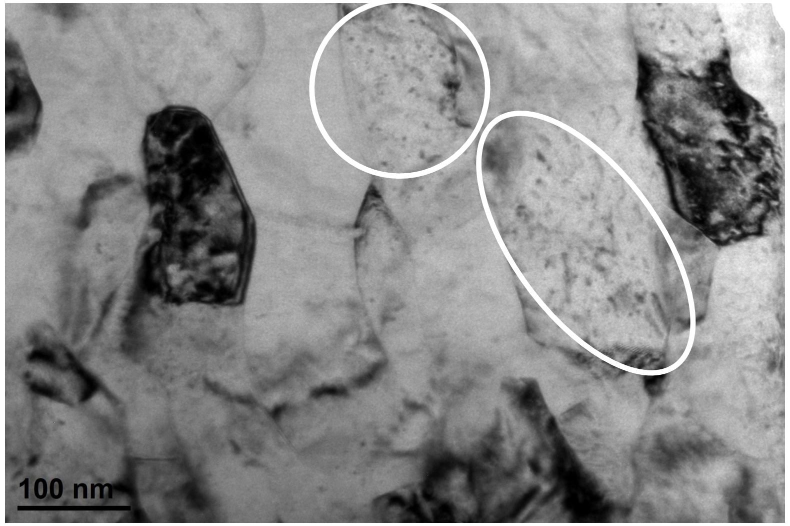
-Arivu, Maalavan, Andrew Hoffman, Jiaqi Duan, Haiming Wen, Rinat Islamgaliev, and Ruslan Valiev. "Severe plastic deformation assisted carbide precipitation in Fe-21Cr-5Al alloy." *Materials Letters* 253 (2019): 78-81.

Reduced irradiation-induced dislocation structures in NC Kanthal-D at RT

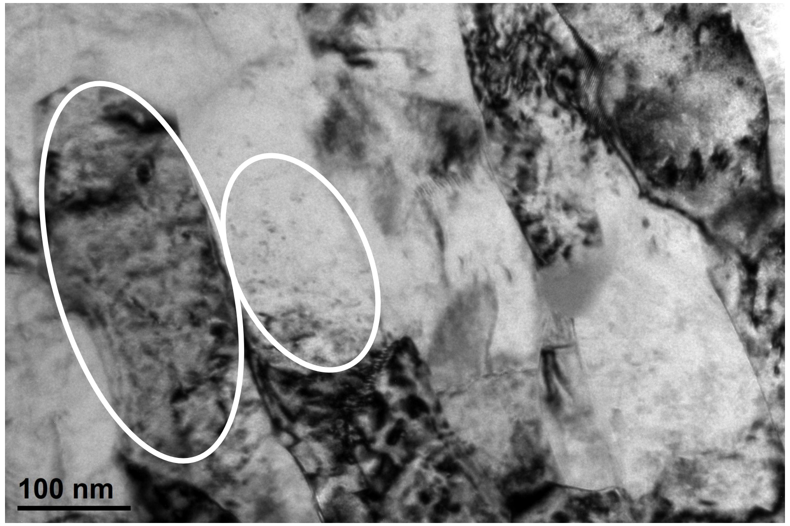
CG 50 dpa RT - Peak dpa region



NC 50 dpa RT - Peak dpa region



BF TEM

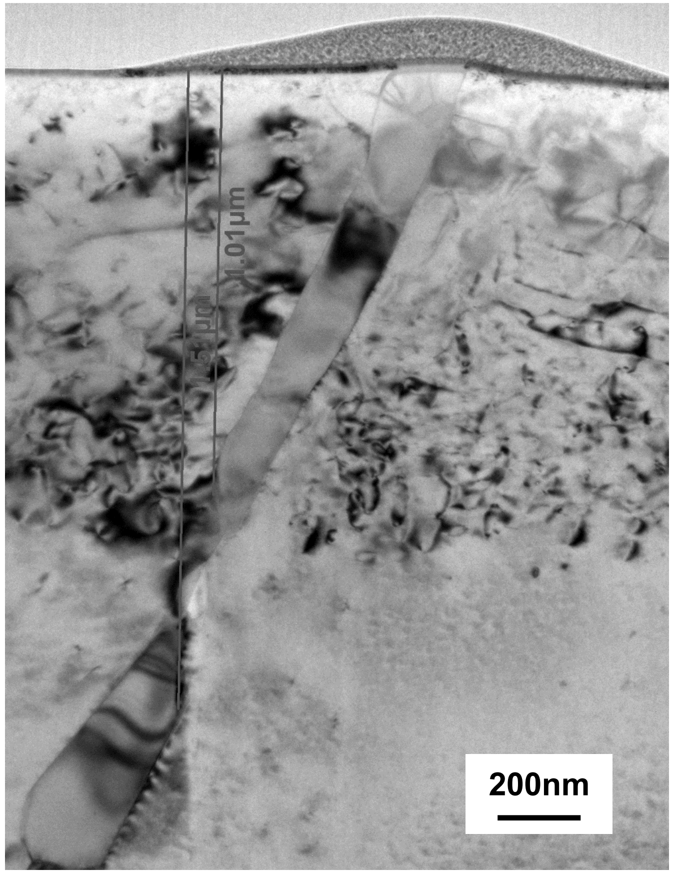


BF TEM

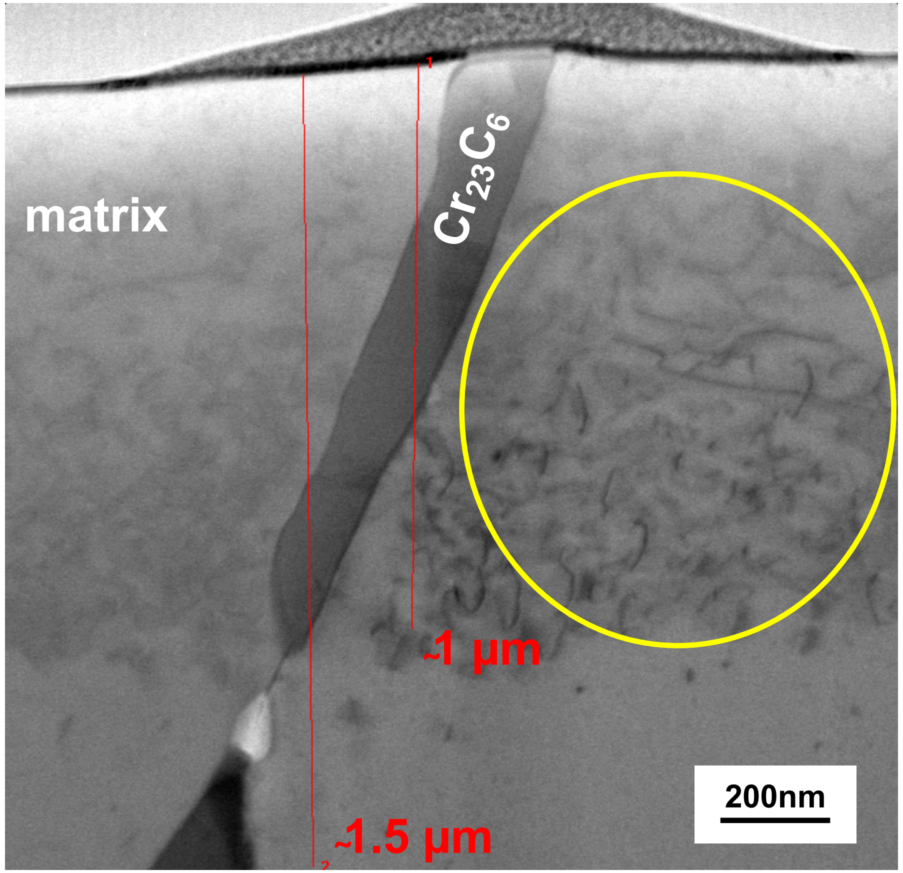
- CG KD shows the presence of dislocation line segments and dislocation loops (yellow circle) in the peak dpa region.
- HPT KD only shows very small dislocation segments and sub-nm defect clusters.

Irradiation-induced dislocation structures in CG Kanthal-D at 500 °C

CG 5 dpa 500C – BF TEM



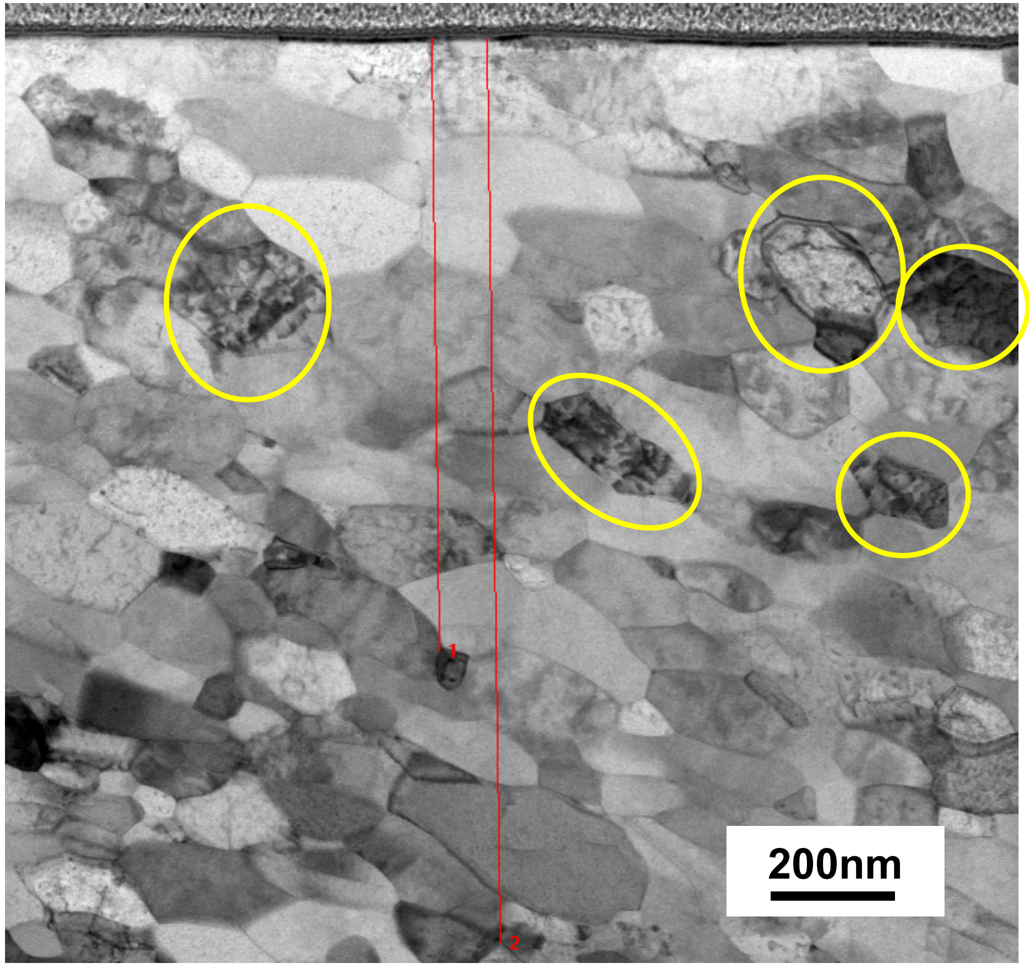
CG 5 dpa 500C – BF STEM



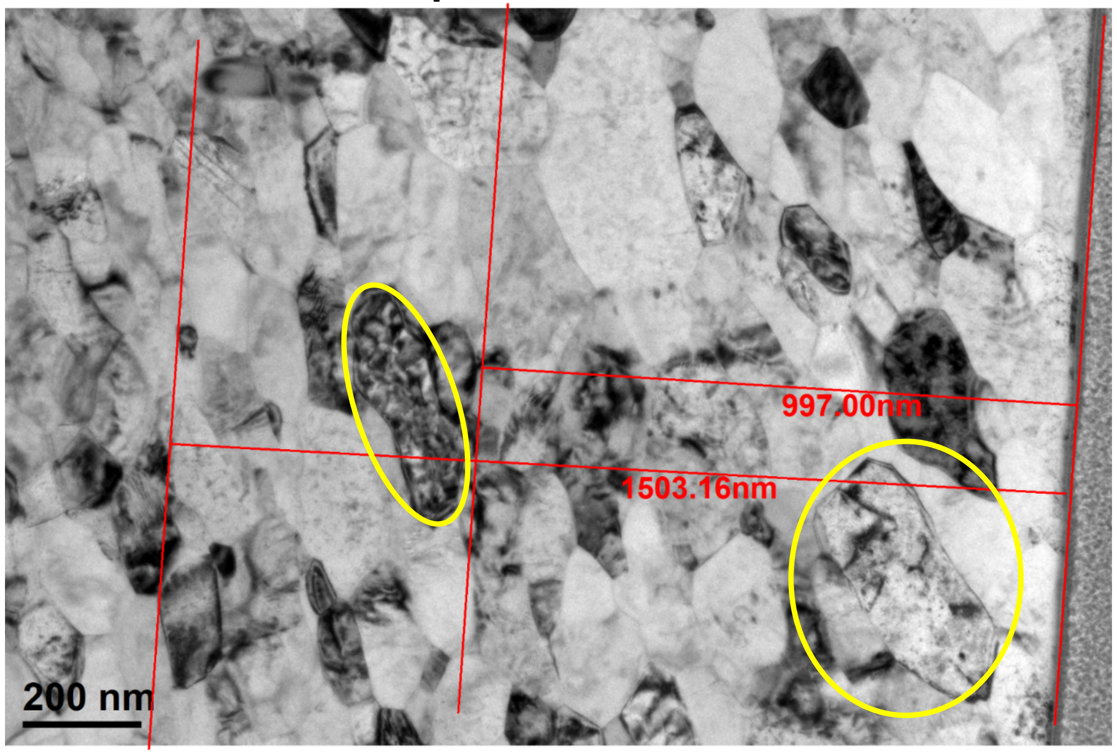
- CG KD shows the presence of dislocation line segments and dislocation loops in the peak dpa region.

Reduced irradiation-induced dislocation structures in NC Kanthal-D at 500 °C

NC 5 dpa 500C – STEM - HAADF



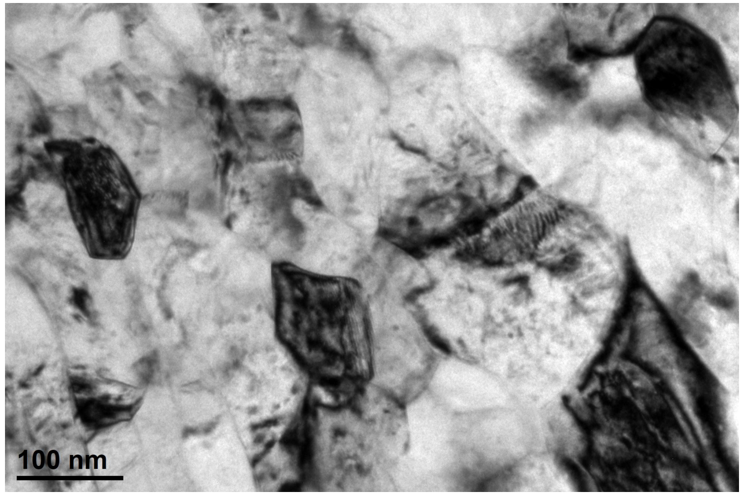
NC 5 dpa 500C – BF TEM

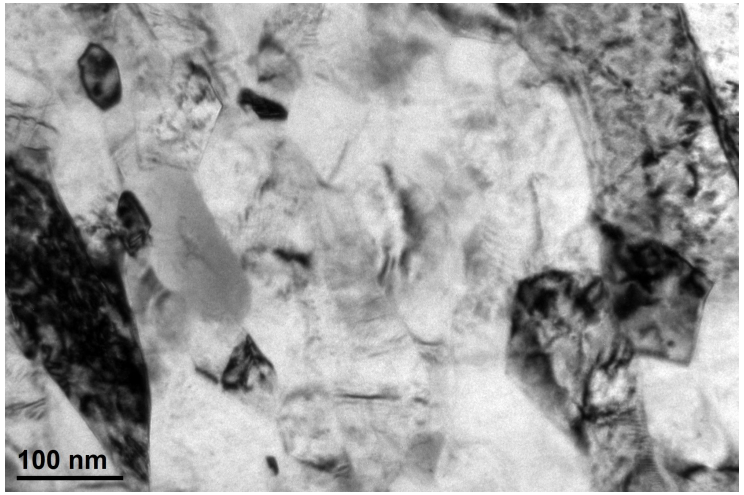


- Highlighted grains show dislocation segments and sub-nm defect clusters.
- **Defect size and density are significantly smaller compared to CG.**

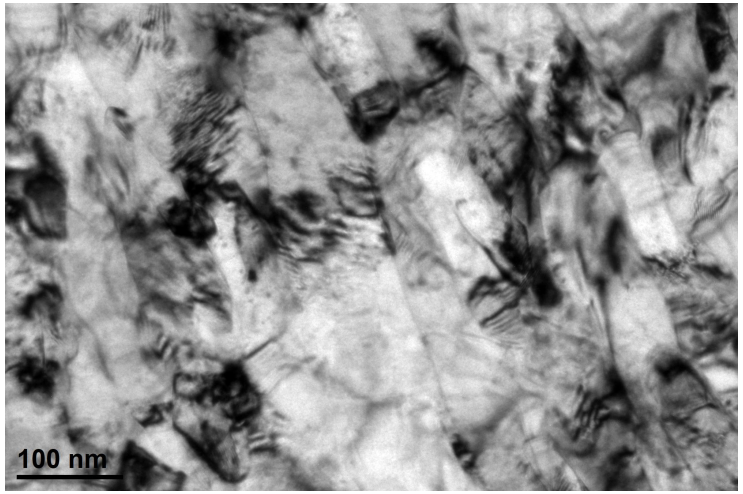
Change in GB curvature and strain relief in 50 dpa, RT irradiated NC KD

NC KD 50 dpa RT – Peak dpa region





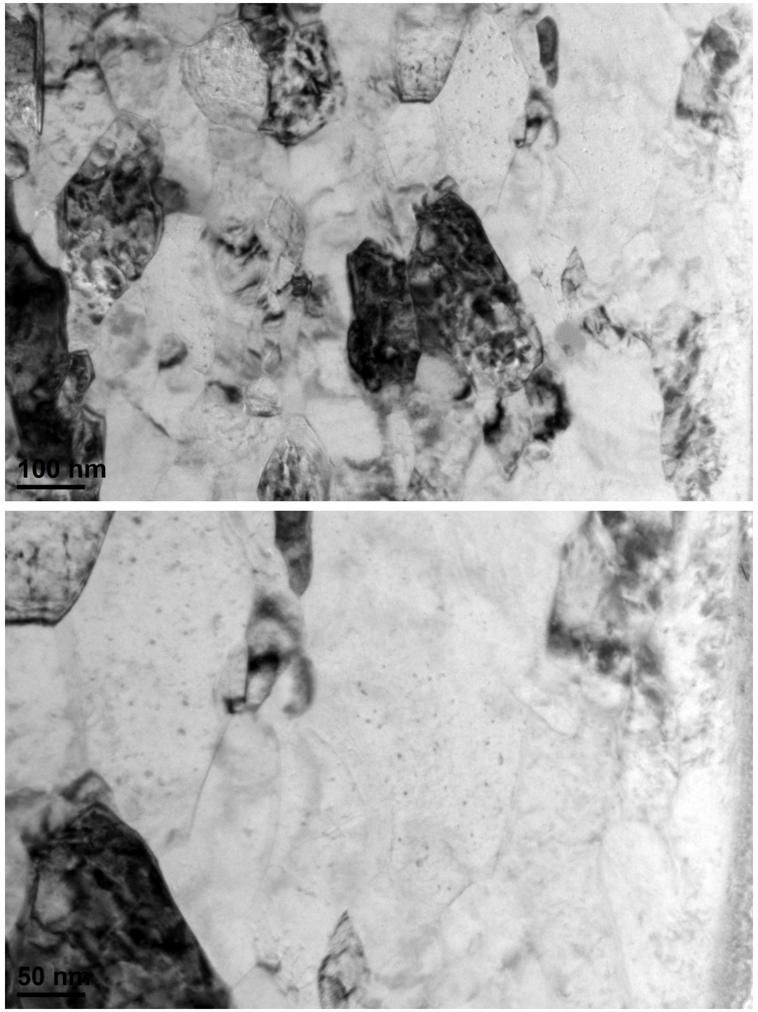
NC KD 50 dpa RT – Unirradiated region



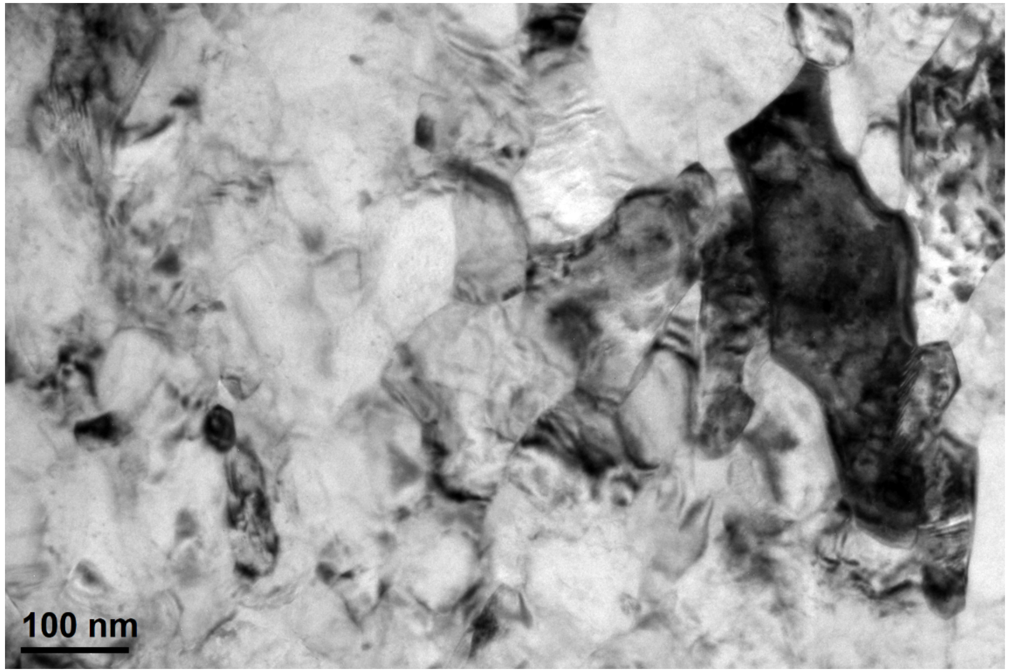
- The grain boundaries become sharper after irradiation, suggesting GB migration.
- The SPD induced strain is relieved in the irradiated region, suggesting dynamic recovery.
- The dynamic recovery is opposite to creation or accumulation of dislocations during irradiation of CG metals.

Change in GB curvature in 5 dpa, RT irradiated NC KD

NC KD 5 dpa RT – Peak dpa region

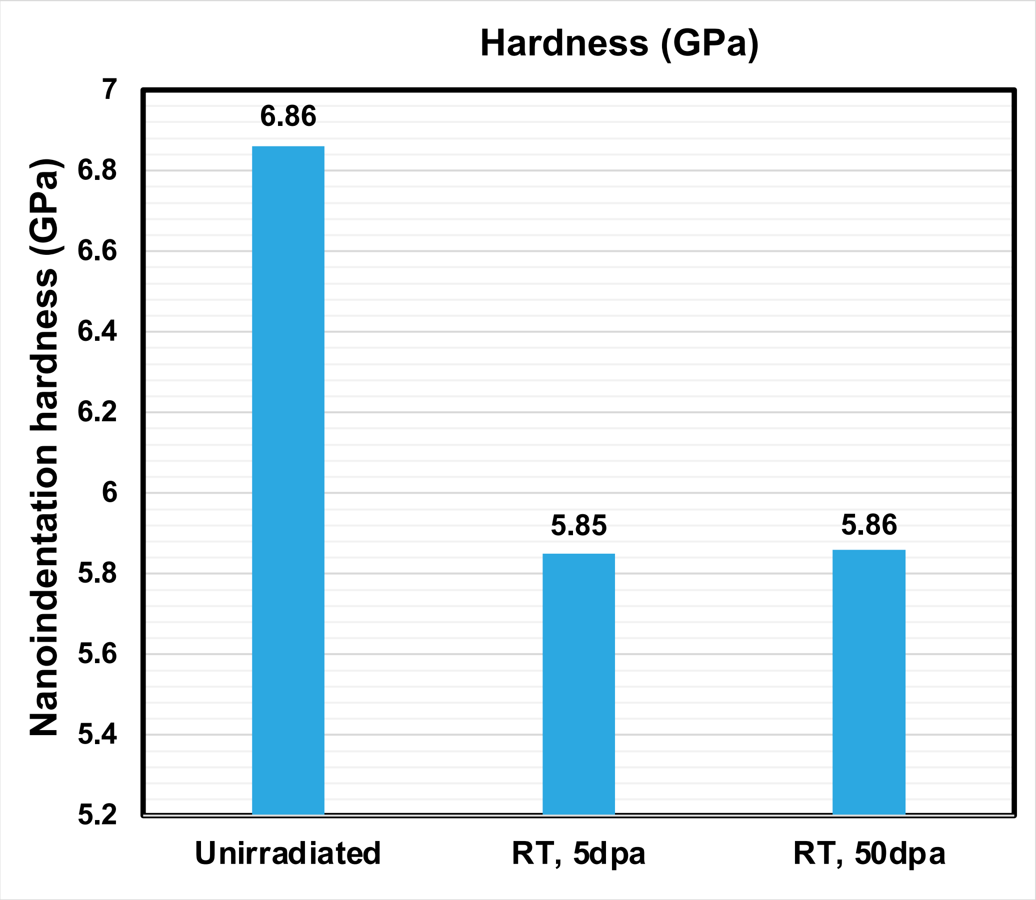


NC KD 5 dpa RT – Unirradiated region



- Although the dose is less, GBs still become sharper in the irradiated region.

Influence of recovery and GB migration during RT irradiation of NC KD on nano-hardness and grain size



Sample	Average grain size (nm)	Hardness (GPa)
Unirradiated HPT	75 ± 40	6.86
5 dpa RT	139.34 ± 38.14	5.85
50 dpa RT	121.67 ± 34.07	5.86

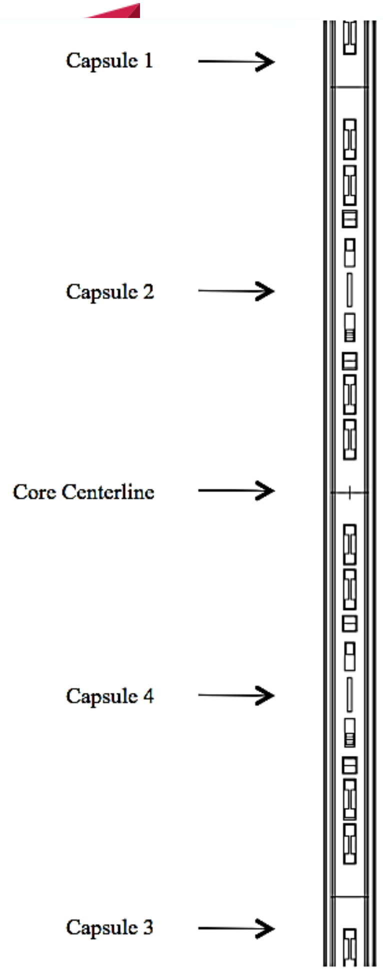
- Recovery and grain boundary migration cause
  - Increase in grain size
  - Decrease in nano-hardness

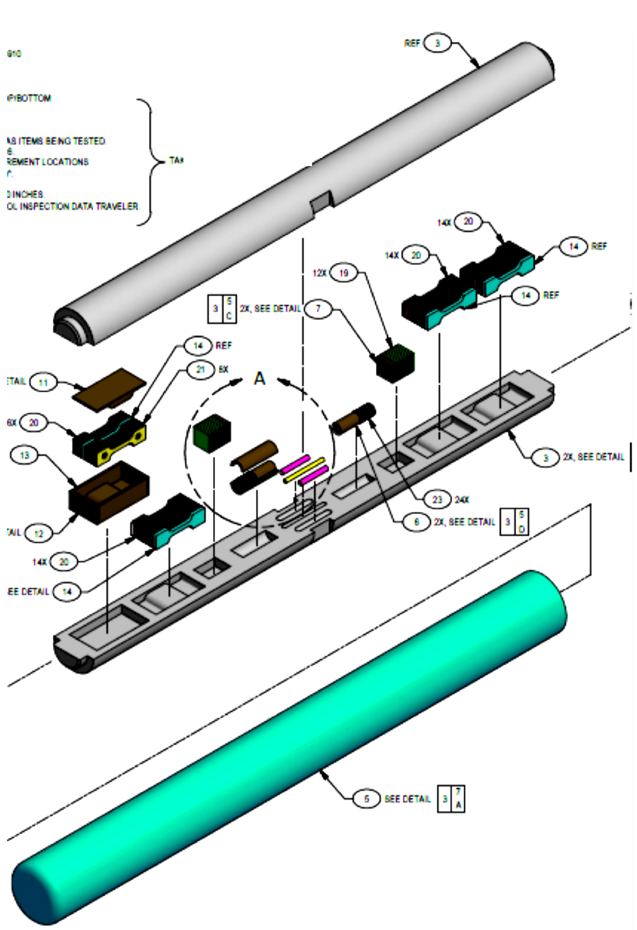
Summary

- **Isothermal aging of CG and ECAP Kanthal-D**
  - **Aging hardening in ECAP Kanthal-D is reduced compared to that in CG**
  - ECAP is found to be thermally stable after 500h of aging at 450 ^{o}C and 500 ^{o}C
  - The increase in hardness is attributed to the precipitation of α’ Cr phase
  - Fe and Al are depleted in the α’ Cr phase whereas Si is enriched
  - **α’ Cr precipitation is influenced by grain size**
  - Al_3Ni precipitation also occurs during aging

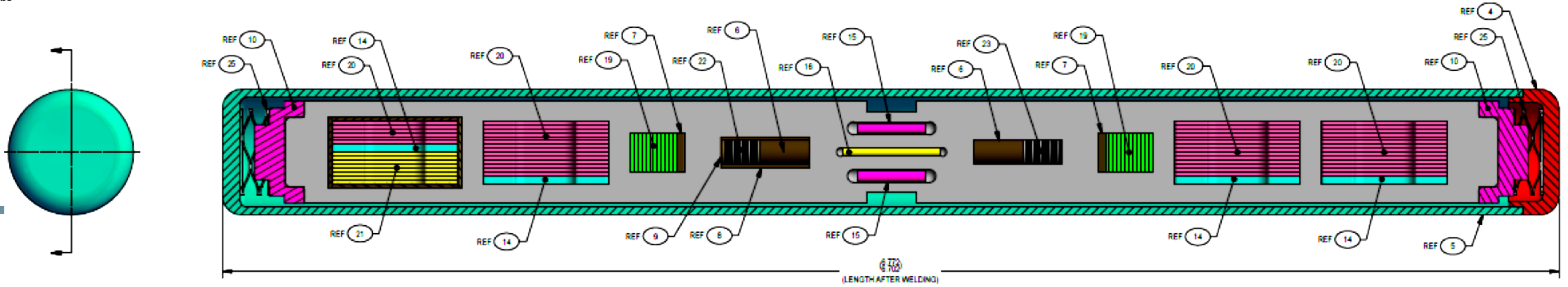
- **Ion irradiation of CG and NC Kanthal-D**
  - **Reduced irradiation-induced precipitation of $Cr_{23}C_6$ in HPT KD**
  - **The dislocation/defect cluster size and density are smaller in NC Kanthal-D compared to CG KD**
  - **Recovery and GB migration occur in HPT KD during RT ion irradiation, causing irradiation-induced softening**

Neutron irradiation





- Conducted at Advanced Test Reactor
- Four irradiation conditions and capsules
  - Capsule 1 at 300 °C to 2 DPA (8 months)
  - Capsule 2 at 300 °C to 6 DPA (2 years)
  - Capsule 3 at 500 °C to 2 DPA (8 months)
  - Capsule 4 at 500 °C to 6 DPA (2 years)
- Tensile, hardness and TEM specimens
- Non-instrumented standard capsule experiments
- Two 2-dpa irradiated capsules shipped from ATR to HFEF
- Disassembly of capsules and scheduling of PIE being conducted



Project Impacts

- **Journal Publications**
  - Hoffman, Andrew, Maalavan Arivu, Haiming Wen, Li He, Kumar Sridharan, Xin Wang, Wei Xiong, Xiang Liu, Lingfeng He, and Yaqiao Wu. "Enhanced Resistance to Irradiation Induced Ferritic Transformation in Nanostructured Austenitic Steels." *Materialia* 13 (2020): 100806.
  - Duan, Jiaqi, Haiming Wen, Caizhi Zhou, Xiaoqing He, Rinat Islamgaliev, and Ruslan Valiev. "Discontinuous grain growth in an equal-channel angular pressing processed Fe-9Cr steel with a heterogeneous microstructure." *Materials Characterization* 159 (2020): 110004.
  - Duan, Jiaqi, Haiming Wen, Caizhi Zhou, Xiaoqing He, Rinat Islamgaliev, and Ruslan Valiev. "Annealing behavior in a high-pressure torsion-processed Fe–9Cr steel." *Journal of Materials Science* (2020): 1-11.

- **Involvement (CAES, INL and ORNL)**
  - Nuclear Science User Facilities (NSUF) Rapid Turnaround Experiment (RTE) titled “Alleviating irradiation-induced precipitation in a Fe-21Cr-5Al alloy via nanostructuring” (19-1761)
  - “Atom probe tomography study of the effect of grain size on a’ Cr precipitation in isothermally aged Fe-21Cr-5Al alloy” at Center for Nanophase Materials Science at Oak Ridge National Laboratory, Proposal ID: CNMS2020-B-00511
  - “Atom probe tomography study of a’ Cr precipitation in ion-irradiated Fe-21Cr-5Al alloy with different grain sizes” at Center for Nanophase Materials Science at Oak Ridge National Laboratory, Proposal ID: CNMS2020-B-00522
  - Nuclear Science User Facilities (NSUF) Rapid Turnaround Experiments (RTE), “Correlative Transmission Electron Microscopy and Atom Probe Tomography Study of Radiation Induced Segregation and Precipitation in Nanostructured SS304" (19-2880)

Project Impacts

- **Conference Presentations**
  - Maalavan Arivu, Andrew Hoffman, Jiaqi Duan and Haiming Wen, "**Thermal Stability of Nanostructured Ferritic and Austenitic Steels**", Progress towards Understanding the Synthesis and Behavior of Metals Far from Equilibrium: A SMD Symposium Honoring Enrique Lavernia on the Occasion of His 60th Birthday, ***2020 TMS Annual Meeting***, February 23-27, San Diego, CA.
  - Haiming Wen, Andrew Hoffman, Jiaqi Duan, Maalavan Arivu, "**Ultrafine-grained and nanocrystalline steels for enhanced mechanical properties and irradiation resistance**", Progress towards Understanding the Synthesis and Behavior of Metals Far from Equilibrium: A SMD Symposium Honoring Enrique Lavernia on the Occasion of His 60th Birthday, ***2020 TMS Annual Meeting***, February 23–27, San Diego, CA.
  - Andrew Hoffman, Maalavan Arivu, Haiming Wen, "**Severe Plastic Deformation Enhanced Segregation and Precipitation in Nanostructured Steels**", Progress towards Understanding the Synthesis and Behavior of Metals Far from Equilibrium: A SMD Symposium Honoring Enrique Lavernia on the Occasion of His 60th Birthday, ***2020 TMS Annual Meeting***, February 23–27, San Diego, CA.
  - Andrew Hoffman, Maalavan Arivu, Haiming Wen, "**Enhanced Austenite Stability in Nanostructured Steels During Ion Irradiation**", Irradiation Effects in Metals and Ceramics, ***2020 TMS Annual Meeting***, February 23–27, San Diego, CA.

Milestones and Deliverables for FY-20

Milestones	**Status**
Pre-irradiation characterization	Complete
Neutron irradiation	On schedule
Post-irradiation examination	Slightly delayed

Deliverables	**Status**
Pre-irradiation characterization report	Met
Conference presentations and journal papers on pre-irradiation characterization	Met
Conference presentations and journal papers on post-irradiation examination	Met

Issues and Concerns

- COVID-19 has limited our progress because we only have limited access to the labs.
- COVID-19 has also impacted NSUF's progress in transferring neutron irradiated samples from ATR to HFEF.
- COVID-19 has also limited NSUF's progress in executing RTE projects.

Milestones and Deliverables for FY-21

- “Atom probe tomography study of the effect of grain size on α’ Cr precipitation in isothermally aged Fe-21Cr-5Al alloy” at Center for Nanophase Materials Science at Oak Ridge National Laboratory, Proposal ID: CNMS2020-B-00511
  - HPT manufactured nanocrystalline samples will be studied
  - More detailed analysis will be carried out
- “Atom probe tomography study of α’ Cr precipitation in ion-irradiated Fe-21Cr-5Al alloy with different grain sizes” at Center for Nanophase Materials Science at Oak Ridge National Laboratory, Proposal ID: CNMS2020-B-00522
- Nuclear Science User Facilities (NSUF) Rapid Turnaround Experiments (RTE), “Correlative Transmission Electron Microscopy and Atom Probe Tomography Study of Radiation Induced Segregation and Precipitation in Nanostructured SS304" (19-2880)
- Disassembly and decontamination of neutron irradiated capsules
- Post-irradiation examination of neutron irradiated samples

Possible Industries for Adoption

- General Electric (GE) Research has collaborated with us on this project, specifically on Kanthal D. They are interested in expanding the collaboration and potentially adopting nanostructured FeCrAl alloys for Accident Tolerant Fuel Cladding.

Contact Information and Questions

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Questions?