CANFSA

Center for Advanced Non-Ferrous Structural Alloys
An Industry/University Cooperative Research Center

Project 56-L: Thermomechanical Processing of Refractory Multi-Principal Element Alloys for Ultrahigh Temperature Performance

Semi-annual Spring Meeting

April 2022

- Student: Adira Balzac (Mines)
- Faculty: Dr. Amy Clarke (Mines)
- Other: Ben Ellyson (Mines)
- Industrial Mentors: TBD

Office of Naval Research
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Science & Technology

COLORADO SCHOOL OF MINES

NSF

IOWA STATE UNIVERSITY

Project 56-L: Thermomechanical Processing of Refractory Multi-Principal Element Alloys for Ultrahigh Temperature Performance

- Student: Adira Balzac (Mines)
- Advisor(s): Amy Clarke (Mines)

Project Duration

PhD: September 2021 to May 2025

- Problem: Ni and Co alloys cannot be operated above 1200°C without coatings and cooling channels that reduce efficiency. RMPEAs can be used at higher temperatures, but thermomechanical processing is challenging.
- Objective: Design RMPEAs with higher temperature performance and develop understanding of alloy and microstructure response to thermomechanical processing above 1000°C.
- Benefit: Refractory MPEAs that can be operated above 1200°C will allow for significant improvements in efficiency.

Recent Progress

- Continued coursework
- Gleeble thermomechanical simulator, arc melter training
- Initial Thermo-Calc, kinetic, and solid solution strengthening modeling for alloy down-selection
- Identified gaps in literature for alloy selection and modeling
- Submitted abstract to MS&T
- Selected material for master alloys and began making alloys

Metrics

Description	% Complete	Status
1. Literature review	20%	●
2. Thermodynamic, kinetic, and solid solution strengthening modeling to select RMPEAs	50%	●
3. High temperature thermomechanical processing of selected RMPEAs	0%	●
4. High temperature thermomechanical processing of RMPEAs with higher oxygen and carbon levels	0%	●
5. Characterization of RMPEAs	0%	●

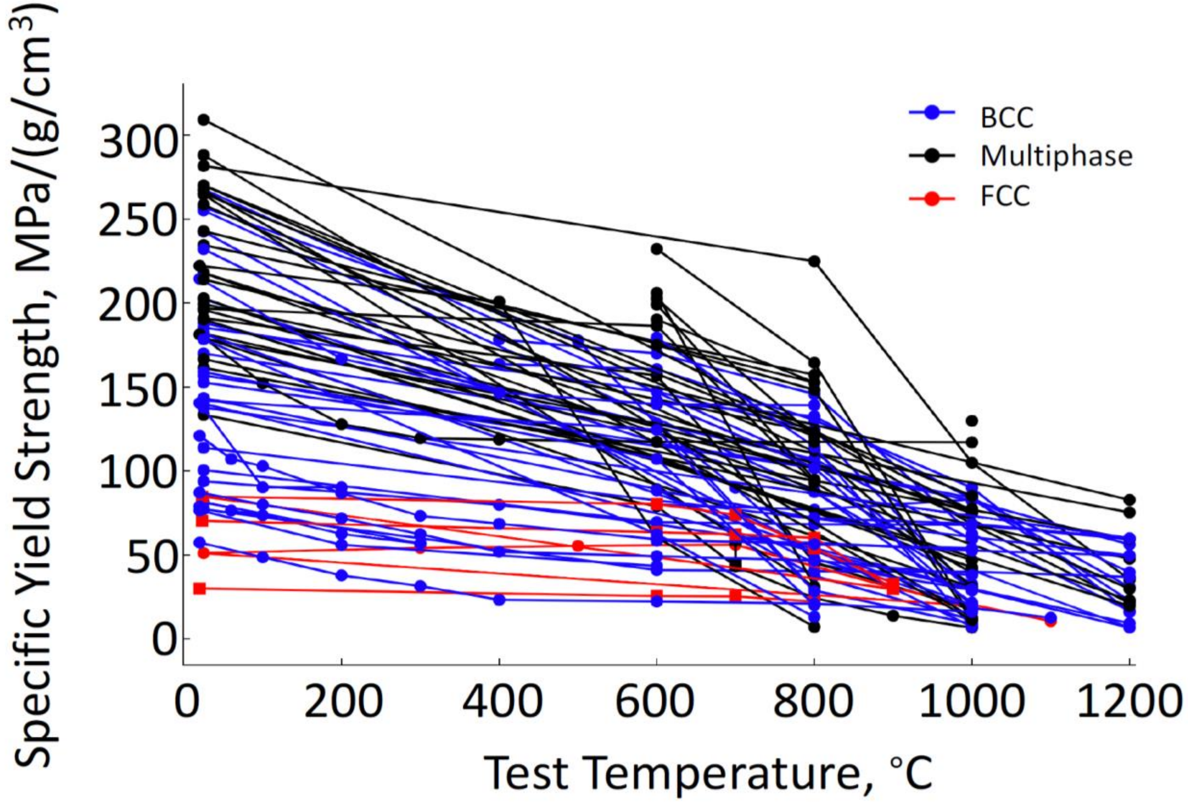
RMPEAs have potential for ultrahigh temperature applications

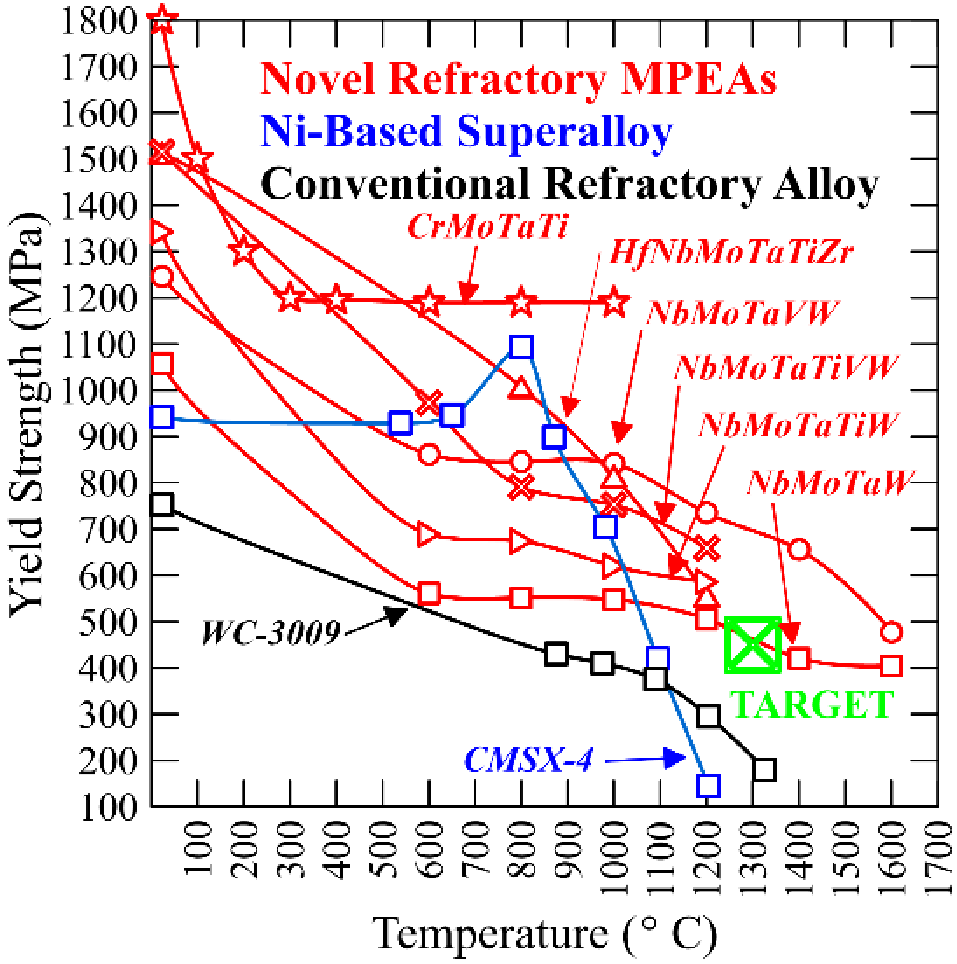
- Jet turbine engines
- Supersonic flight
- Nuclear reactors

Wikimedia

Limited options for refractory properties

- Current refractory alloys have limited operability above 1200 °C
- Limits efficiency and component lifetime [4]

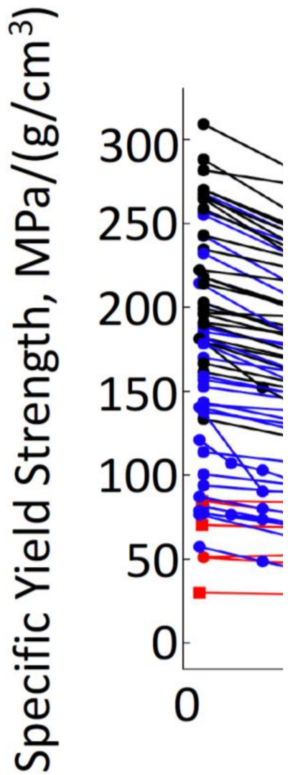


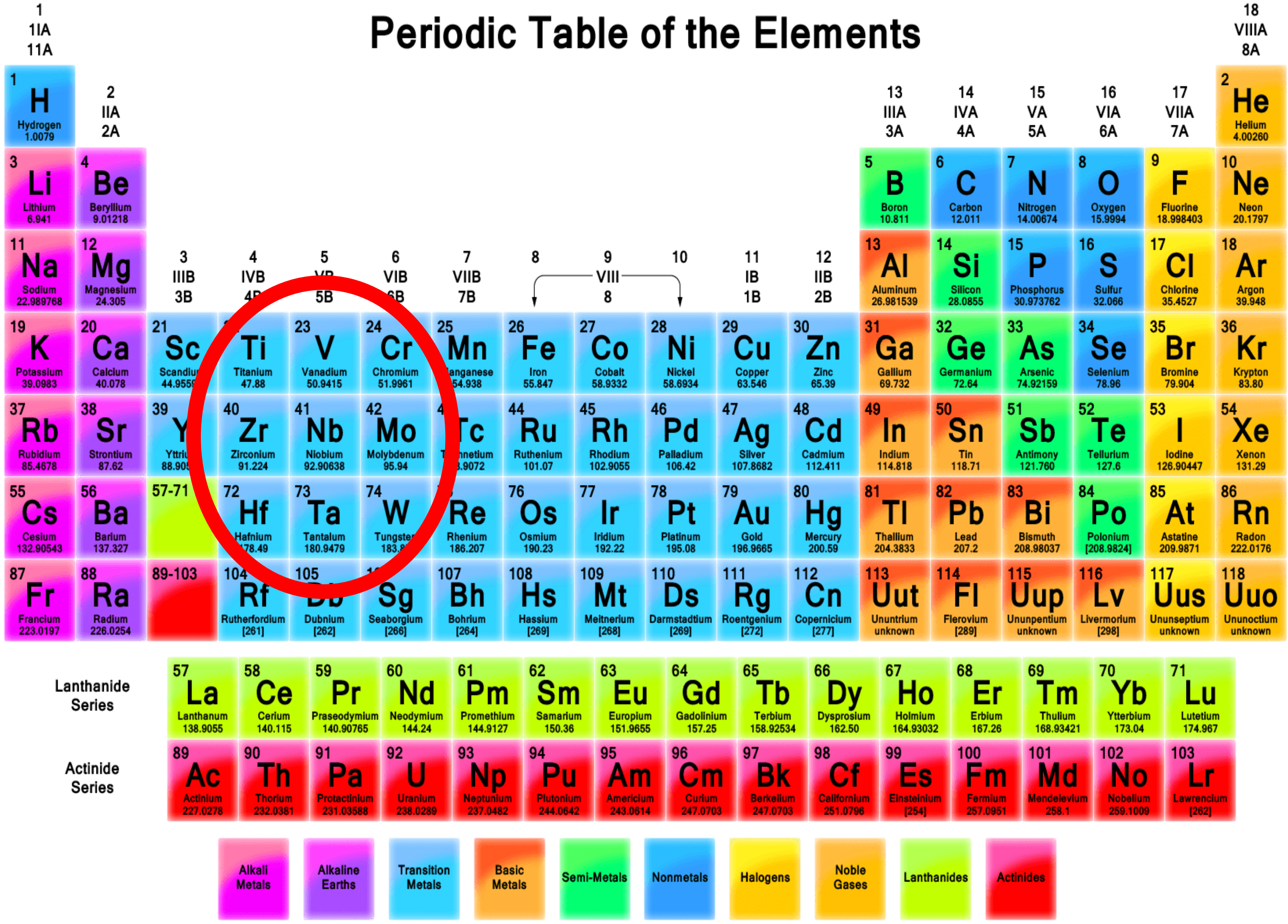


A. J. Clarke et. al. 2021.

Limited options for refractory properties

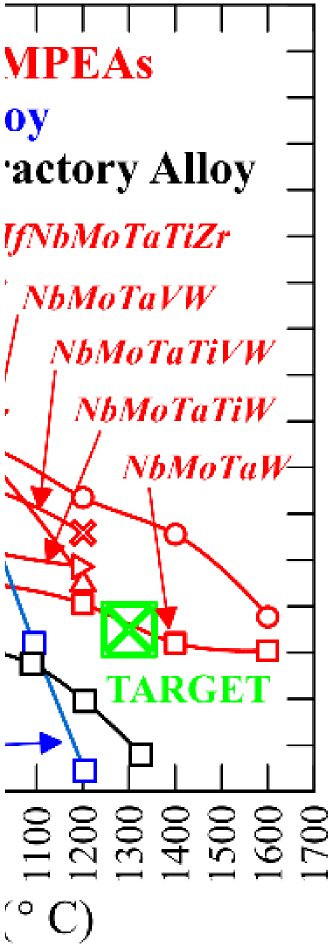
- Current refr
  operability
- Limits effici



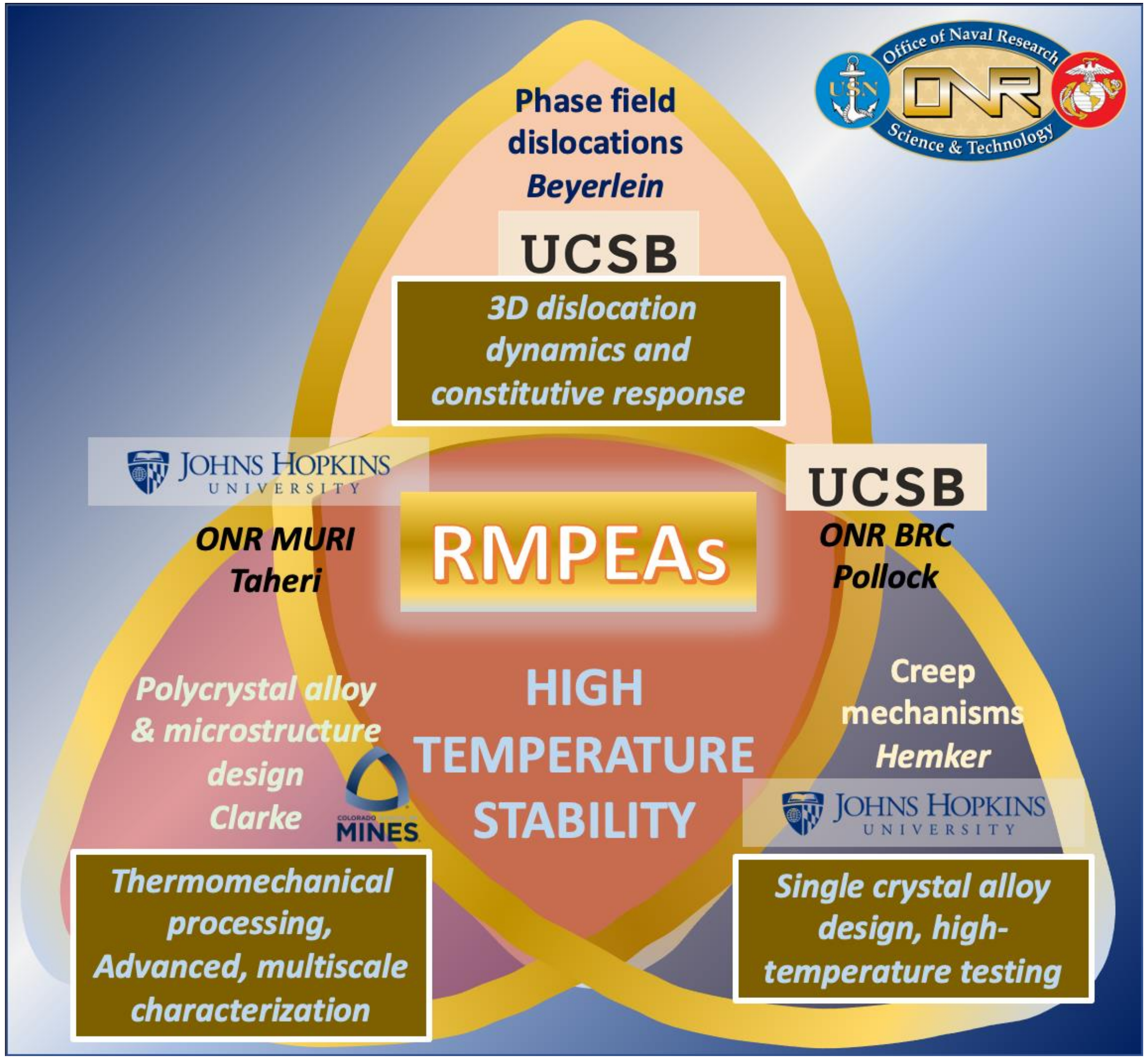


Test Temperature, °C

Todd Helmenstine, sciencenotes.org



Collaborative research



Phase field dislocations
Beyerlein
UCSB

3D dislocation dynamics and constitutive response

JOHNS HOPKINS UNIVERSITY
ONR MURI
Taheri

RMPEAs

UCSB
ONR BRC
Pollock

Polycrystal alloy & microstructure design
Clarke
COLORADO MINES

HIGH TEMPERATURE STABILITY

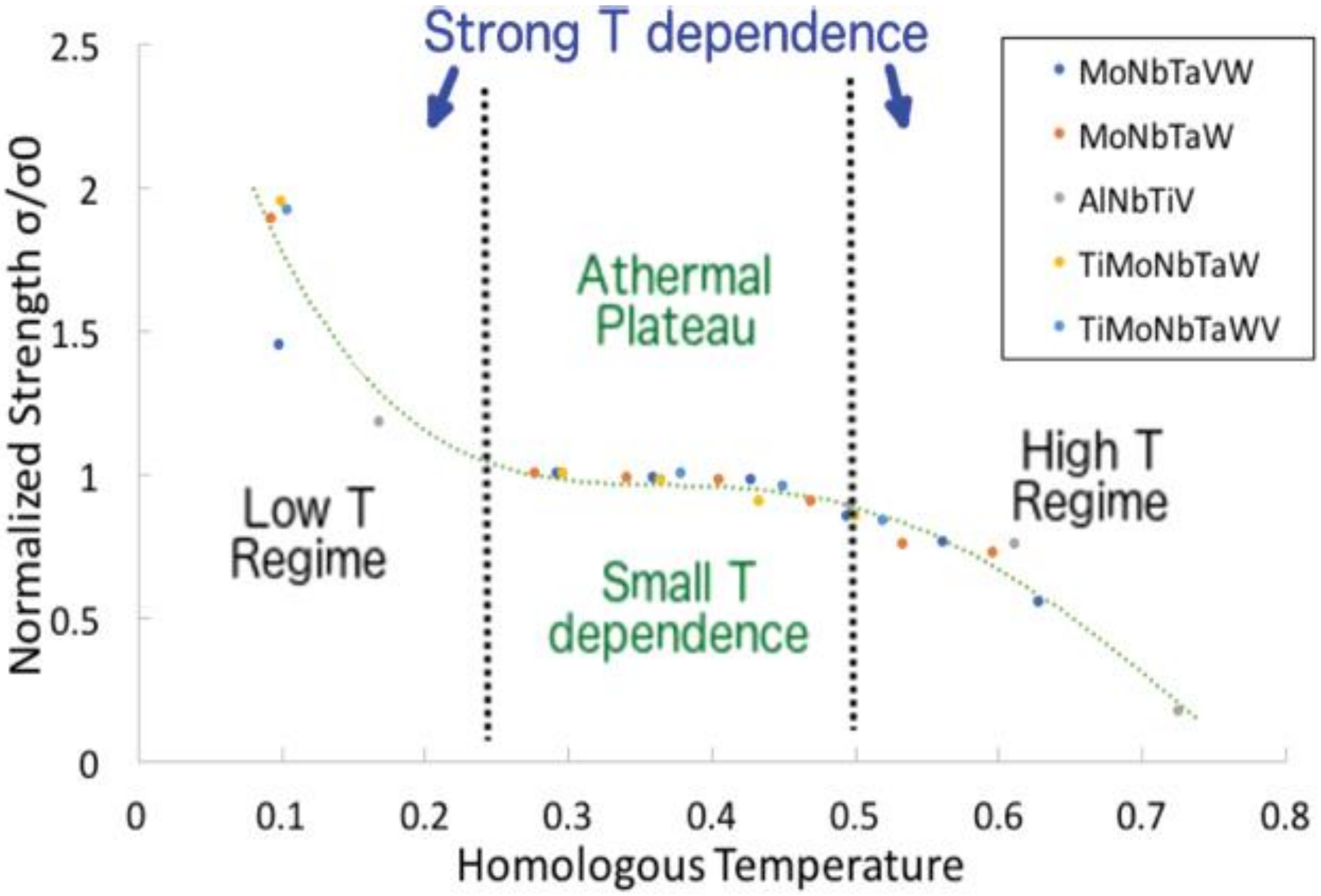
Creep mechanisms
Hemker
JOHNS HOPKINS UNIVERSITY

Thermomechanical processing, Advanced, multiscale characterization

Single crystal alloy design, high-temperature testing

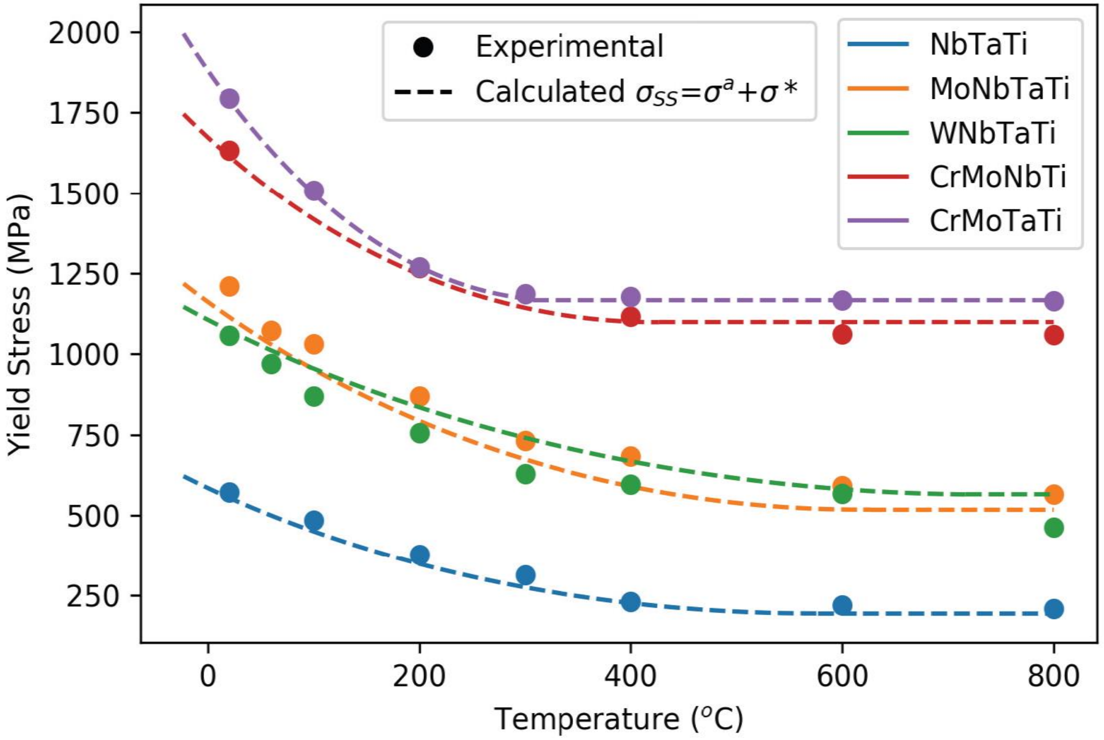
A. J. Clarke et. al. 2021.

Temperature dependence of yield stress limits thermomechanical processing window

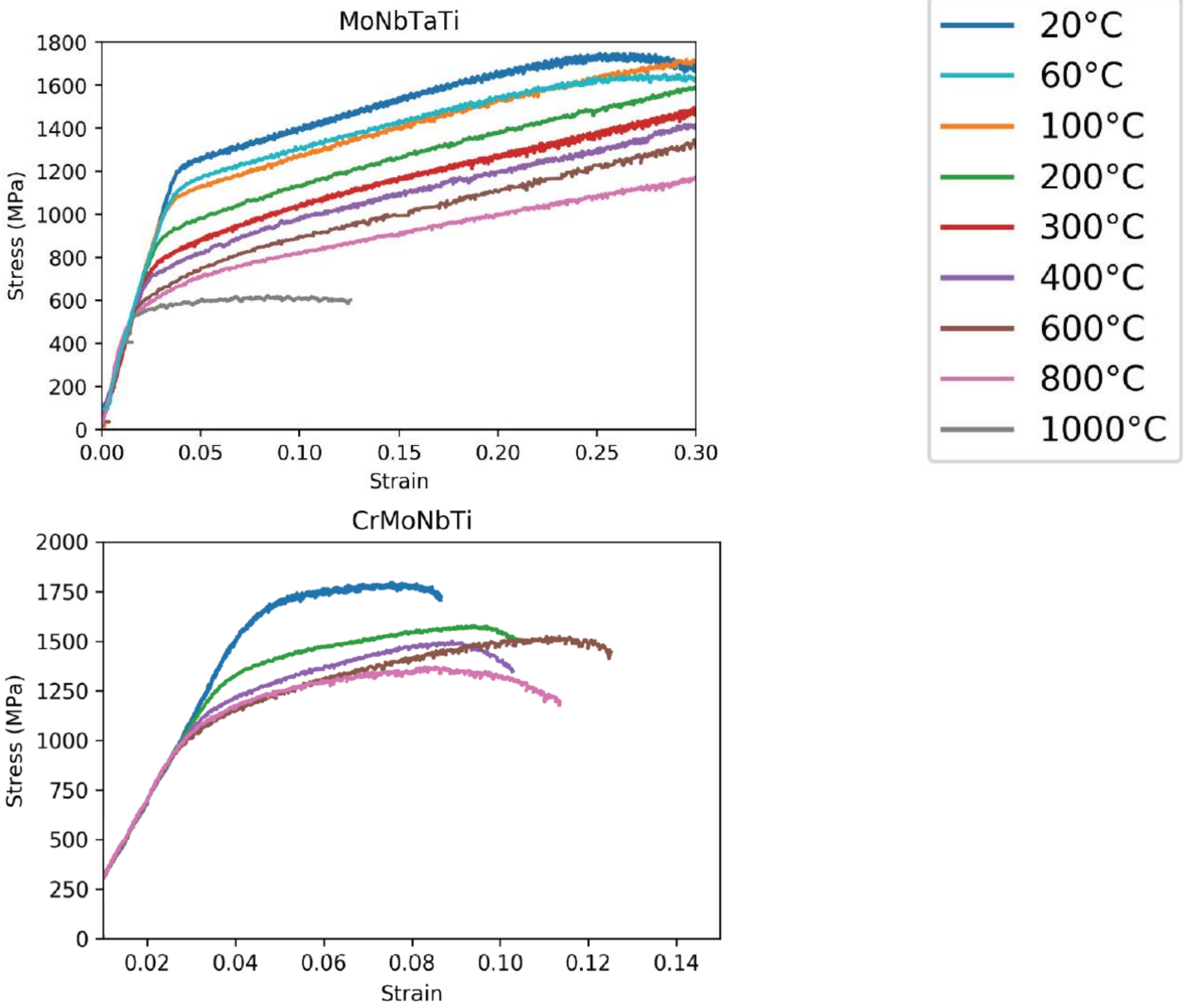


F.G. Coury, Solid Solution Strengthening Mechanisms in High Entropy Alloys, 2018.

Predicted strength informs TMP

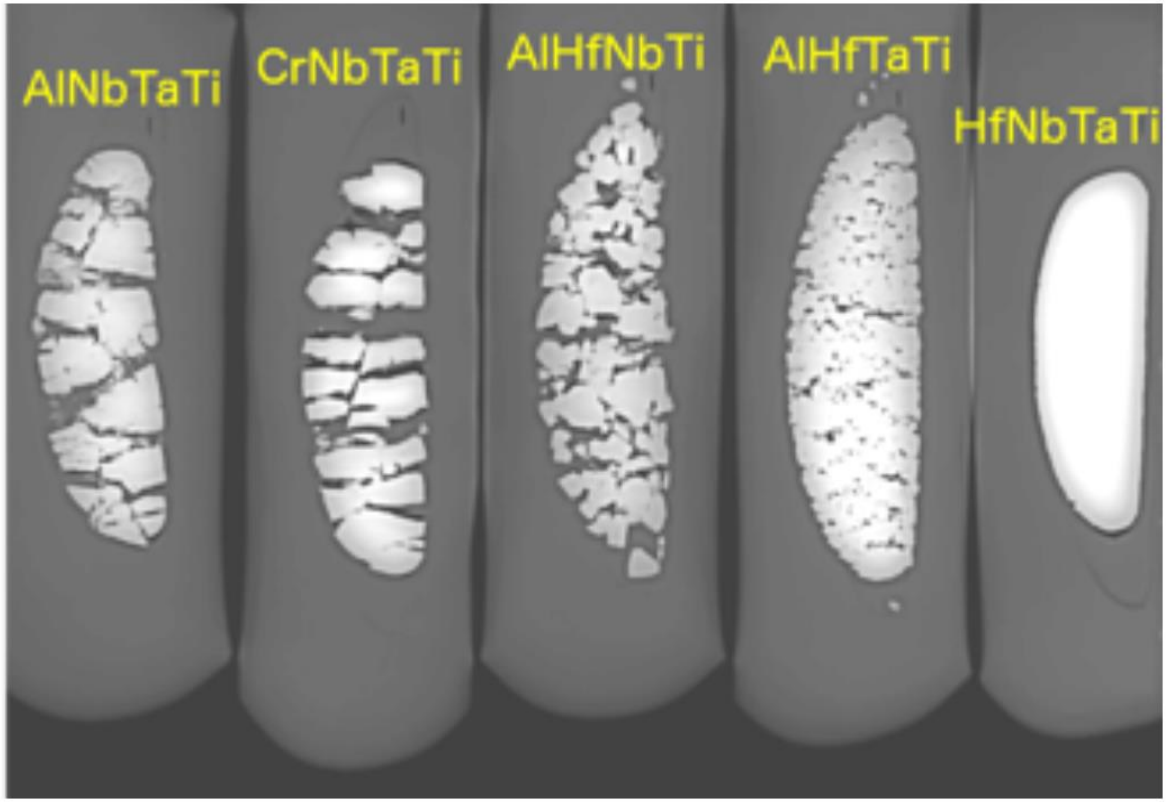


F.G. Coury, Solid Solution Strengthening
Mechanisms in High Entropy Alloys, 2018.



Difficulty in thermomechanical processing

- Presence of intermetallic phases leads to brittle failure

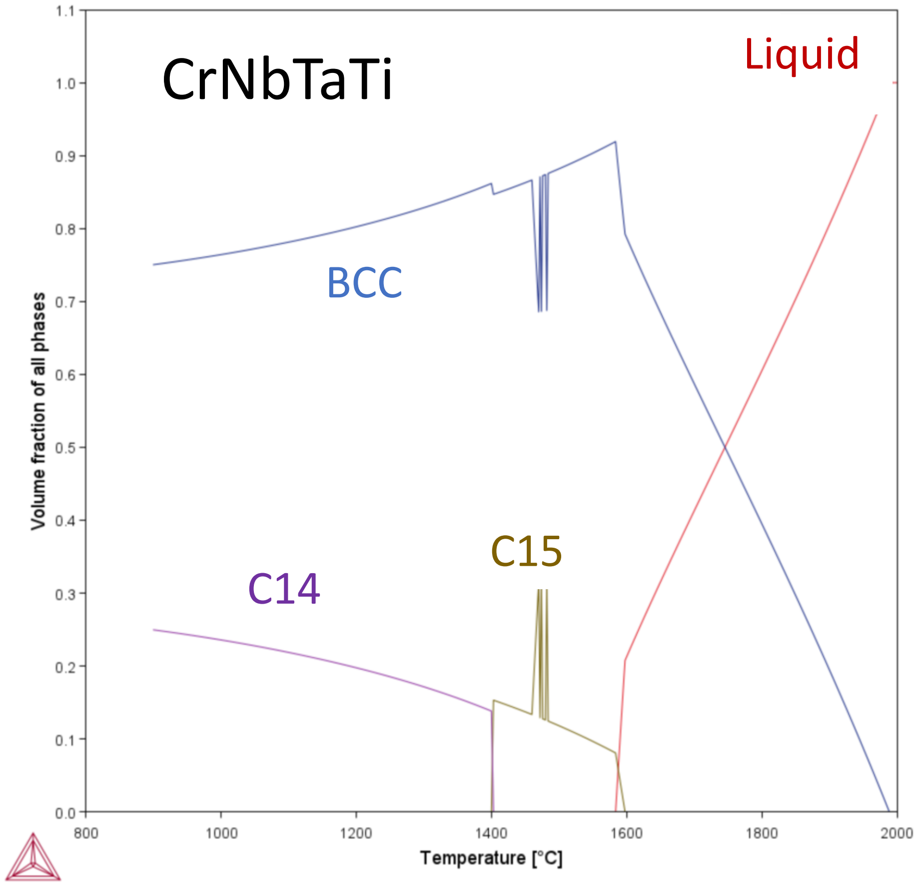


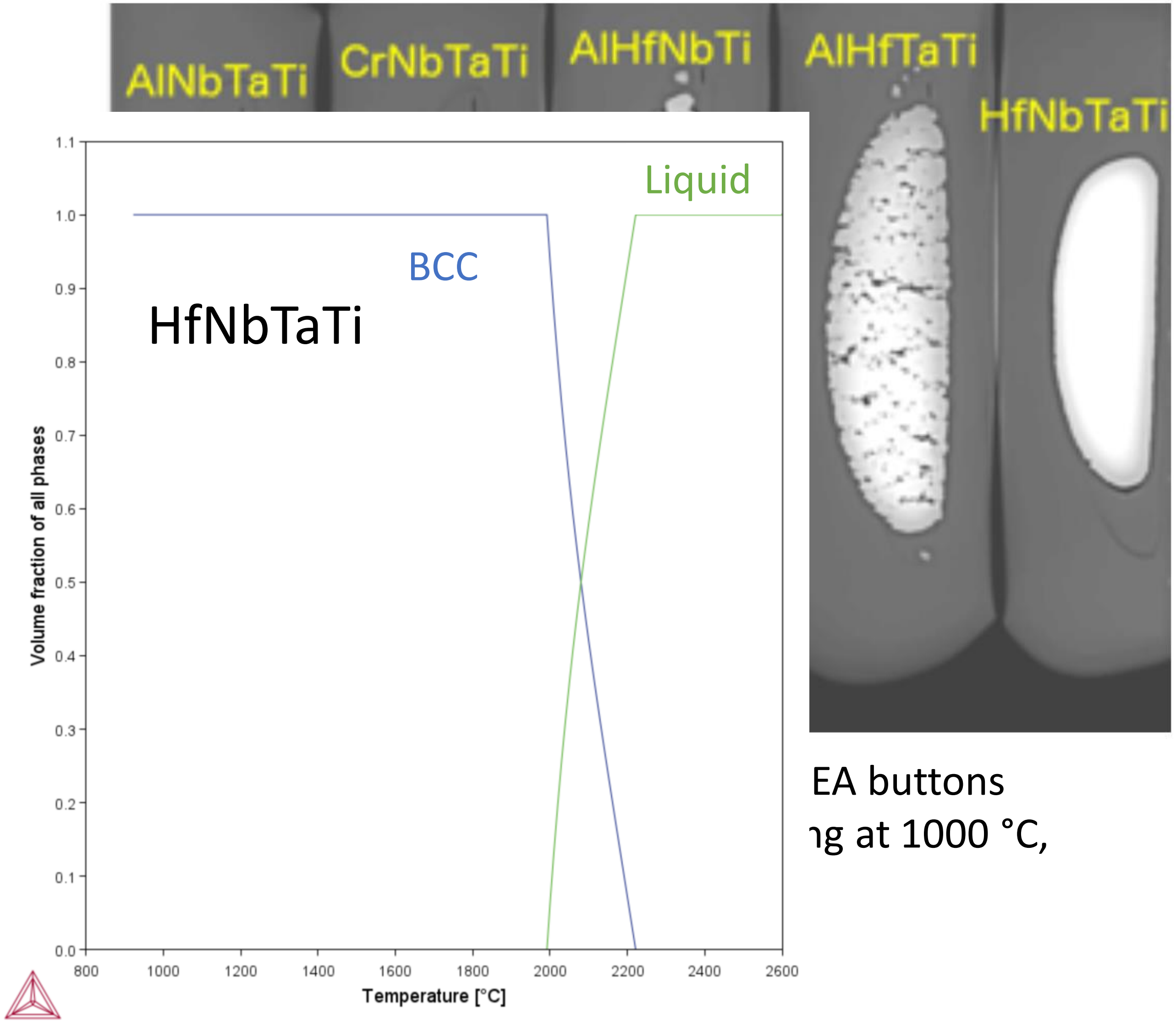
X-ray radiographs of selected RMPEA buttons canned in mild steel after hot rolling at 1000 °C, courtesy of ATI

A. J. Clarke et. al. 2021.

Difficulty in thermomechanical processing

- Presence of intermetallic phases leads to brittle failure





EA buttons
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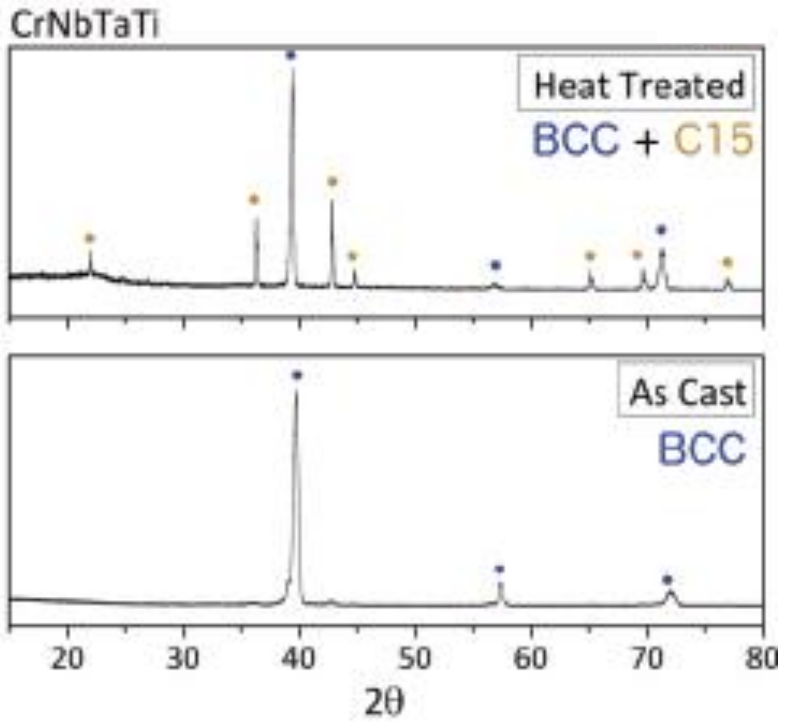
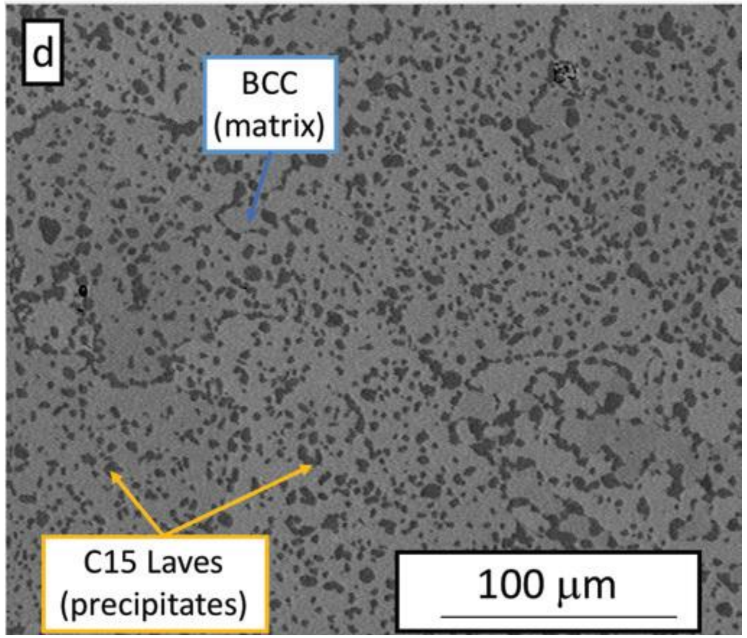
Phase stability at elevated temperatures

- Formation of deleterious phases
- Homogenization of microstructure



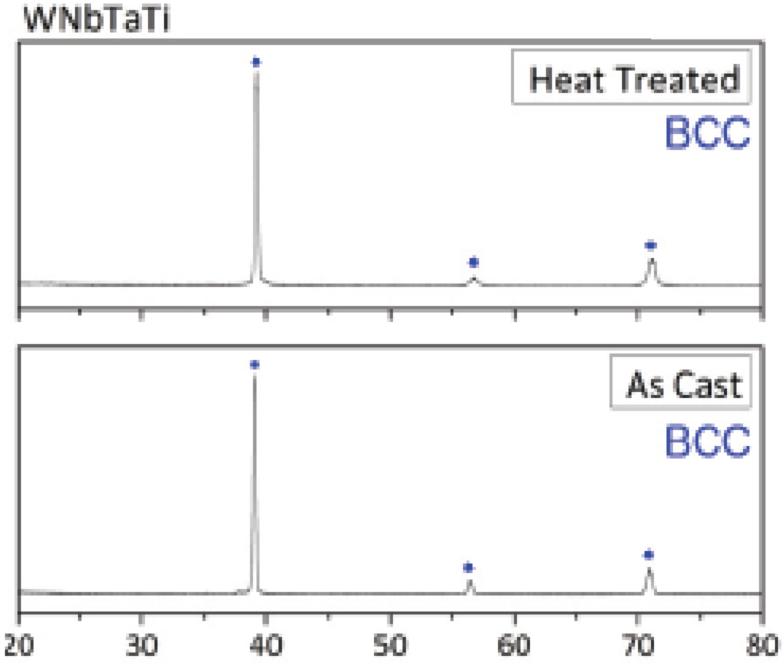


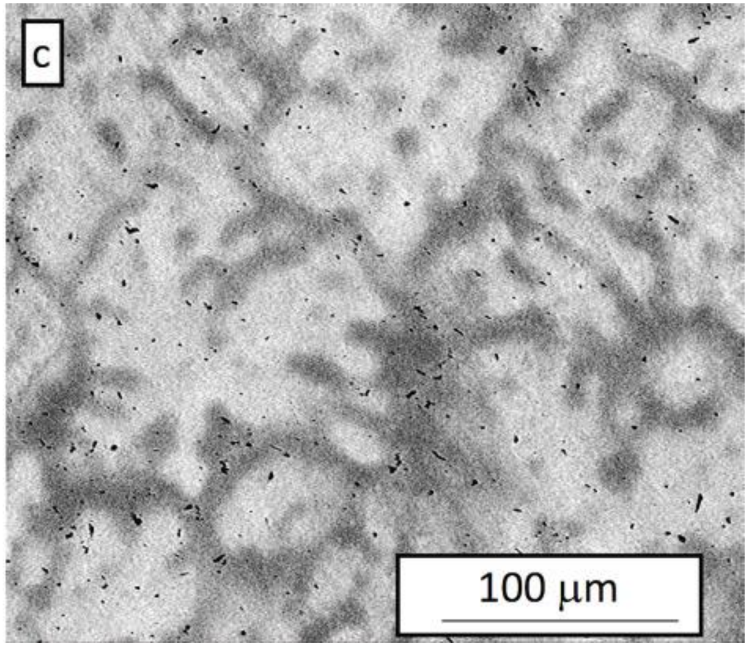
CrNbTaTi following heat treatment at 1400 C for 35 hours

F.G. Coury, Solid Solution Strengthening Mechanisms in High Entropy Alloys, 2018.

Phase stability at elevated temperatures

- Formation of deleterious phases
- Homogenization of microstructure



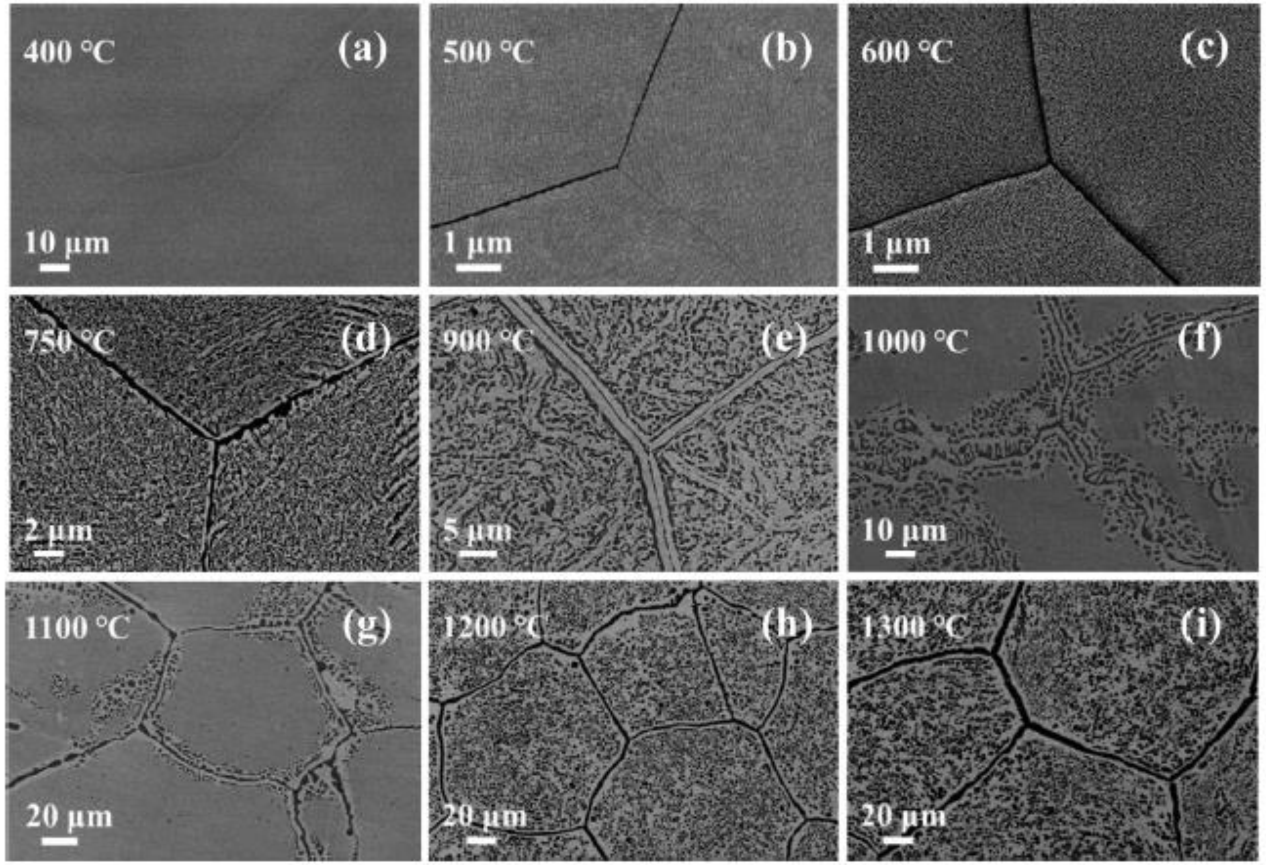


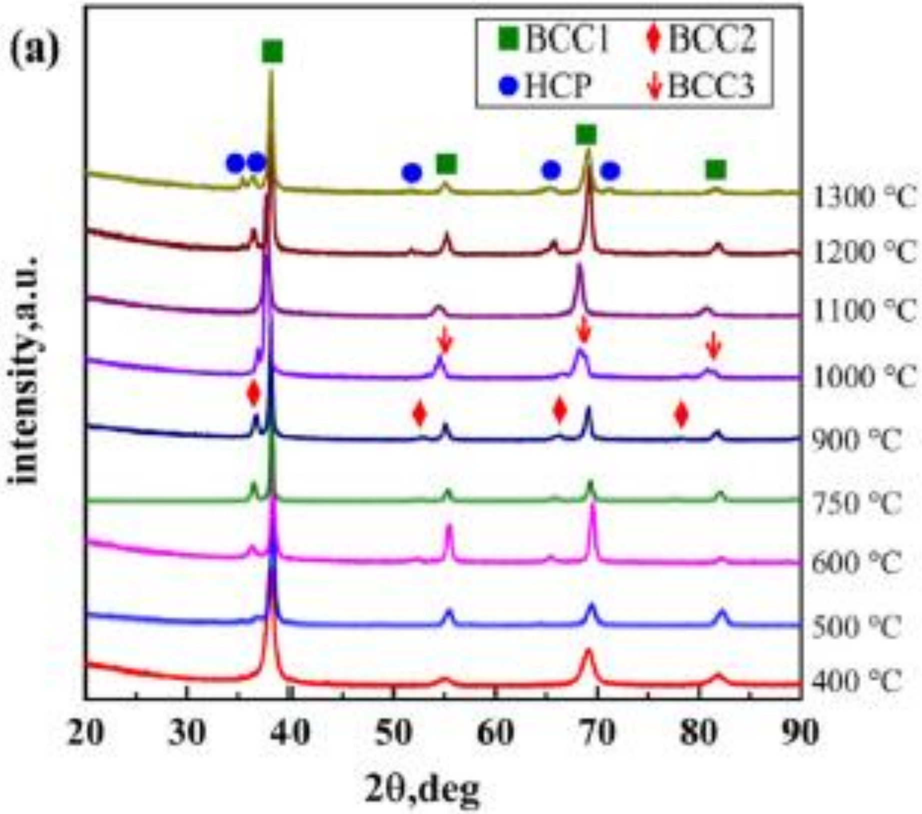
WNbTaTi following heat treatment at 1400 C for 35 hours

F.G. Coury, Solid Solution Strengthening Mechanisms in High Entropy Alloys, 2018.

Limited predictive ability of models

- CALPHAD models limited by experimental data
- Literature focus on equimolar compositions

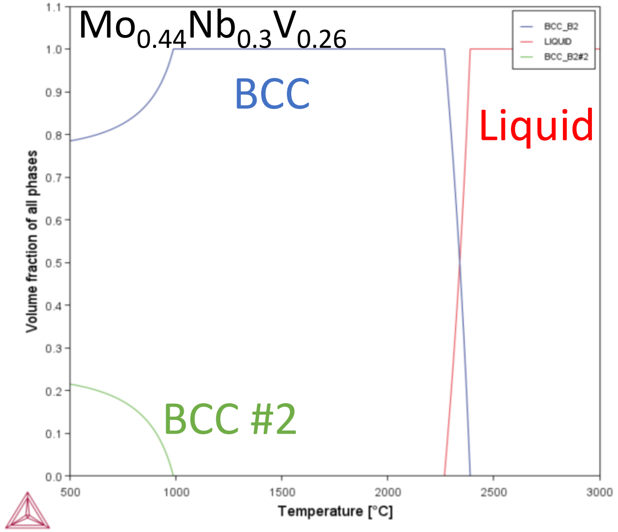


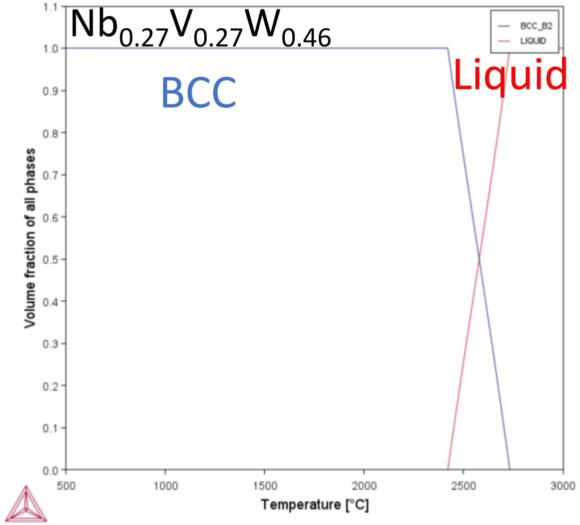


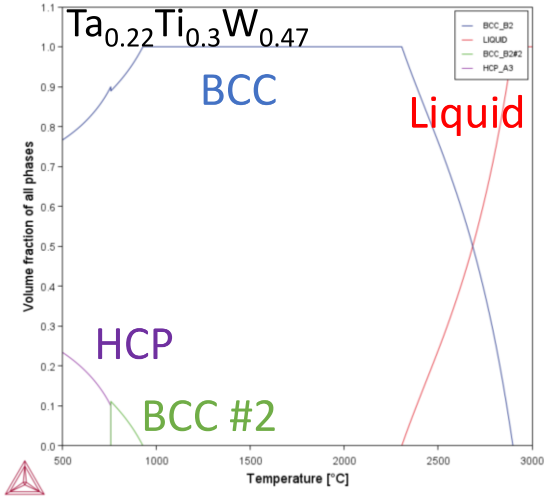
XRD and BSE of NbTaTiZr following annealing for 100 hours

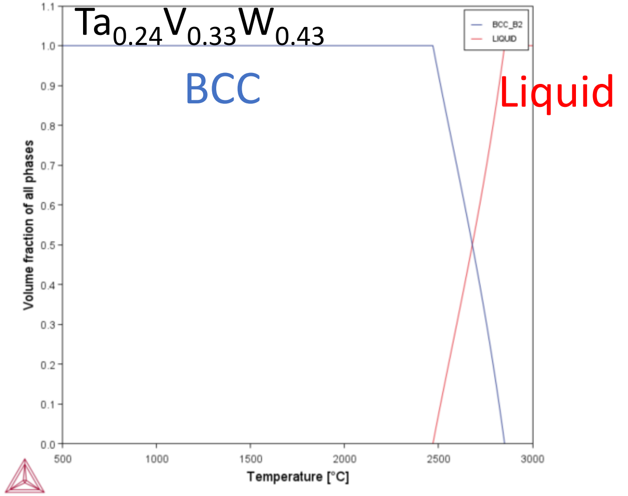
Cao et. al. Journal of Materials Science & Technology (2022).

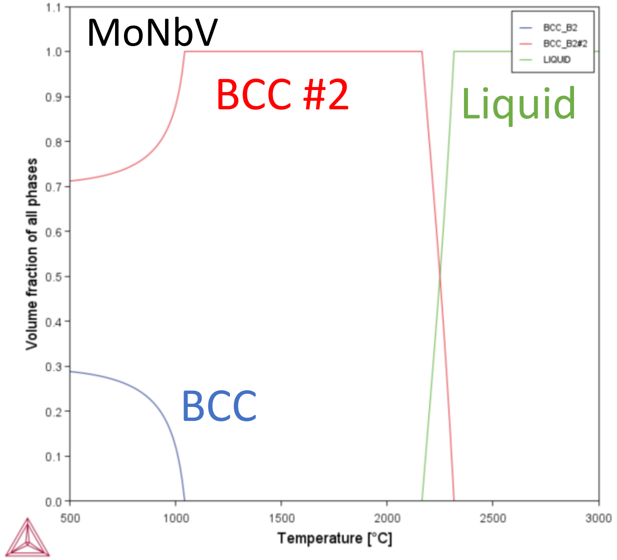
Initial ternary alloy selection

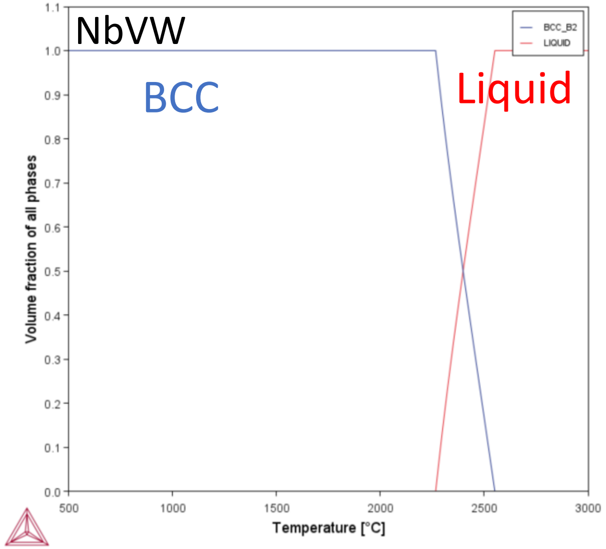


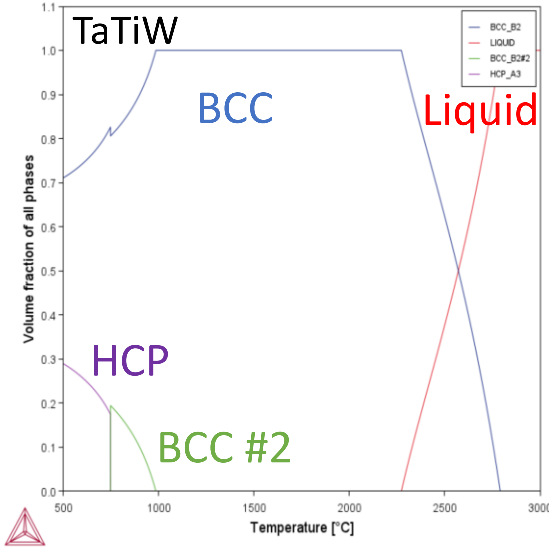


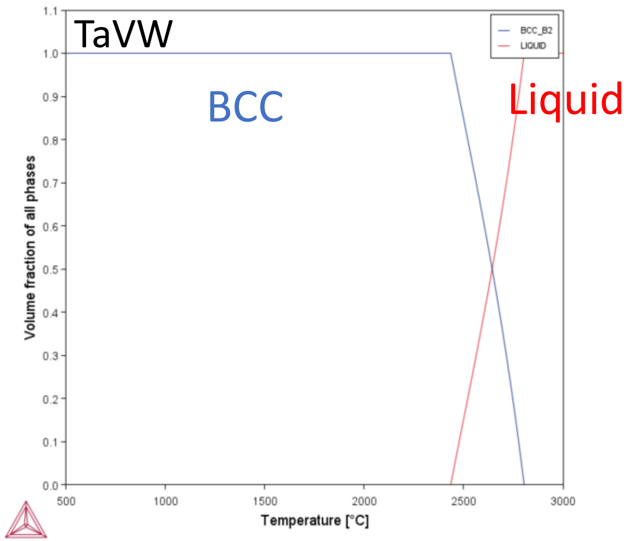






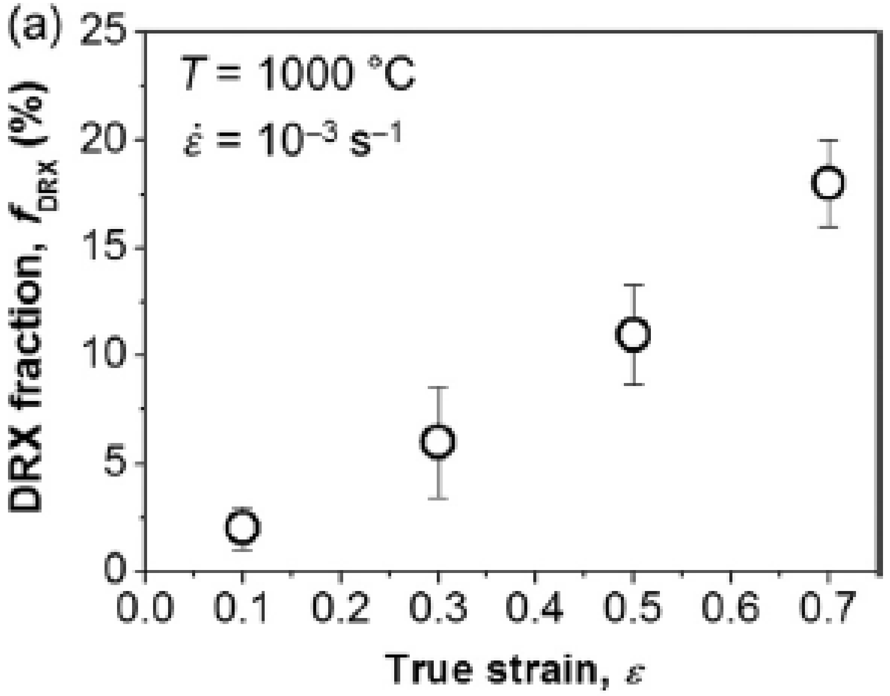




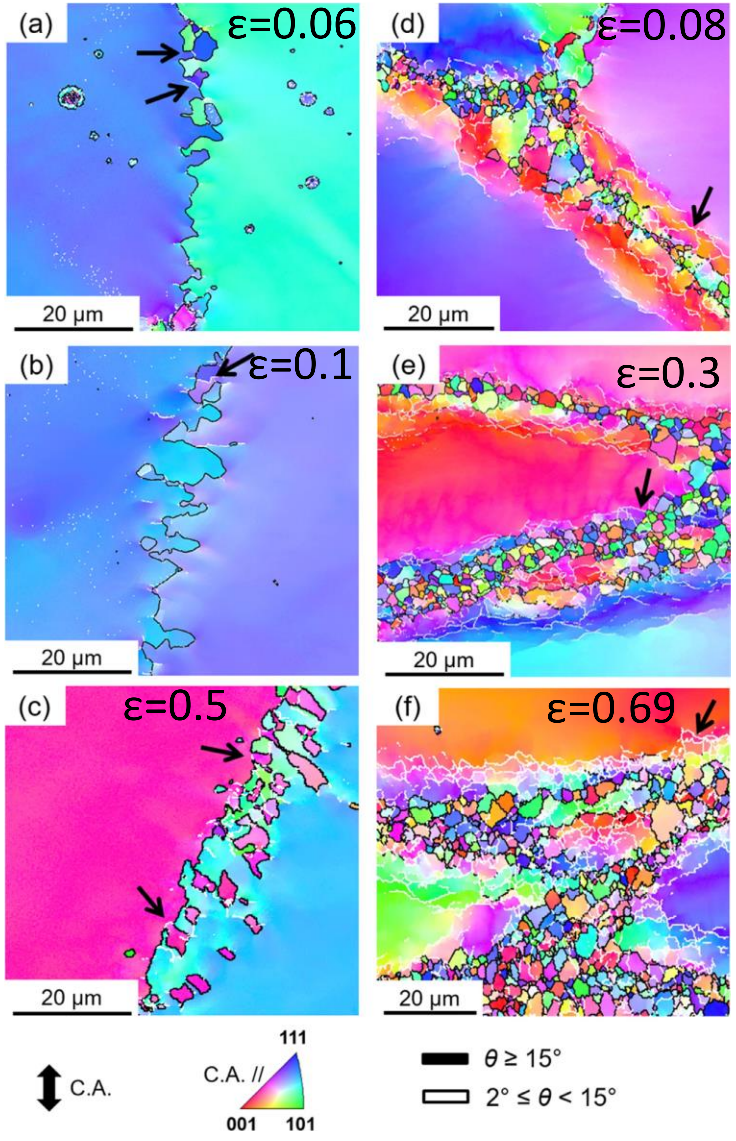


TMP to control microstructures

- Recrystallization
  - Heterogeneous necklace structure



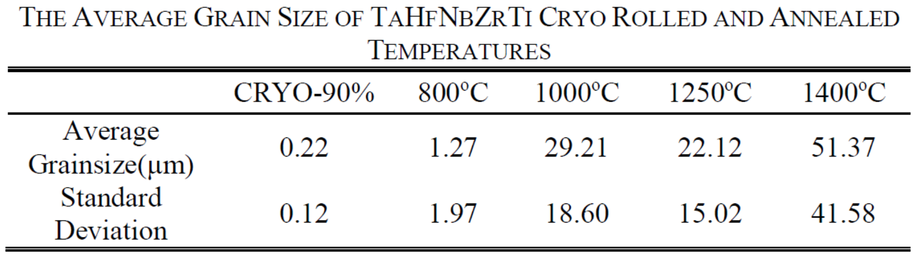
DRX fraction in NfNbTaTiZr hot compressed at 1000 °C and at a rate of 10^{-3} s^{-1}



Eleti et. al. Acta Materialia (2020).

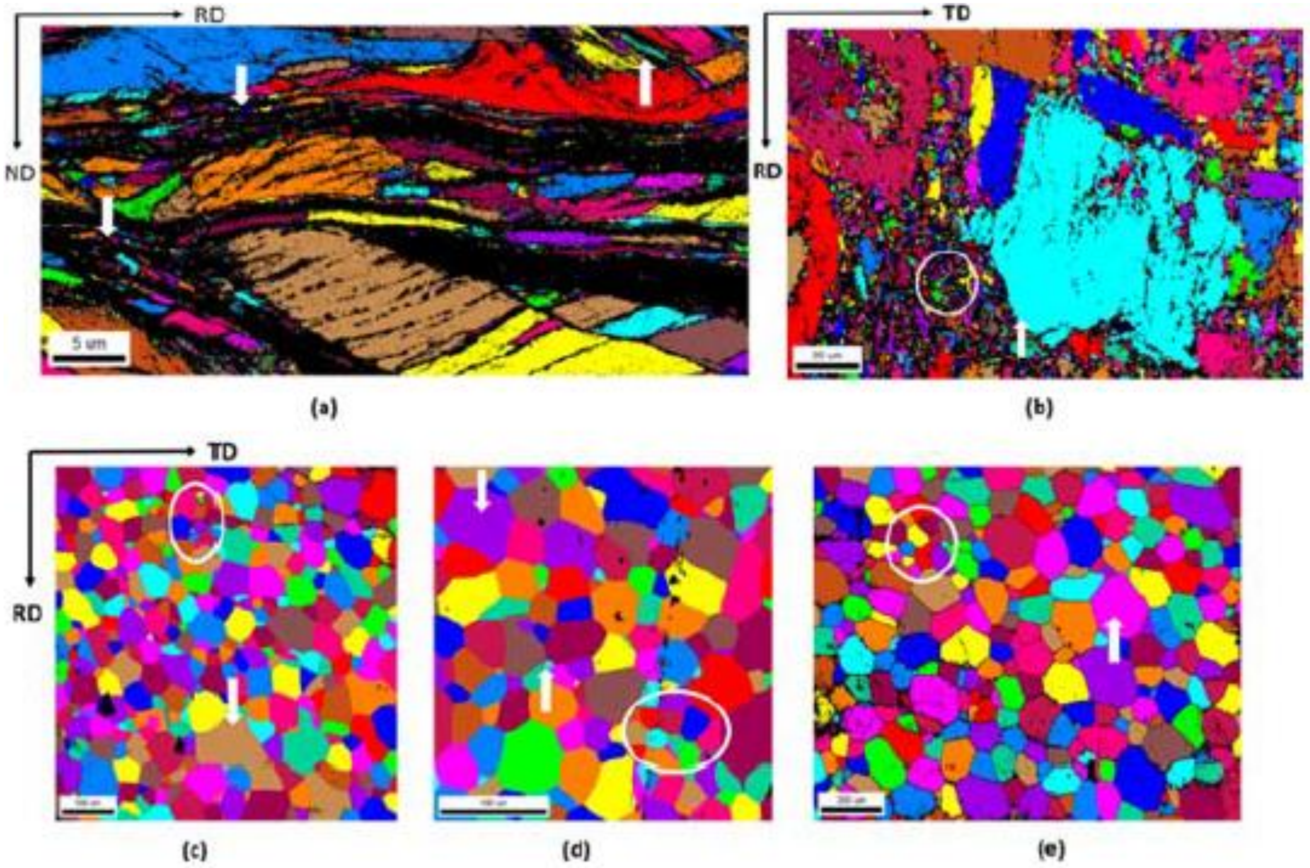
TMP to control microstructures

- Dynamic recrystallization
  - Heterogeneous necklace structure
  - Cryo-rolling and annealing



The Average Grain Size of TaHfNbZrTi Cryo Rolled and Annealed Temperatures

	CRYO-90%	800°C	1000°C	1250°C	1400°C
Average Grainsize(µm)	0.22	1.27	29.21	22.12	51.37
Standard Deviation	0.12	1.97	18.60	15.02	41.58



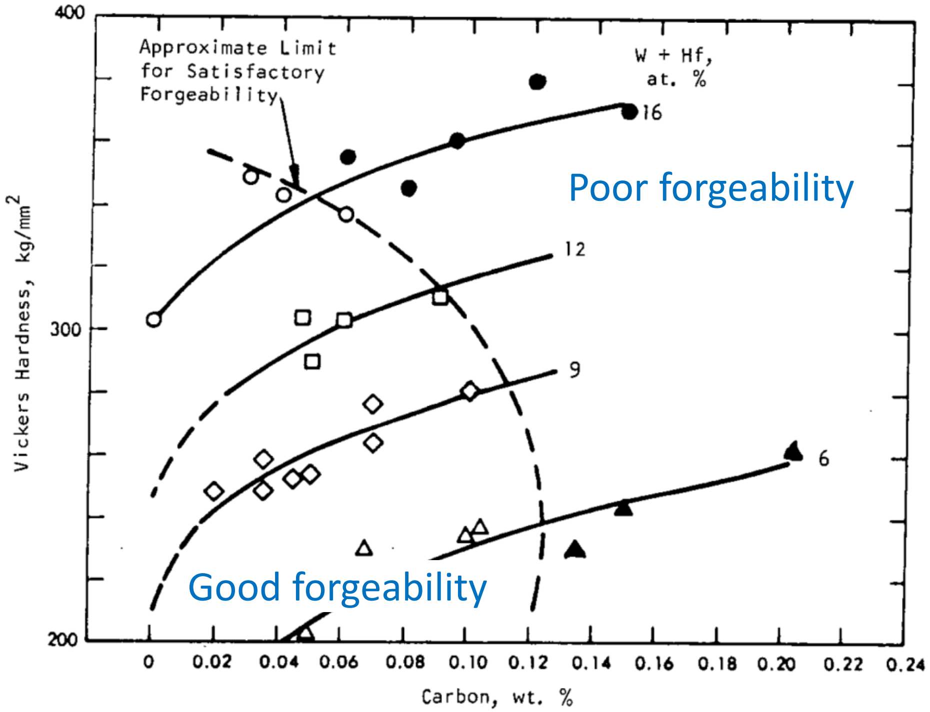
(a) (b)

(c) (d) (e)

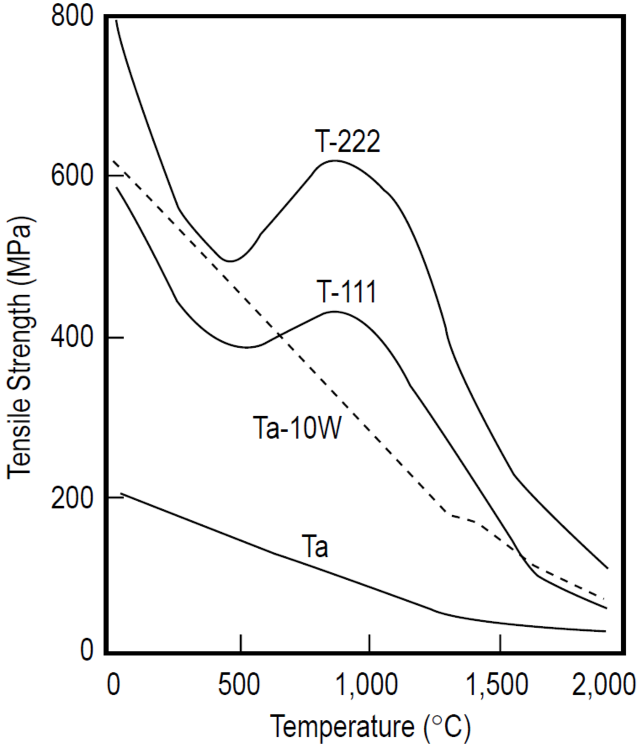
EBSD of HfNbTaTiZr (a) cryo-rolled to 90% reduction and annealed at (b) 800 °C, (c) 1000 °C, (d) 1250 °C, (3) 1400 °C for 1 hour

Veeresham, International Journal of Materials and Metallurgical Engineering (2021).

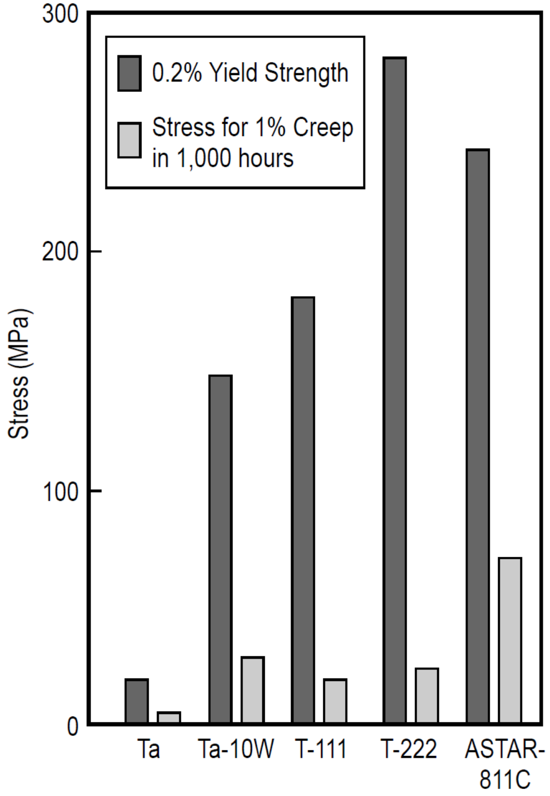
Effects of interstitials on conventional refractory alloys



Effect of carbon on as-cast hardness of Ta-W-Hf



Temperature dependence of UTS of Ta and Ta alloys

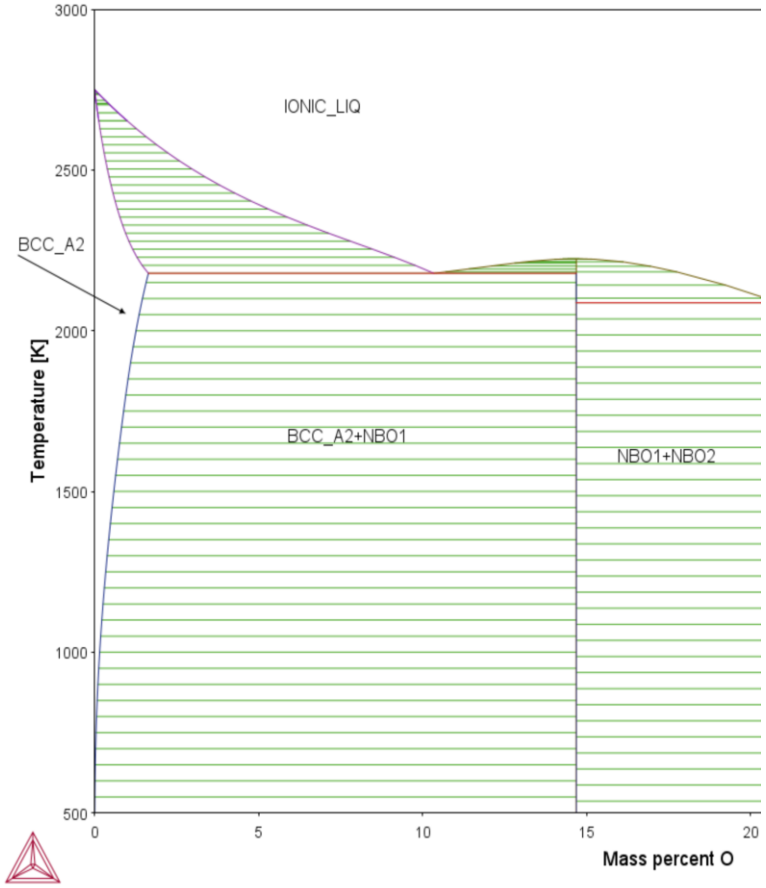


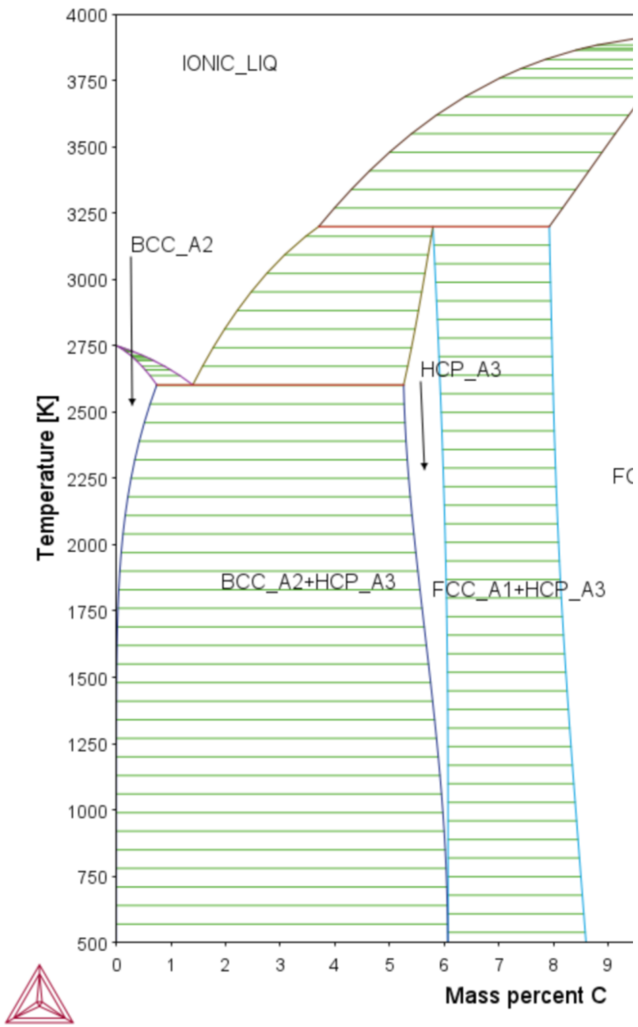
Tensile yield strength and 1% creep strength of Ta and Ta alloys at 2400 °F (1316 °C)

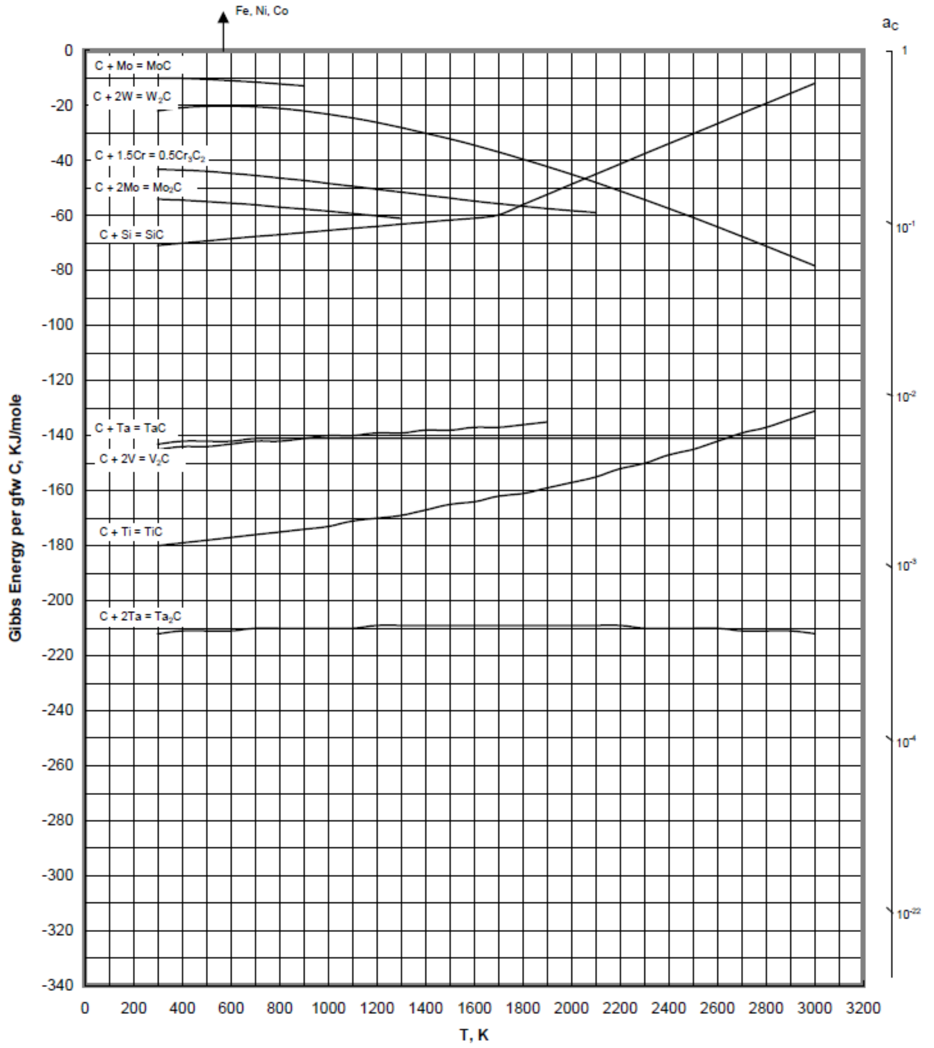
R.W. Buckman, Jr., R.R. Begley, NASA, Report No. NASA SP-245, 1970, pp. 19-37
R.W. Buckman, Jr., JOM, 2000, 53:40-41

Exploring the role of oxygen and carbon on RMPEAs

- Interstitial C, O



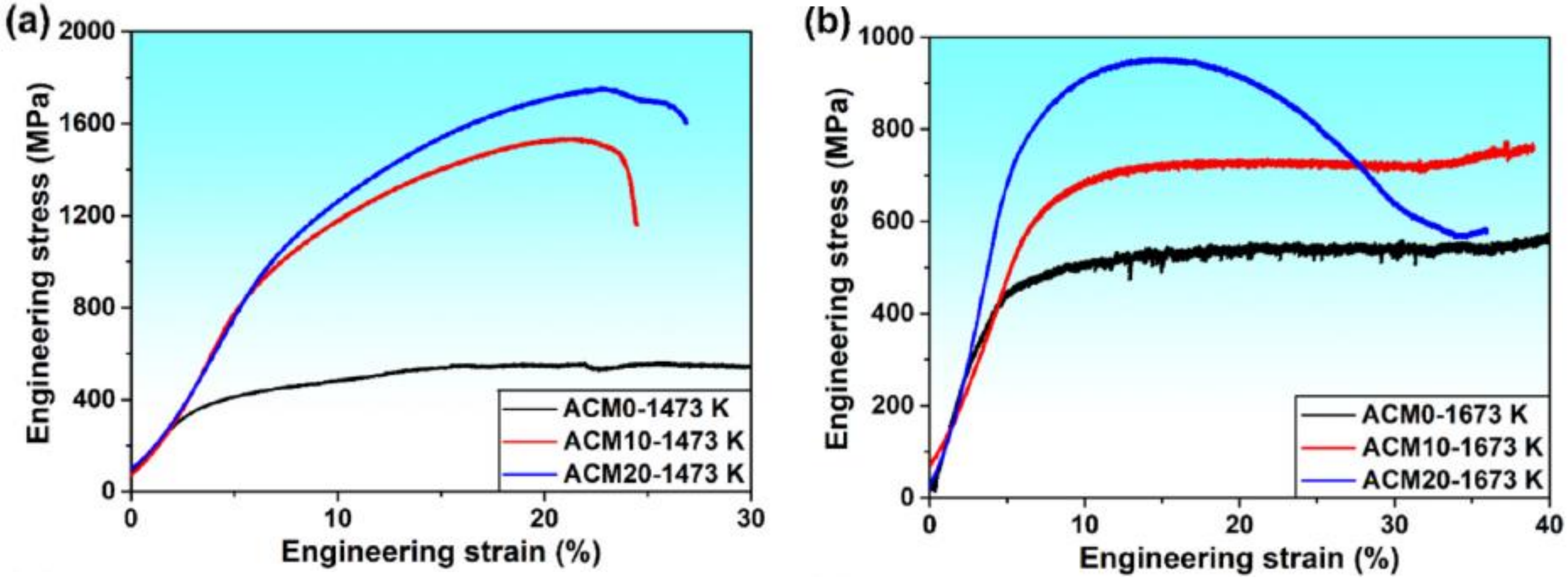




Courtesy Noah Philips, ATI

Interstitial effects

- NbTaW$_{0.5}$(Mo$_2$C)$_x$ (x=0-0.25)

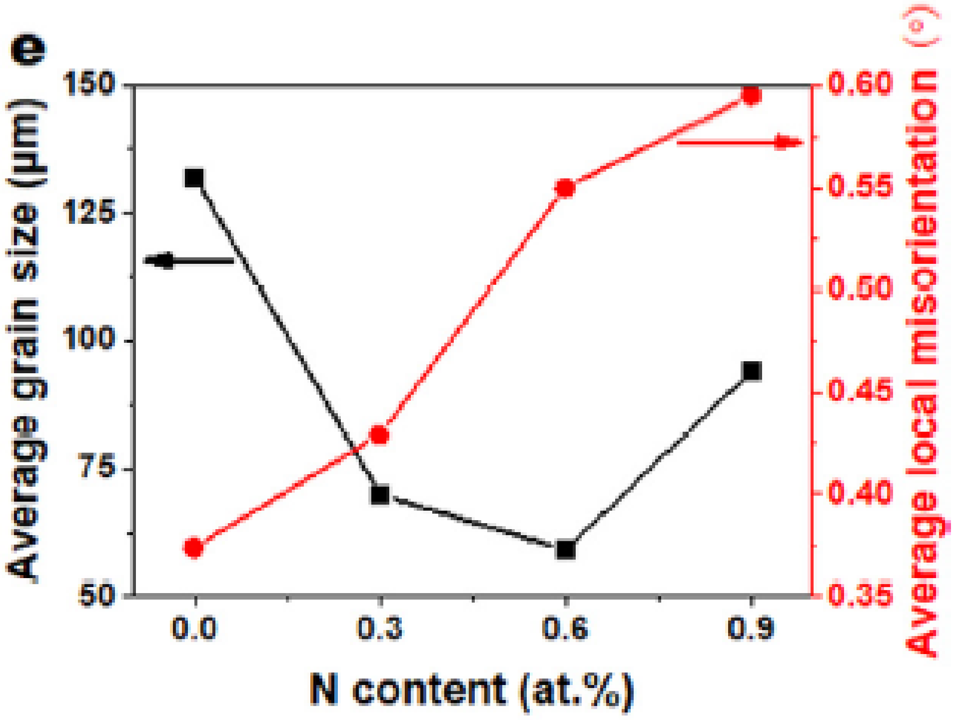


Compressive stress-strain curves at (a) 1200 C and (b) 1400 C

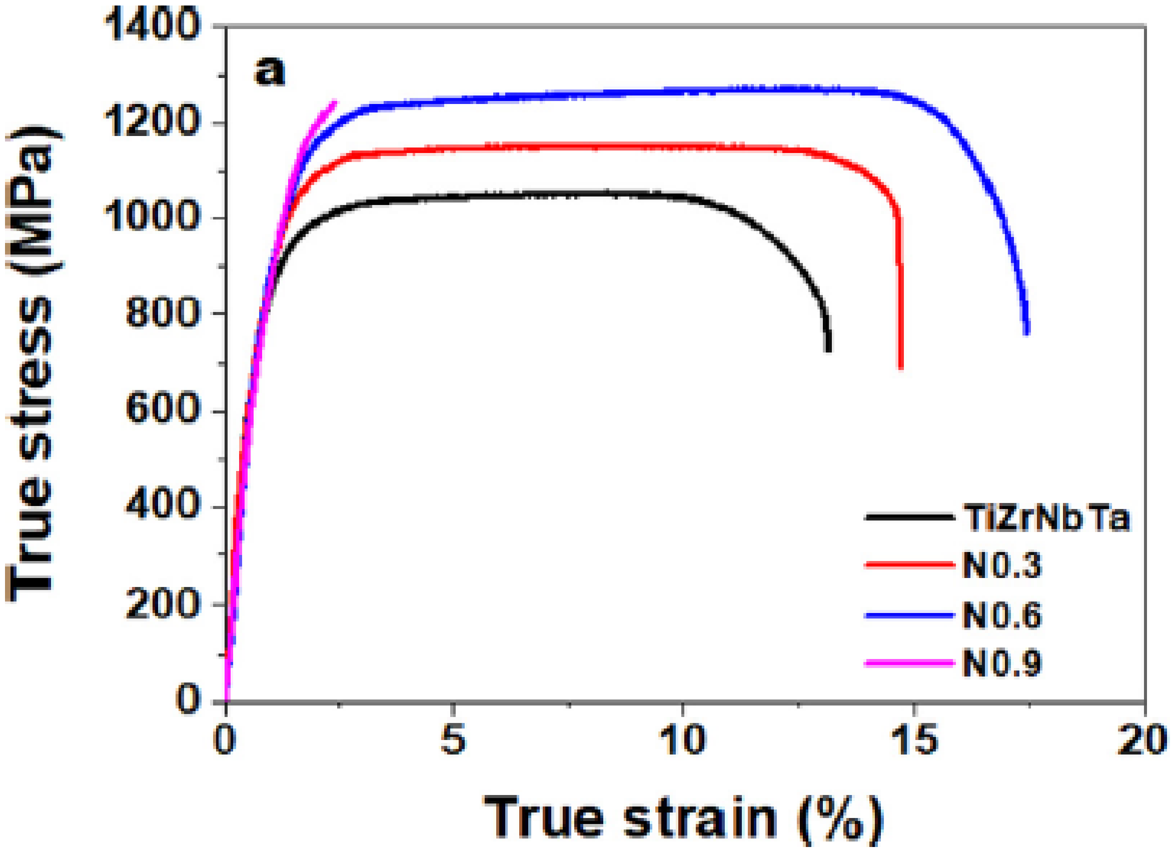
Wu et. al., Journal of Alloys and Compounds (2022).

Interstitial effects

- $NbTaW_{0.5}(Mo_2C)_x$
- Nitrogen doped NbTaTiZr



Effect of nitrogen content on average as-cast grain size



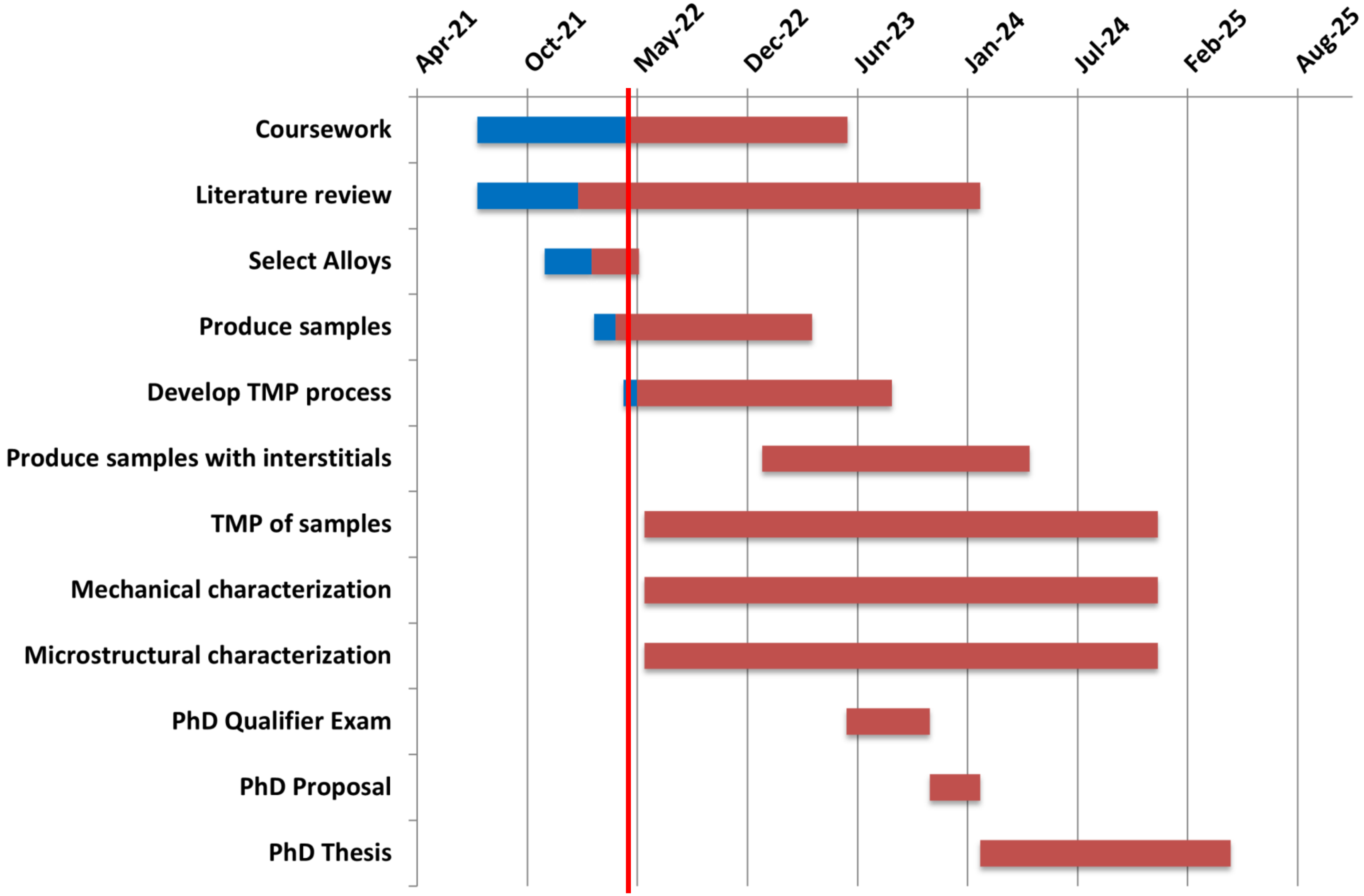
Tensile stress-strain curves for as-cast $(TiZrNbTa)_{100-x}N_x$

Wang et. al. Materials and Design (2022).

Next steps

- Equilibrium phase data
  - Identify off-equimolar compositions of interest
  - Develop heat treatment to reach equilibrium state
  - Characterization of equilibrium structure
  - NbTaTi, NbTiZr, MoNbV, NbVW, TaTiW, TaVW
- Identify quaternary compositions of interest
  - TC-EARS and CALPHAD modeling
- Initial characterization and thermomechanical processing
  - Arc melting to produce buttons
  - Gleeble thermomechanical simulations
  - SEM, TEM, XRD

Gantt Chart


Apr-21
Oct-21
May-22
Dec-22
Jun-23
Jan-24
Jul-24
Feb-25
Aug-25
Coursework
Literature review
Select Alloys
Produce samples
Develop TMP process
Produce samples with interstitials
TMP of samples
Mechanical characterization
Microstructural characterization
PhD Qualifier Exam
PhD Proposal
PhD Thesis

Challenges & Opportunities

- Making material
  - Melting compositions containing W difficult due to high melting temperature
- Studying equilibrium structures
  - Long times and high temperatures needed
  - Stability of as-cast microstructure
- Thermomechanical processing
  - Gleeble
- Characterization
  - SEM, TEM, and XRD

Thank you!

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abalzac@mines.edu

References

[1] A. J. Clarke, Technical proposal: Thermomechanical processing of refractory multi-principal element alloys for ultrahigh temperature performance.

[2] O.N. Senkov, D.B. Miracle, K.J. Chaput, J.P. Couzinie, Development and exploration of refractory high entropy alloys - A review, Journal of Materials Research. 33 (2018) 3092–3128. https://doi.org/10.1557/jmr.2018.153.

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[7] C.C. Wojcik, Thermomechanical processing and properties of niobium alloys, in: International Symposium Niobium, 2001: pp. 163–173.

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[13] M. Veeresham, Microstructure and texture evolution of cryo-rolled and annealed ductile TaNbHfZrTi refractory high entropy alloy. International Journal of Materials and Metallurgical Engineering (2021), 15(11).

[14] R.W. Buckman, Jr., R.R. Begley, NASA, Report No. NASA SP-245, 1970, pp. 19-37

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