CANFSA

Center for Advanced Non-Ferrous Structural Alloys

An Industry/University Cooperative Research Center

Project 46: Influence of Microstructure on the Oxidation Behaviors of Refractory Complex Concentrated Alloys (RCCAs)

Semi-annual Fall Meeting

October 2021

- Student: Noah Welch (ISU)
- Faculty: Dr. Peter C. Collins (ISU)
- Industrial Mentors: Dr. Todd Butler (AFRL)

COLORADO SCHOOL OF MINES   NSF   IOWA STATE UNIVERSITY

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- Student: Noah Welch (ISU)
- Advisor(s): Peter Collins (ISU)

Project Duration

PhD: Fall 2020 to Spring 2024

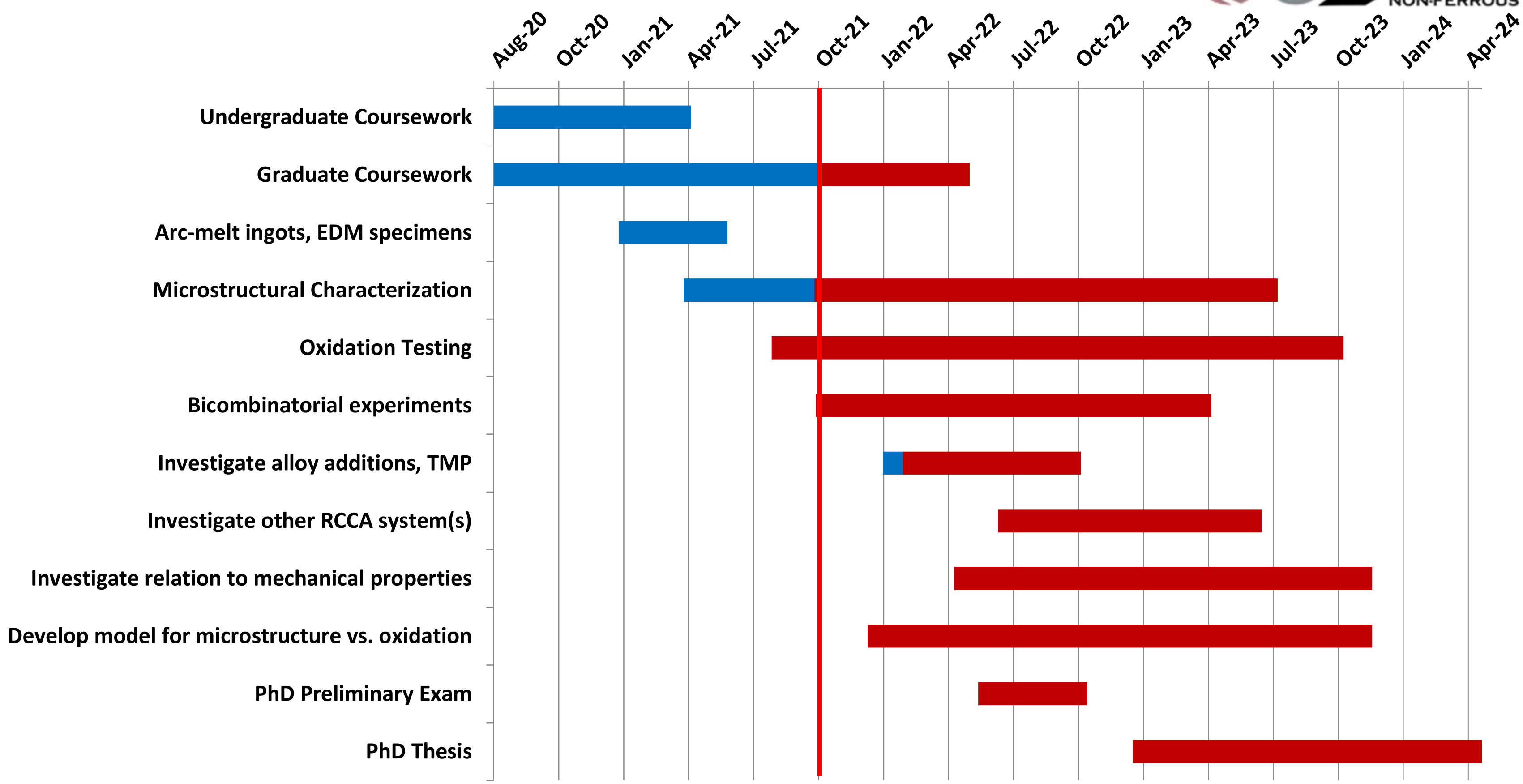
- Problem: The oxidation mechanisms in RCCAs and the influence of microstructure on oxide formation are poorly understood.
- Objective: Investigate microstructural influence on the oxidation properties of RCCAs, specifically TaTiCr.
- Benefit: RCCAs show great promise for future use in advanced, high-temperature structural applications.

Recent Progress
- Extensive literature review for pickling Ta and Cb alloys
- Development of SOP for pickling procedure
- Implementation of safety standards in accordance with environmental health & safety
- Compression test and oxidation test specimens pickled
- Preparing for TGA oxidation tests

Metrics

Description	% Complete	Status
1. Literature review	70%	●
2. Cast specimens at desired compositions for oxidation tests, characterize microstructure.	75%	●
3. Induce microstructural changes using TMP and measure effect on oxidation performance	0%	●
4. Determine oxidation behavioral dependence on microstructure	0%	●
5. Investigate expansibility to other RCCA systems	0%	●

Progress



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Microstructural Characterization
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Bicombinatorial experiments
Investigate alloy additions, TMP
Investigate other RCCA system(s)
Investigate relation to mechanical properties
Develop model for microstructure vs. oxidation
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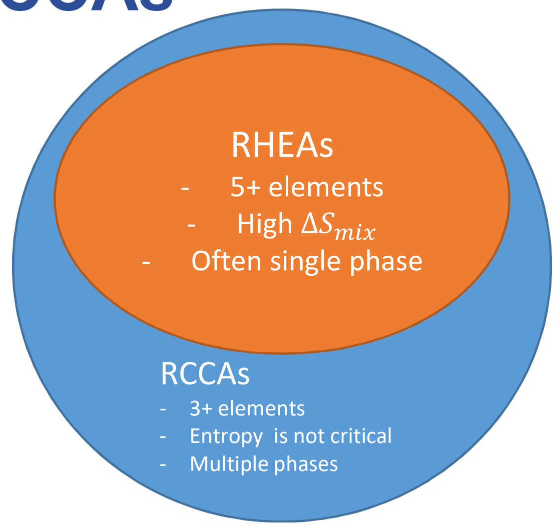
PhD Thesis

RCCAs

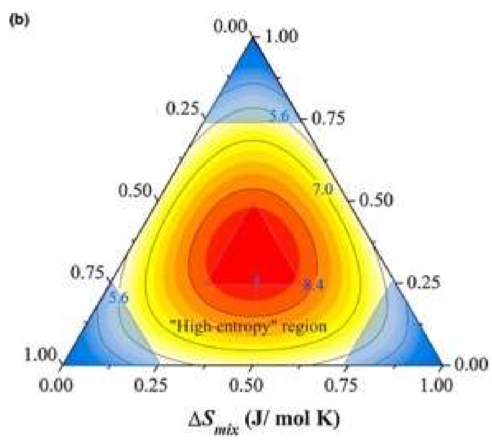


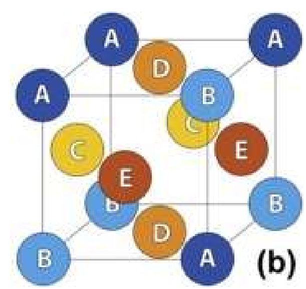
RCCAs are a broader class of refractory high entropy alloys (RHEAs).

Due to containing fewer constituents, they have lower configurational entropy.

- Multiple phases present, often cubic + Laves

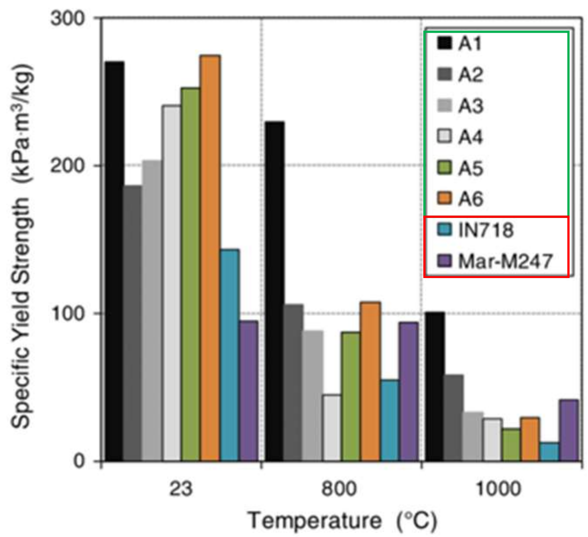
Disordered cubic structures are the most common matrix phase.





Ye, et al., *Materials Today, 2016*
Miracle, et al., *Journal of Alloys and Compounds, 2019*

Industrial Relevance



RHEA's
RCCA's

Ni-based
superalloys

Comparison of refractory high entropy alloys (RHEA) and RCCA specific yield strength to two Ni-based superalloys

Implications:

- Displace Ni-based superalloys as prominent advanced structural alloys
  - Improved oxidation performance and mechanical properties
- Framework for future alloy development

Applications:

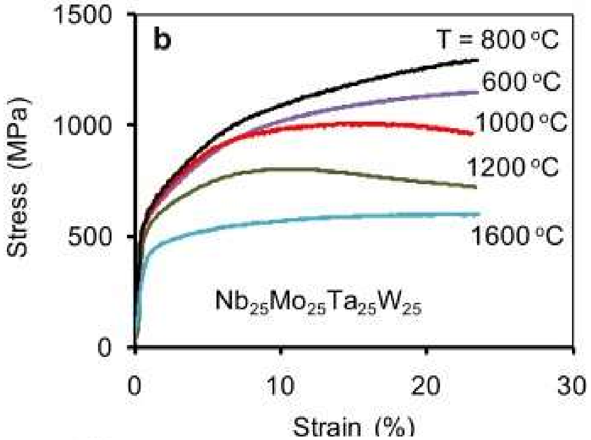
- High temperature, structural applications
- Turbine blades, heat exchangers, boiler housings

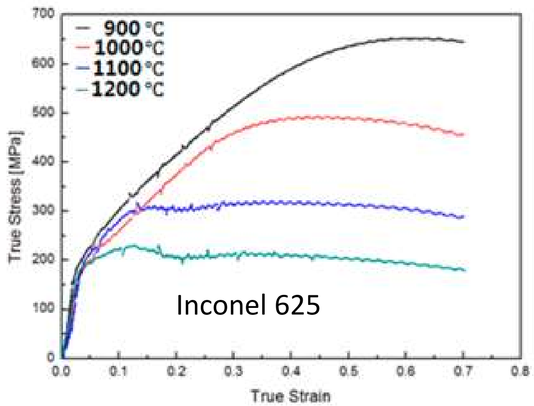
Benefits:

- Higher operating temperatures
- Better oxidation performance
- Improved high-temperature processes

Senkov, et al., *JOM, 2014*

Mechanical Properties





The disordered structure often contributes to high yield strengths and low ductility in RCCAs.

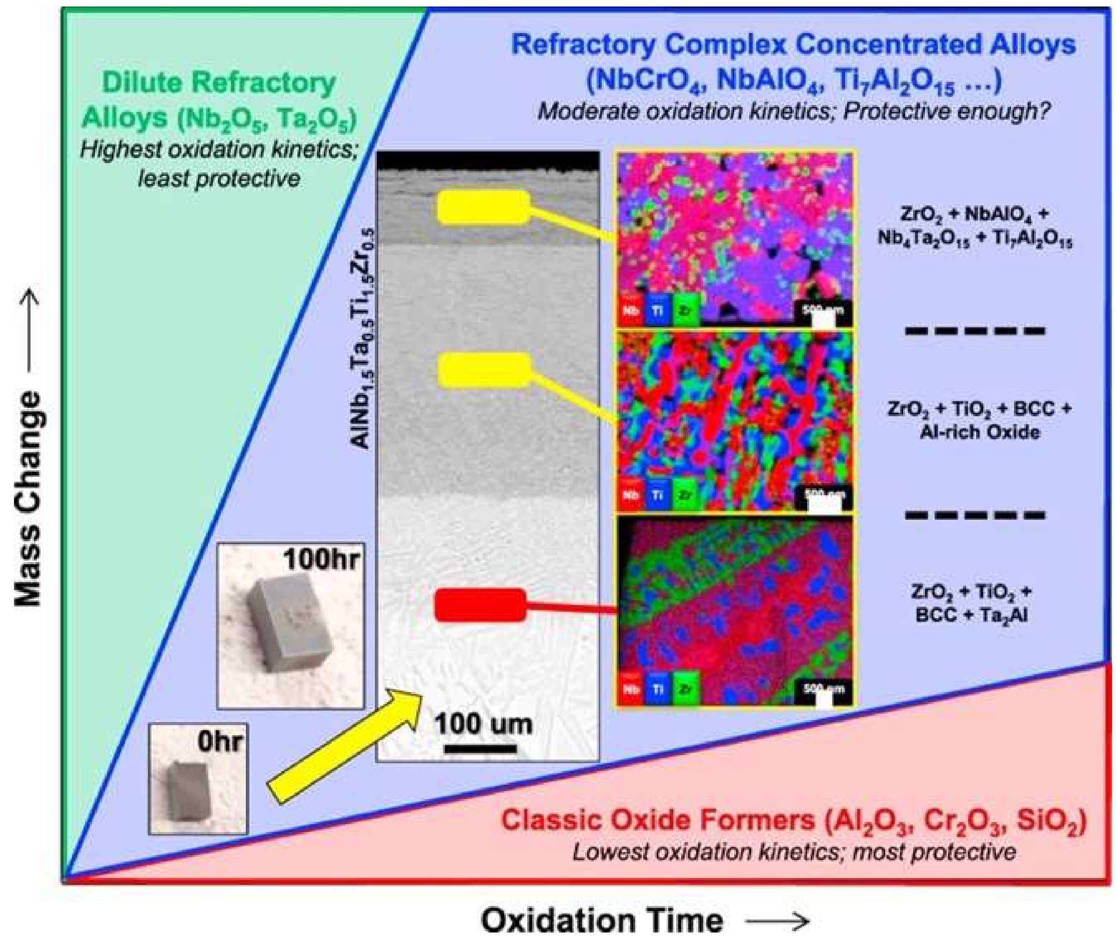
Variance in performance is dependent on constituents, processing conditions, etc.

Mechanical properties and oxidation performance is competitive with Ni-based superalloys.

Observed room temperature ductility may inhibit processing for engineering applications.

Senkov, et al., *Intermetallics, 2011*
Jeong, et al., *Metals, 2019*

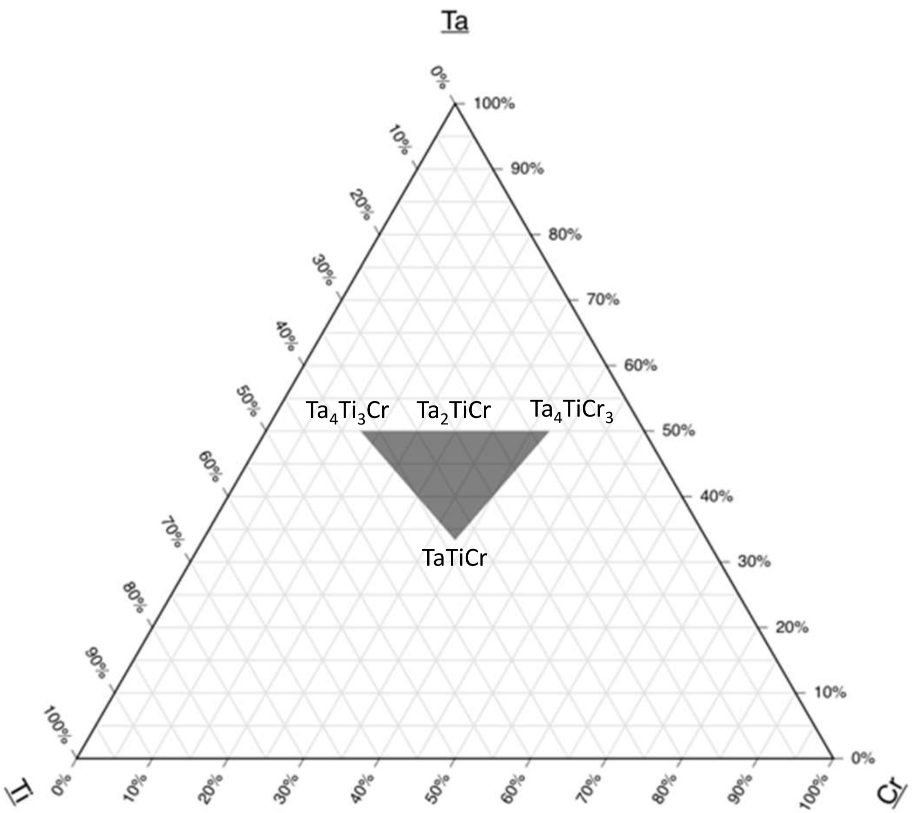
Oxidation Performance



Butler, et al., *Journal of Alloys and Compounds, 2019*

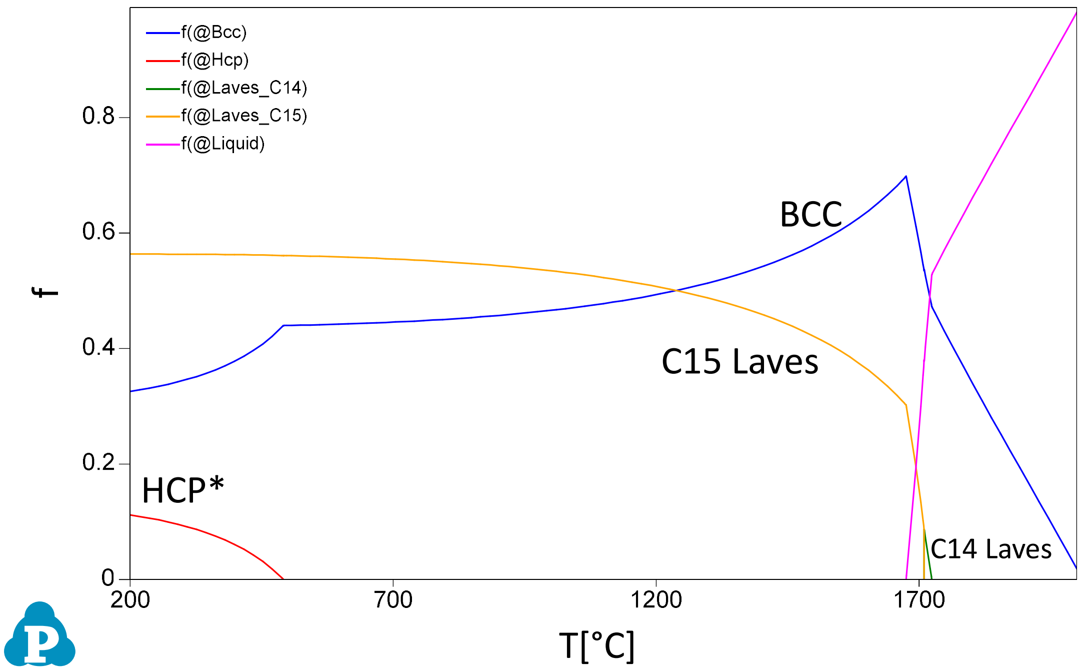
- Unique, complex oxide structures not found in conventional alloys
  - Intermediate oxidation rate between dilute alloys and classic oxide formers
- Most experiments on as-cast/annealed condition
  - Microstructural contributions need to be investigated further

TaTiCr Compositional Range



- Characterize compositional range
  - Orbits RCCA compositional space
- Determine optimal composition range to maximize oxidation and mechanical properties
- Pared range will be used in compositionally graded additive manufactured specimens

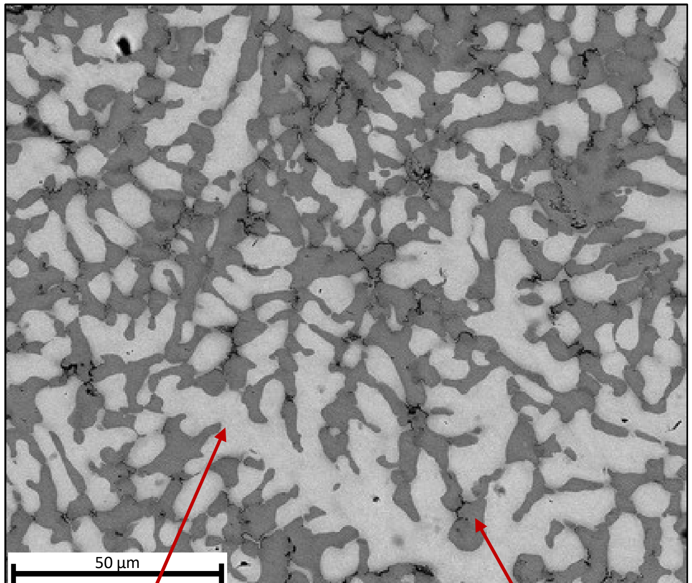
TaTiCr Phases



*Not expected to form due to sluggish kinetics

- Ta + Ti form BCC solid solution for large temperature range
  - Ti + Cr BCC decomposes from 1000-1400 °C
- Ta and Ti both form Laves intermetallic with Cr
  - $TaCr_2$, $TiCr_2$
- High temperature C14 (Hexagonal) Laves nucleates from melt and transforms into C15 (Cubic) upon cooling

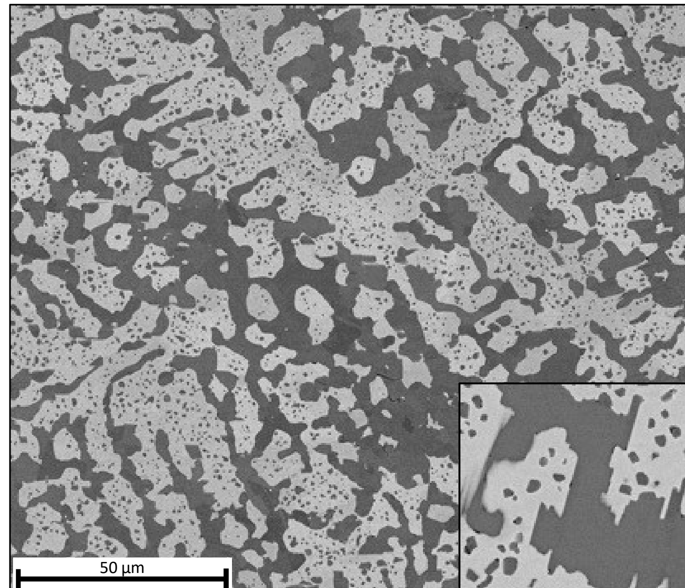
Microstructure Characterization – Ta_4TiCr_3

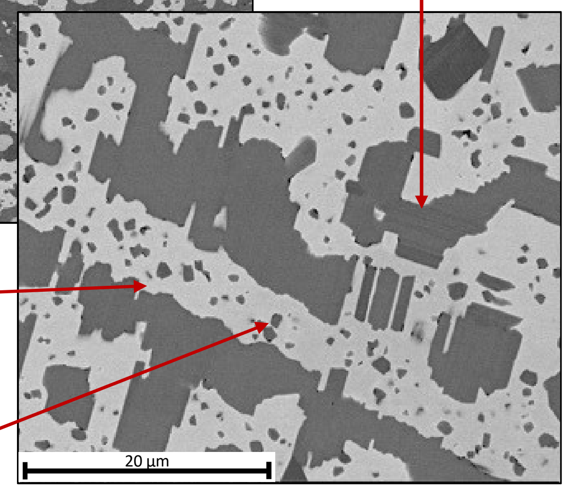


BCC dendrites

Coarse interdendritic Laves

HIP 3 hrs, 30 ksi
1400 °C





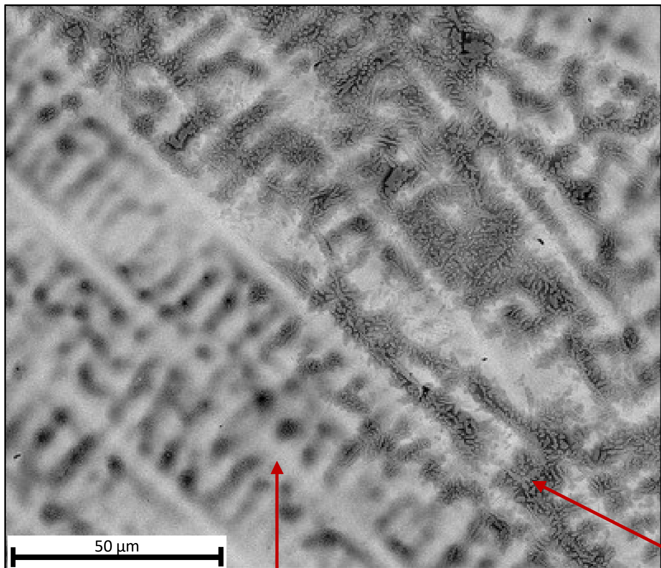
Retained C14 Laves

Dendrite morphology refinement

Fine Laves precipitates inside dendrites

Hardness: 710 HV (60.2 HRC)
Density: 12.69 g/cm^3

Microstructure Characterization – TaTiCr



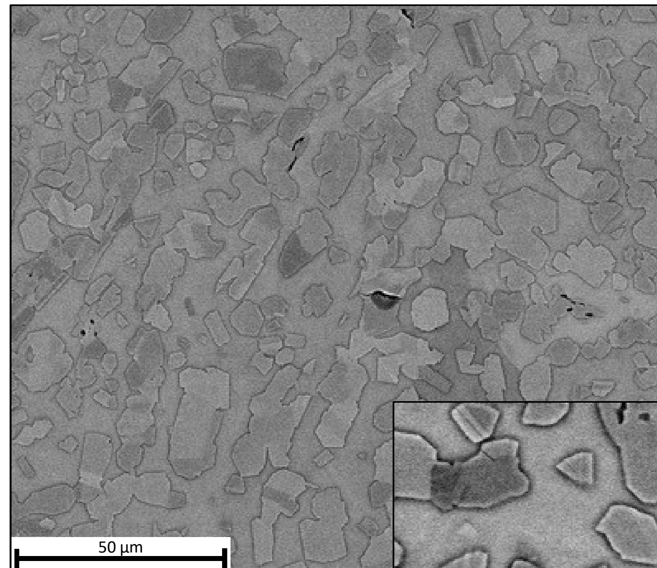
Cored* Ta-rich dendritic grains

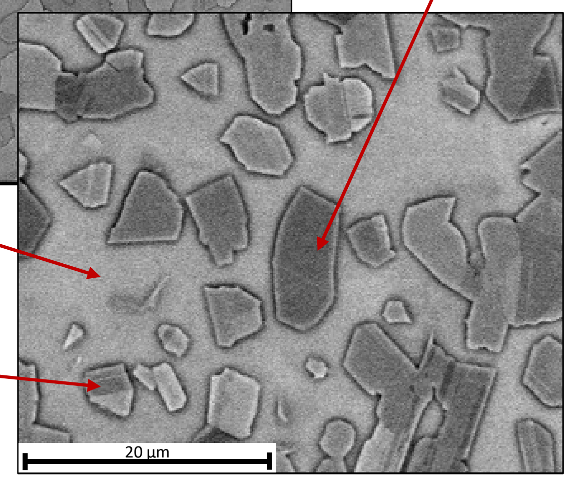
Fine Laves precipitates

*Coring is an artifact resulting from the partition coefficients between constituent elements, leading to the first-freezing component forming a highly concentrated "core" within each dendrite.

Hardness: 574 HV (53.5 HRC)
Density: 8.40 g/cm^3

HIP 3 hrs, 30 ksi
1400 °C →



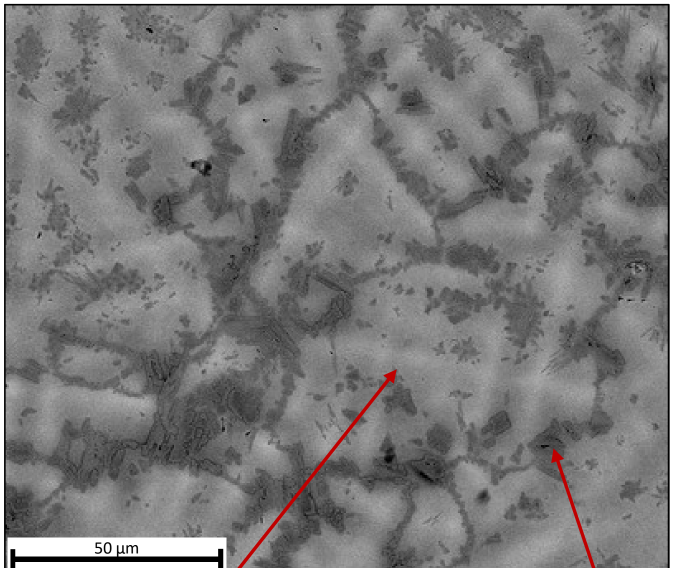


Coarsened Laves particles

Ti – rich BCC matrix

Transformation twinning: C14 → C15

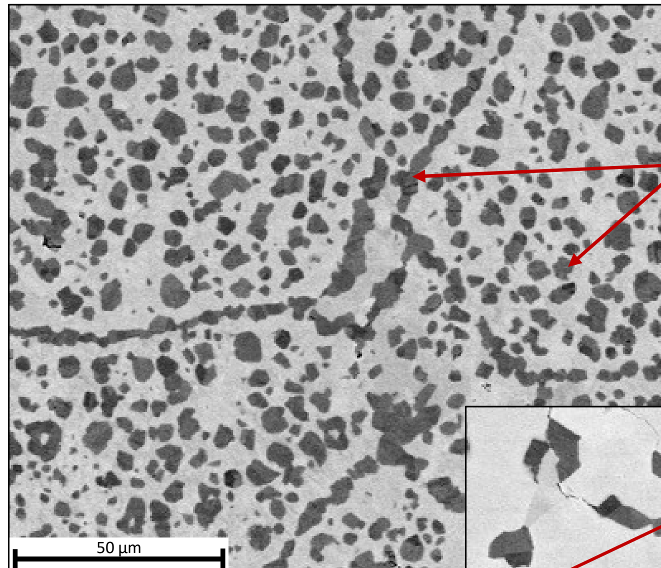
Microstructure Characterization – Ta_2TiCr

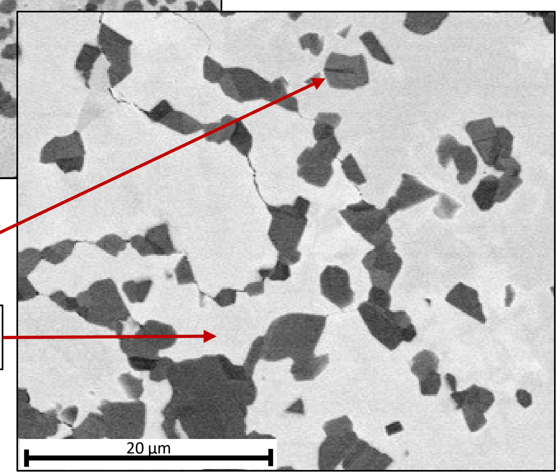


Cored dendritic grains

Laves precipitates on grain boundaries

HIP 3 hrs, 30 ksi
1400 °C





GB and intragranular Laves coarsening

Transformation twinning

Ta – rich BCC matrix

Hardness: 564 HV (53.2 HRC)
Density: 11.95 g/cm^3

Microstructure – Ta_4Ti_3Cr

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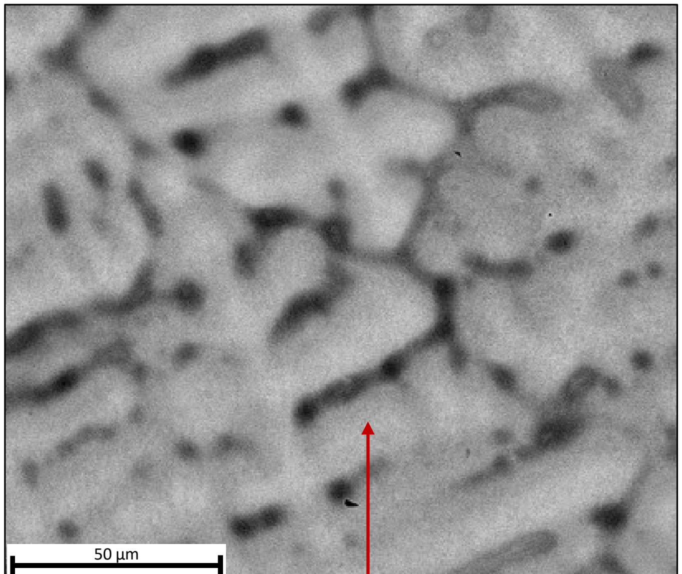
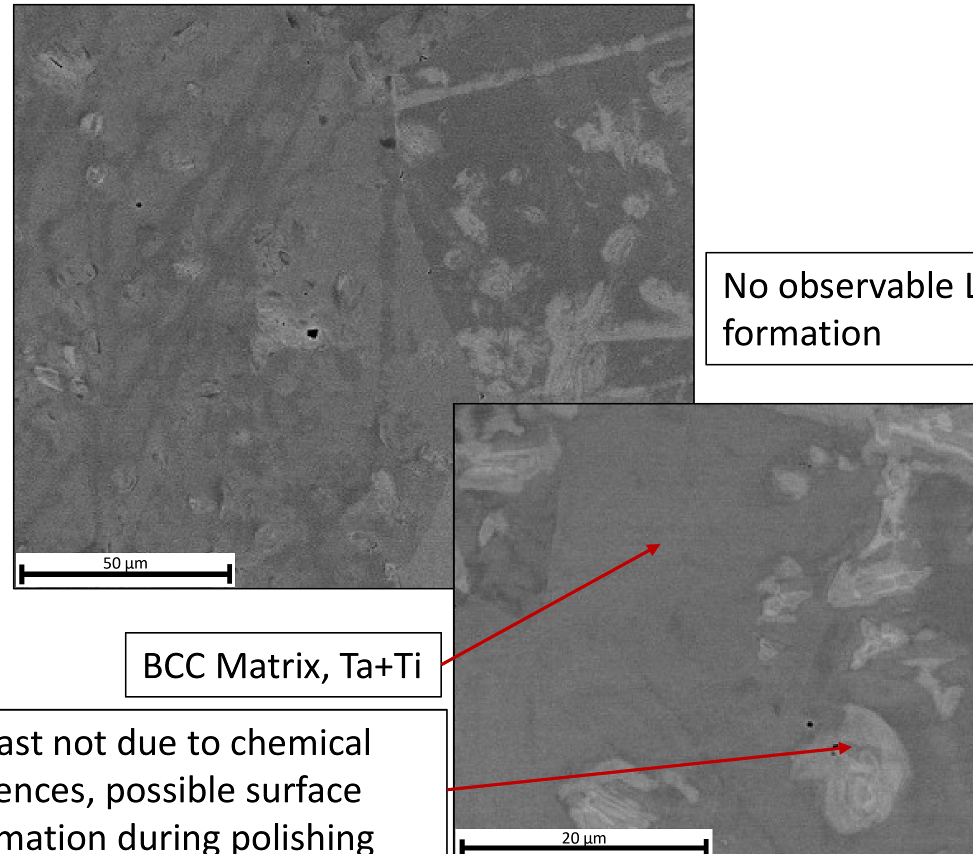


Coarse dendritic grains

HIP 3 hrs, 30 ksi
1400 °C



No observable Laves formation

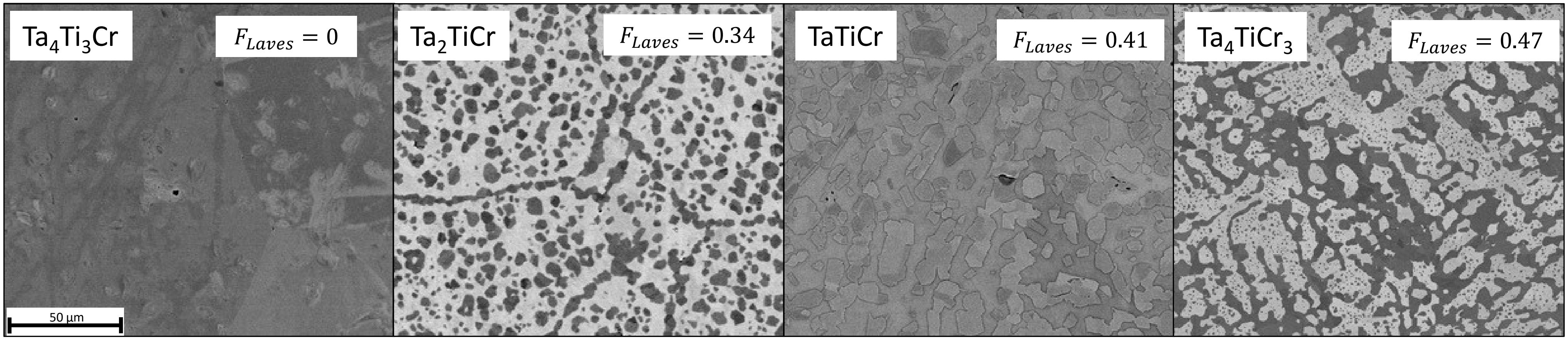
BCC Matrix, Ta+Ti

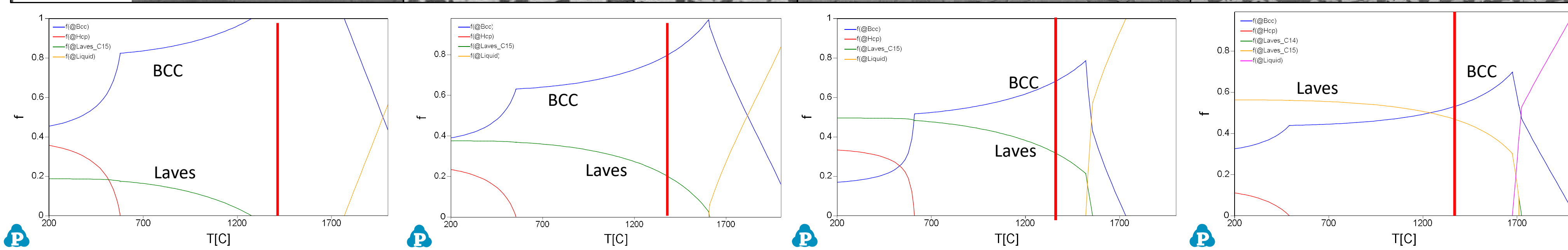
Contrast not due to chemical differences, possible surface deformation during polishing

Hardness: 363 HV (36.9 HRC)
Density: 11.79 g/cm^3

Microstructure

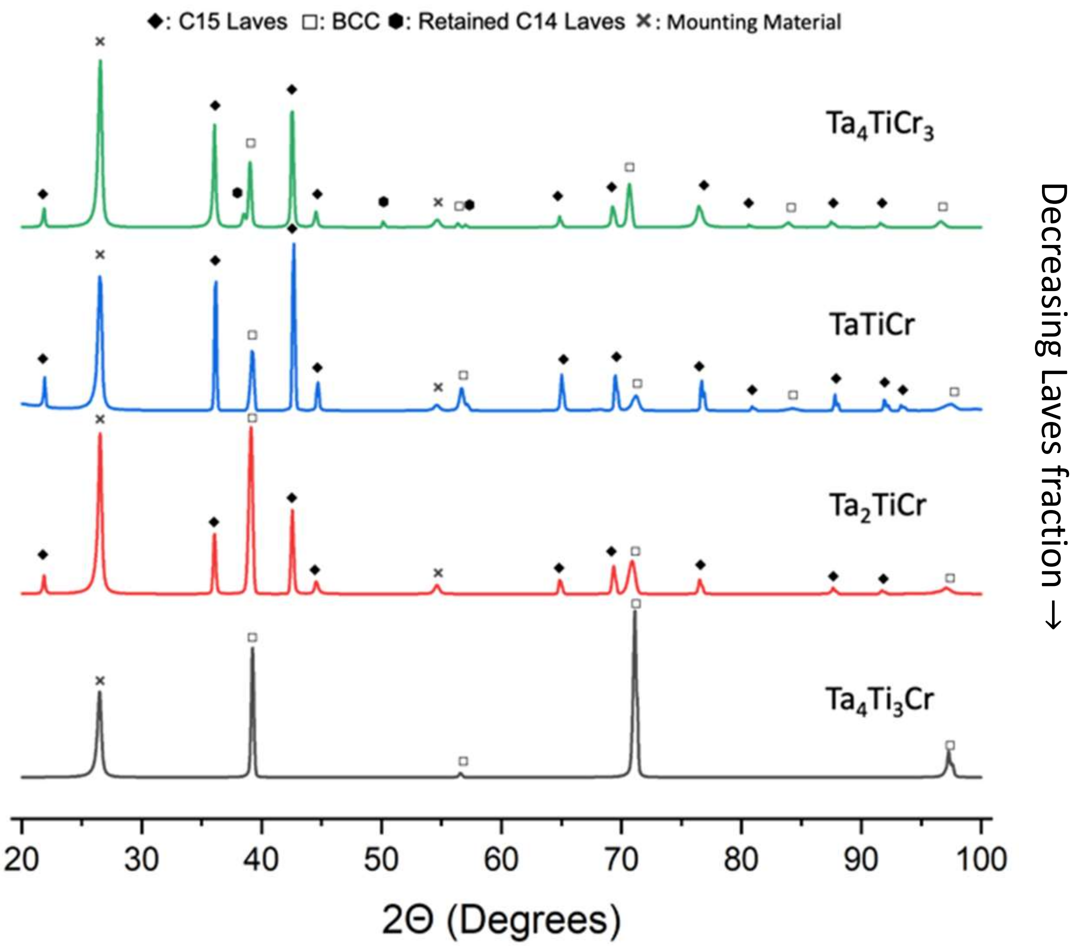
Increasing Laves fraction, increasing Cr % →





Sluggish kinetics are responsible for quasi-quenched state after cooling from 1400 °C . (Cooling rate 15 °C /min)

XRD Phase Verification



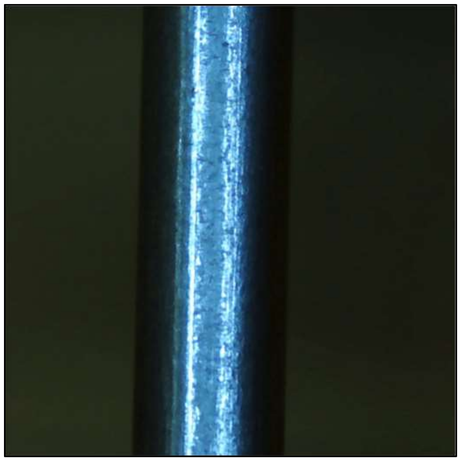
	Ta_4TiCr_3	$TaTiCr$	Ta_2TiCr	Ta_4Ti_3Cr
C15 Laves	7.047	7.024	7.036	-
BCC	3.264	3.243	3.254	3.247

Lattice parameters of phases (Å)

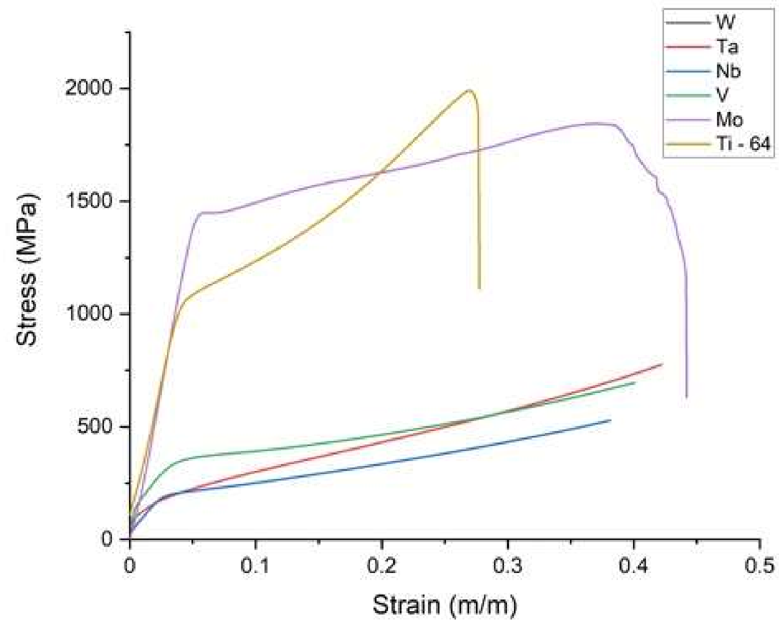
Laves phase fraction directly correlated with Cr %
Plan to verify phases using TEM selected area diffraction

Compression Tests

L/D ratio: 3



L/D ratio: 2

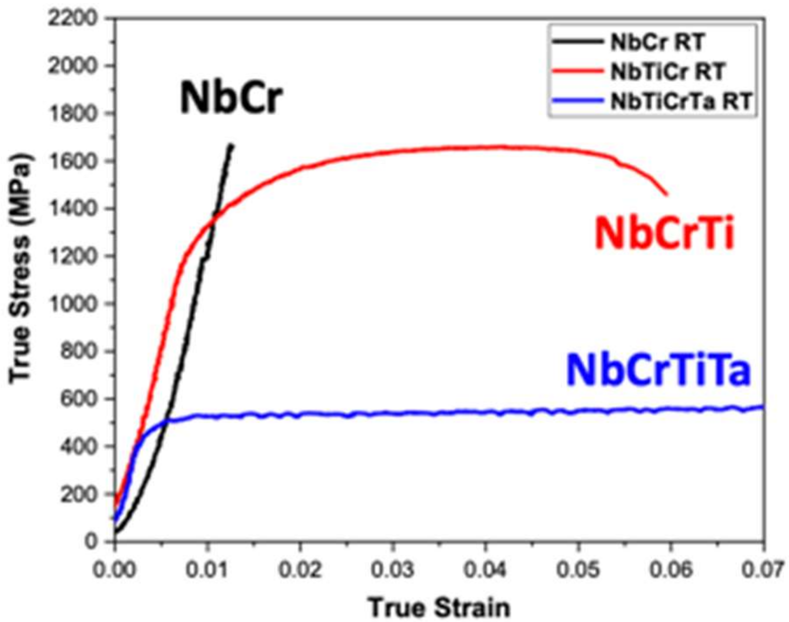


L/D = 2 greatly reduces buckling during tests, providing more accurate results

Procedure following ASTM E9.

Tested on W, Ta, Nb, Mo, V, and Ti-64

Compression Tests



When compared with similar systems (NbCrTi and NbCrTiTa) the ternary TaTiCr composition will likely exhibit an intermediate ductility

- Increasing Laves fraction would expect a lower ductility, higher compressive strength

Butler, AFOSR, 2020.

Pickling Procedure

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SPECIFICATIONS FOR CLEANING, FUSION WELDING, AND POSTHEATING TANTALUM AND COLUMBIUM ALLOYS

by T. J. Moore, P. E. Moorhead
and K. J. Bowles
Lewis Research Center
Cleveland, Ohio
July, 1971

Adapted from NASA specification TM-X67879

10 minute acid bath in solution consisting of:
1 part hydrofluoric acid
1 part nitric acid
4 parts sulfuric acid
2 parts water

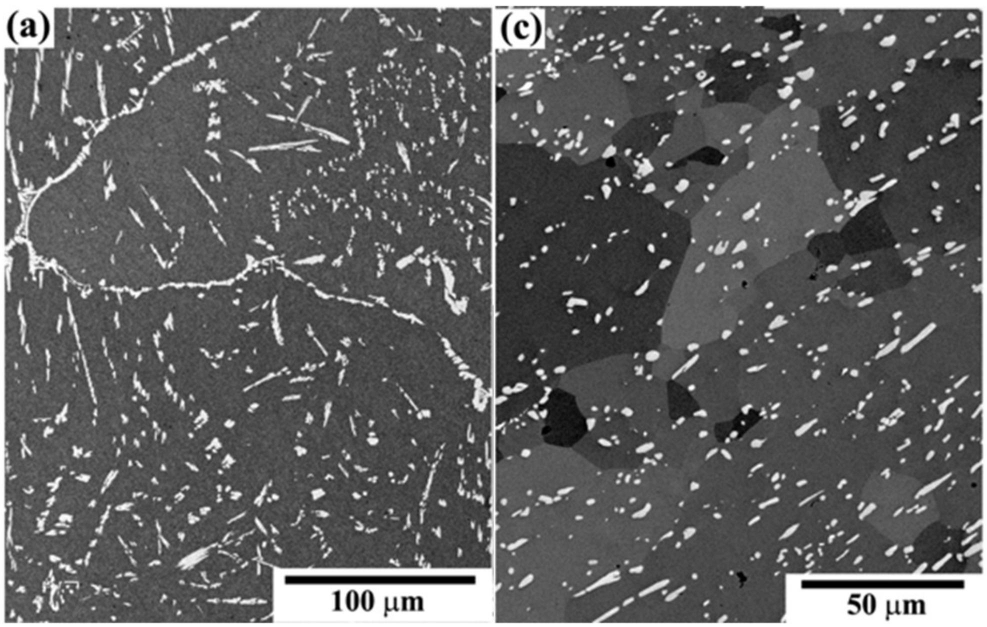
Unmixed tantalum could be seen after pickling

Chemistry likely altered in rest of specimens

Post-EDM

Post-pickle

Thermal-Mechanical Processing



Fe_2Nb Laves in Fe-25%Al-3%Nb , forged at 1150 °C , $\varepsilon = 2.3$

There is not always a direct correlation between grain size and oxidation performance

- Diffusion mechanisms are T dependent.
- Tradeoff between O ions diffusing in or metal ions diffusing out

High temperature thermal-mechanical processing (TMP) to break up and disperse Laves phase.

High Laves volume fraction may inhibit processing

Morris, et al., *Intermetallics, 2012*

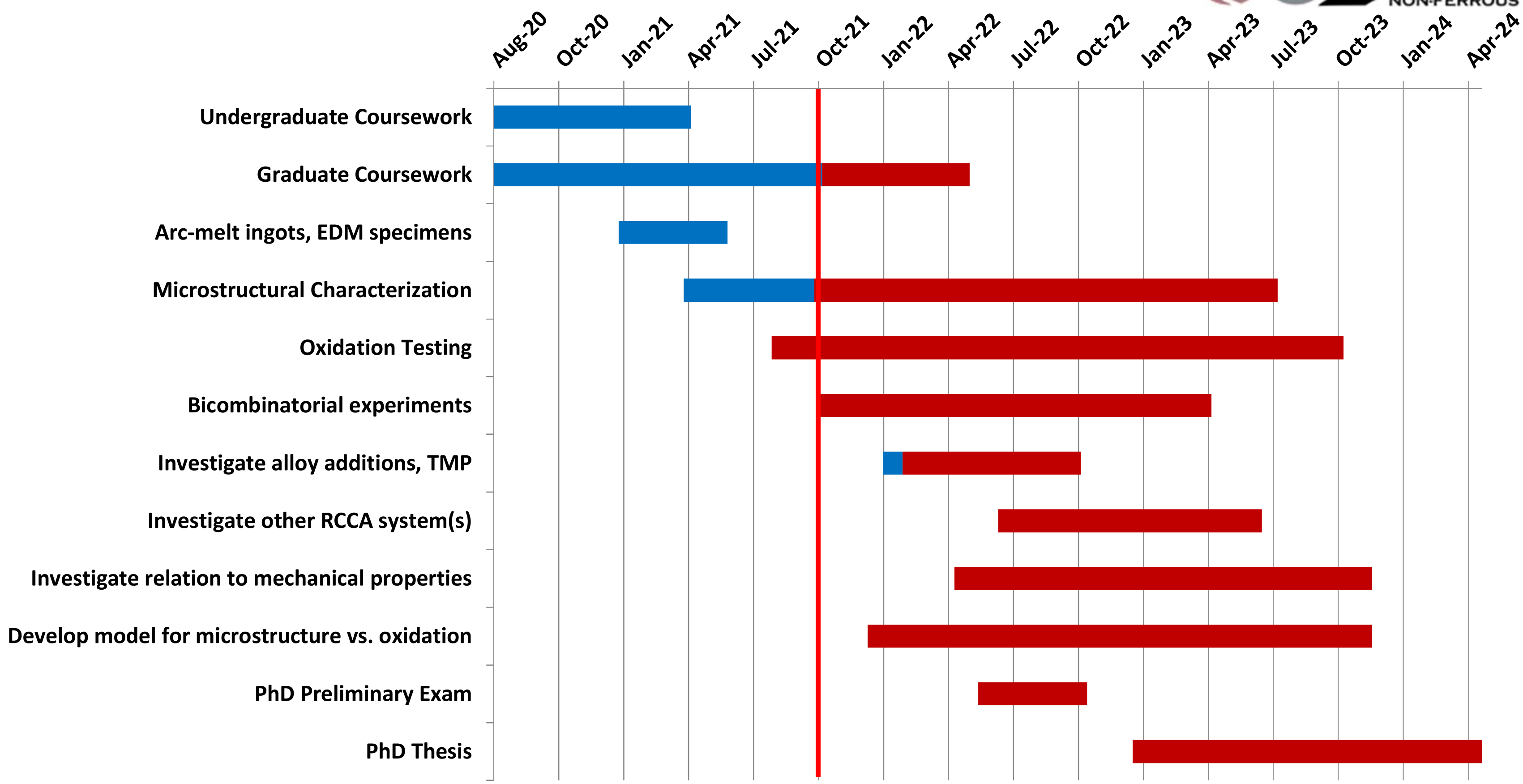
Future Work

- Oxidation Tests
  - TGA, Open air and reduced oxygen atmosphere to simulate flight conditions
- Complete characterization
  - Continue characterizing mechanical, chemical, and physical properties of the alloy system
- Define ideal composition range
  - 4 initial compositions will be narrowed down to a smaller range based on oxidation and mechanical performance
- Bicombinatorial Experiments
  - Additive manufactured specimen with composition gradient
  - Gleeble system induces thermal gradient orthogonal to composition gradient
  - Gather oxidation vs. composition data rapidly for decided composition range
- Compression tests after remaking specimens
  - Room temperature, elevated temperature compression tests
  - Lower priority, not critical for understanding oxidation behaviors

Challenges & Opportunities

- Remake compression specimens
  - Find alternative use for current specimens
- New alloy system
  - TaTiCr system not characterized
  - Similar systems may not be best model for performance
- Development of “in-house” compression test procedure
  - Faster assessment of compression strength
- AM capabilities
  - Difference in T_M may cause issues in homogeneity
  - Opportunity to further develop AM for refractory alloys

Progress



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Acknowledgments

- Dr. Peter Collins - ISU
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- Bobby Puerling - Mines
- Matt Besser - Ames Laboratory Metals Preparation Center (MPC)
- Ben Lehs - Priority Custom Machining (PCM)

Thank You!

Questions?

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