Project 43-L: Thermodynamics of Refractory Alloys

Semi-annual Spring Meeting

April 2022

- Student: Bobby Puerling (Mines)
- Faculty: Amy Clarke (Mines), Jonah Klemm-Toole (Mines)
- Industrial Mentors: Andy Deal (KCNSC), Wes Everhart (KCNSC), Noah Philips (ATI), Andrew Kustas (SNL)

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Project 43-L: Thermodynamics of Refractory Alloys

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- Student: Bobby Puerling (Mines)
- Advisor(s): Amy Clarke (Mines), Jonah Klemm-Toole

Project Duration
Master's: Jan. 2020 to August 2022

- Problem: Gaps exist in the thermodynamic databases where refractory alloys are concerned.
- Objective: Compile thermodynamic data for compositions of interest, assess the phase stability of MoNbTa with heat treatments, and characterize microstructures.
- Benefit: Improve databases for thermodynamic predictions.

Recent Progress

- Additional heat treatments at 1700˚C are completed and samples are being analyzed
- Second nesting doll diffusion chamber heat treatment trial completed

Metrics		
Description	**% Complete**	**Status**
1. Literature review	95%	●
2. Comparison of published phase diagrams to Thermo-Calc predicted phase diagrams	100%	●
3. Create heat treatment method utilizing DICTRA and Scheil simulations	100%	●
4. Perform heat treatment, microstructural characterization, and assess phase stability	75%	●
5. Input experimental data into Thermo-Calc and compare new predictions to experimental data	5%	●

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Background

- HEAs/MPEAs/CCAs (High Entropy Alloys/Multi-Principal Element Alloys/Complex Concentrated Alloys) popular for research during last 15 years
- Growing need for advanced structural metallic alloys capable of ultrahigh temperature performance in extreme environments
  - Recent research into MPEAs consisting of only, or primarily, refractory metals (RMPEAs)
- Limited knowledge of refractory alloys beyond binaries
  - Extremely high melting temperatures lead to experimental difficulties
- Fabrication of RMPEAs challenging
  - Need for discovery/development of RMPEAs with capability to be fabricated (some room temperature ductility) while maintaining high temperature strength (thermomechanical processing)
  - Need for discovery/development of RMPEAs for additive manufacturing

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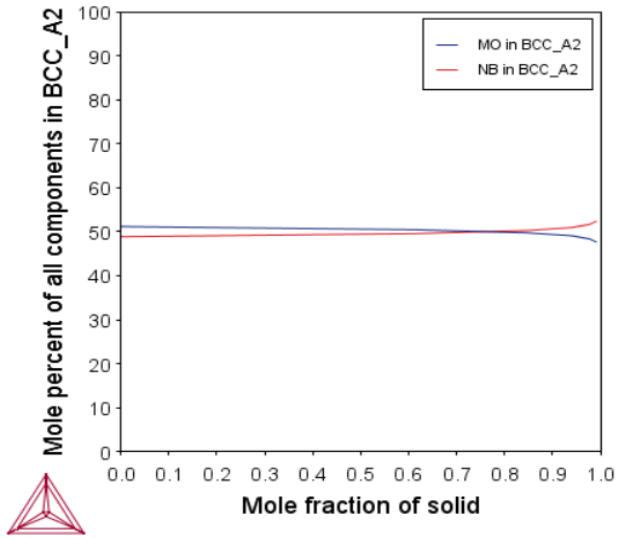
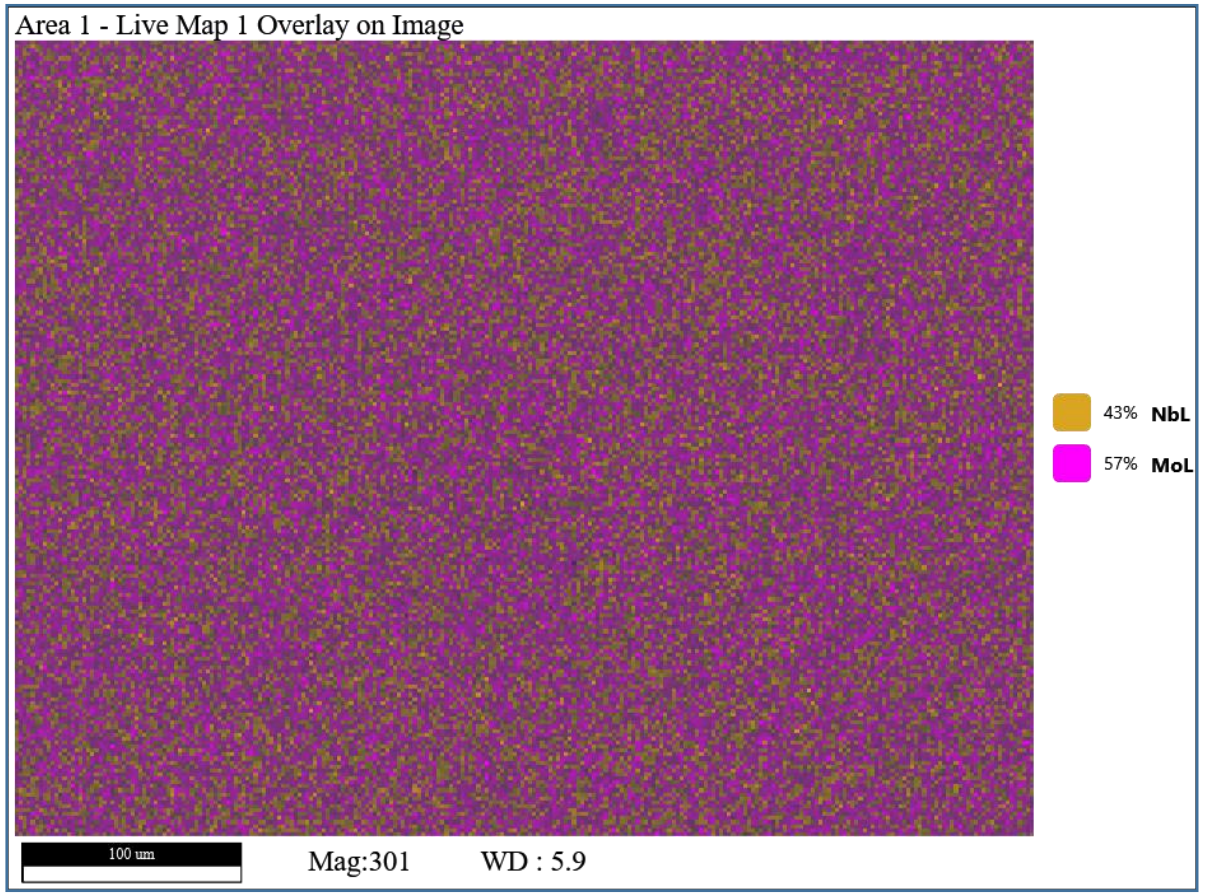
Diffusion Couples

- Pure Ta with MoNb binaries
- Melting Temperatures
  - Mo = 2623 ˚C
  - Nb = 2477 ˚C
- Minimal solidification segregation





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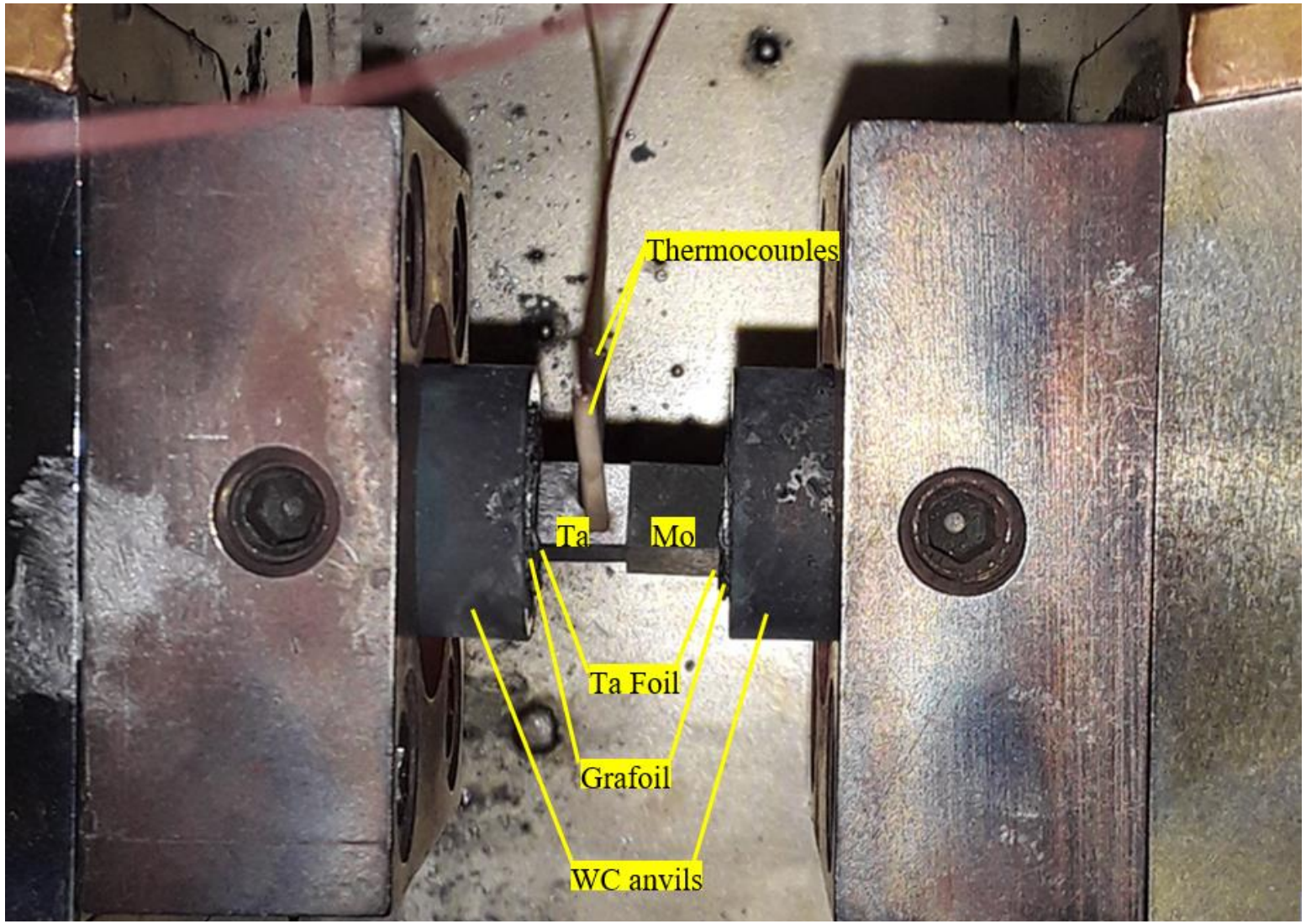
Diffusion Couples



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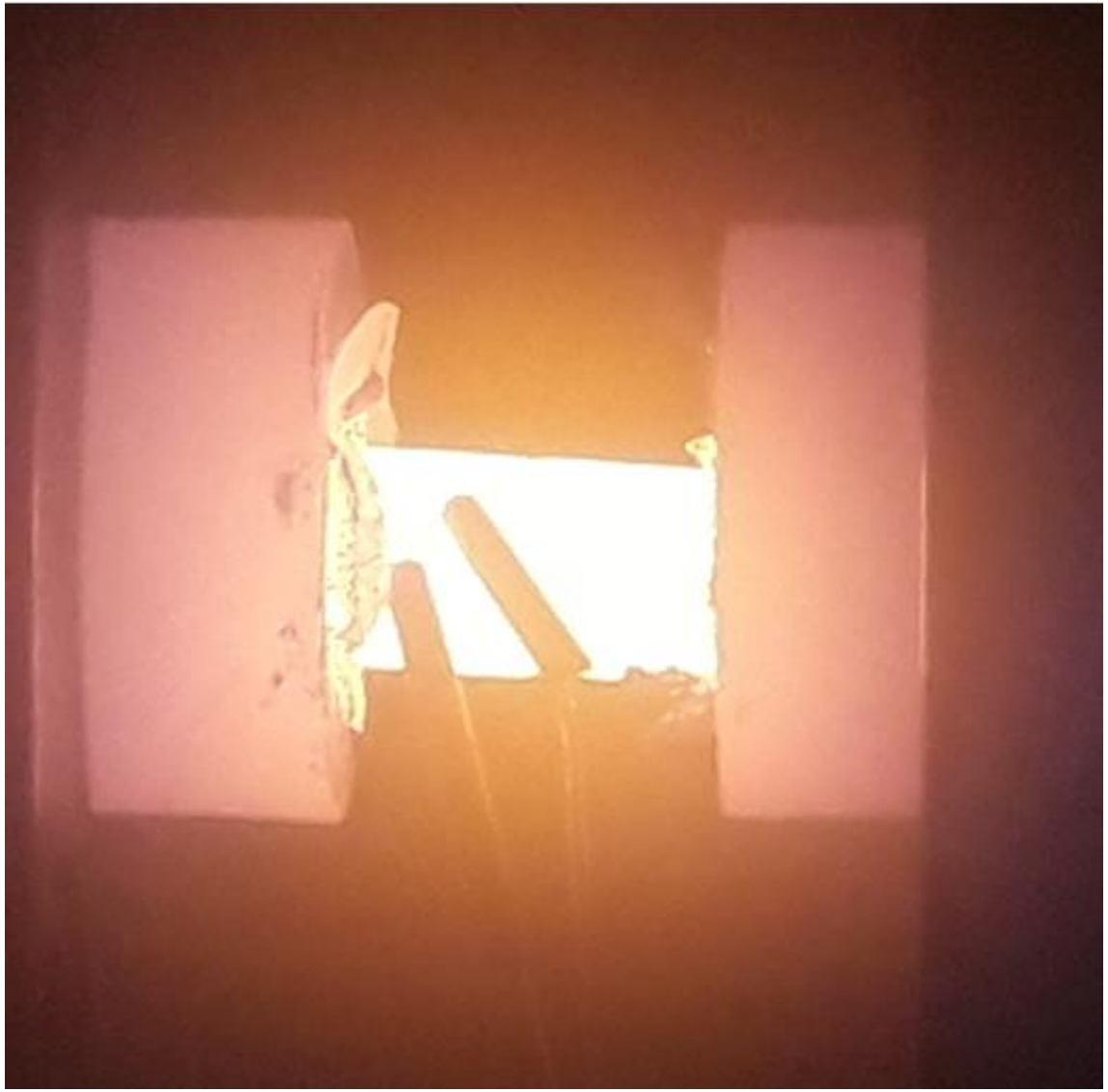
Diffusion Couples

- 1st sample set
  - Apply 2kN compression
  - Ramp to 1200 ˚C over 4 min
    - Compress 1/4mm during ramp
  - Hold at 1200 ˚C for 30 min
    - Compress 1mm during hold
- Other sample sets
  - Apply 2kN compression
  - Attempted ramp to 1200 ˚C over 4 min
    - Thermocouples failed at ~900 ˚C



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Heat Treatment

- 500h @ 1700˚C in static Ar
  - 100h segments
- Nb7.5Ta and Nb30Mo witness samples
  - One each pulled every 100h
- Three diffusion couple sample sets
  - 1st: interface ground with SiC before joining in gleeble
  - 2nd and 3rd: interface ground with AlO before joining in gleeble
    - 3rd sent to KCNSC for analysis
  - No discernable difference between the sample sets

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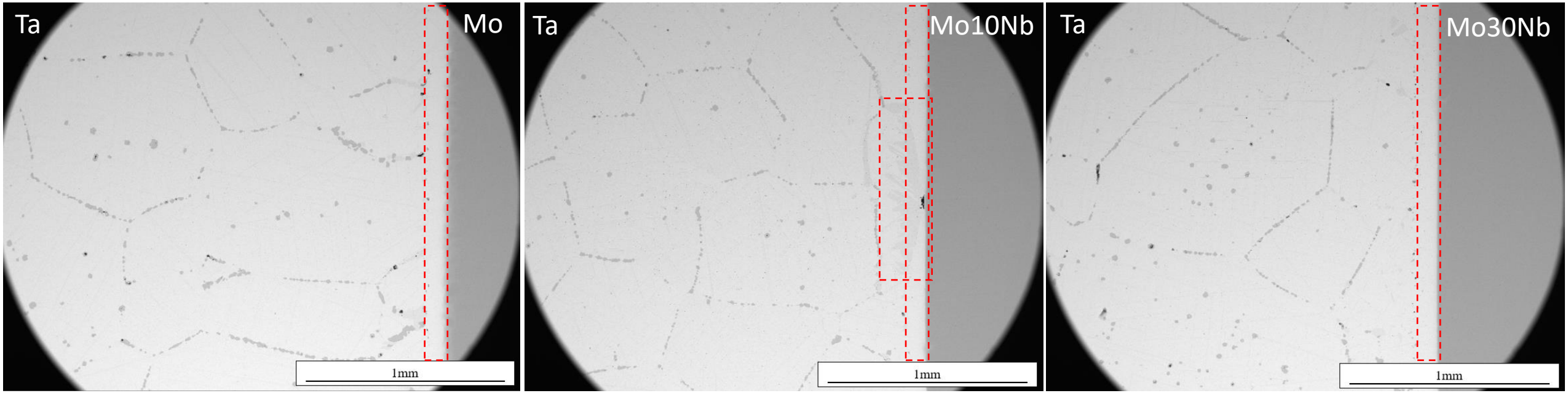
Ta-Mo, Ta-Mo10Nb, Ta-Mo30Nb

500h @ 1700˚C in static Ar



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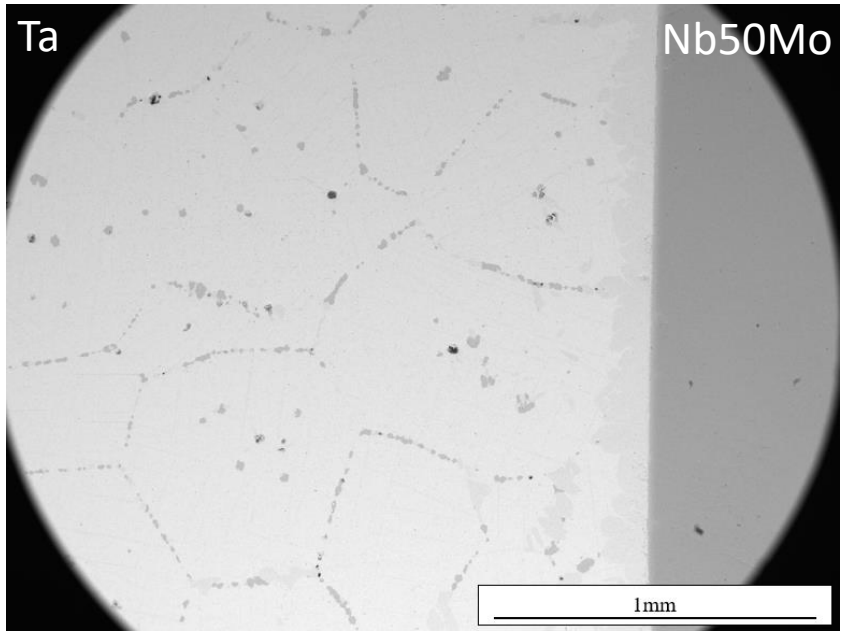
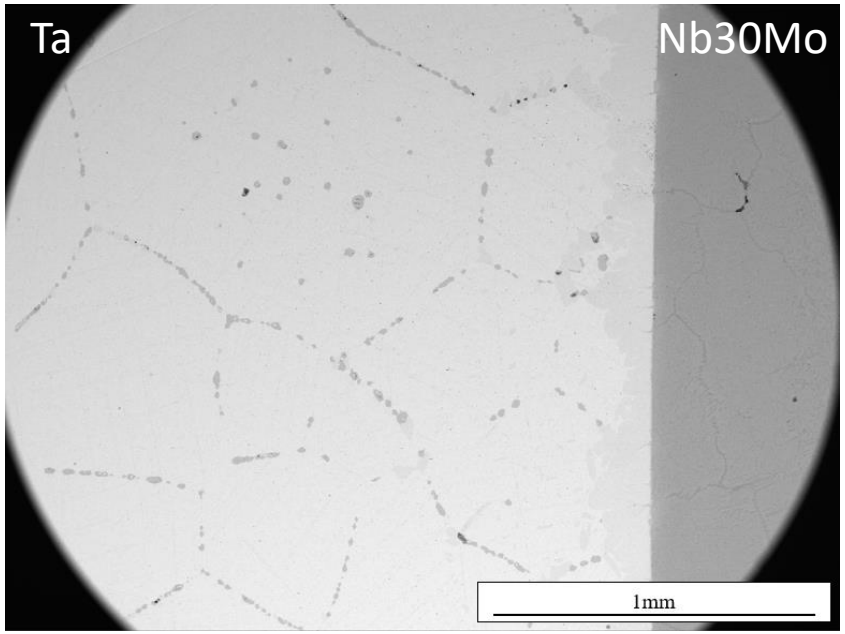
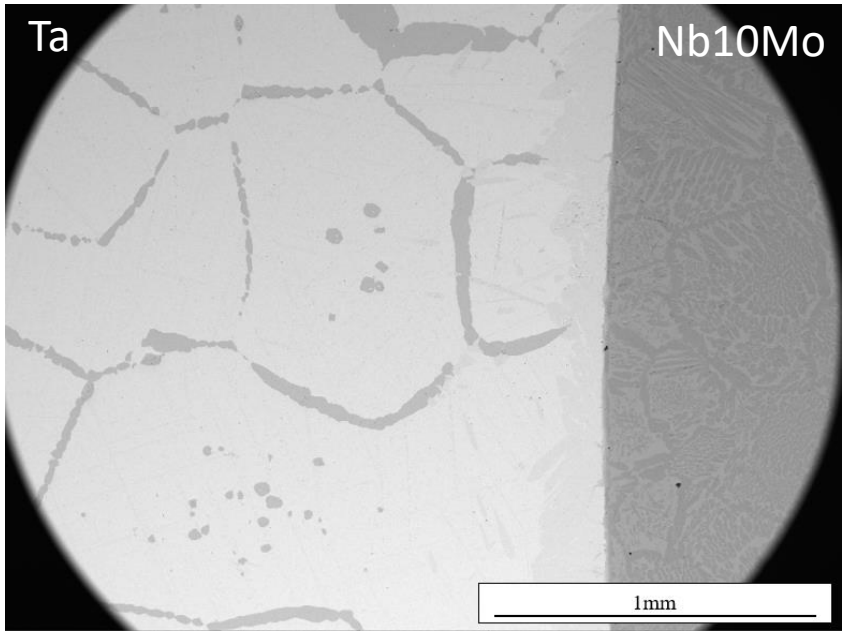
Ta-Nb50Mo, Ta-Nb30Mo, Ta-Nb10Mo

500h @ 1700˚C in static Ar







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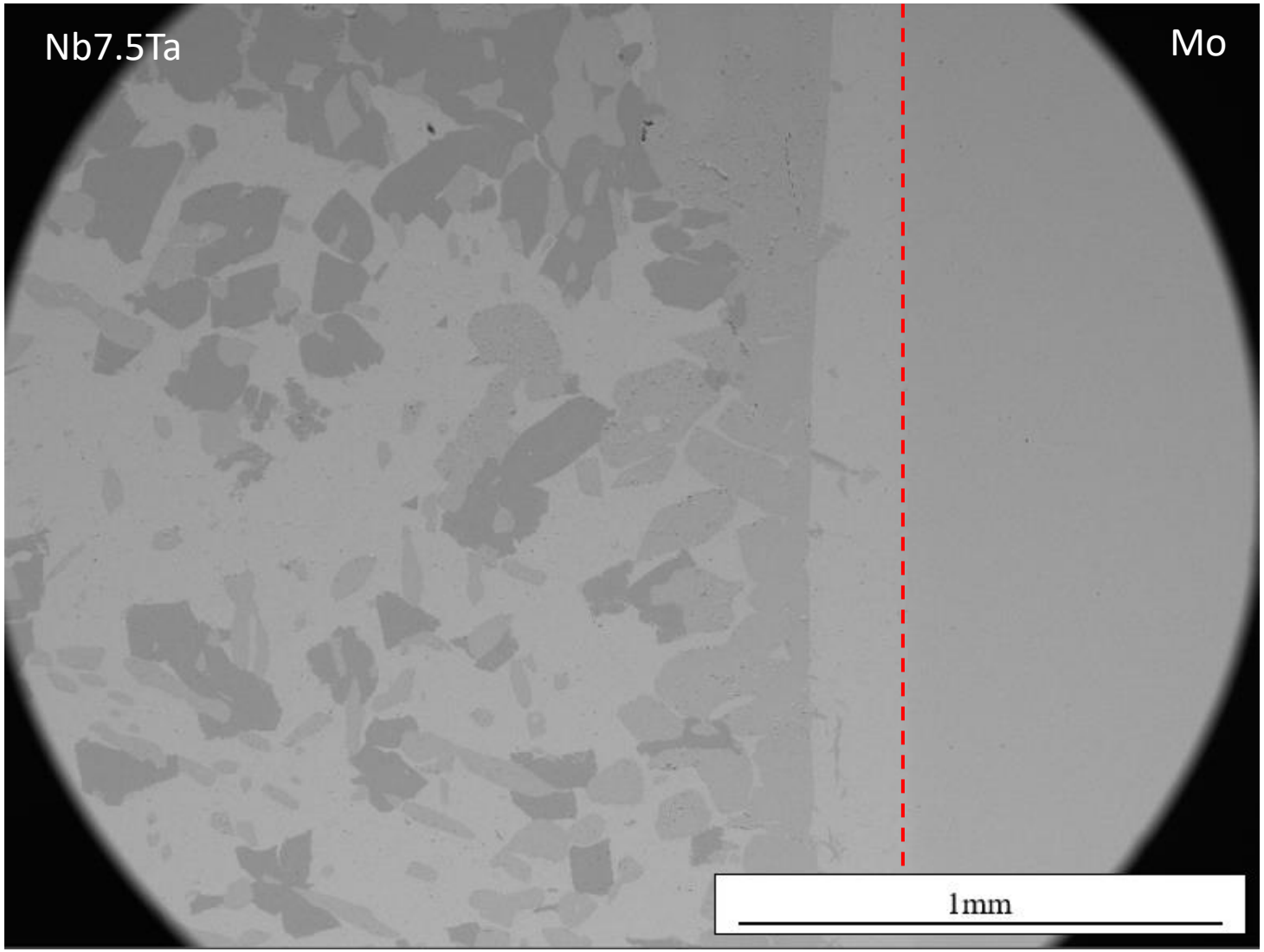
Mo-Nb7.5Ta

500h @ 1700˚C in static Ar



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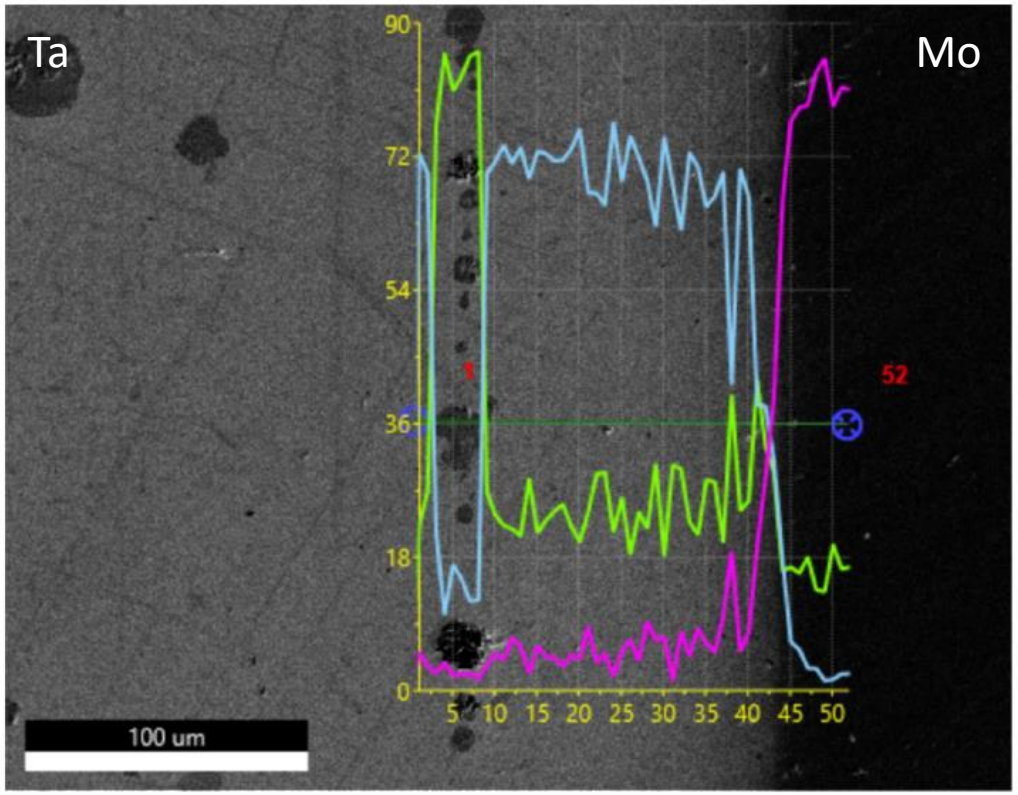
Ta-Mo EDS Line Scans

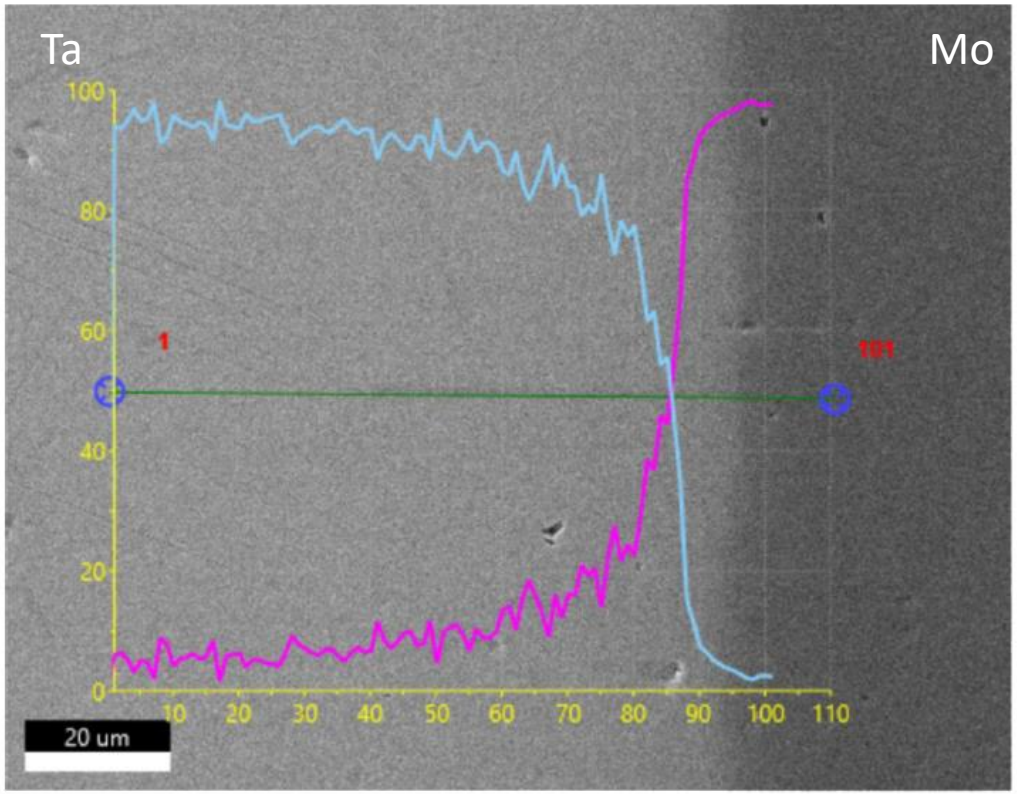
500h @ 1700˚C in static Ar

5keV



O K
Ta M
Mo L

30keV



Mo L
Ta L

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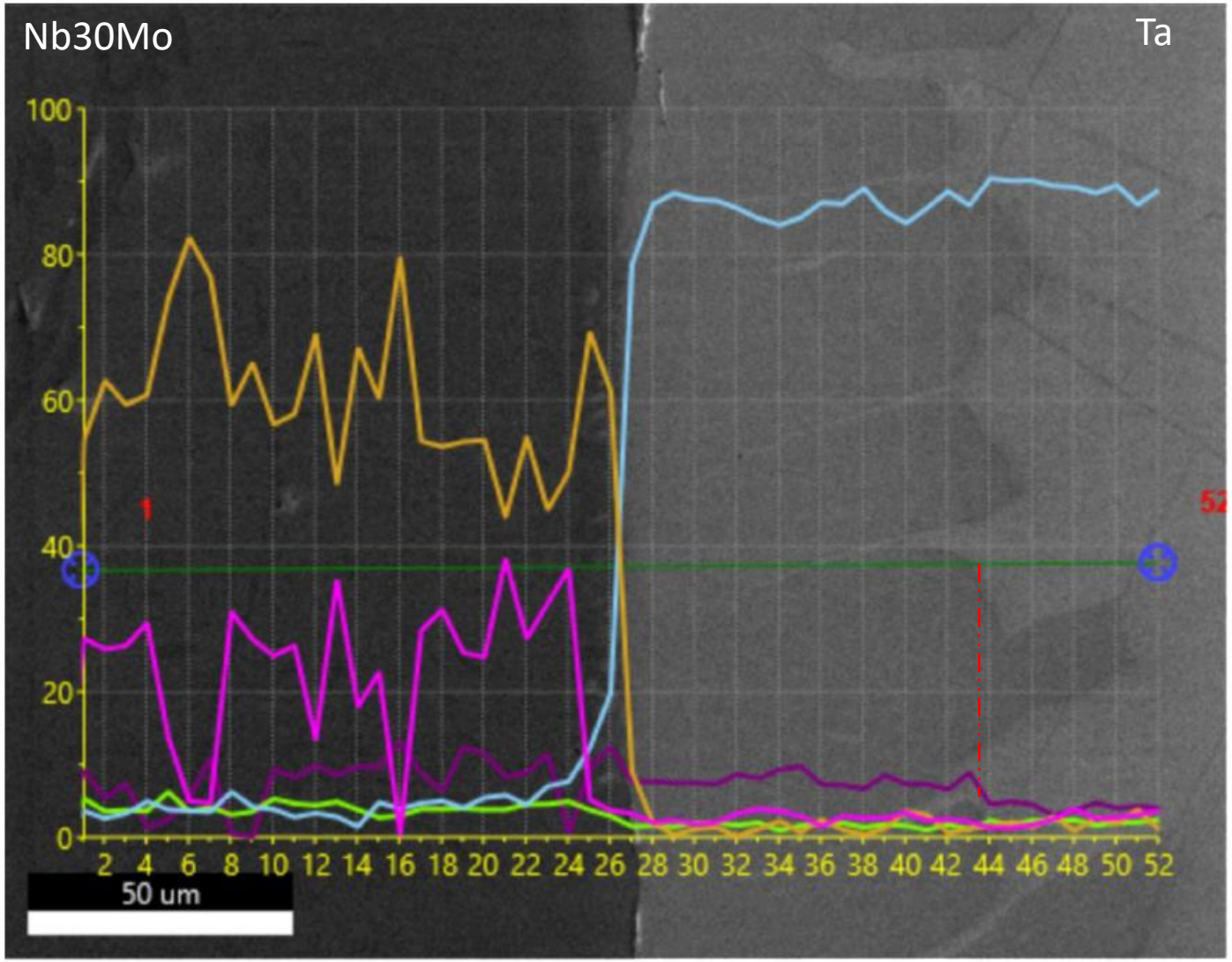
Ta-Nb30Mo EDS Line Scan

500h @ 1700˚C in static Ar



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Tantalum Carbide at Diffusion Couple Interface

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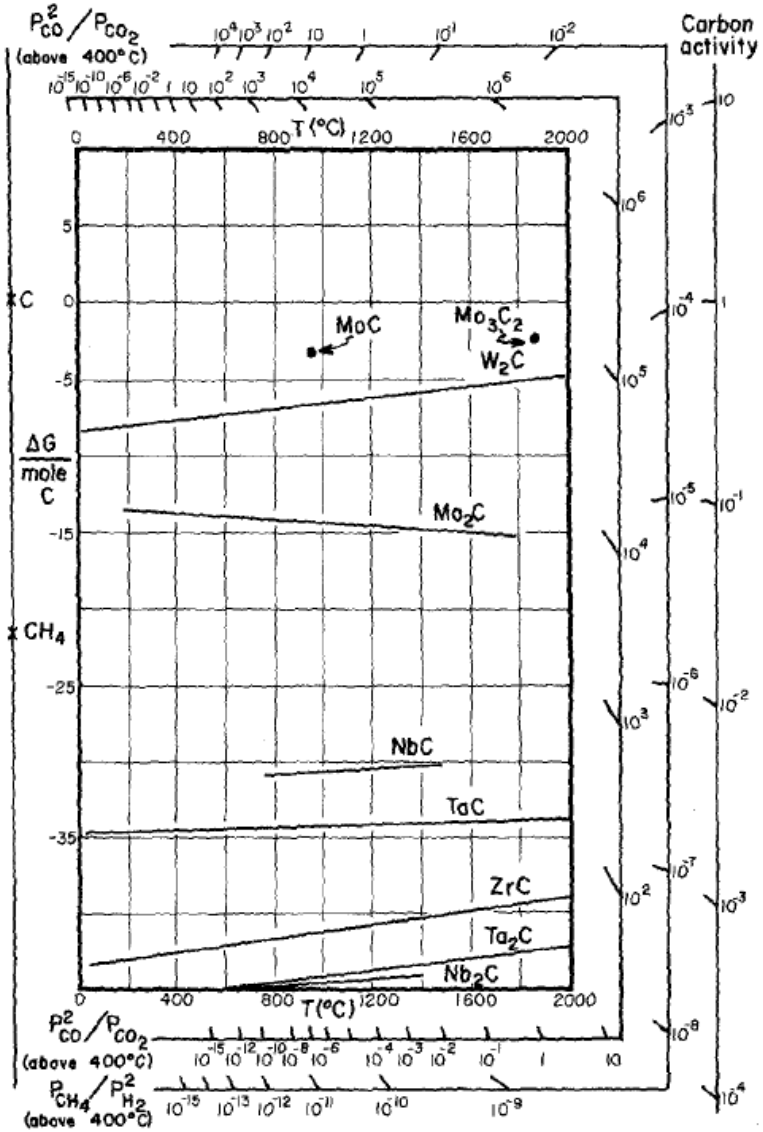
- Ta likes C more than Mo and Nb
- Mo does not like C
- Hypothesis
  - C diffuses faster in Nb than Ta
  - Ta takes C from MoNb side of diffusion couple
  - Not enough C in high Mo binaries to form tantalum carbide at interface
- Need to verify diffusivity of C in Nb and Ta



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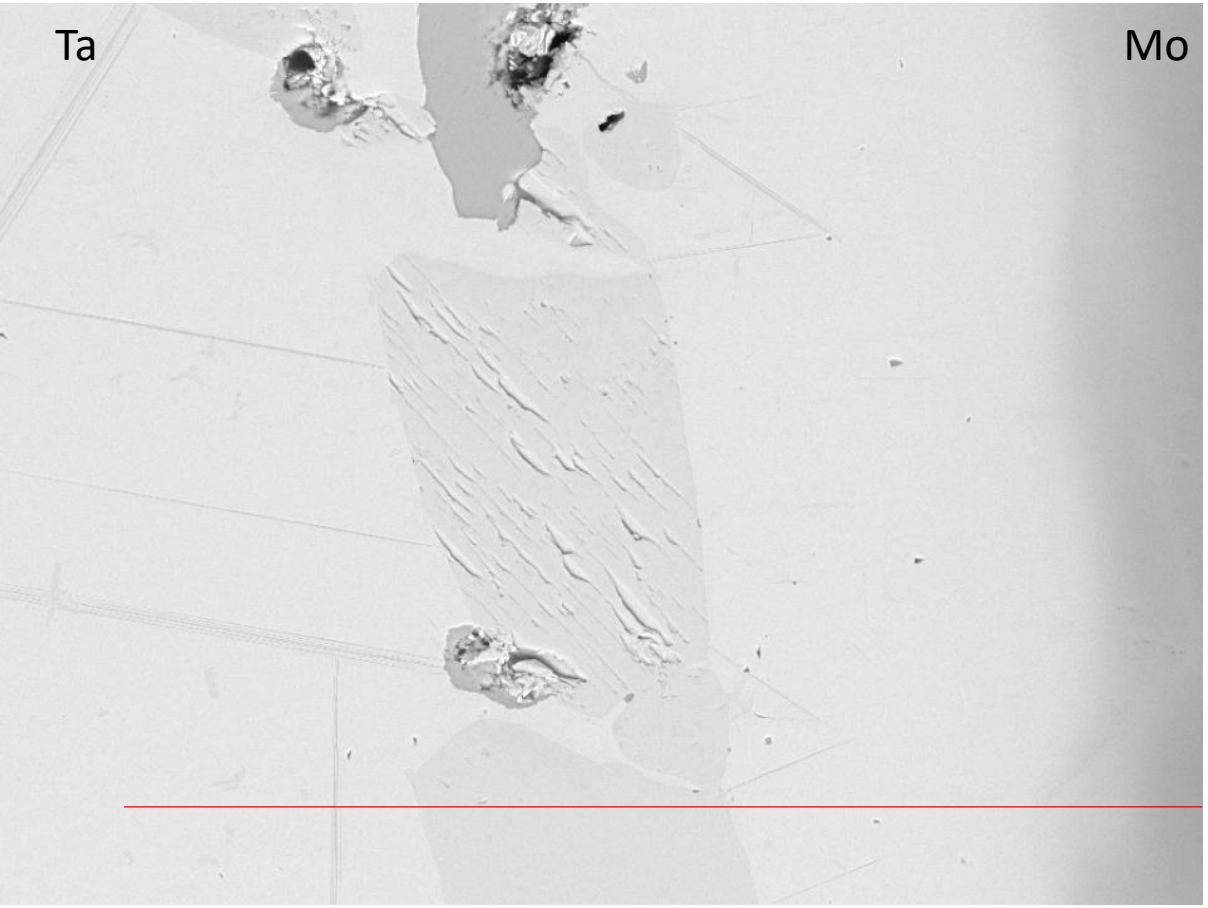
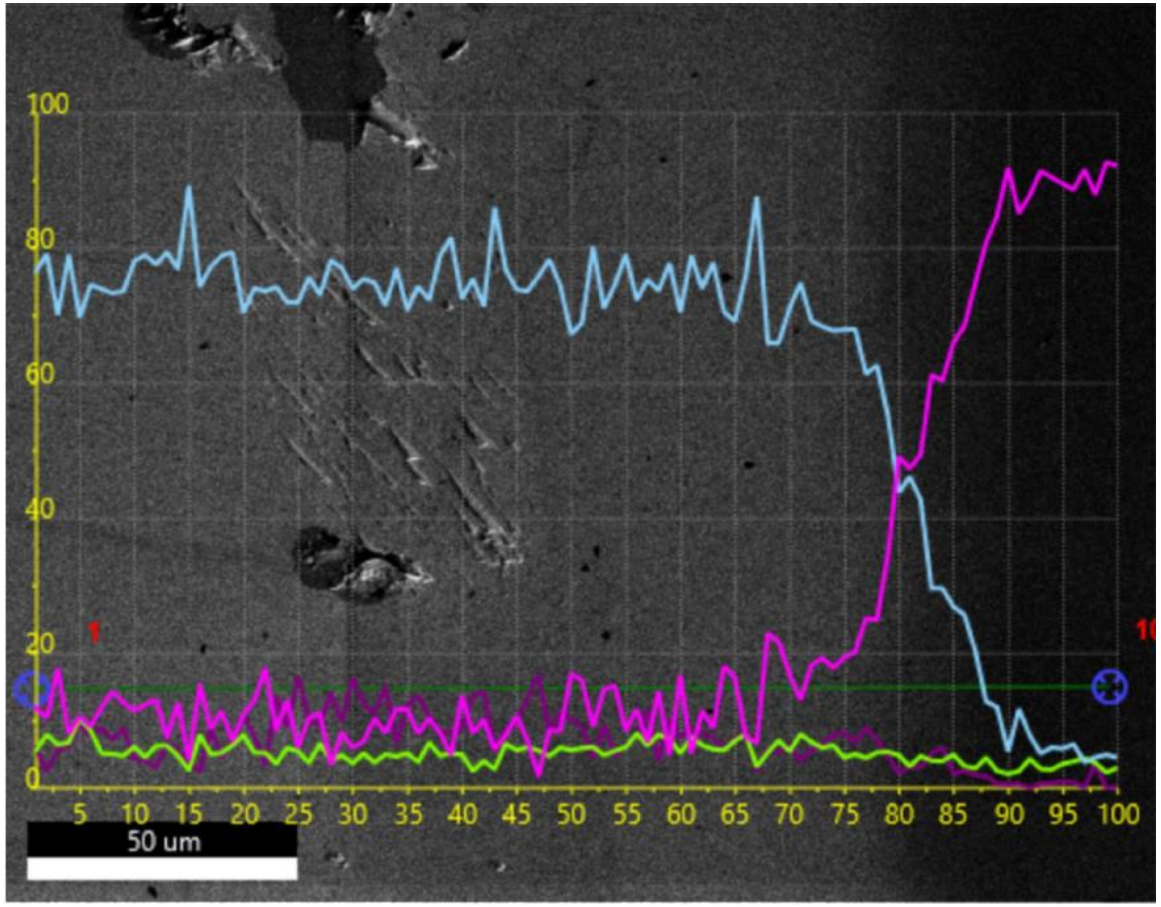
Ta-Mo Denuded Zone EDS Line Scan

500h @ 1700˚C in static Ar





Takeaway: Denuded zone has same composition as bulk Ta.

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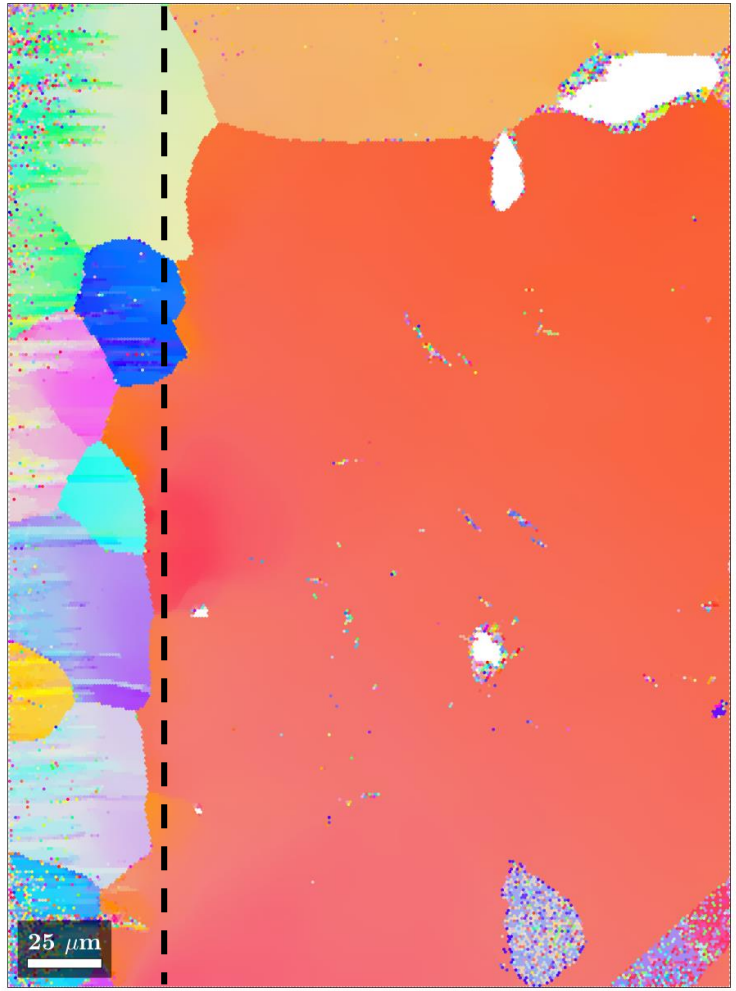
Ta-Mo Denuded Zone EBSD

500h @ 1700˚C in static Ar



Takeaway: Denuded zone is not recrystalization.

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Additional Heat Treatment

- 68h @ 1700˚C in flowing Ar
  - Attempted 100h
- Nb30Mo and Nb7.5Ta
  - Compare to witness samples from previous heat treatment
- No oxides or carbides present
- Nitrogen present

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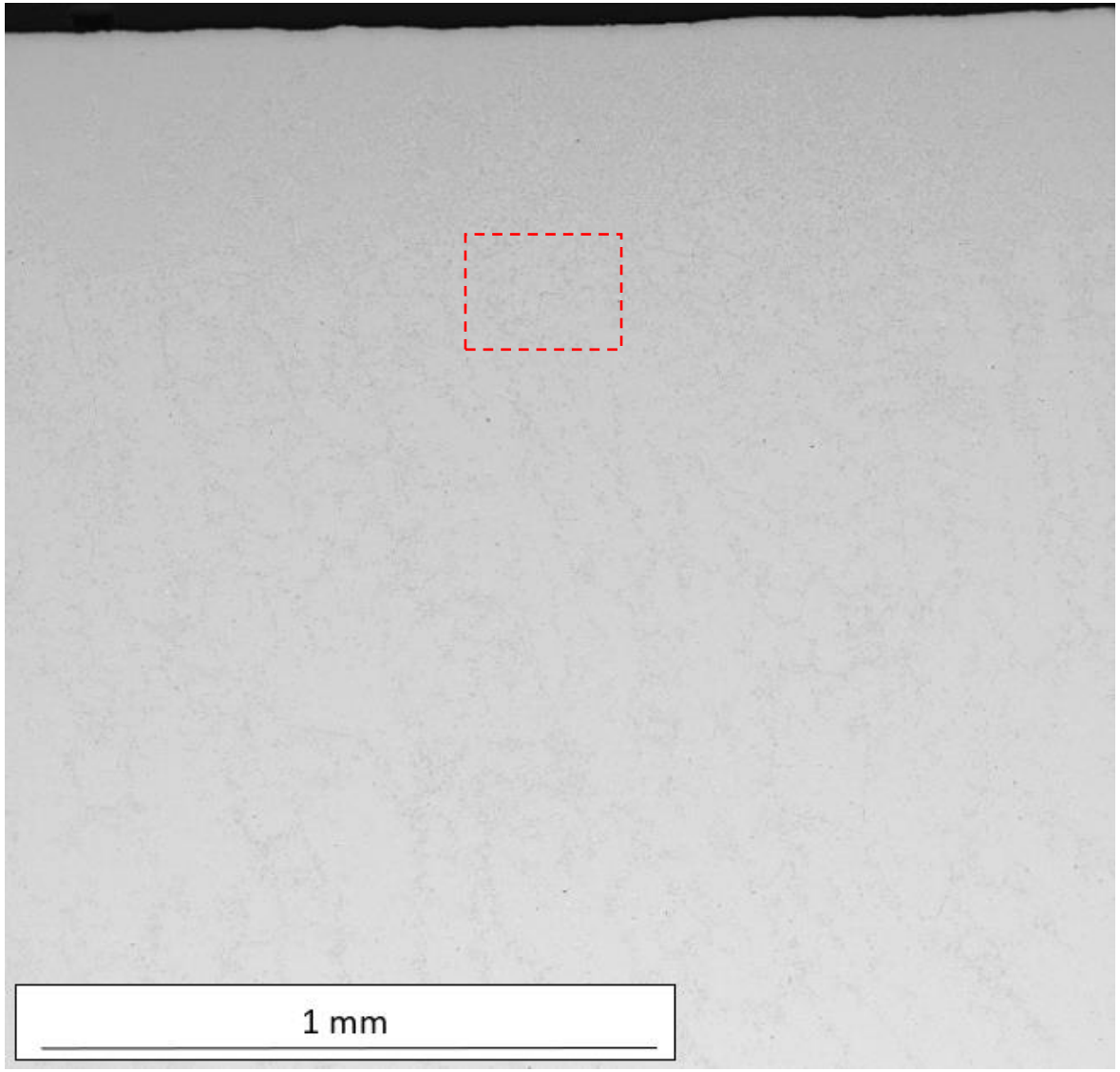
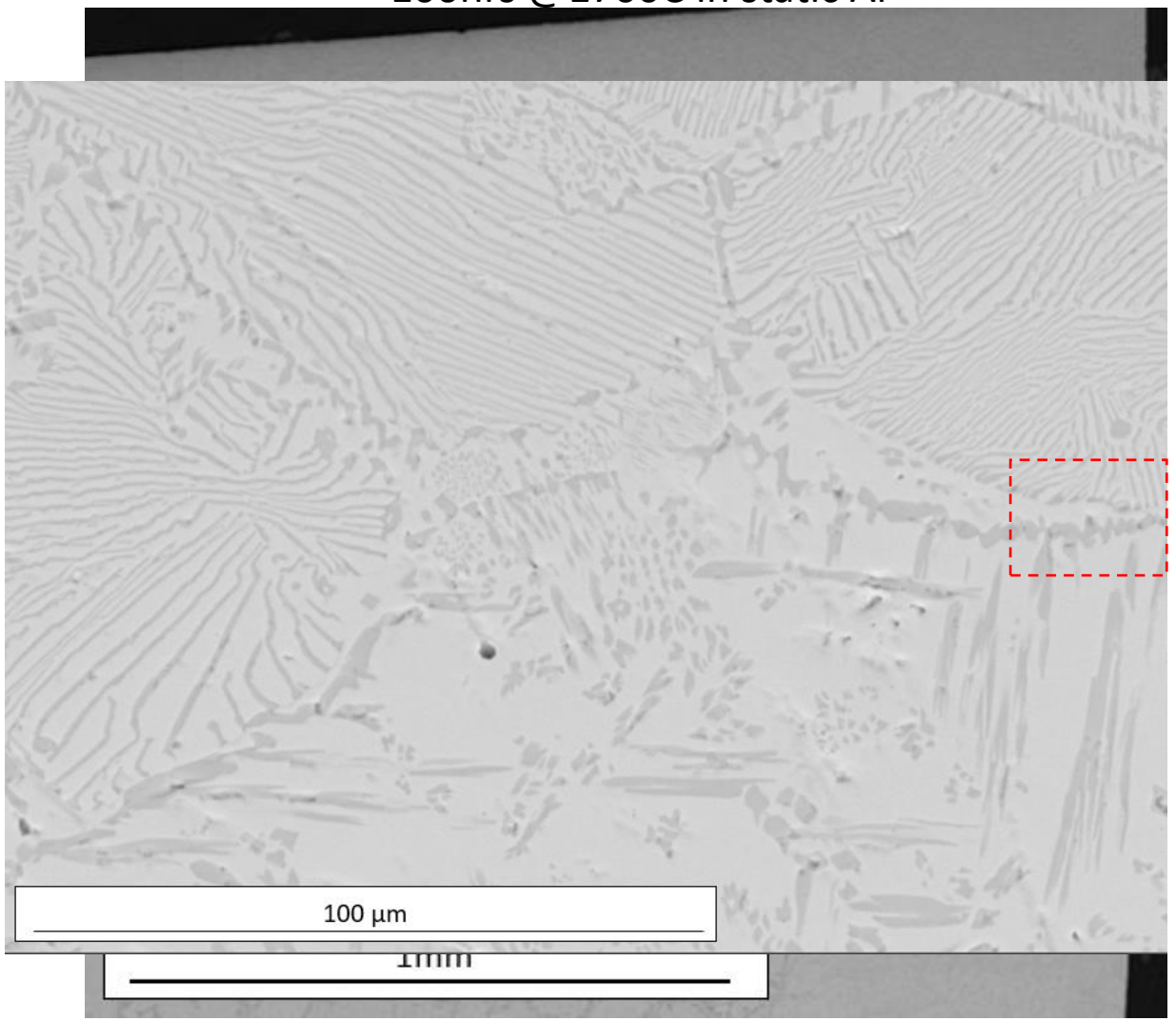
Nb30Mo Flowing vs Static Ar

68hrs @1700C in flowing Ar



100hrs @1700C in static Ar



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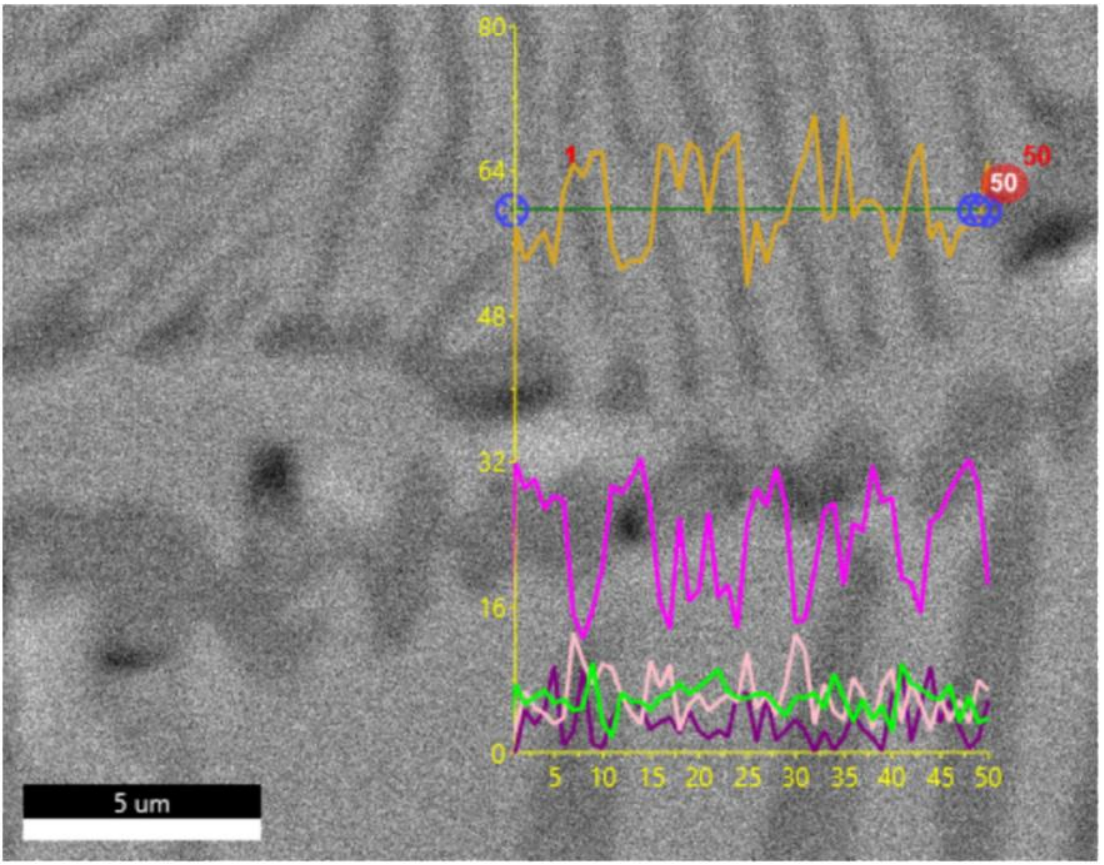
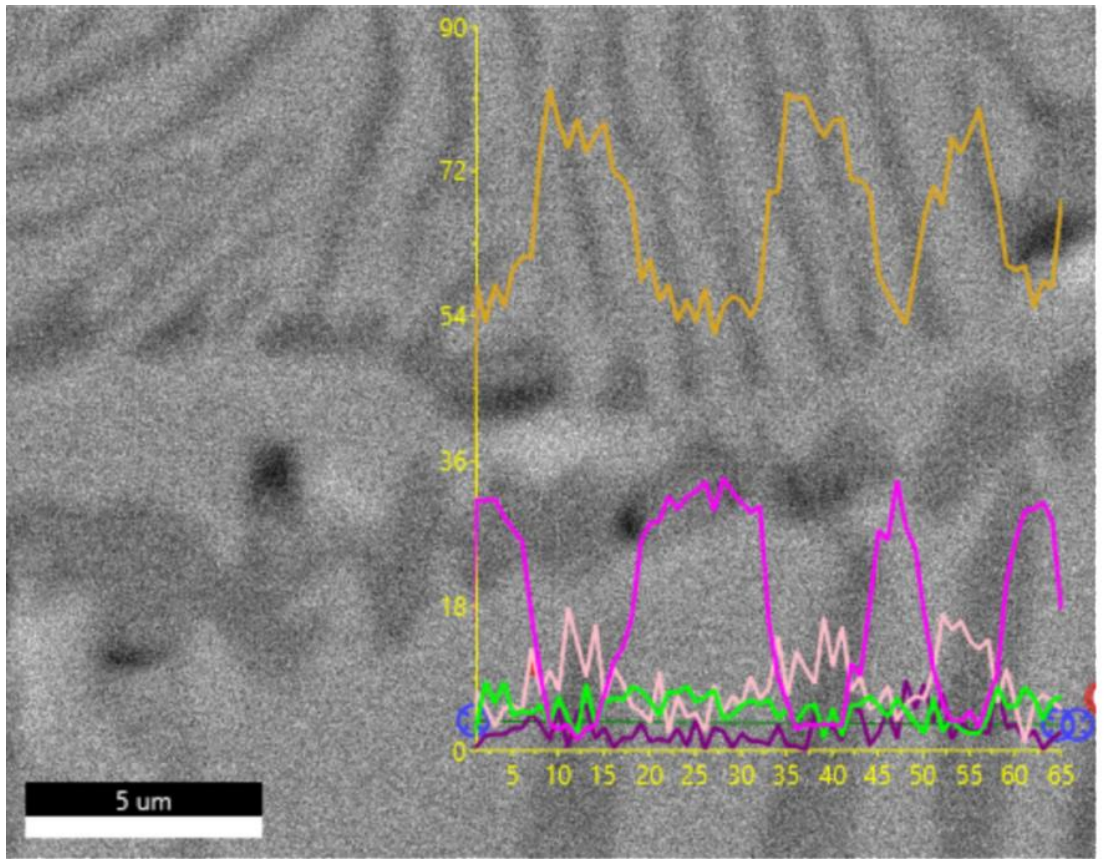
Nb30Mo EDS Line Scan

68h @ 1700˚C in flowing Ar





Takeaway: Dark areas are high in N.

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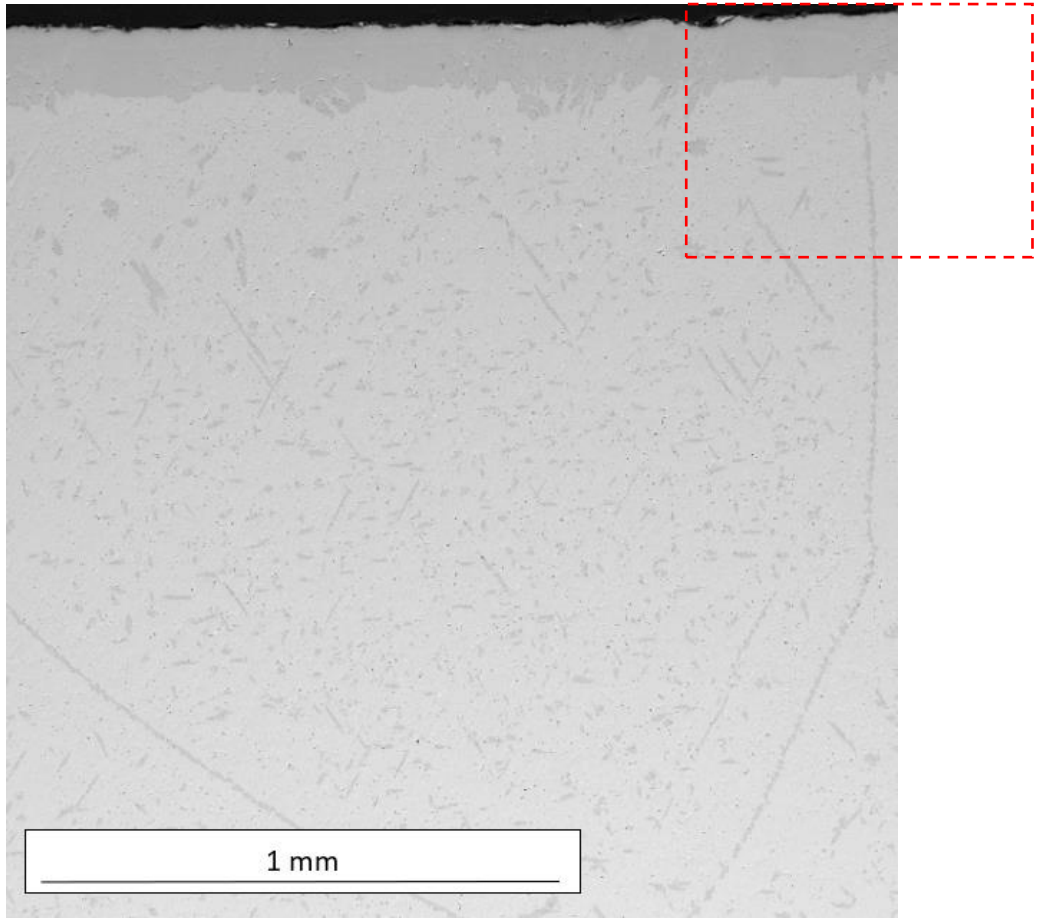
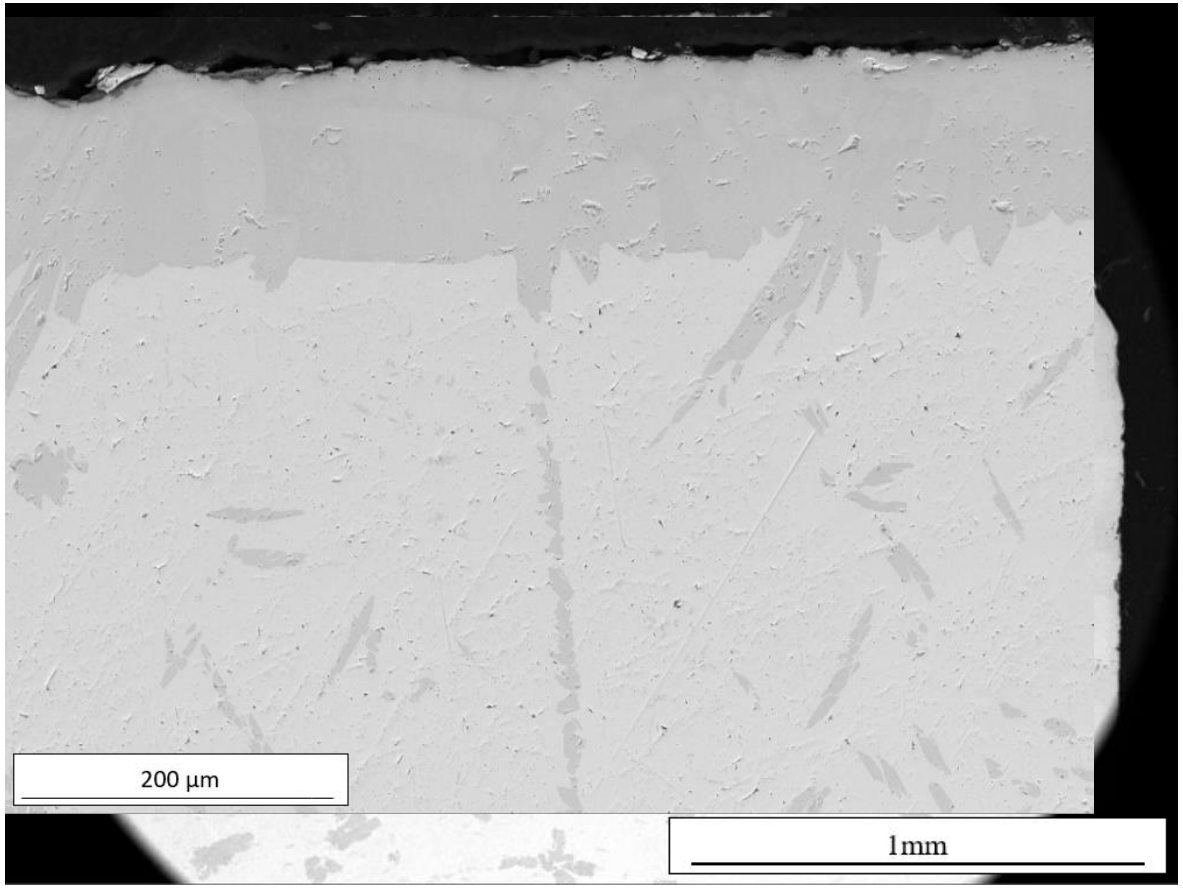
Nb7.5Ta Flowing vs Static Ar

68hrs @1700C in flowing Ar



100hrs @1700C in static Ar



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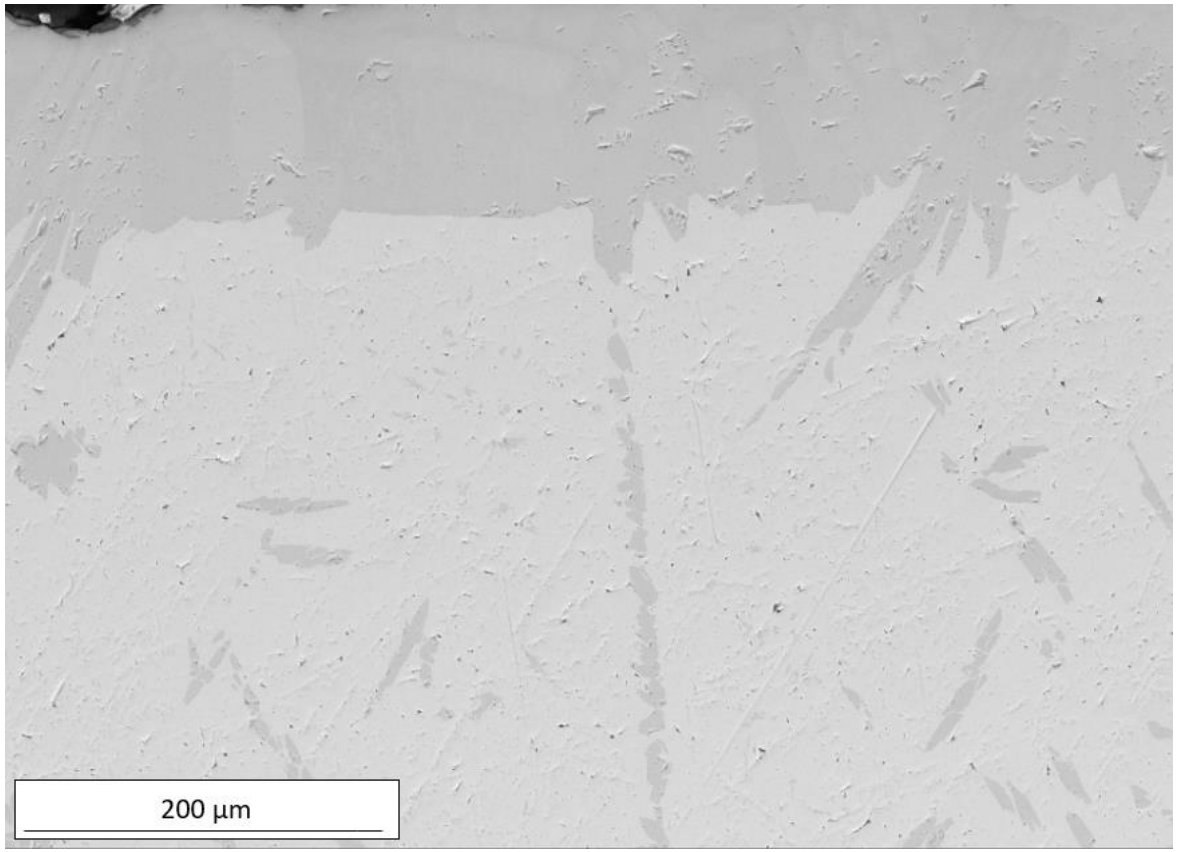
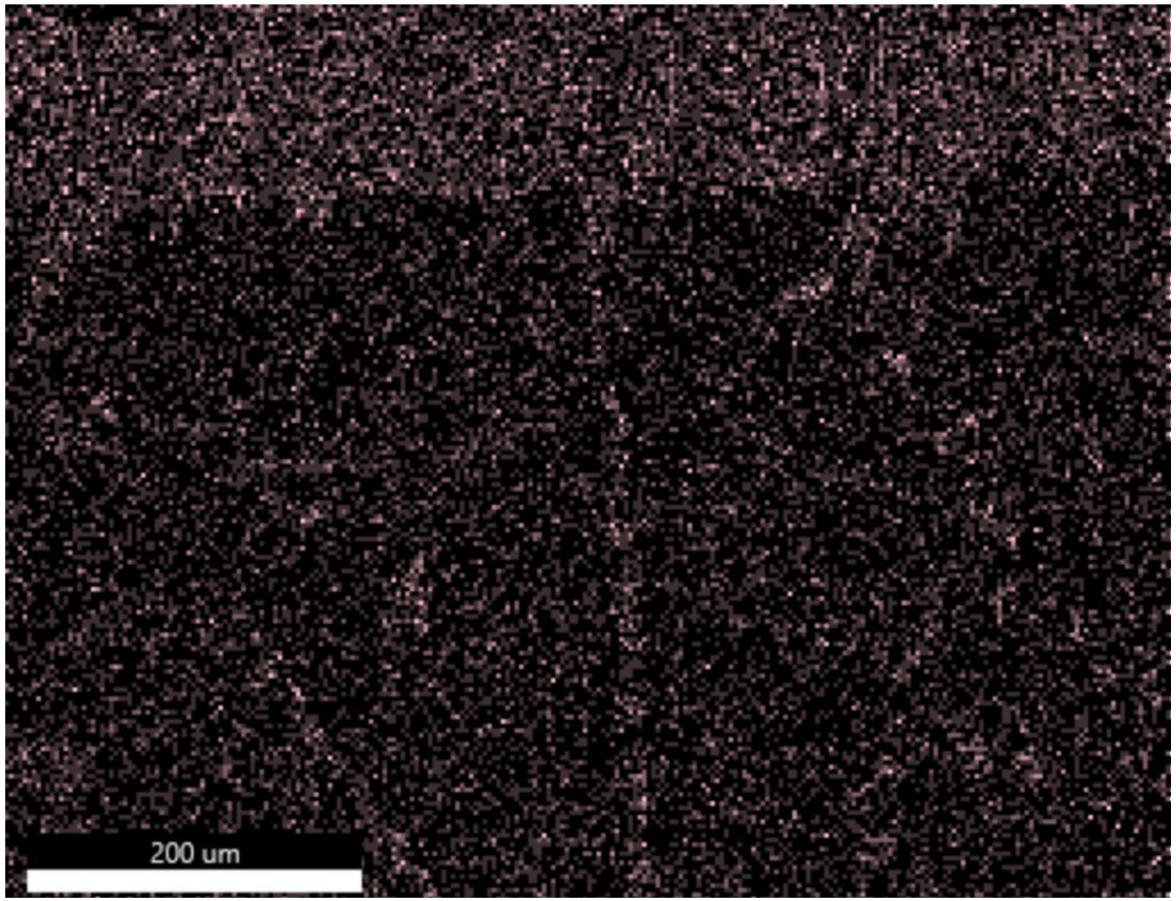
Nb7.5Ta EDS Nitrogen Map

68h @ 1700˚C in flowing Ar





Takeaway: Dark areas are high in N.

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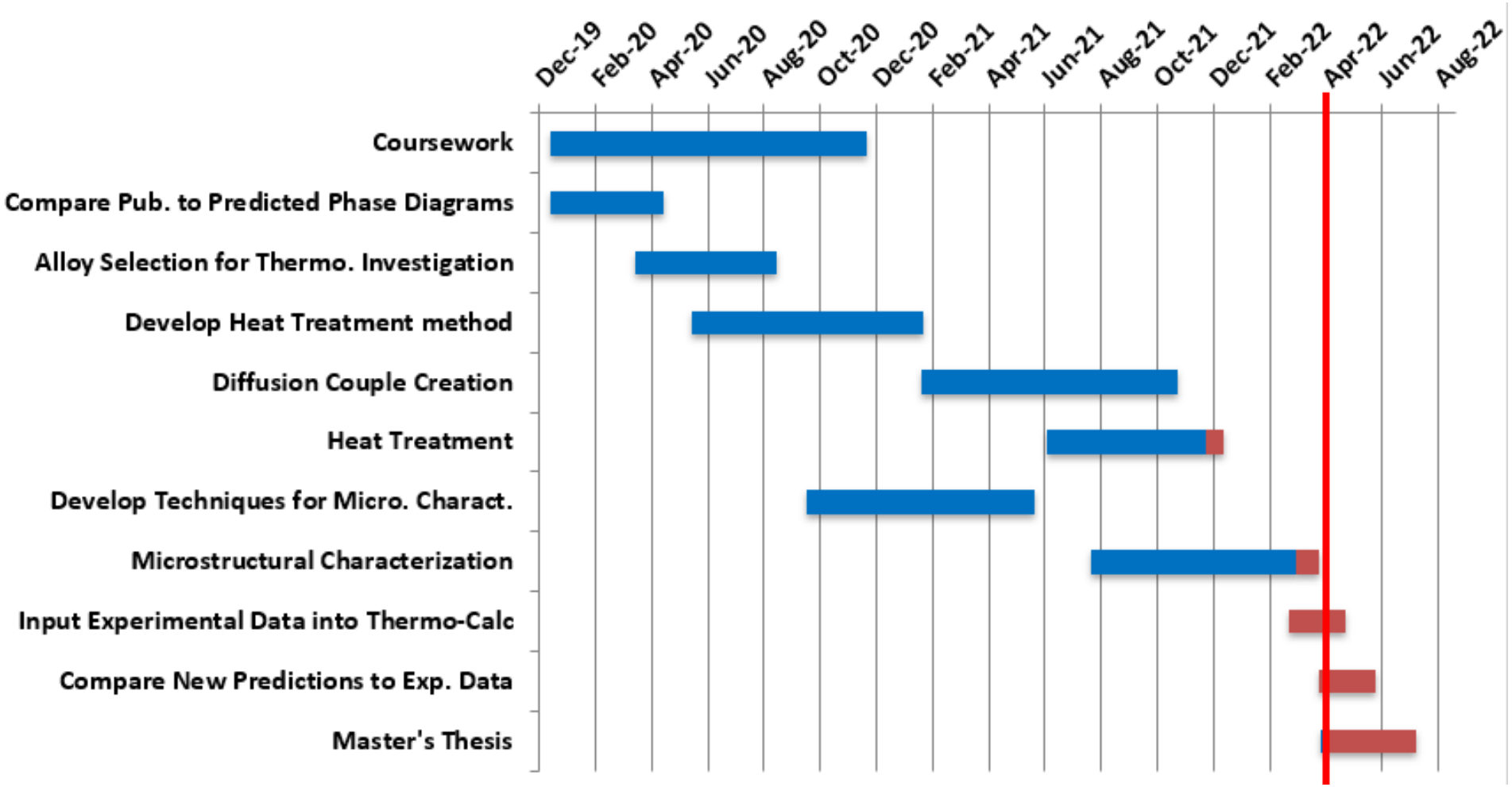
Gantt Chart



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Challenges & Opportunities

- Challenges so far
  - Heat treatments
    - Hot press had vacuum issues that took multiple weeks to fix
    - Finding furnace for long term heat treatments
    - Oxygen, carbon, and nitrogen contamination
  - Juggling a baby and research responsibilities
- Opportunities
  - Developing process for heat treating refractories alloys at Mines
  - Spending a lot of time with my daughter

Thank you!

Bobby Puerling
rppuerling@mines.edu

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[4] D. B. Miracle, O. N. Senkov, J. M. Scott, G. B. Wilks, and Air Force Research Lab Wright-Patterson Afb Oh Materials And Manufacturing Directorate, “Mechanical Properties of Nb25Mo25Ta25W25 and V20Nb20Mo20Ta20W20 Refractory High Entropy Alloys (Postprint),” May 2011.

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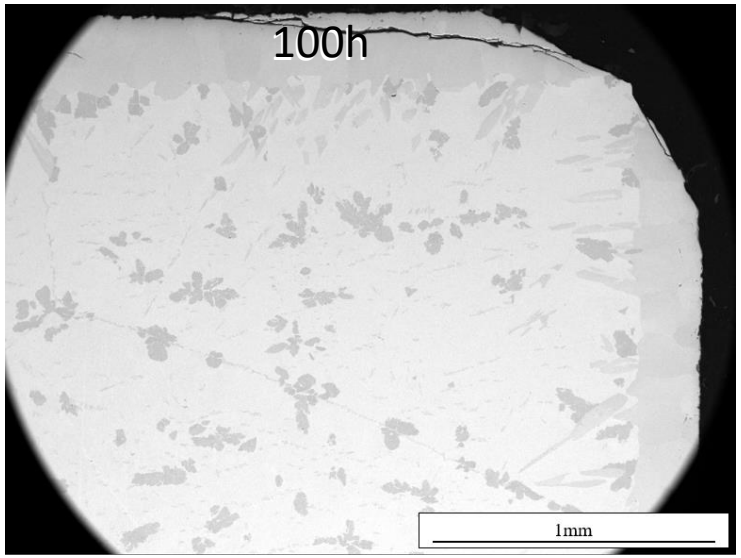
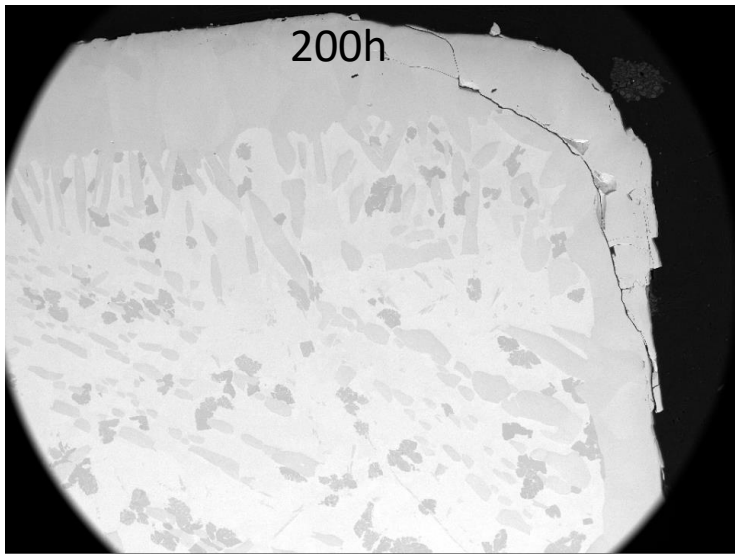
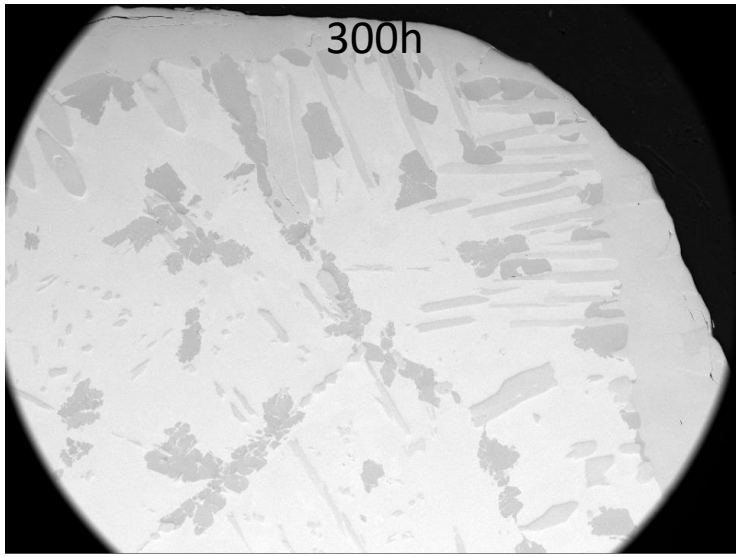
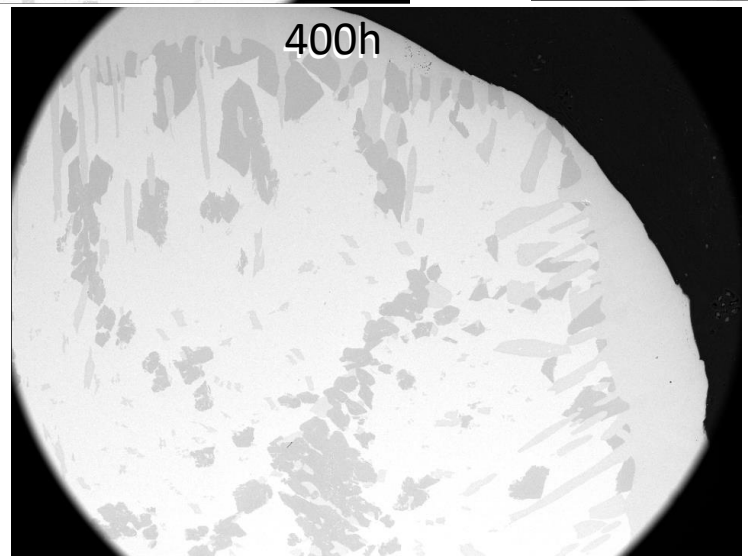
Nb7.5Ta Witness Samples

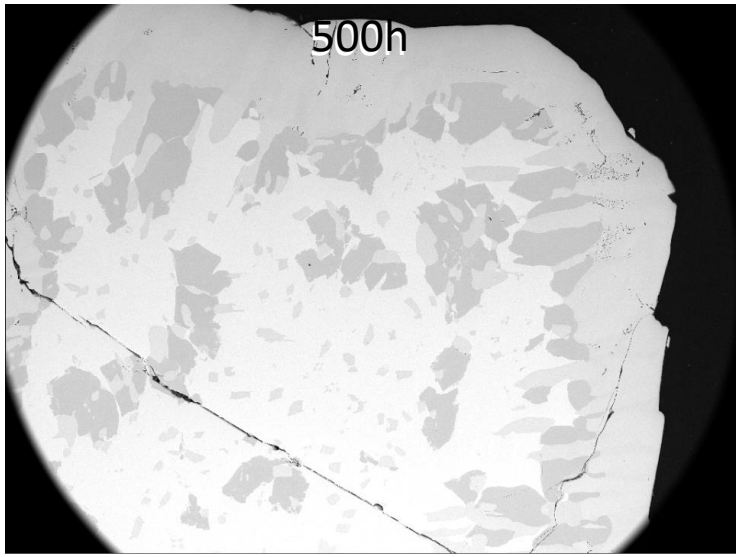
1700˚C in static Ar











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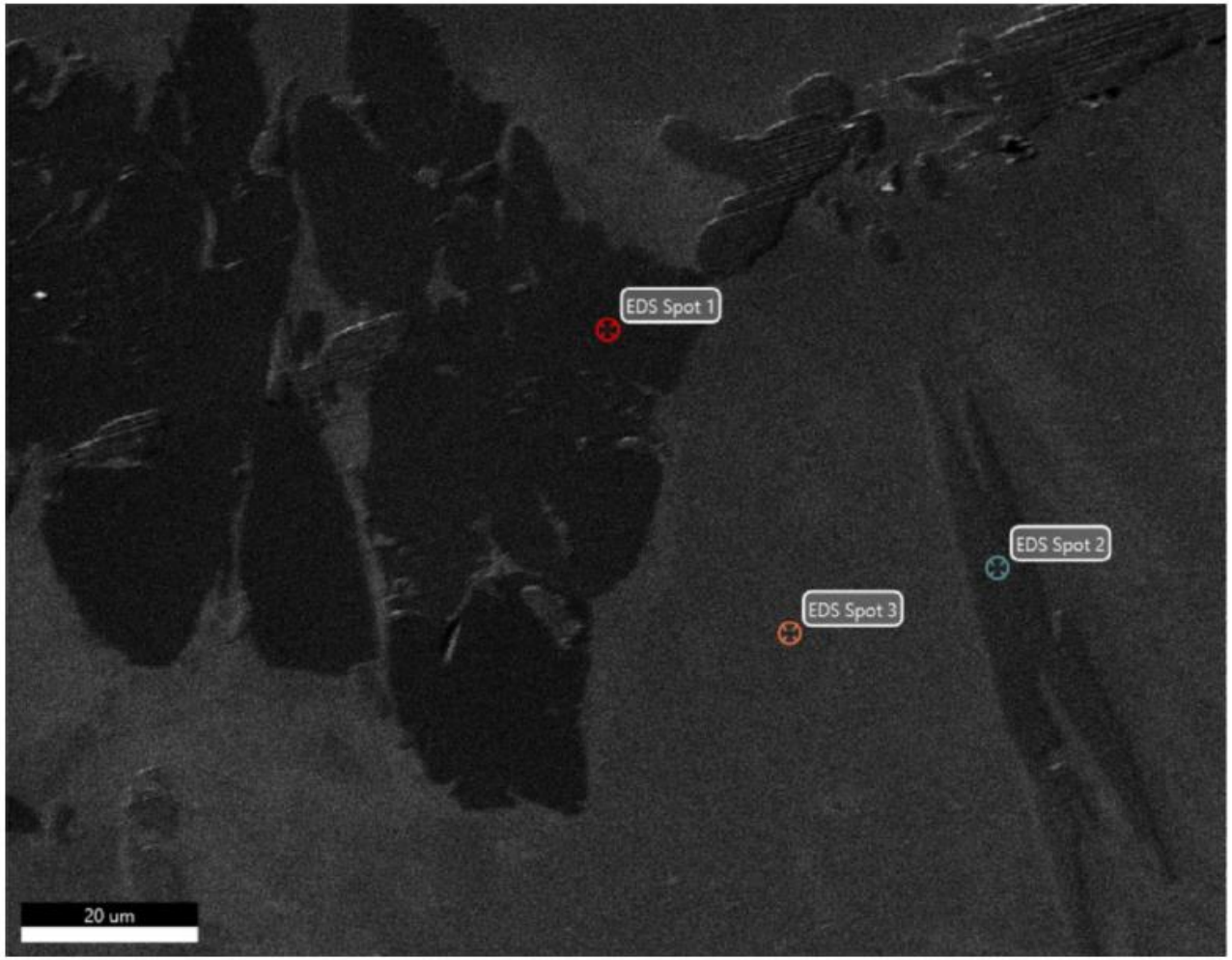
Nb7.5Ta EDS Spot Scans

100h @ 1700˚C in static Ar



Takeaway: O and C contamination.

Smart Quant Results

Element	Weight %	Atomic %	Error %
Witness Samples | Nb7.5Ta 100hrs | Area 3 | EDS Spot 1			
C K	7.63	23.36	17.64
O K	21.52	49.48	10.84
NbL	66.18	26.21	10.03
TaM	4.68	0.95	19.43
Witness Samples | Nb7.5Ta 100hrs | Area 3 | EDS Spot 2			
C K	17.13	56.43	14.98
O K	4.53	11.2	17.5
NbL	73.62	31.34	9.76
TaM	4.72	1.03	21.84
Witness Samples | Nb7.5Ta 100hrs | Area 3 | EDS Spot 3			
C K	6.38	31.97	21.19
O K	3.08	11.61	19.03
NbL	83.4	54.05	9.68
TaM	7.14	2.38	13.77

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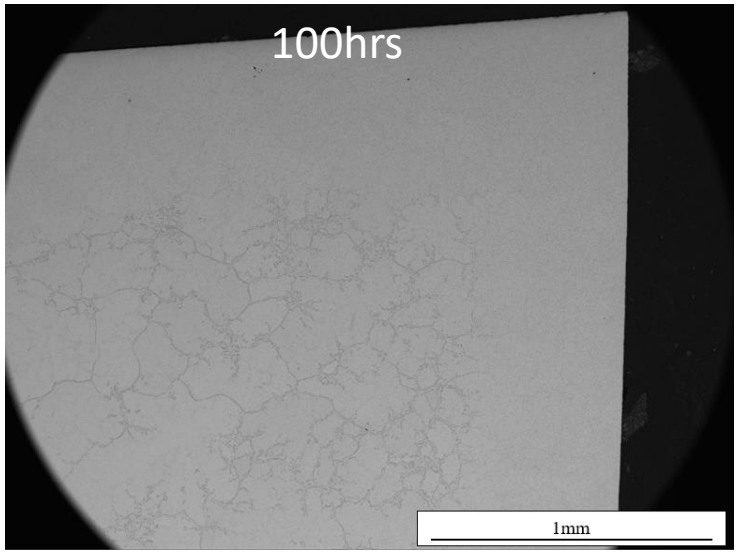
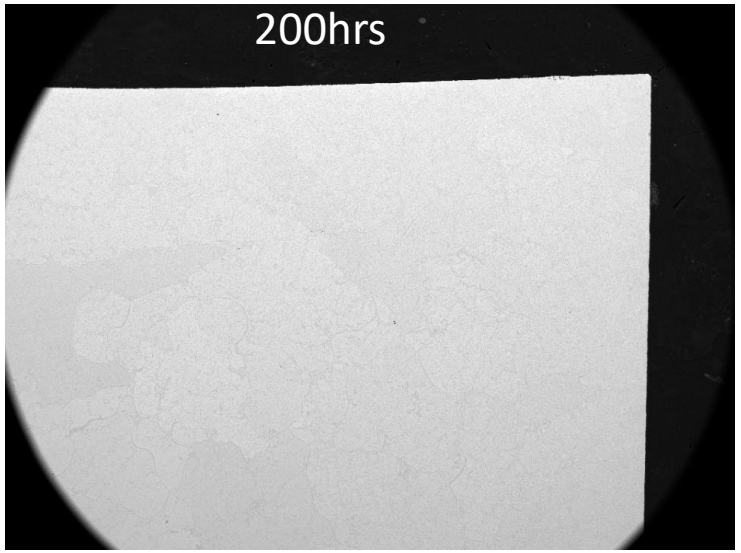
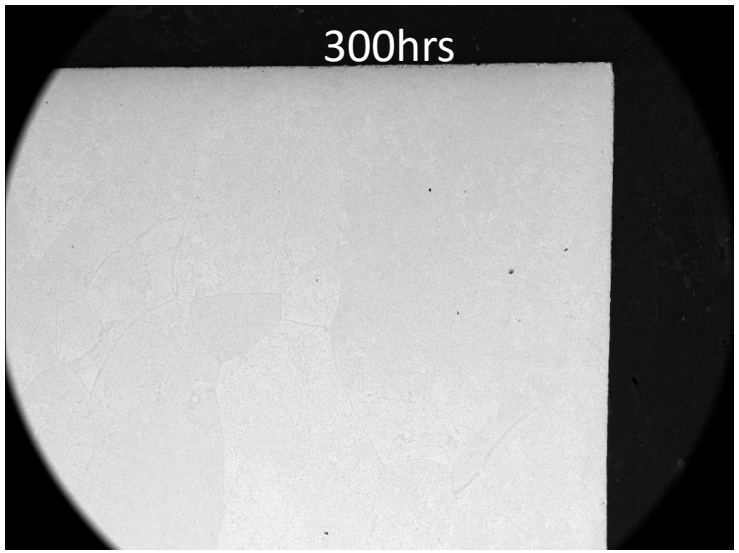
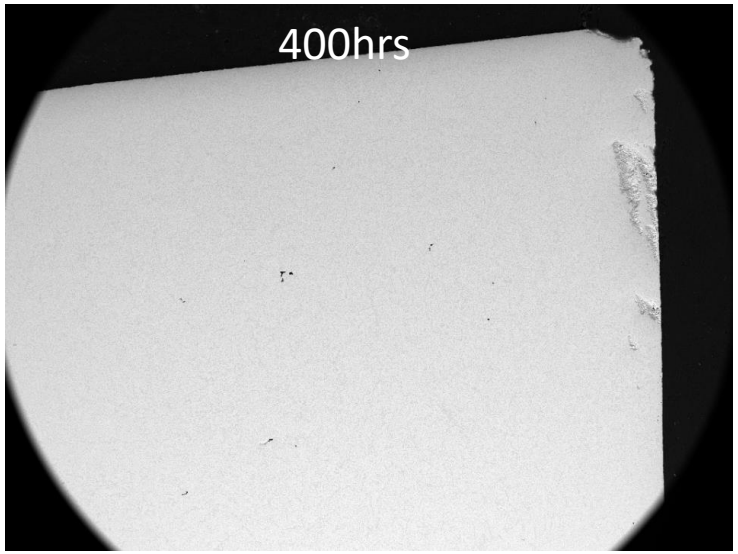
Nb30Mo Witness Samples

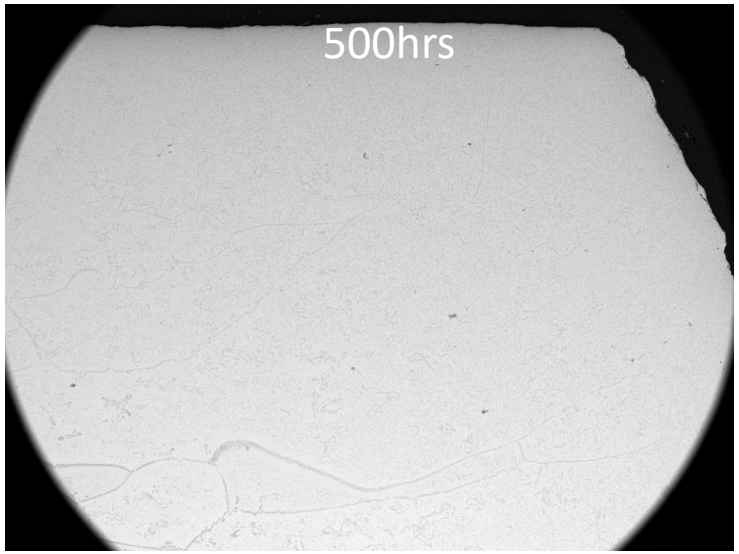
1700˚C in static Ar











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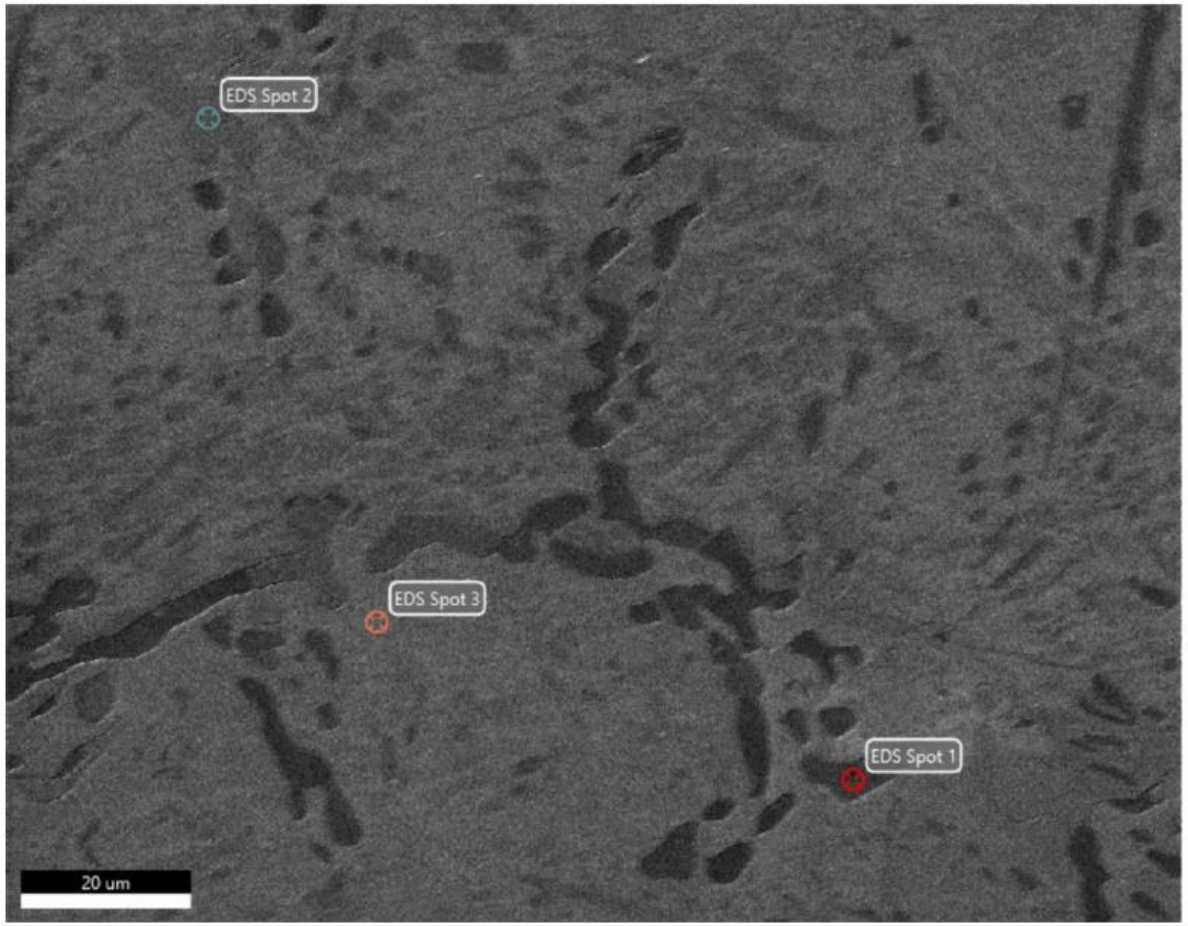
Nb30Mo EDS Spot Scans

100h @ 1700˚C in static Ar



Smart Quant Results

Element	Weight %	Atomic %	Error %
Witness Samples | Nb30Mo 100hrs | Area 8 | EDS Spot 1			
C K	9.87	28.14	16.86
N K	0.47	1.14	89.72
O K	21.26	45.51	10.88
NbL	68.25	25.16	9.33
MoL	0.15	0.05	99.99
Witness Samples | Nb30Mo 100hrs | Area 8 | EDS Spot 2			
C K	20	58.37	13.78
N K	3.57	8.93	26.45
O K	2.13	4.68	25.75
NbL	73.25	27.64	9.2
MoL	1.05	0.38	87.29
Witness Samples | Nb30Mo 100hrs | Area 8 | EDS Spot 3			
C K	14.34	53.54	15.44
N K	0.01	0.02	99.99
O K	2.38	6.68	20.3
NbL	54.37	26.24	10.09
MoL	28.9	13.51	14.91

Takeaway: O and C contamination.

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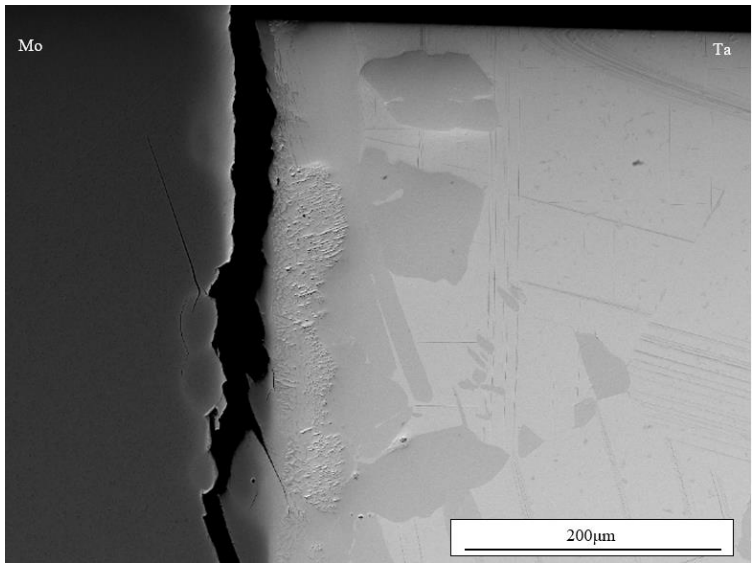
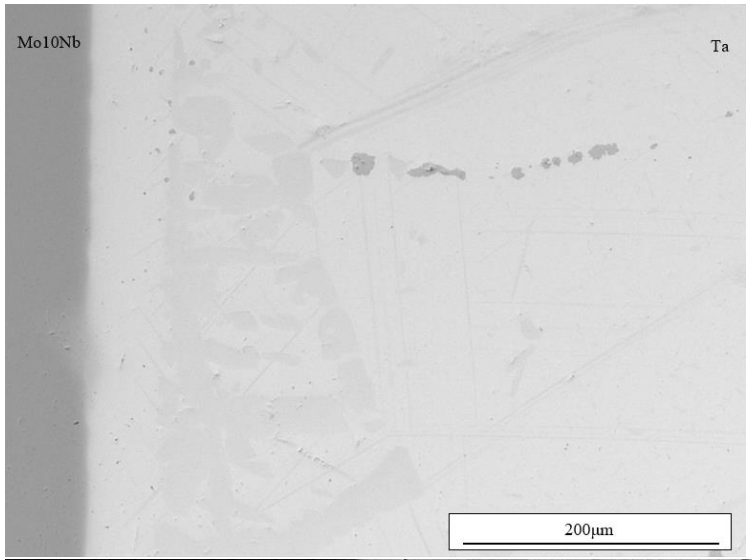
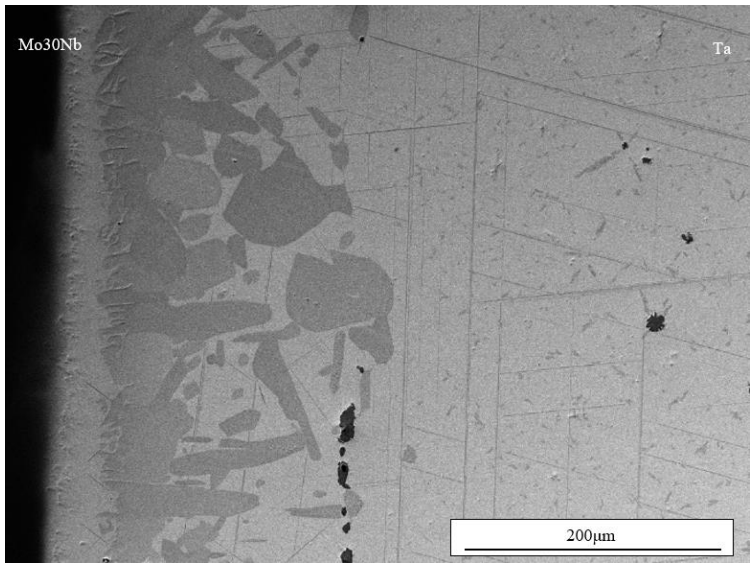
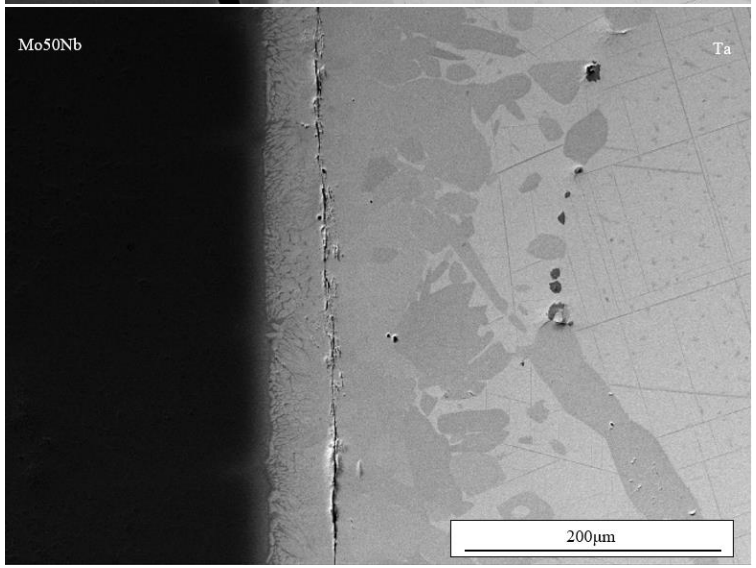
BSE Images of Diffusion Couples

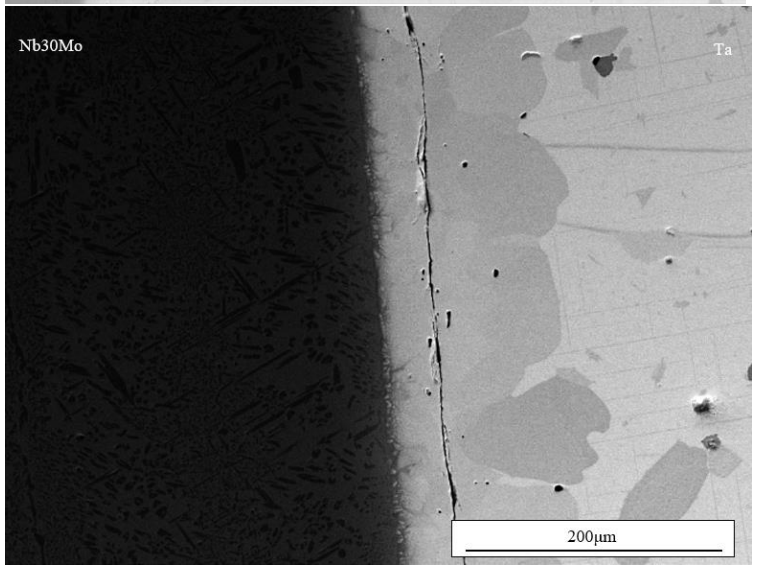
420h @ 1700˚C in static Ar

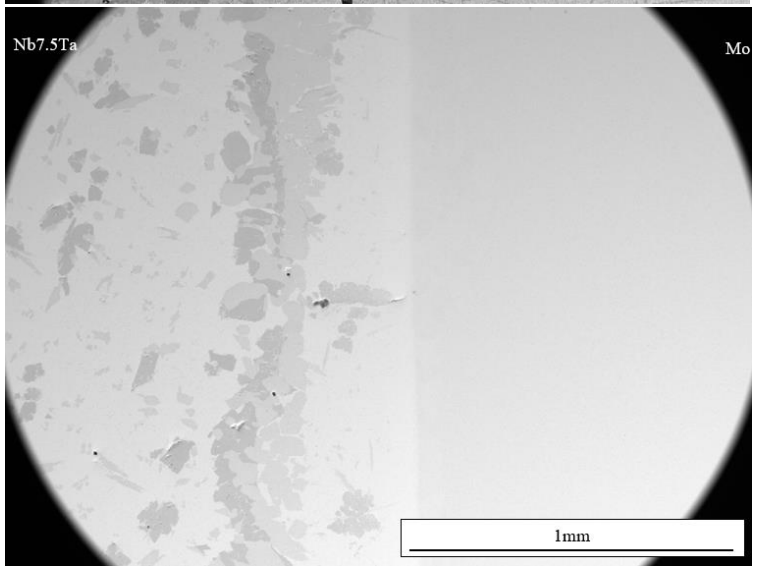












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