AMM Program Review
Dec 4–6, Knoxville, Tennessee

Enhancing irradiation tolerance of steels via nanostructuring by innovative manufacturing techniques

MISSOURI S&T

Haiming Wen
wenha@mst.edu

Department of Materials Science and Engineering
Department of Mining and Nuclear Engineering
Missouri University of Science and Technology

Acknowledgements

- Students and postdoc working on the project: Andrew Hoffman, Jiaqi Duan, and Maalavan Arivu.
- Rinat Islamgaliev from Ufa State Aviation Technical University is thanked for providing samples.
- Nuclear Science User Facility is acknowledged for supporting neutron irradiation work, especially Keith Jewell (NSUF Technical Lead) and Katie Anderson and Leslie Soderquist (Experiment Manager).
- Co-PIs: James Cole, Yongfeng Zhang, Isabella van Rooyen at INL.
- This research is financially supported by U.S. Department of Energy, Office of Nuclear Energy through the NEET-NSUF (Nuclear Energy Enabling Technology - Nuclear Science User Facility) program (award number DE-NE0008524).

Why We Go into NANO

Strengthening mechanisms:

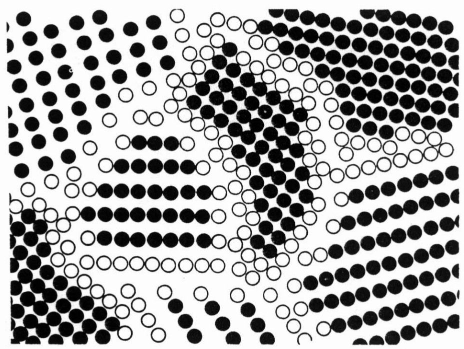
A. Work hardening: dislocation-dislocation interaction

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:

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

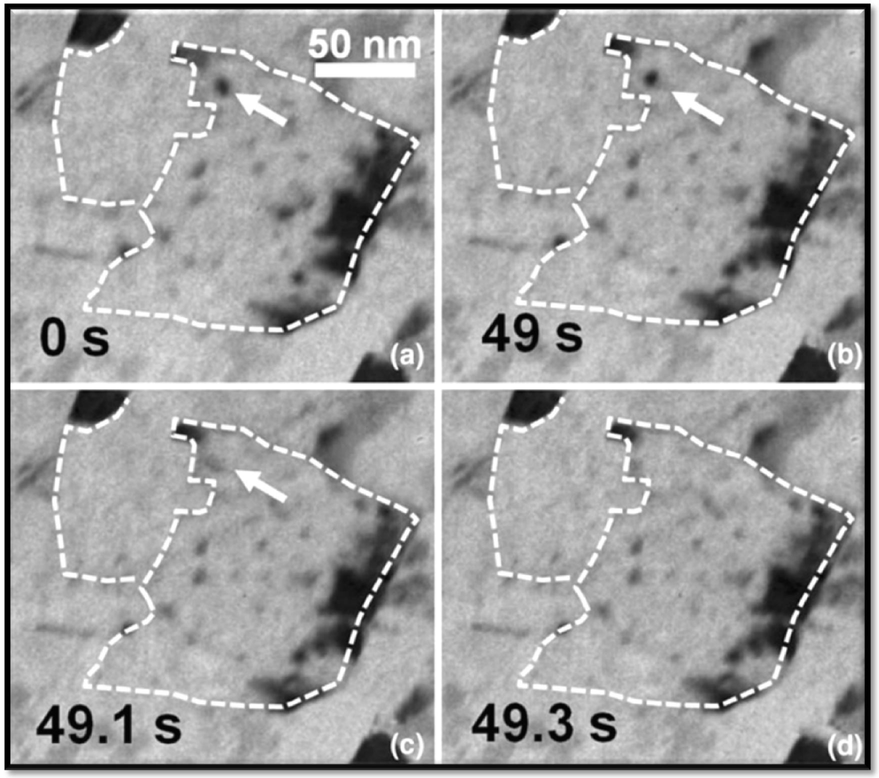
σ_0, k_y : material constants

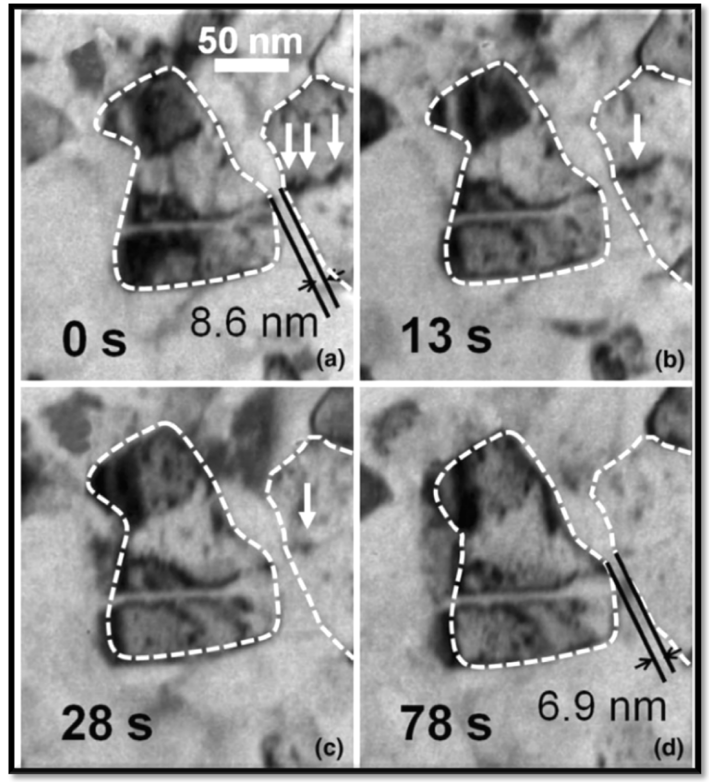
Nanocrystalline material: single or multiple-phase polycrystals with structural features (typically grains) smaller than 100 nm

- D=5 nm, fraction of GBs=50%
- 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

GBs as Sinks for Irradiation Defects

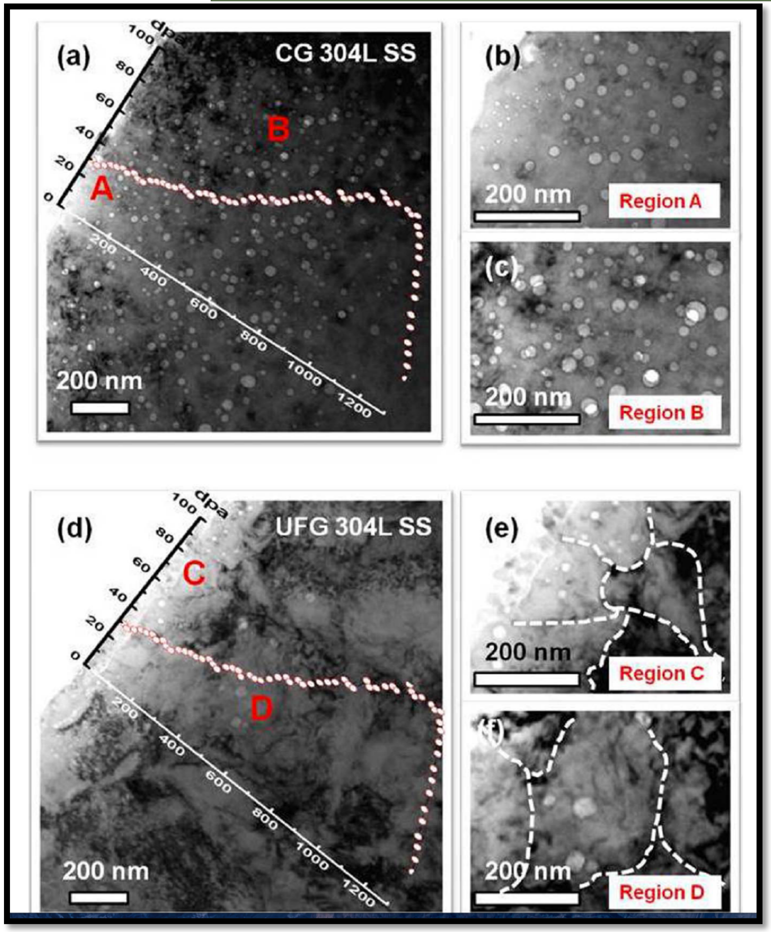




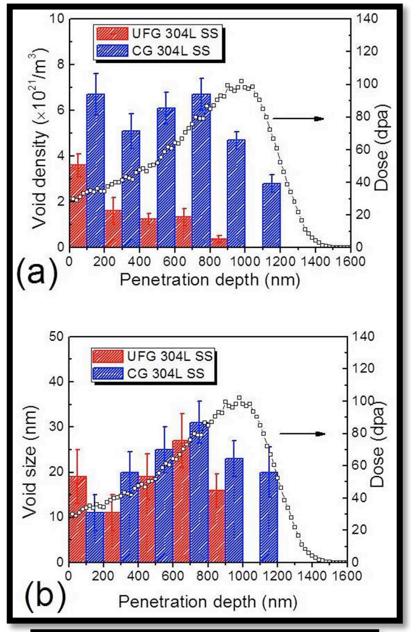
- In-situ TEM imaging during ion irradiation of NC Ni films
- Grain boundaries as sinks for irradiation-induced dislocation loops and segments

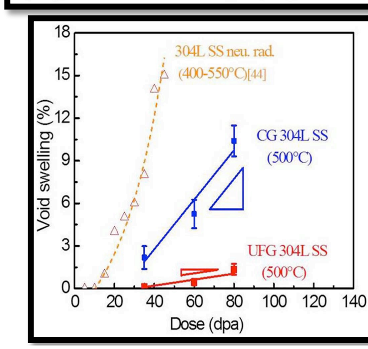
Sun C, et al., Metall Mater Trans A 44 (2013) 1966

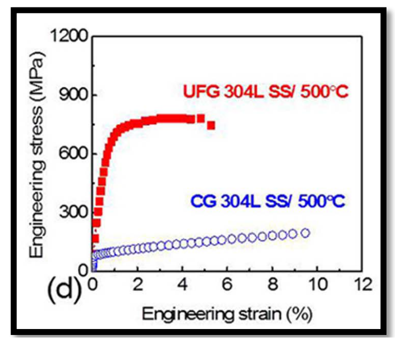
Ion Radiation Resistance of UFG 304 Steel



Sun C, et al., Scientific Reports 5 (2015) 7801

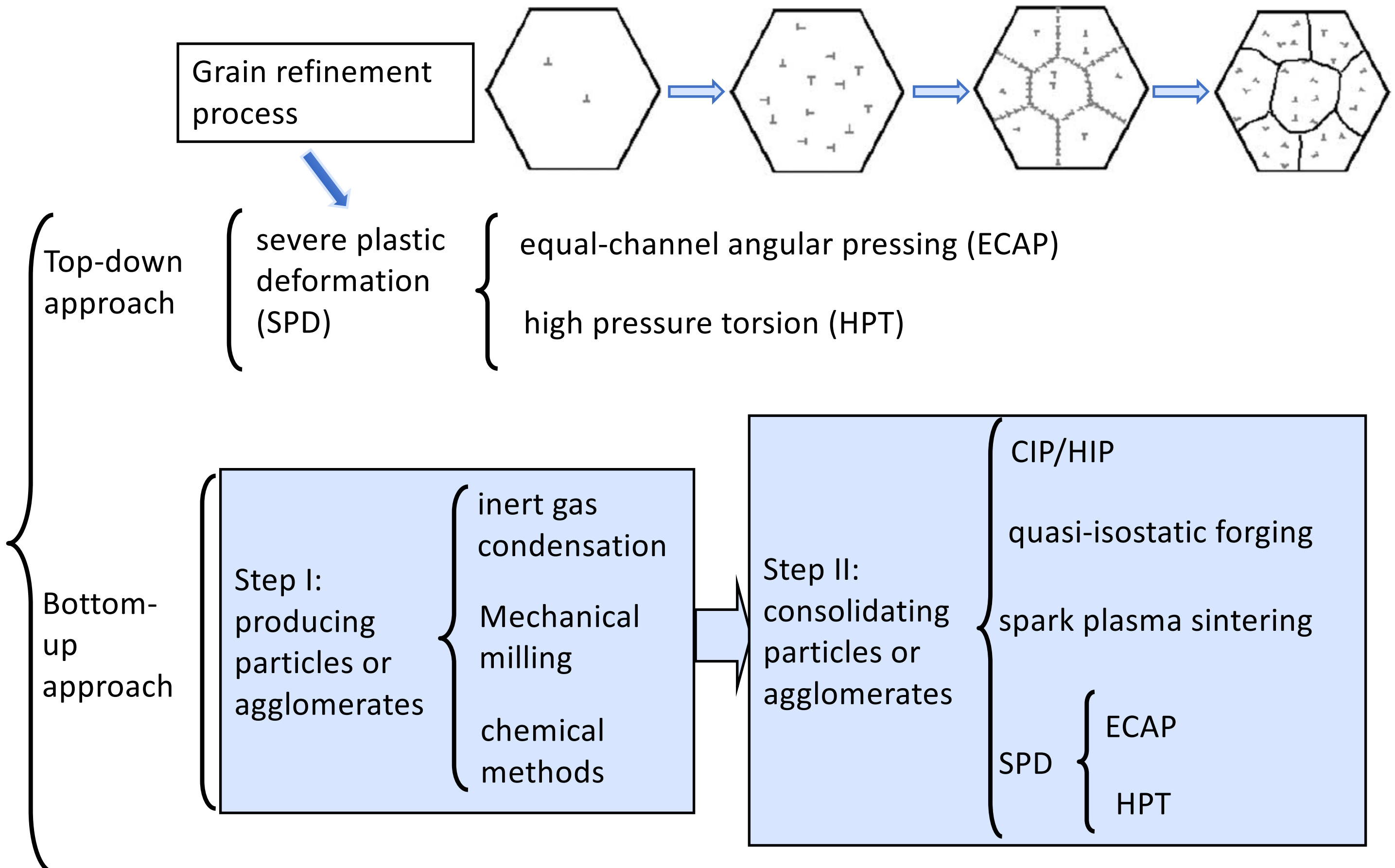






- Much smaller void density and void swelling in UFG sample
- Much higher strength of UFG sample

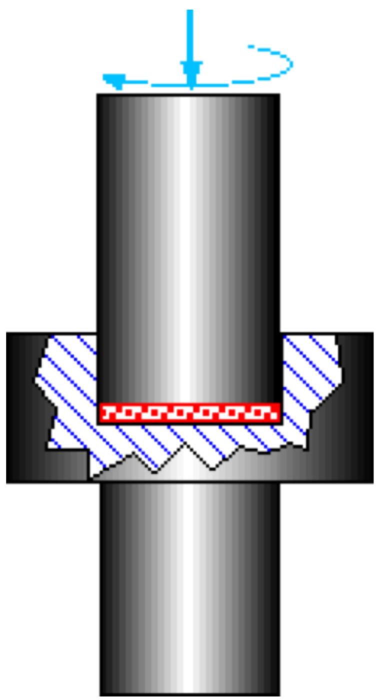
Manufacturing of bulk nanostructured metals



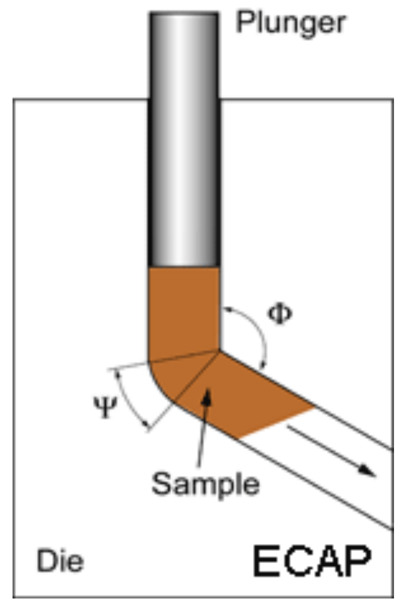
Lavernia EJ, et al., Progress in Materials Science 51 (2006) 1

Severe plastic deformation (SPD)

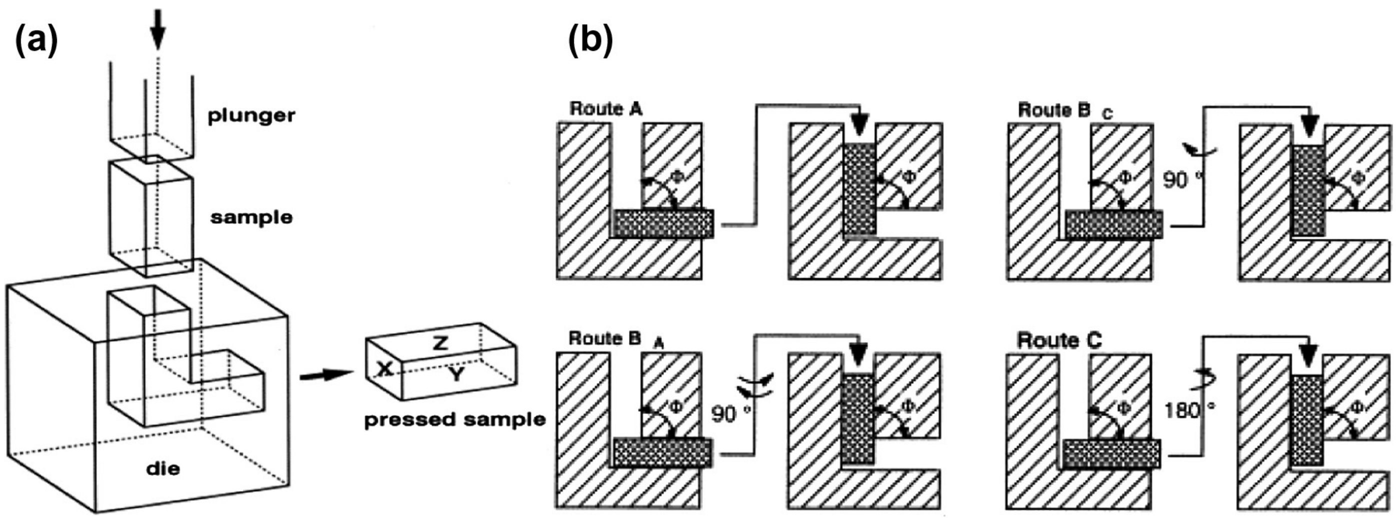
High pressure torsion (HPT)



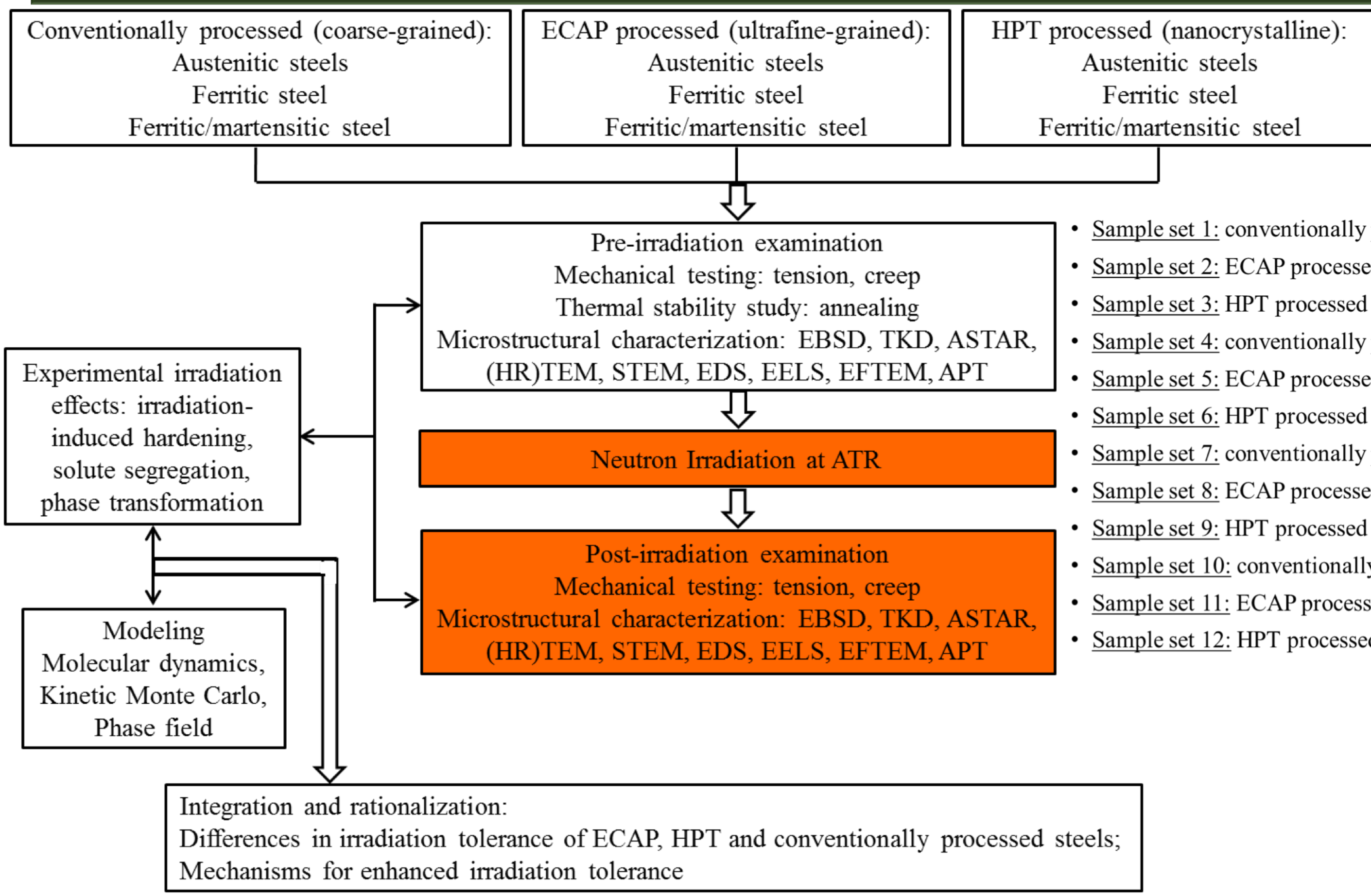
Equal-channel angular pressing (ECAP)



Equal-channel angular pressing



NEET-NSUF Project: Enhancing Irradiation Tolerance of Steels Via Nanostructuring



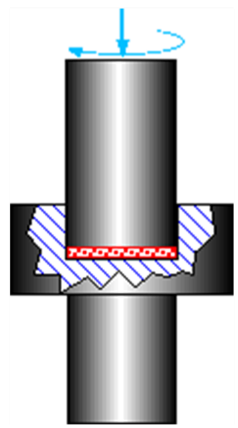
- Sample set 1: conventionally processed (coarse-grained) austenitic 316 steel
- Sample set 2: ECAP processed (ultrafine-grained) austenitic 316 steel
- Sample set 3: HPT processed (nanocrystalline) austenitic 316 steel
- Sample set 4: conventionally processed (coarse-grained) austenitic 304 steel
- Sample set 5: ECAP processed (ultrafine-grained) austenitic 304 steel
- Sample set 6: HPT processed (nanocrystalline) austenitic 304 steel
- Sample set 7: conventionally processed (coarse-grained) F/M Grade 91 steel
- Sample set 8: ECAP processed (ultrafine-grained) F/M Grade 91 steel
- Sample set 9: HPT processed (nanocrystalline) F/M Grade 91 steel
- Sample set 10: conventionally processed (coarse-grained) ferritic Kanthanl D
- Sample set 11: ECAP processed (ultrafine-grained) ferritic Kanthanl D
- Sample set 12: HPT processed (nanocrystalline) ferritic Kanthanl D

Funded by DOE, Office of Nuclear Energy through the NEET-NSUF program (award number DE-NE0008524). **10/1/2016 – 09/30/2023.**

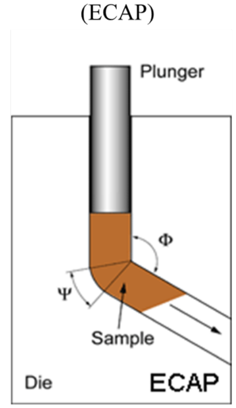
Sample Preparation Using Severe Plastic Deformation

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	-
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	-

High pressure torsion (HPT)

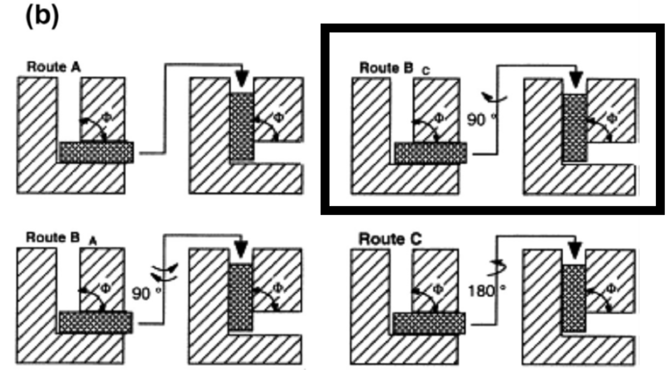


Equal-channel angular pressing (ECAP)

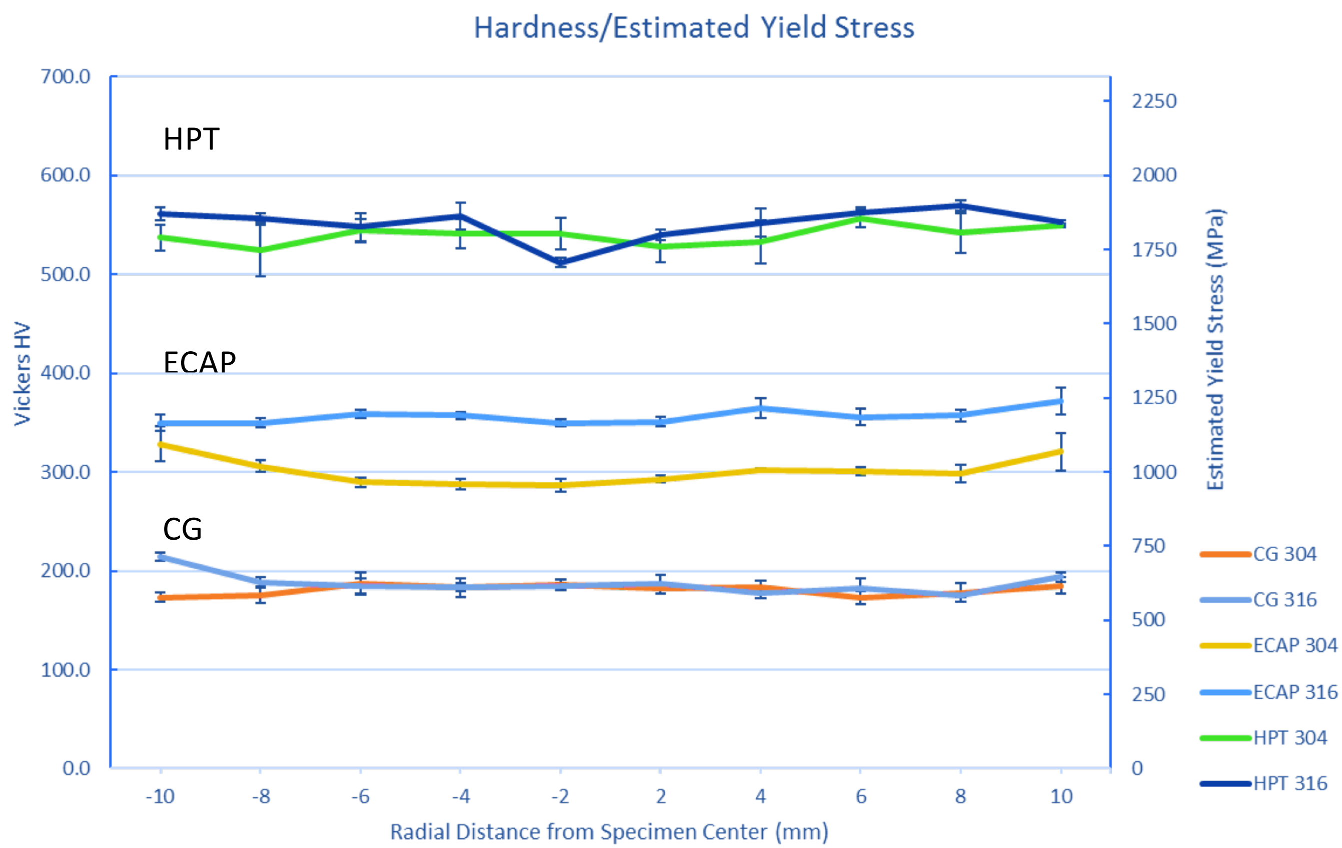


Material	Technique	Temp (°C)	# of passes/turns
SS 304	HPT	300	10
SS 316	HPT	300	10
Grade 91	HPT	300	10
Kanthal D	HPT	300	10
SS 304	ECAP	450	6
SS 316	ECAP	380	6
Grade 91	ECAP	300	6
Kanthal D	ECAP	520	6

(b)

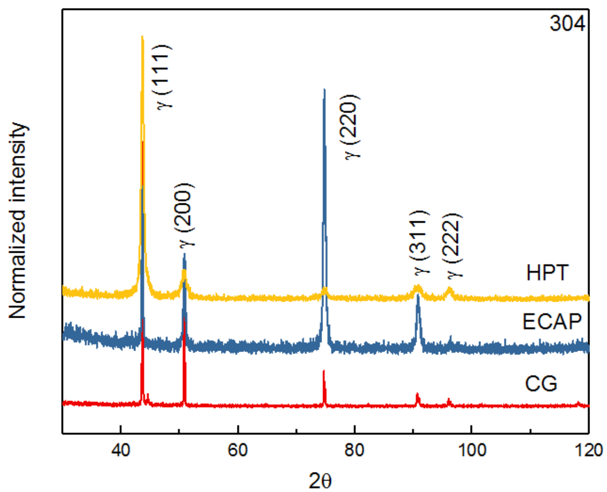


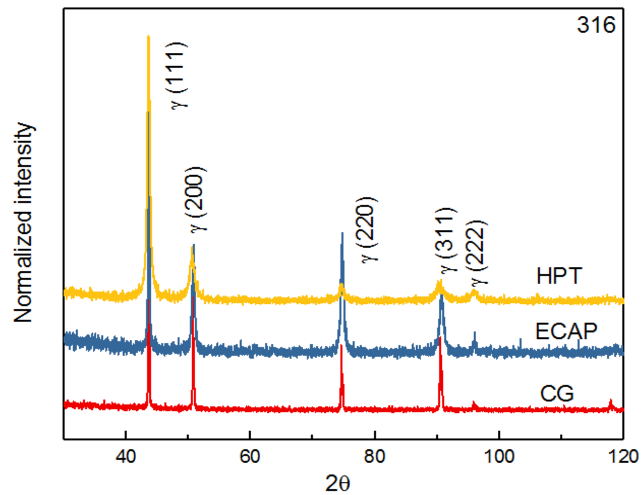
Hardness Testing of Austenitic Steels



- Hardness tested using Vickers microindenter
- HPT samples having extremely high microhardness (~540 Hv, ~1.8 GPa estimated tensile strength)
- Hardness of HPT higher due to smaller grain size, higher strain, and more precipitate hardening
- Difference between the hardness of ECAP 316 and 304 may come from the difference in processing temperature (380 vs 450 °C)

XRD Results for Austenitic Steels

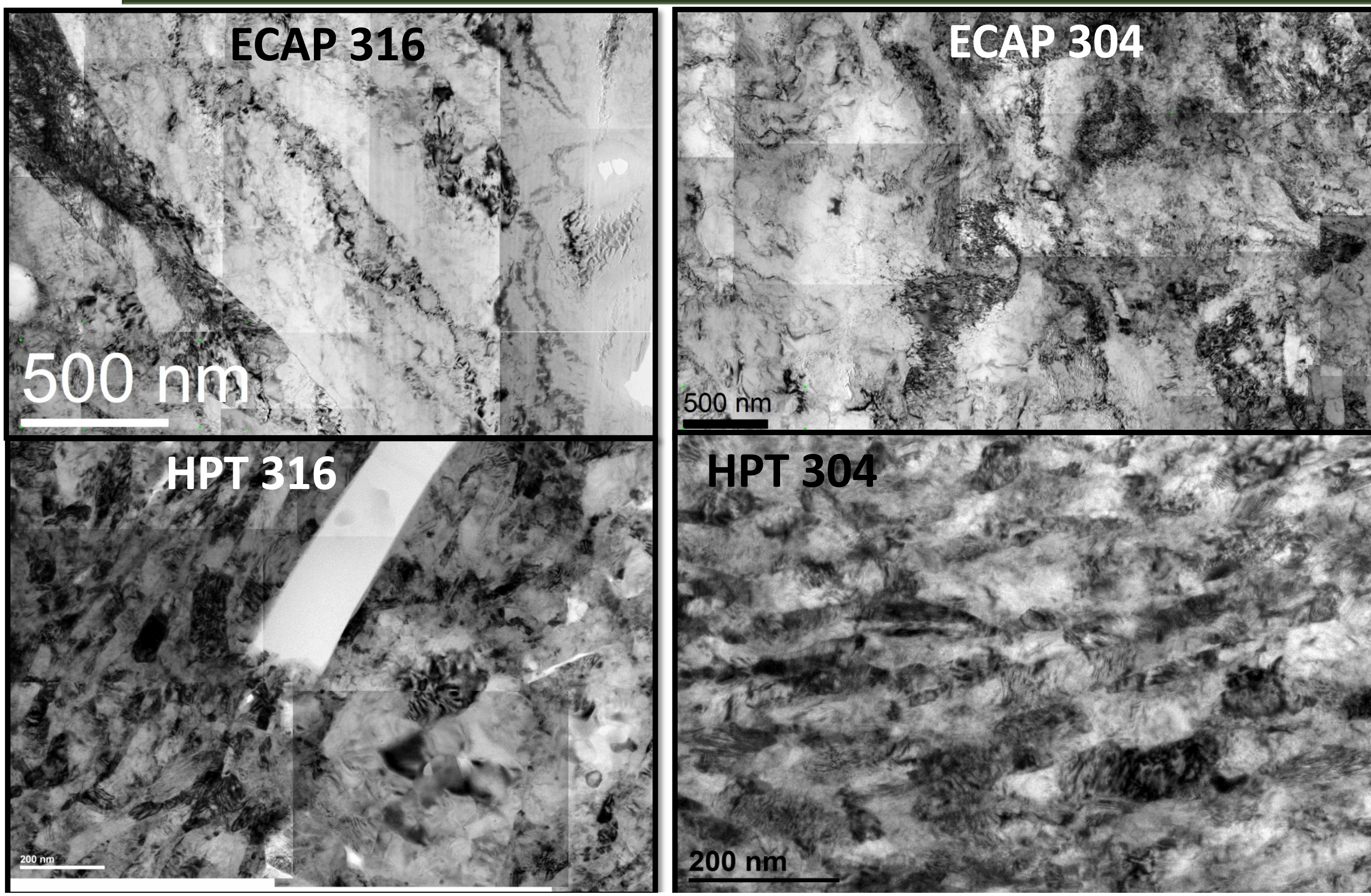




Sample	Strain (%)	CSD Size (nm)	Dislocation ρ (m^-2)
HPT 316	0.38	28	2.6 x 10^15
HPT 304	0.43	36	2.3 x 10^15
ECAP 316	0.33	58	1.1 x 10^15
ECAP 304	0.17	67	5.0 x 10^14
CG 316	0.013	281	8.9 x 10^12
CG 304	0.047	349	2.6 x 10^13

- **Only austenite peaks in all samples**
- **Significant texture in γ-220 after ECAP in both samples**
- **Significant peak broadening due to dislocations/small grains**
- **CSD and micro-strain estimated using Williamson-Hall method**
- **HPT samples have smallest crystallite sizes, largest micro-strains and highest dislocation densities**

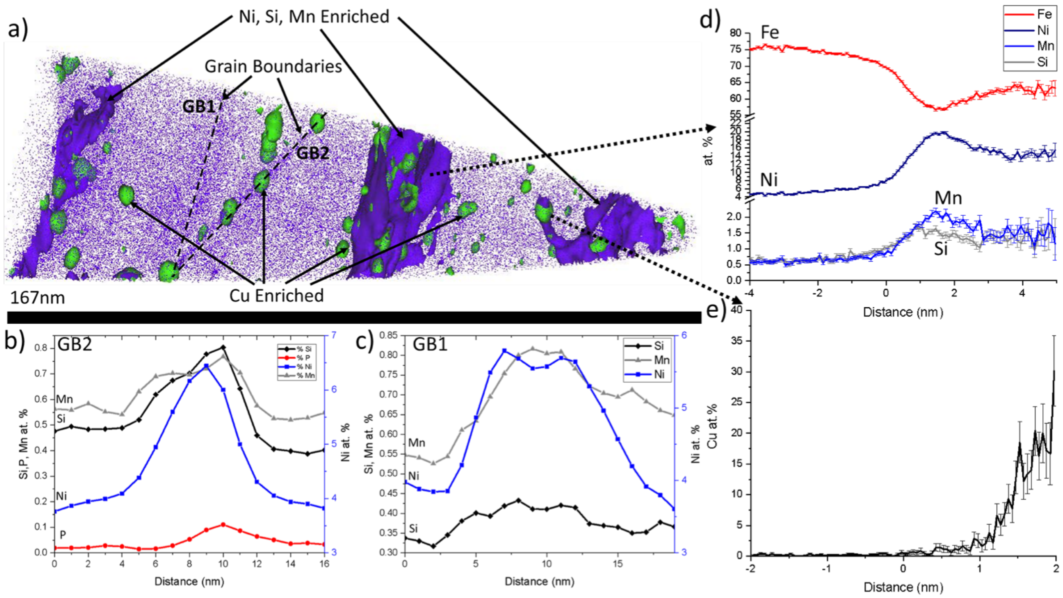
Grain Structure/Dislocations in Austenitic Steels

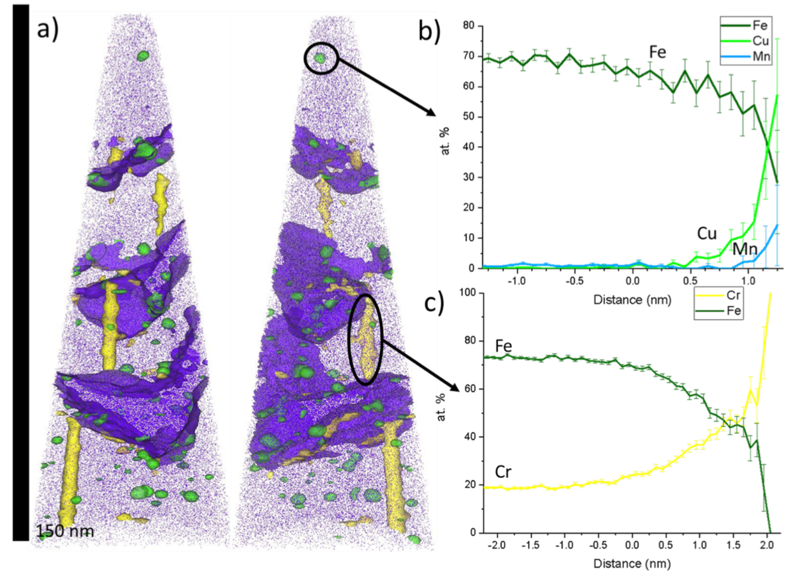


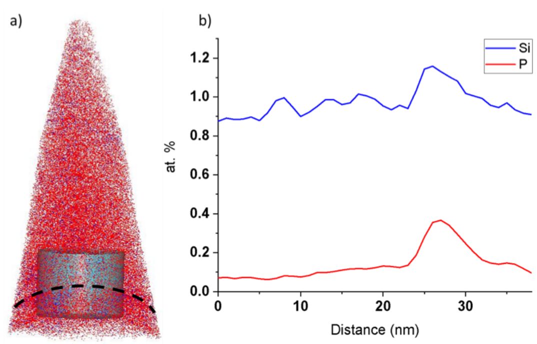
- **ECAP** show many dislocation networks/cells
- Grain size difficult to measure in TEM

- **HPT** samples have much more defined grain structure with many equiaxed grains
- Grain size on the order of 150 nm

Segregation/Precipitation in 304 after HPT

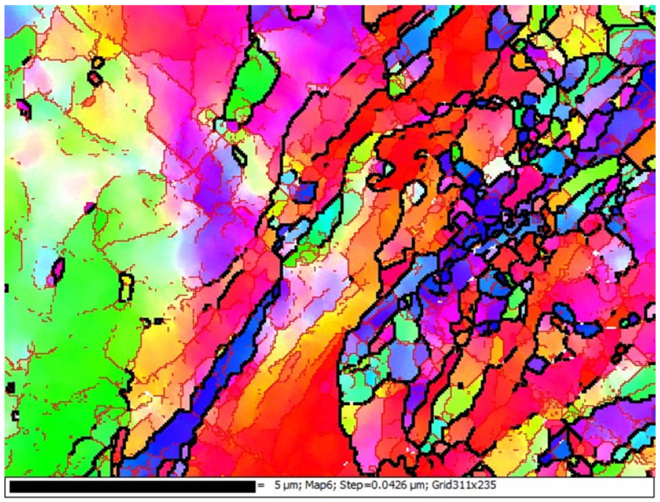


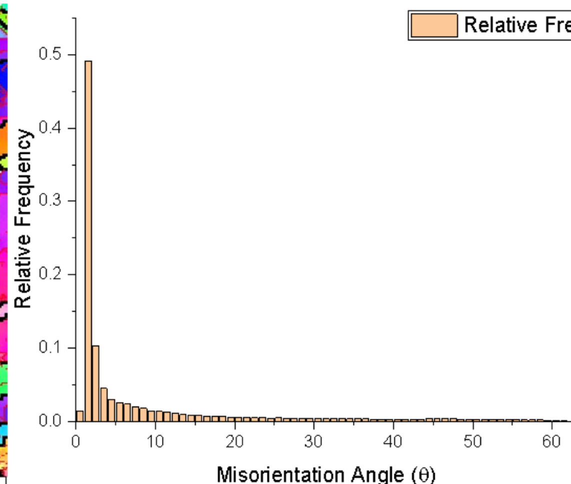


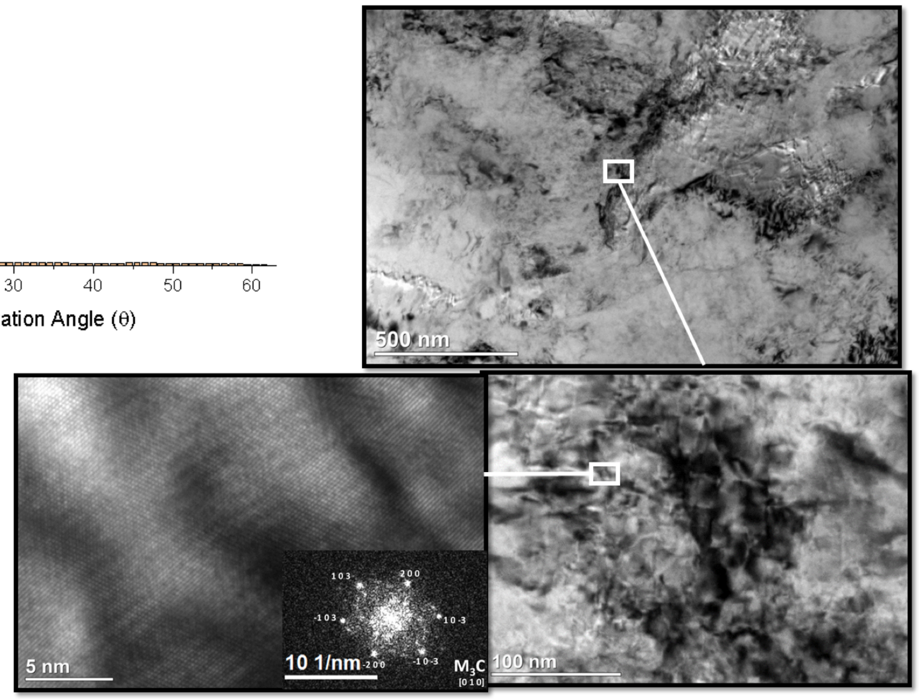


- Significant segregation of Mn, Si, Ni, and P along grain boundaries
- Cu nanoprecipitates near/along grain boundaries, Ni-Mn-Si enriched particles along grain boundaries, needle like Cr particles
- Segregation behavior attributed to high defect density/flux

As ECAPed 304 microstructure

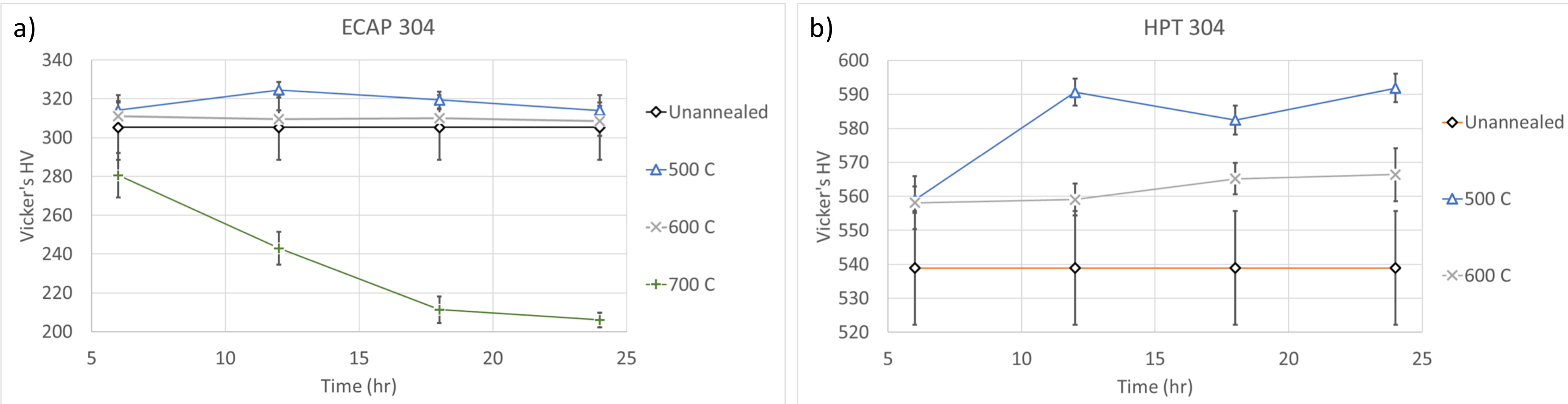






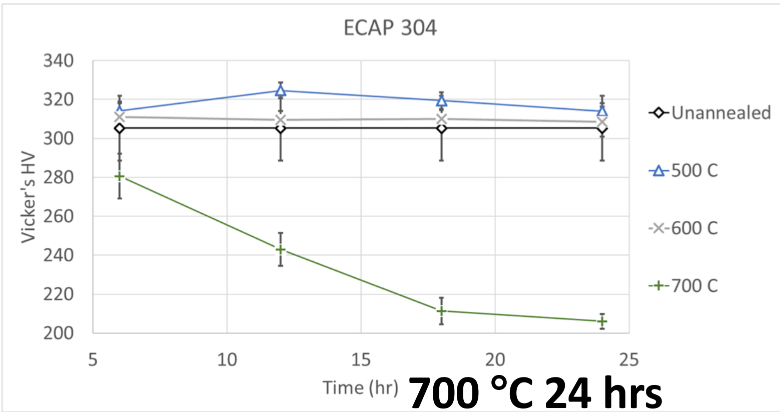
- Large number of low angle grain boundaries
- Microstructure not homogeneous (still in early stages of grain refinement)
- Some signs of carbides forming in dislocation dense regions

Annealing of ECAP and HPT 304

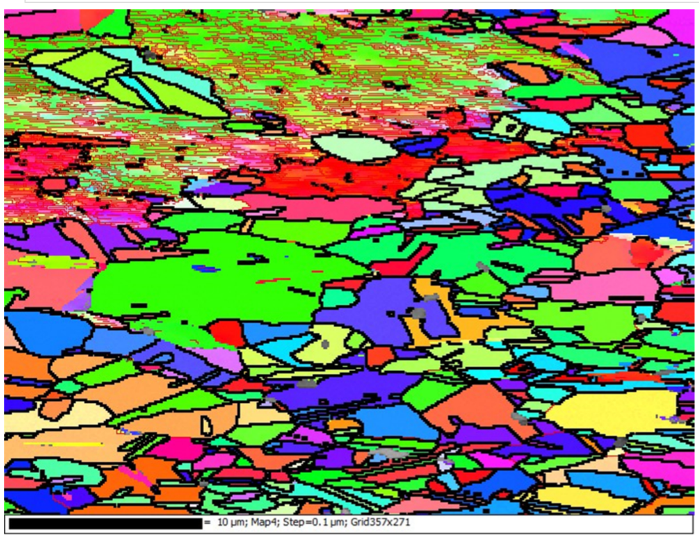


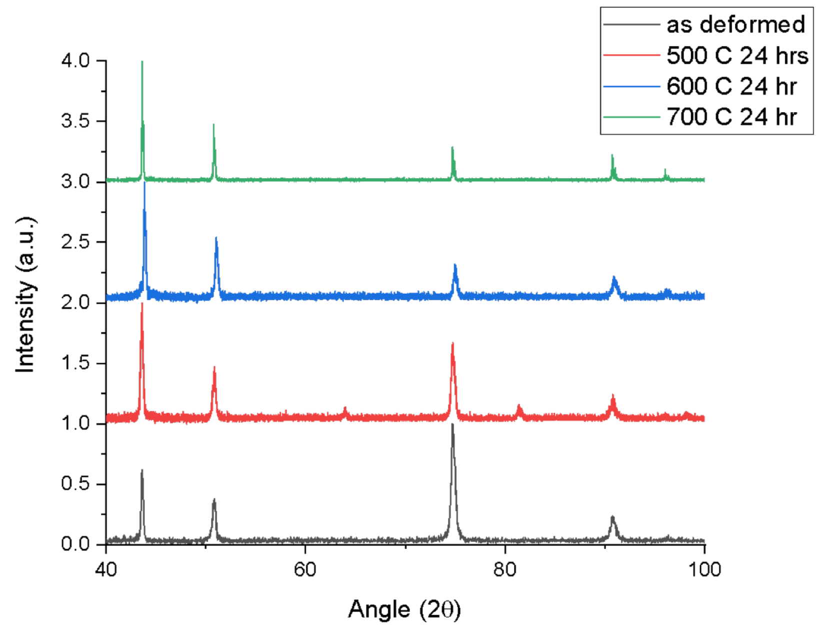
- **Microhardness measured after thermal annealing as a measure of retained properties after annealing**
- **Both ECAP and HPT samples are shown to be stable up to 600 °C**
- **Noticeable increase in hardness in the HPT 304 sample at 500 °C possibly due to the formation of precipitates**

Annealing Effects on ECAP 304



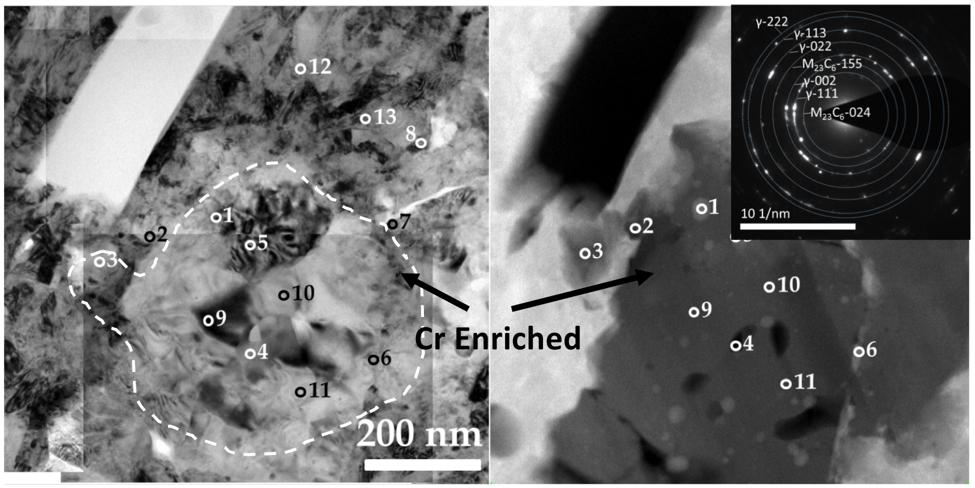
700 °C 24 hrs

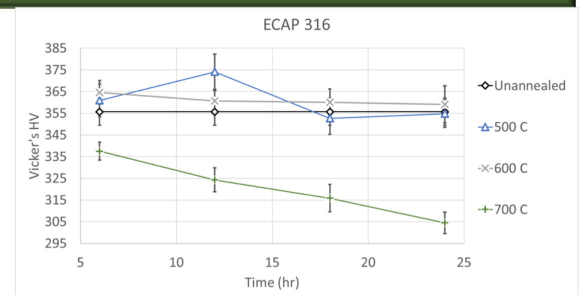


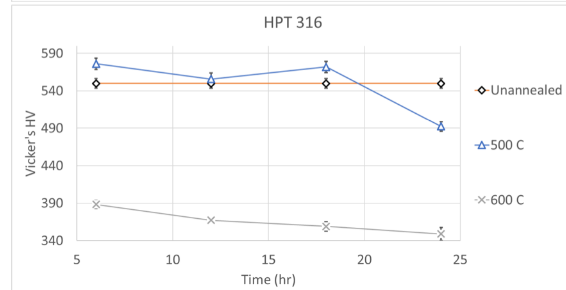


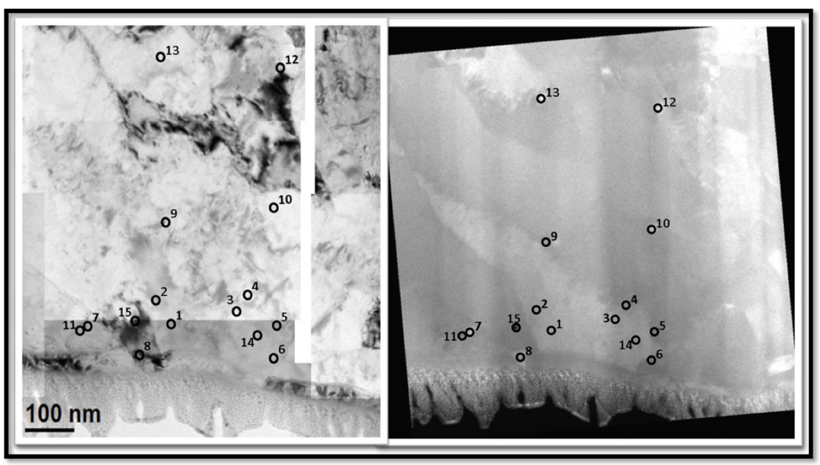
- No decrease in hardness after annealing below 700 C
- Increase in annealing temperature causes decrease in texture
- Significant recrystallization after annealing at 700 C, Cr enriched M_3C precipitation also occurs

Overview of ECAP and HPT 316



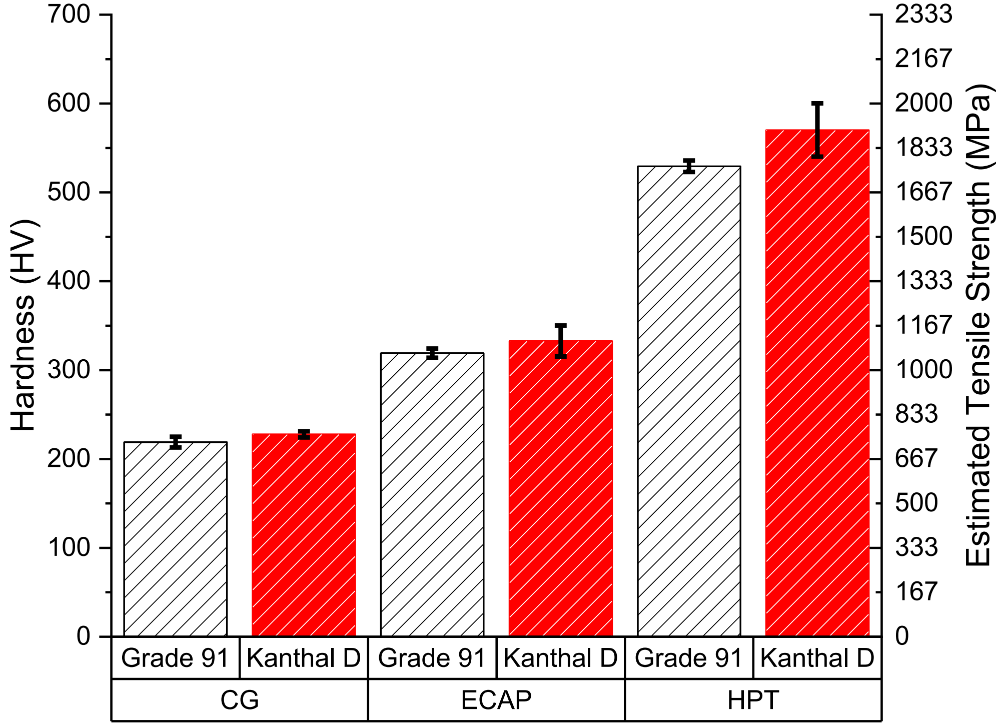


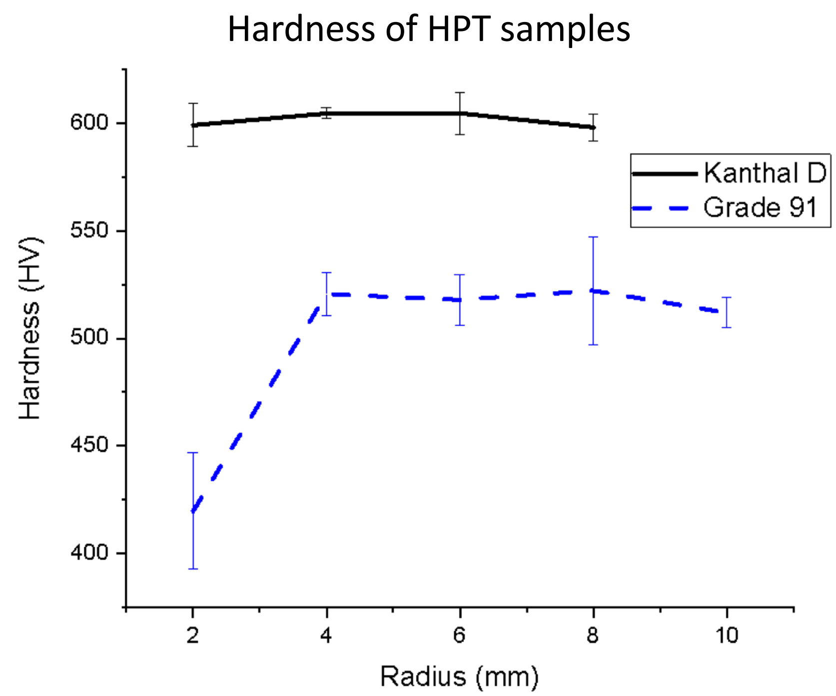




- **Cr enriched (assumed to be carbides) regions in HPT 316**
- **No secondary phases in ECAP 316**
- **ECAP and HPT 316 have different thermal stability, ECAP stable up to 600 C, HPT stable up to 500 C**

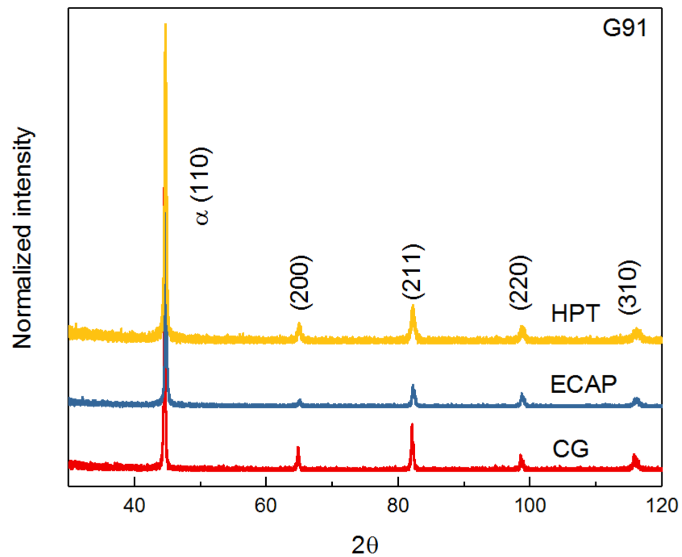
Hardness Testing of Ferritic Steels

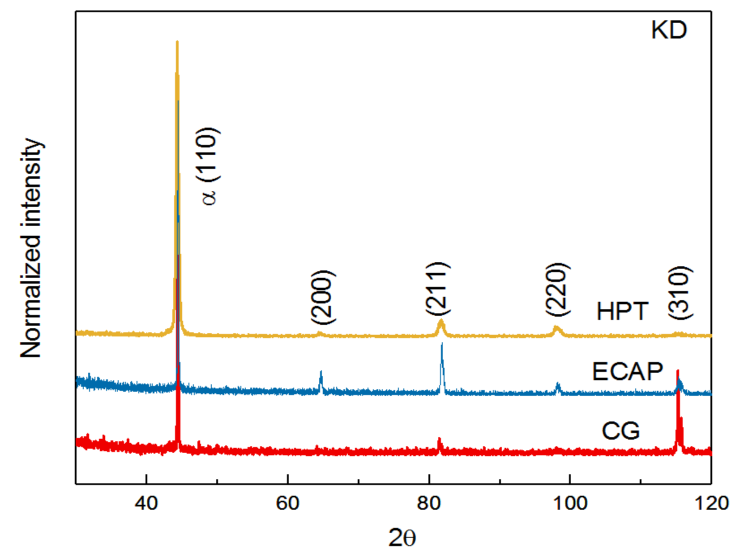




- Improvement in hardness after SPD not as dramatic as in austenitic steels
- HPT Grade 91 shows uniform hardness up to ~4mm; HPT Kanthal D shows uniform hardness up to ~2mm
- Hardness of HPT ferritic steels not as uniform as HPT austenitic steels

XRD Results for G91 and Kanthal-D

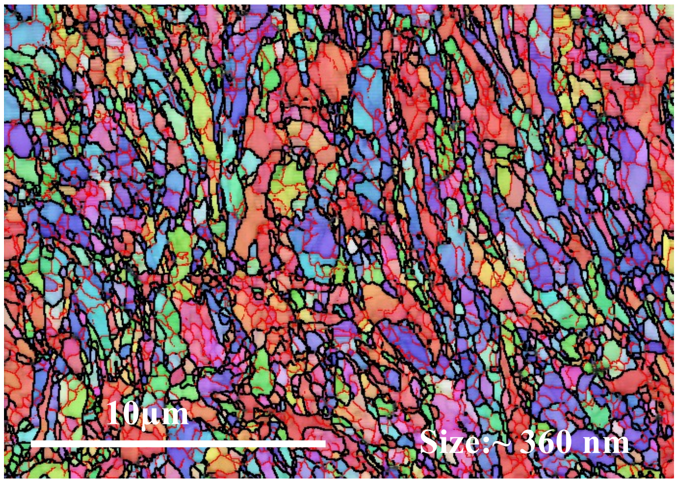


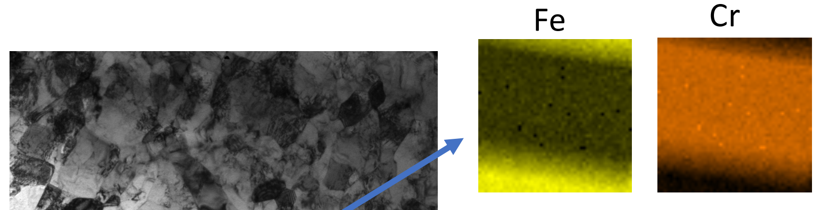


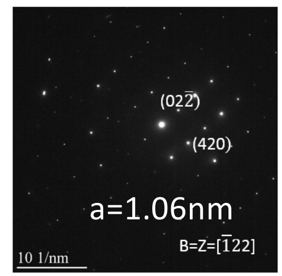
Sample	Microstrain (%)	Crystallite size (nm)	Dislocation ρ (m^-2)
CG	0.054	149	5.0 x 10^13
ECAP	0.146	80	2.7 x 10^14
HPT	0.42	43	1.4 x 10^15

Sample	Microstrain (%)	Crystallite size (nm)	Dislocation ρ (m^-2)
CG	0.021	280	1.1 x 10^13
ECAP	0.087	101	1.2 x 10^14
HPT	0.29	40	1.0 x 10^15

Microstructure of ECAP G91

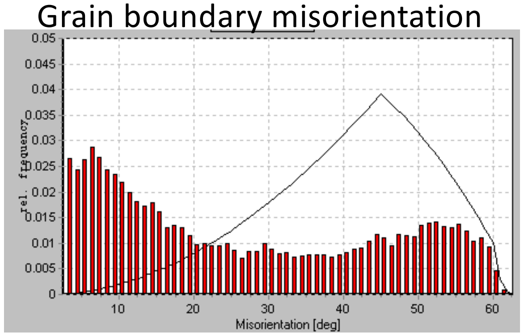






$M_{23}C_6$

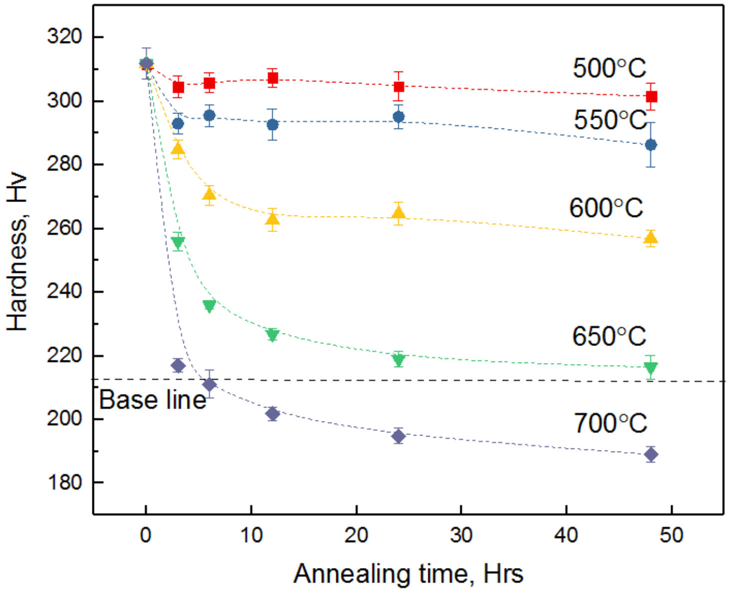
Grain boundary misorientation

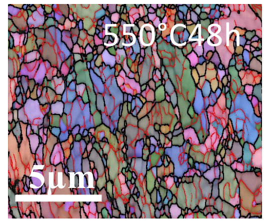


$M_{23}C_6$ M=Cr, Mo
Average: 116 nm
Number density: 0.46×10^{12} m $^{-2}$
Area Fraction: 2.1%

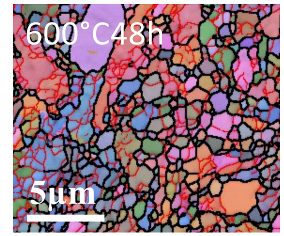
MX M=Nb, V
Average: 59 nm
Number density: 0.32×10^{12} m $^{-2}$
Area Fraction: 0.41%

Annealed microstructure of ECAP G91

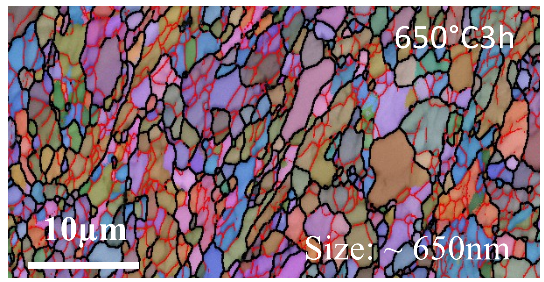


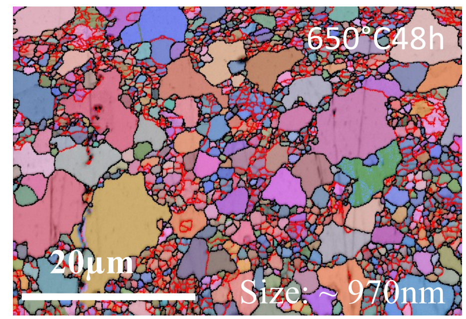


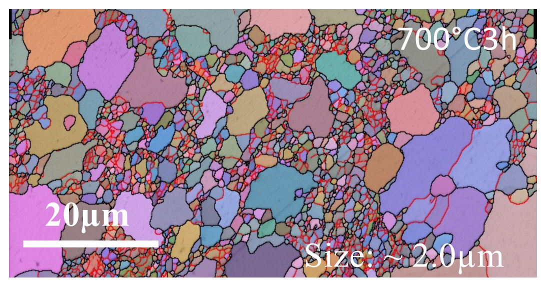
Size: ~ 440nm

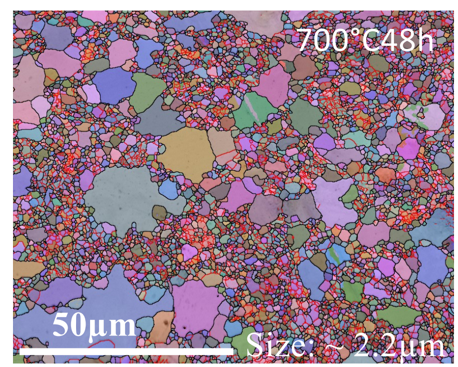


Size: ~ 620nm





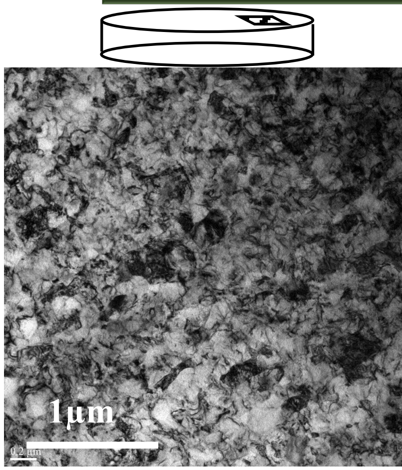


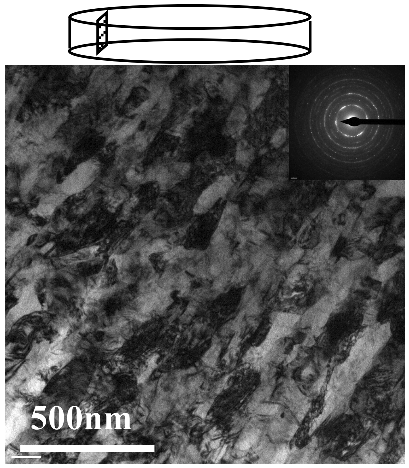


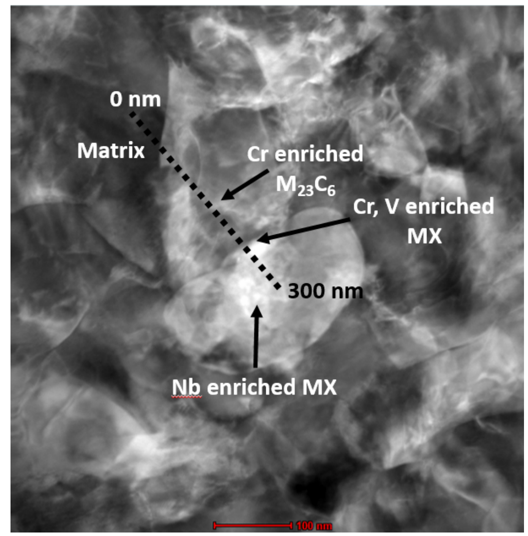
Microstructure is stable up to 500-550°C

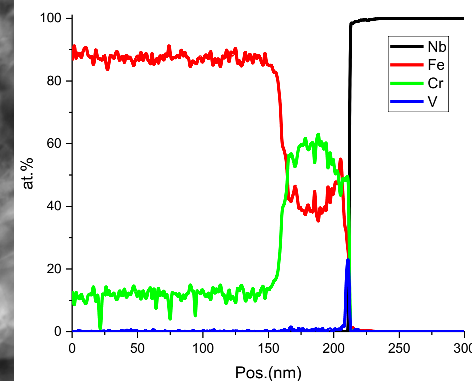
Very inhomogeneous microstructure formed during annealing above 650°C, suggesting recrystallization.

Microstructure of HPT G91

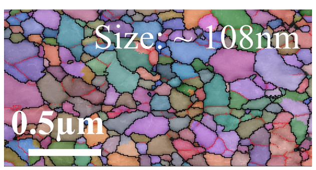


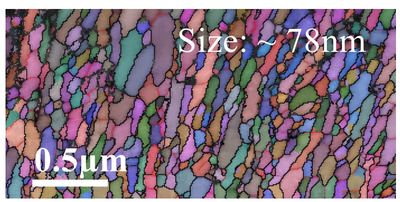


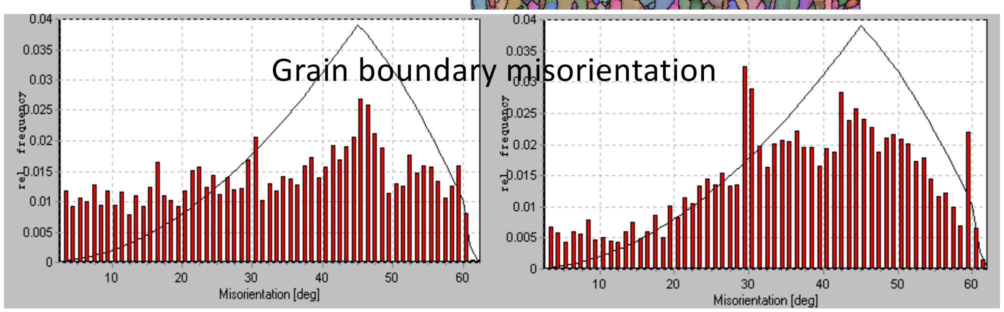




TKD







$M_{23}C_6$

Average: 47 nm

Number density ： 2.7×10^{12} m $^{-2}$

Fraction: 2.3%

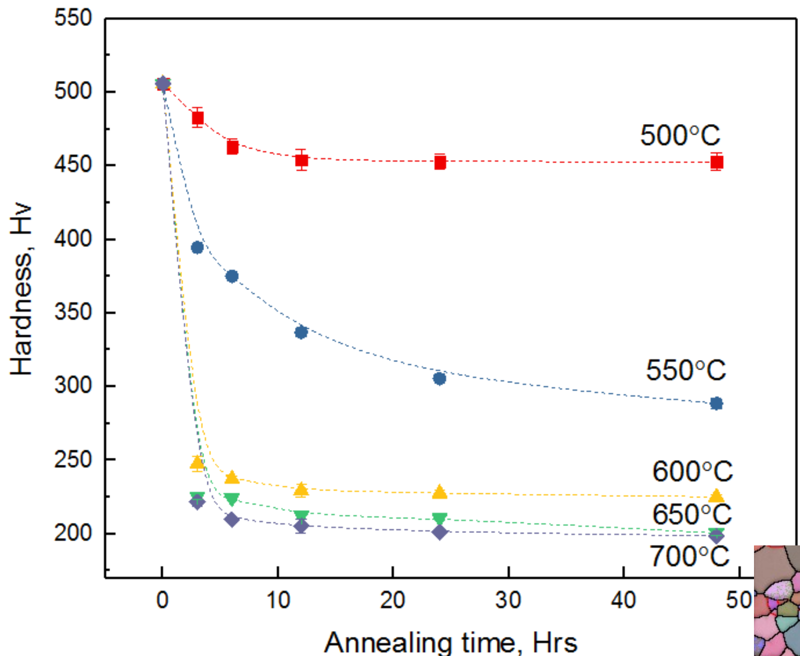
MX

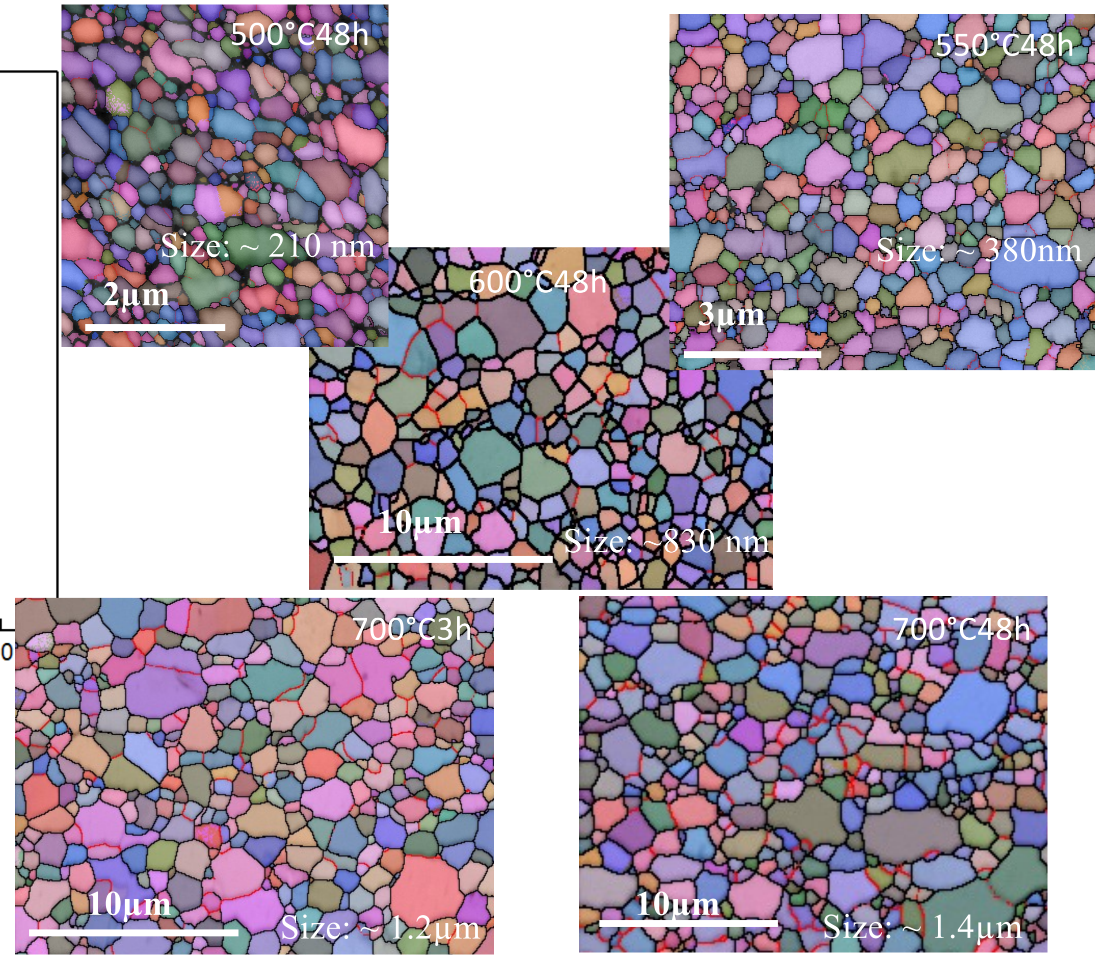
Average: 20 nm

Number density ： 3.3×10^{12} m $^{-2}$

Fraction: 0.47%

Annealed microstructure of HPT G91



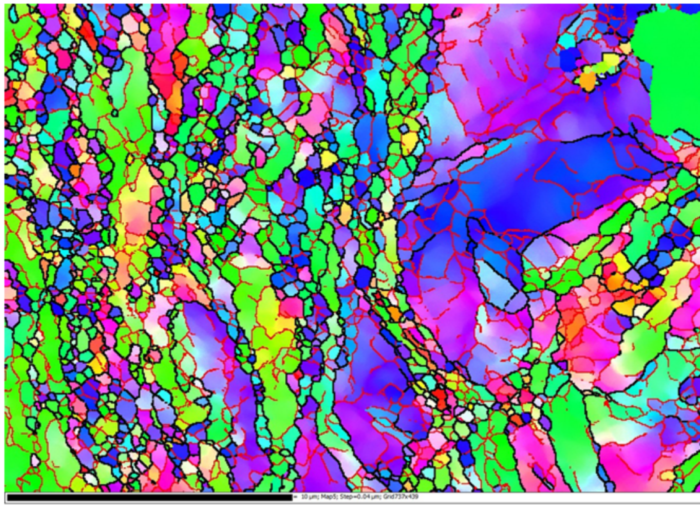


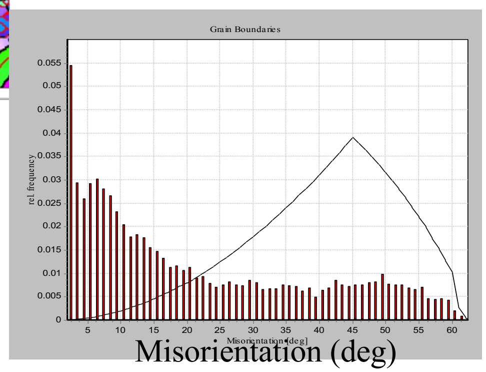
Grains grow in a homogenous manner (homogenous grain growth) at all annealing temperatures.

Grain growth leads to decrease in hardness

Microstructure of HPT and ECAP Kanthal-D

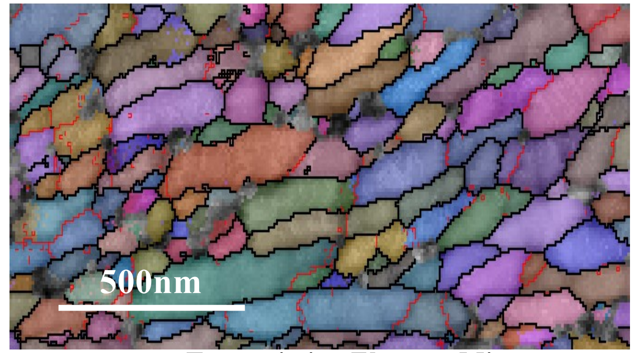
ECAP



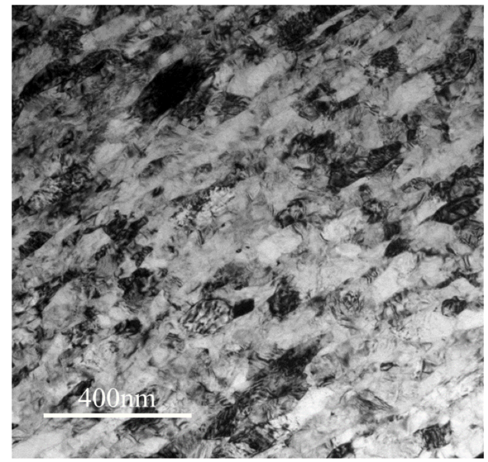


HPT

Transmission Kikuchi Diffraction



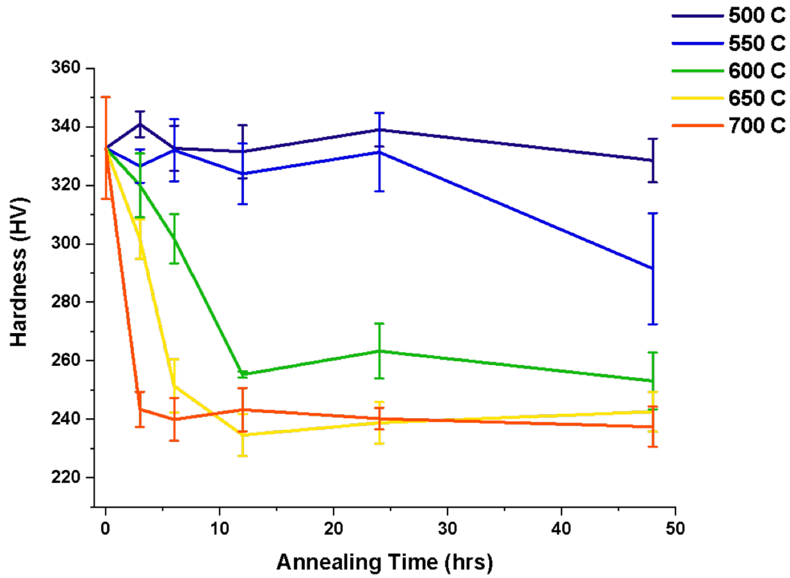
Transmission Electron Microscopy



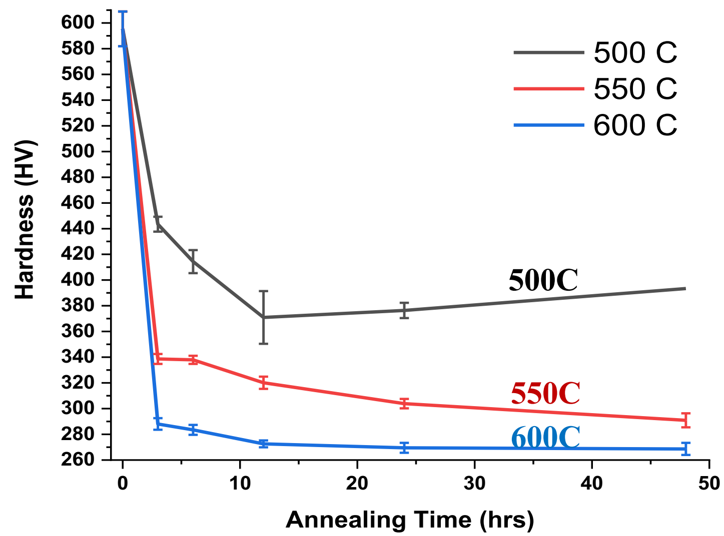
- HPT has grain size ~100nm with homogenous microstructure
- ECAP has grain size ~500nm with inhomogeneous microstructure

Thermal Stability of SPD Kanthal-D

ECAP annealed at various temperatures

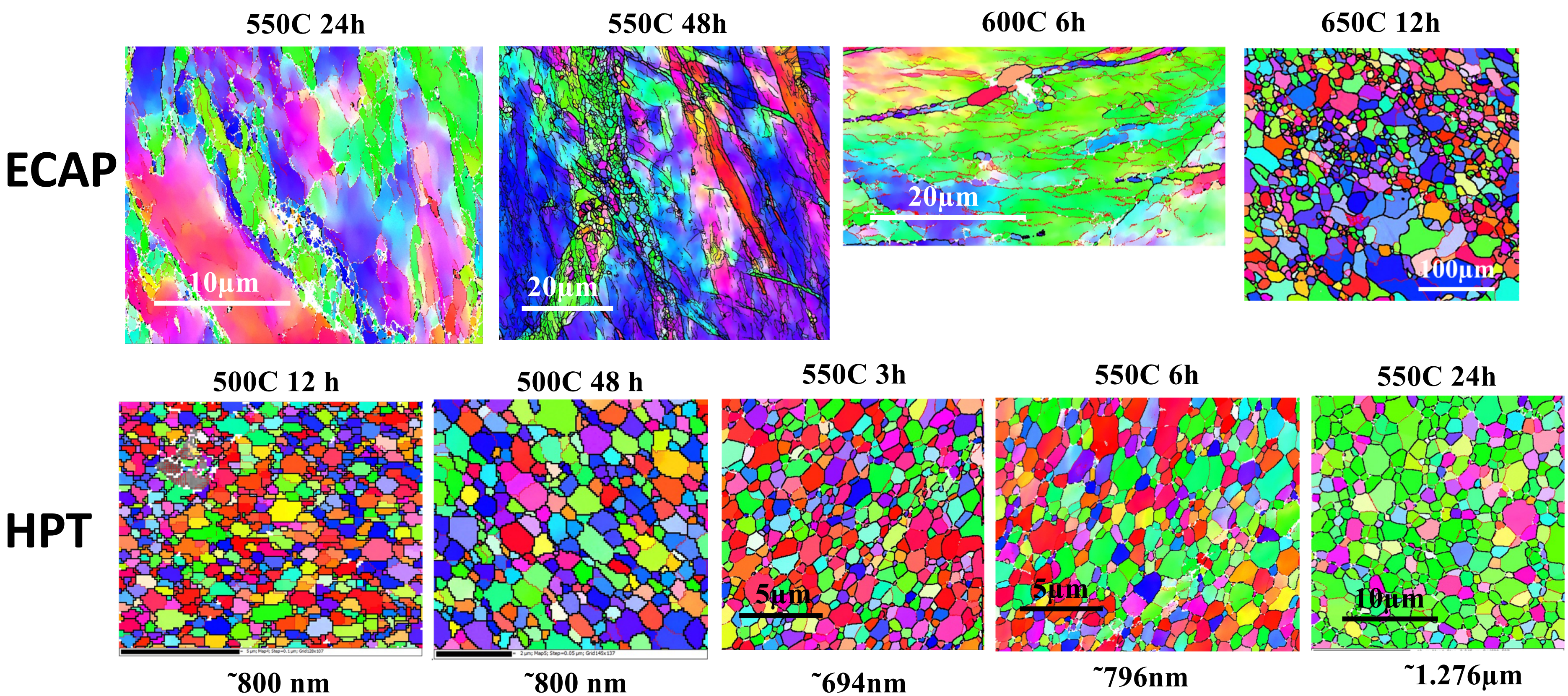


HPT annealed at various temperatures



- **ECAP stable up to ~550 C**
- **HPT unstable at 500 C showing significant drop in hardness**
- **Difference in stability maybe be due to difference in grain boundary characteristics**

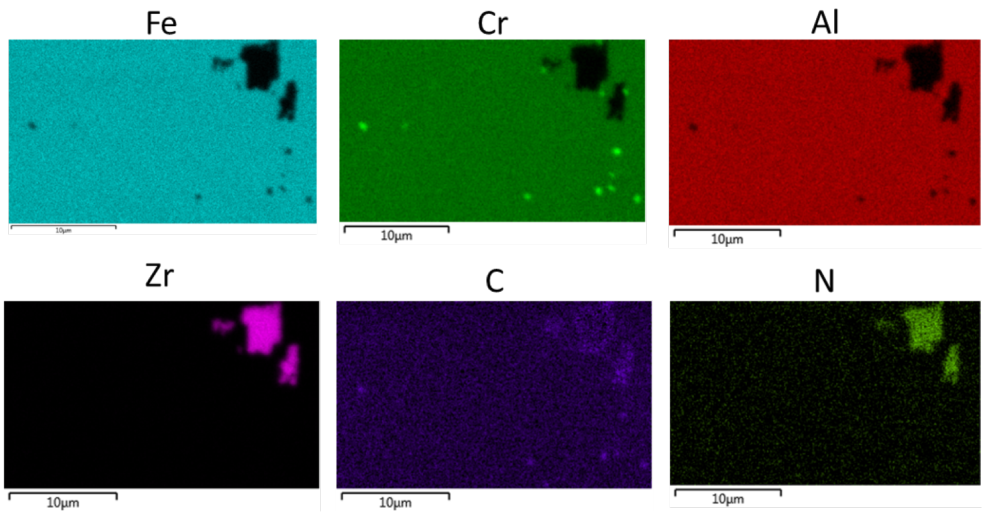
Microstructure of annealed SPD Kanthal-D



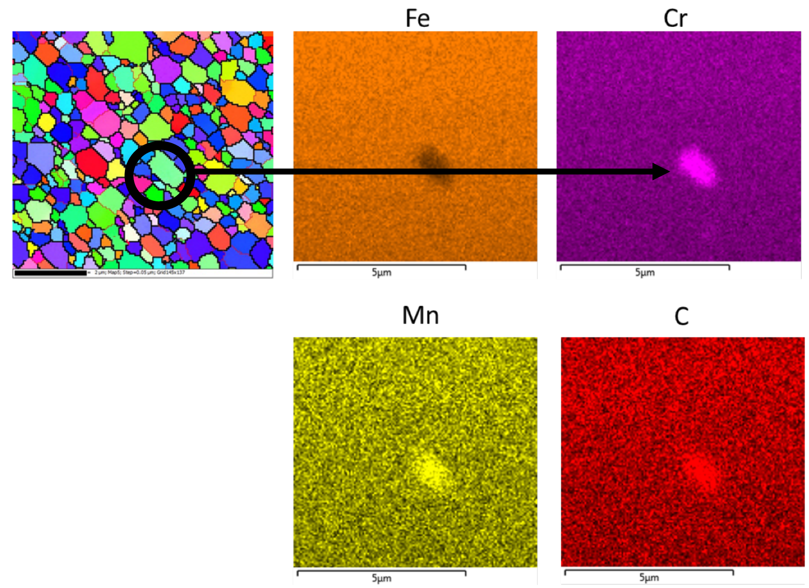
- Microstructure of ECAP barely changed after annealing at 550 C; recrystallization occur at 650 C
- Significant grain growth in HPT after annealing at and above 500 C

Cr Carbide Precipitation

As ECAPed (Processed at 520 C)



HPT annealed at 500 C

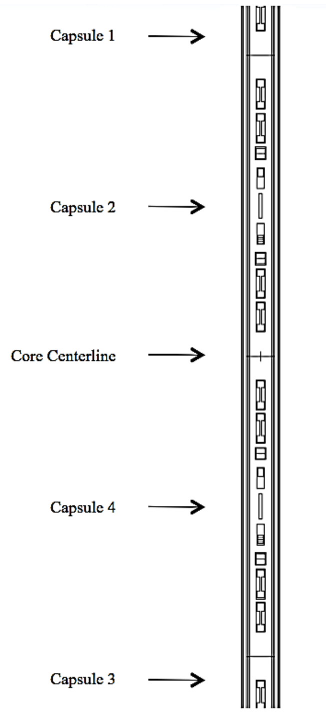


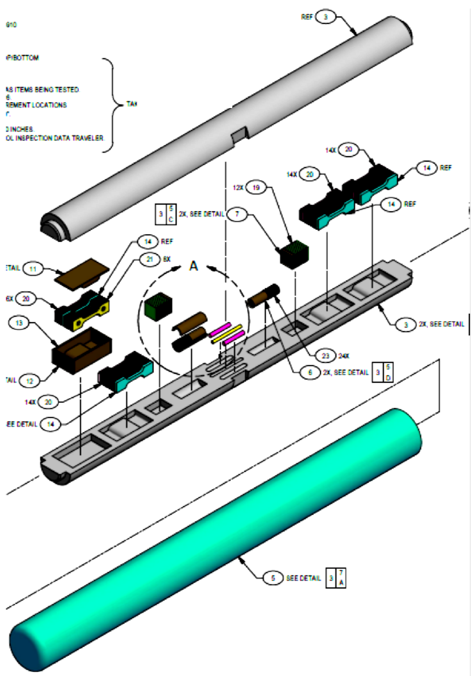
- Cr enriched carbides found in ECAP Kanthal-D
- No Cr enriched carbides in as HPTed sample, but they appear after annealing at 500 C
- No Cr enriched carbides in coarse grained Kanthal-D after annealing at 500 C
- Grain refinement enhances carbide precipitation at ~500 C

Summary of Pre-irradiation Characterization

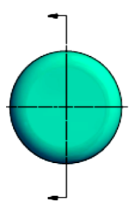
- **HPT and ECAP processing significantly improves the hardness/strength of steels.**
- **Grain size of HPT samples is smaller (~100nm) than ECAP samples (~400nm), and dislocation density of HPT samples is higher than ECAP samples.**
- **ECAP samples show texture while HPT samples do not.**
- **Second-phase particles found in each sample:**
  - **ECAP 304: small amount of $M_{23}C_6$ and M_3C**
  - **HPT 304: Ni-Mn-Si precipitates, Cr precipitates, and Cu-rich precipitates**
  - **ECAP 316: no second-phase particles/precipitates found so far**
  - **HPT 316: cementite and Cr-rich $M_{23}C_6$**
  - **HPT Grade 91: Cr-rich $M_{23}C_6$, Nb-rich MX phase**
  - **ECAP Grade 91: Cr-rich $M_{23}C_6$, Nb-rich MX phase**
  - **HPT Kanthal-D: ZrN particle**
  - **ECAP Kanthal-D: Cr-rich carbides, ZrN particle**
- **Both ECAP and HPT 304 samples shown to be thermally stable up to 600 °C, ECAP 316 stable up to 600 °C, HPT 316 stable up to 500 °C, ECAP Grade 91 stable up to 550 °C, HPT Grade 91 stable up to 500 °C, ECAP Kanthal-D stable up to 550 °C, HPT Kanthal-D unstable above 500 °C**

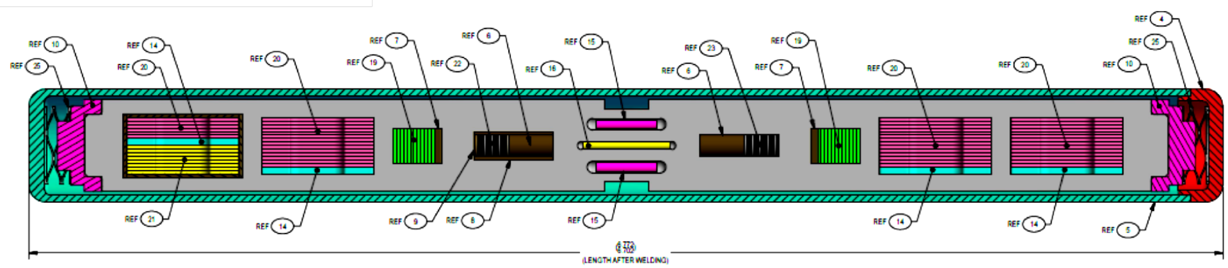
Neutron irradiation





- Conducted at Advanced Test Reactor
  (Samples in ATR since June 2018)
- 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
- Melt wires and SiC to monitor temperature
- Flux wires to measure flux
- ~500 specimens in total





AMM Program Review

Dec 4–6, Knoxville, Tennessee

Enhancing irradiation tolerance of steels via nanostructuring by innovative manufacturing techniques

MISSOURI S&T

Haiming Wen

wenha@mst.edu

Department of Materials Science and Engineering

Department of Mining and Nuclear Engineering

Missouri University of Science and Technology

Questions?