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Diffusion Bonding of Cu to Nb

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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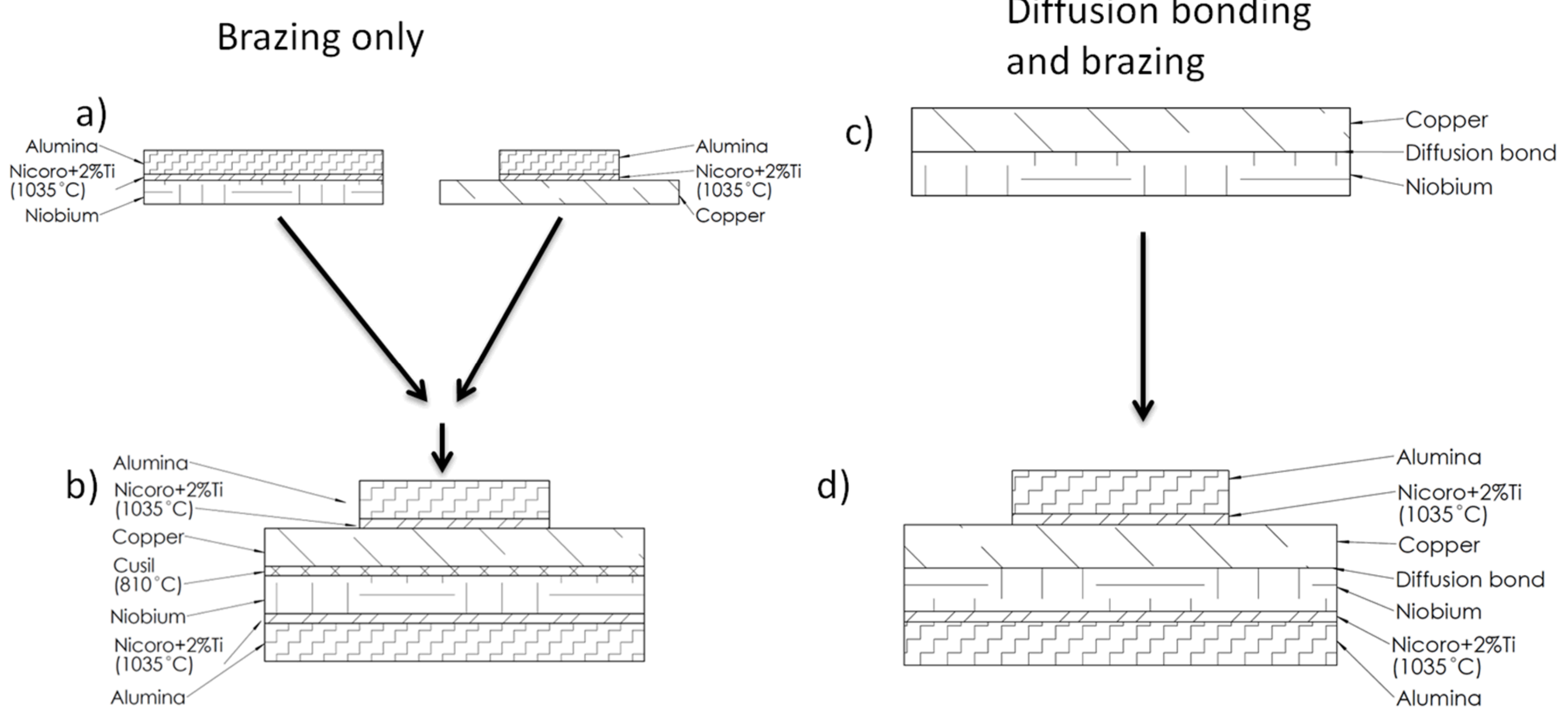
Objectives

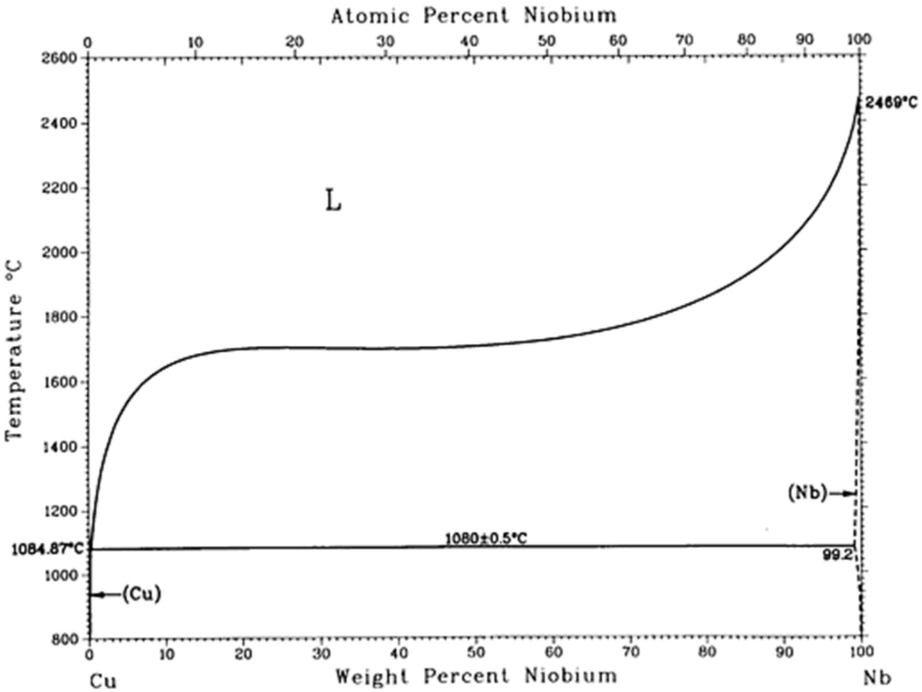
- Introduction
- Why Cu and Nb?
  - Material properties
  - Literature review
- What is diffusion bonding?
  - Parameters affecting bonding
- Experimental procedure
- Results
- Conclusions
- Future work

Introduction

- Join two ceramic components
- Current method multiple braze cycles
  - Alumina to Nb, Cu to Nb, Cu to alumina
- Goal: Join two ceramic components
  with an optimized diffusion bonded
  Cu-Nb substrates

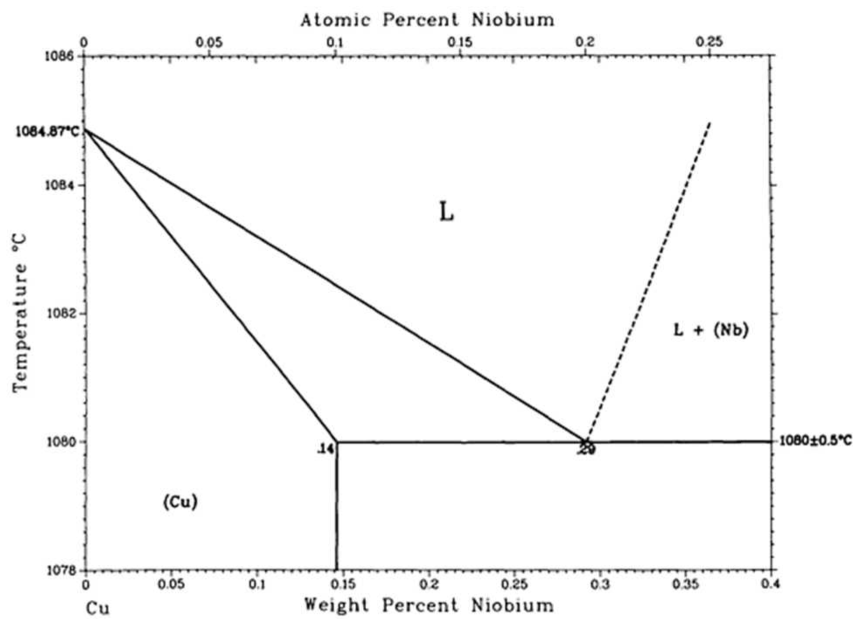


Why Cu and Nb?



Cu-Nb phase diagram

Advantages
-Braze ability
-No intermetallic formation



Enlargement of the Cu-rich portion of the Cu-Nb system.

Difficulties
-Limited solubility
-Different melting temperatures

T. Massalski, Binary alloy phase diagrams, 1, 938-939, (1986)

Material properties: Cu and Nb

Crystal structure and physical properties for Cu and Nb [15, 16]

	Cu	Nb
Crystal structure	FCC	BCC
Atomic radius, [pm]	128	146
Cell parameter 'a', [pm]	361.49	330.04
Space-group	Fm-3m	Im-3m
CTE, [µm/m/K]	16.5×10^{-6}	7.3×10^{-6}
Melting point, [°C]	1084	2469

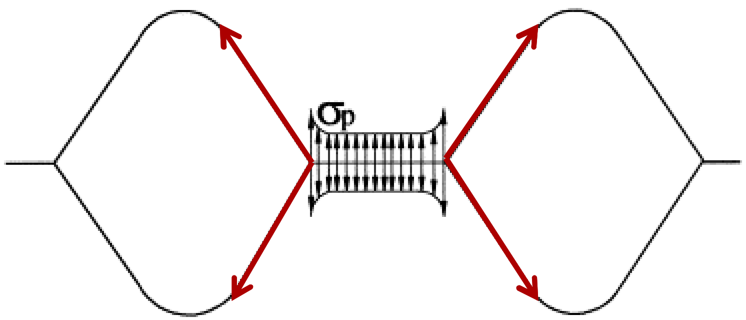
$\boxed{T_m(Cu) << 0.5\, T_m(Nb)}$

Cu-Nb diffusion bonding research

- **The diffusion bonding of Cu to Nb has not been presented in any research**
- **The diffusion of Cu into Nb or Nb into Cu has not been presented or observed in any research.**
- Research on ARB (accumulative roll bonding) of Cu to Nb, and annealing nanolayerd Cu-Nb stacks
  - No diffusion was observed or presented in either
  - ARB demonstrated tensile strengths of the Cu-Nb stack both parallel and perpendicular to the rolling direction; tensile strength:1 GPa
- Other diffusion bonded materials
  - Cu-alumina
  - Nb-alumina

What is diffusion bonding?

- Solid state joining of similar or dissimilar components
- Mechanisms during diffusion bonding
  - Deformation mechanisms
  - Diffusion mechanisms



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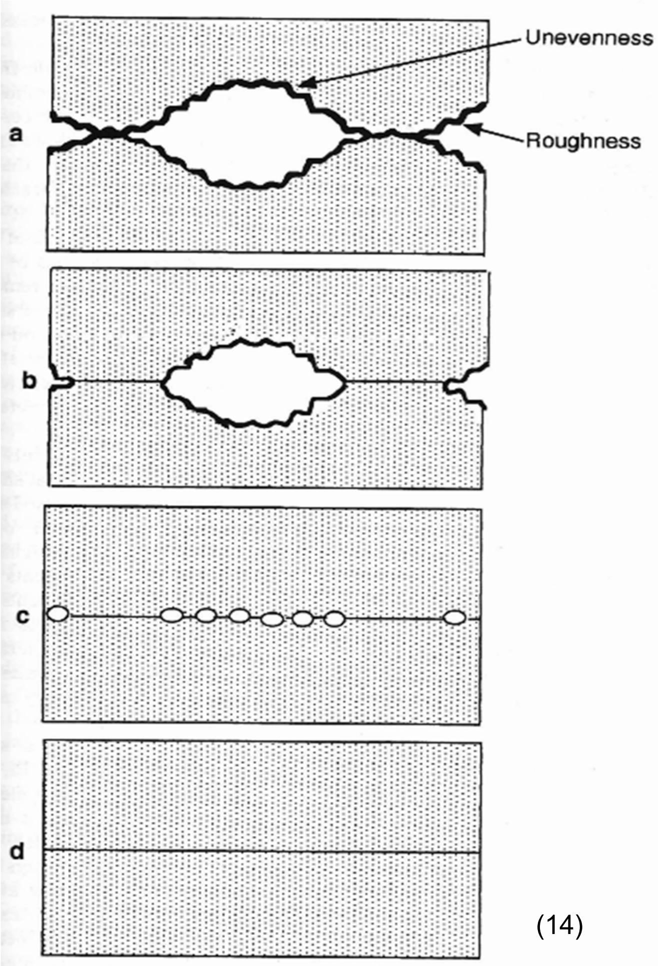

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Maxwell relation*

$$\left(\frac{\partial \mu}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial N}\right)_{T,p}$$

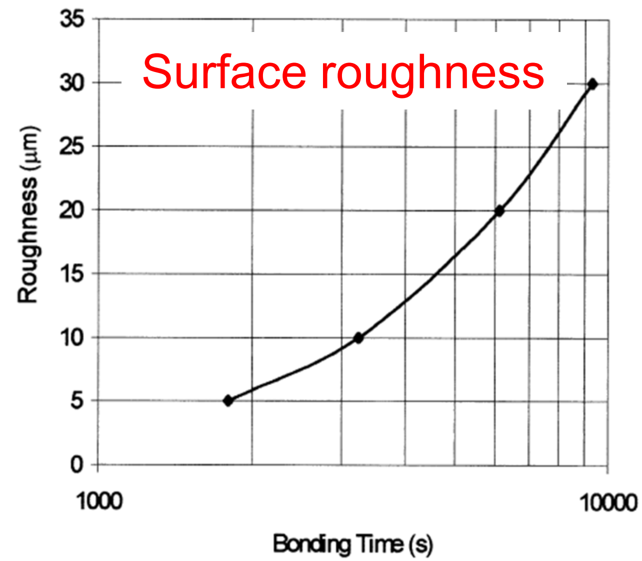
Derived from
Gibbs free energy eq.*

$$\mu = -\sigma dT + \nu dp; \frac{S}{N} = \sigma, \frac{V}{N} = \nu$$

*K. Stowe, *Introduction to statistical mechanics and thermodynamics*, John Wiley and sons, New York, 209-231, (1984)

Parameters that affect bonding

- Surface preparation
  - Surface roughness
  - Cleanliness
- Temperature
- Pressure
- Time



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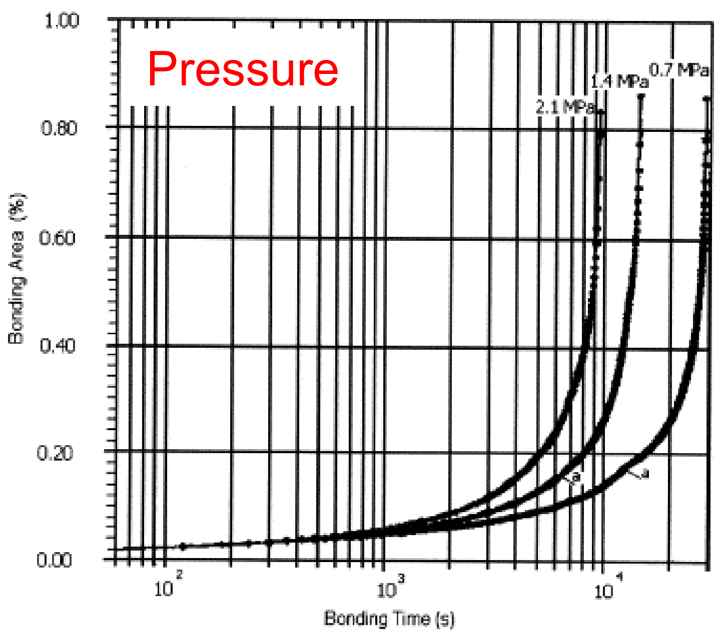

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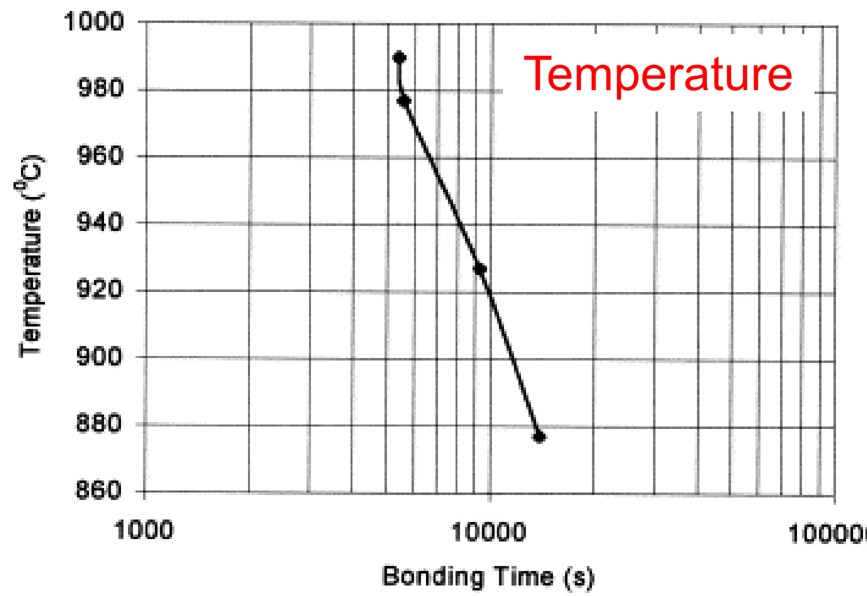

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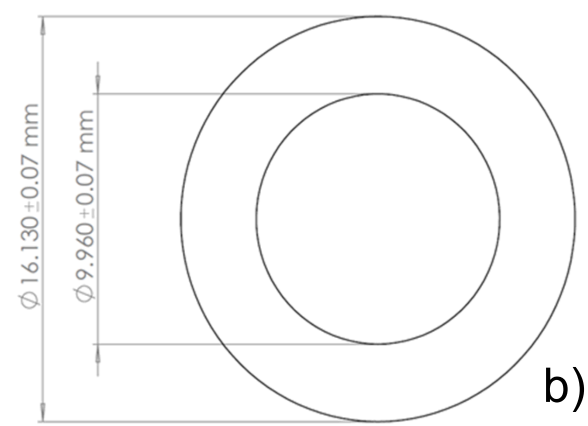
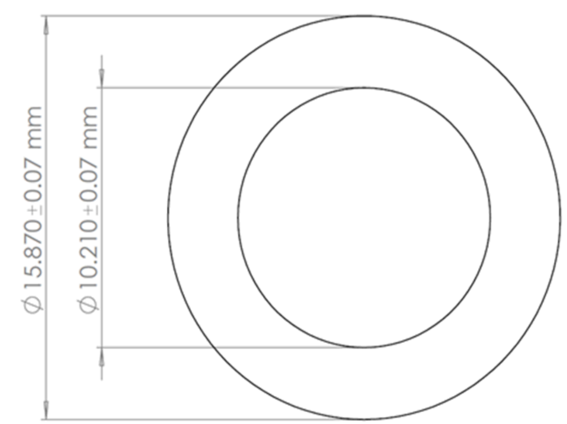
Sample preparation for diffusion bonding and brazing

- Diffusion bonding
  - Cut samples
  - Degrease samples in a Lenium vapor degreaser
  - Vacuum anneal Nb 1400^{o}C
- Brazing
  - Wire EDM Cu-Nb washers from bonded substrates (image a)
  - Bake Cu-Nb substrates (800^{o}C) to remove machining oils
  - Punch Nicoro®+2%Ti braze washers 9image b)

a)



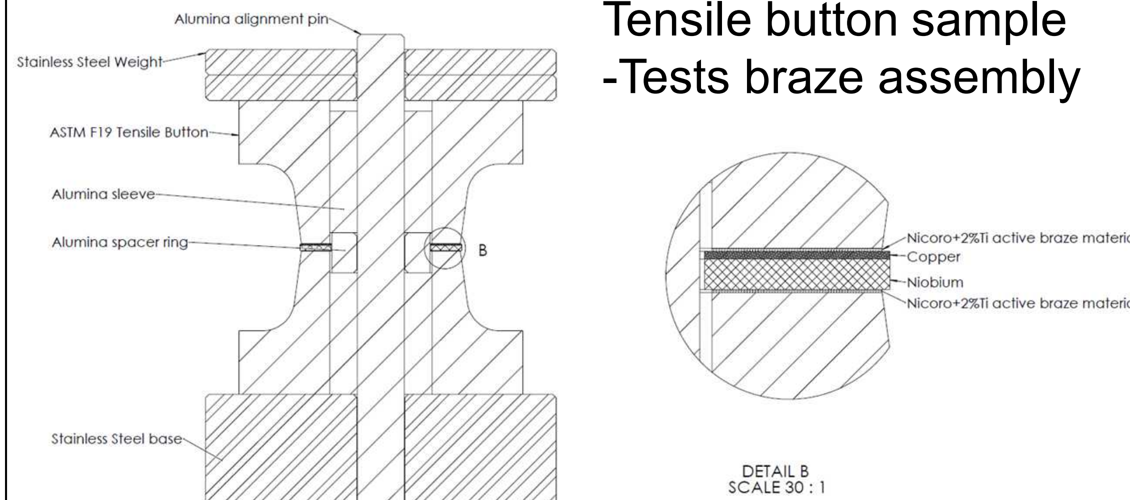
b)



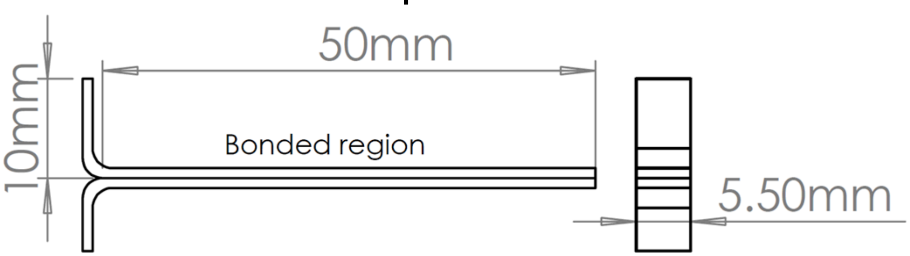
Sample analysis for diffusion bonding and brazing

- Braze samples with Nicoro®+2%Ti
- Helium leak check with
  He mass spec leak detector
- SEM, EDS, and TEM
- Mechanical testing
  - Hardness test
  - Peel test
  - Tensile test

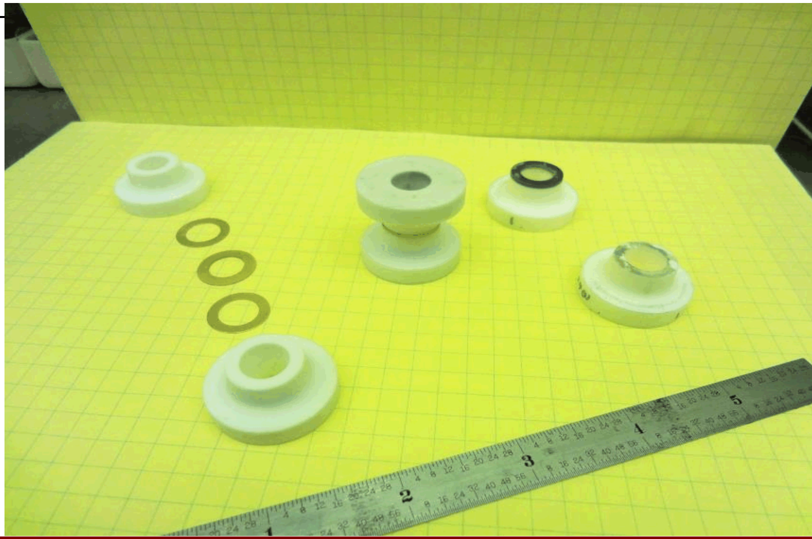
Tensile button sample
-Tests braze assembly



Peel test sample



-Tests diffusion bonded interface



Experiments

- Design of experiments to determine best bonding parameters

	Temperature [°C]	Pressure [Mpa (KSI)]	Time [Hours]	Material thickness Cu [µm]	Nb [µm]	Load applied [°C]
Run 1	950	10.3 (1.5)	0.5	127	508	950
Run 2	950	4.1 (0.6)	3	127	508	950
Run 3	1000	6.9 (1.0)	1.5	127	508	1000
Sample 1	1035	4.1 (0.6)	3	50.8	1016	1035
Run 4	1035	4.1 (0.6)	3	127	508	1035
Sample 2	1050	4.1 (0.6)	3	50.8	254	1050
Run 5	1050	4.1 (0.6)	3	127	508	1050
Run 6	1050	10.3 (1.5)	0.5	127	508	1050

Samples 1 and 2 were initial experiments
Sample 1: SEM, and tensile buttons
Sample 2: SEM
Run 1,2,4: SEM
Run 3,5,6: SEM, and tensile buttons
Run 1, 3, 5, 6: TEM

Optimization experiments

- Experiments to determine optimal bonding parameters
  - Based on SEM results from initial experiments

	Temperature [^{o}C]	Pressure [Mpa (KSI)]	Time [Hours]	Material thickness		Load applied [^{o}C]
				Cu [µm]	Nb [µm]	
Run 7	1050	10.3 (1.5)	0.25	127	508	1050
Run 8	1050	4.1 (0.6)	1.5	127	508	1050
Run 9	1050	4.1 (0.6)	0.5	127	508	1050

Run 7, 8, 9: SEM

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Recap: Experiments

- Design of experiments to determine best bonding parameters

	Temperature [°C]	Pressure [Mpa (KSI)]	Time [Hours]	Material thickness		Load applied [°C]
				Cu [µm]	Nb [µm]	
Run 1	950	10.3 (1.5)	0.5	127	508	950
Run 2	950	4.1 (0.6)	3	127	508	950
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Sample 1	1035	4.1 (0.6)	3	50.8	1016	1035
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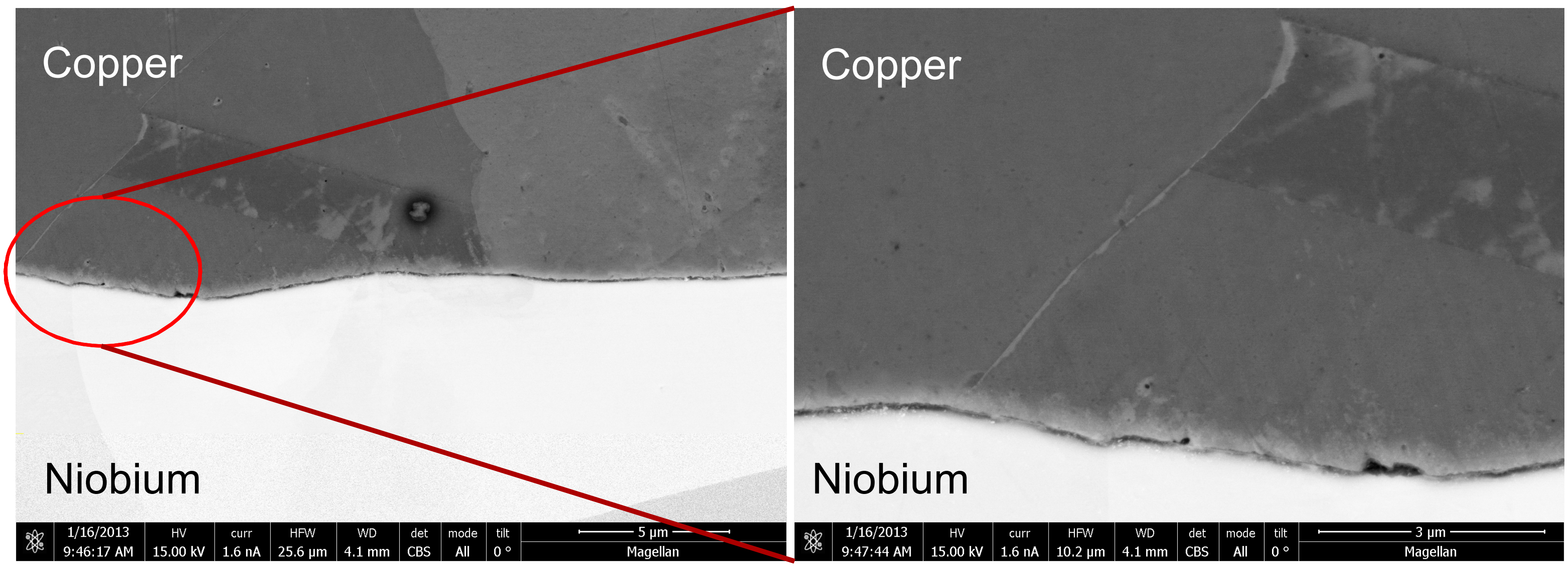
Samples 1 and 2 were initial experiments
Sample 1: SEM, and tensile buttons
Sample 2: SEM
Run 1,2,4: SEM
Run 3,5,6: SEM, and tensile buttons
Run 1, 3, 5, 6: TEM

Diffusion interface formation

- Diffusion interface formed by Cu surface self diffusion
  - Cu conforms to Nb surface
- Surface self diffusivity for Cu and Nb at 950^0C
  - Cu: $5.2x10^{-5}cm^2/sec$
  - Nb: $7.7x10^{-10}cm^2/sec$
    - $D_{Nb} << D_{Cu}$
- Cu has a much higher surface self diffusivity rate than Nb
  - Positively effects Coble creep mechanisms
  - Leads to the closure of microvoids
  - Uniformly voidless diffusion interface is formed

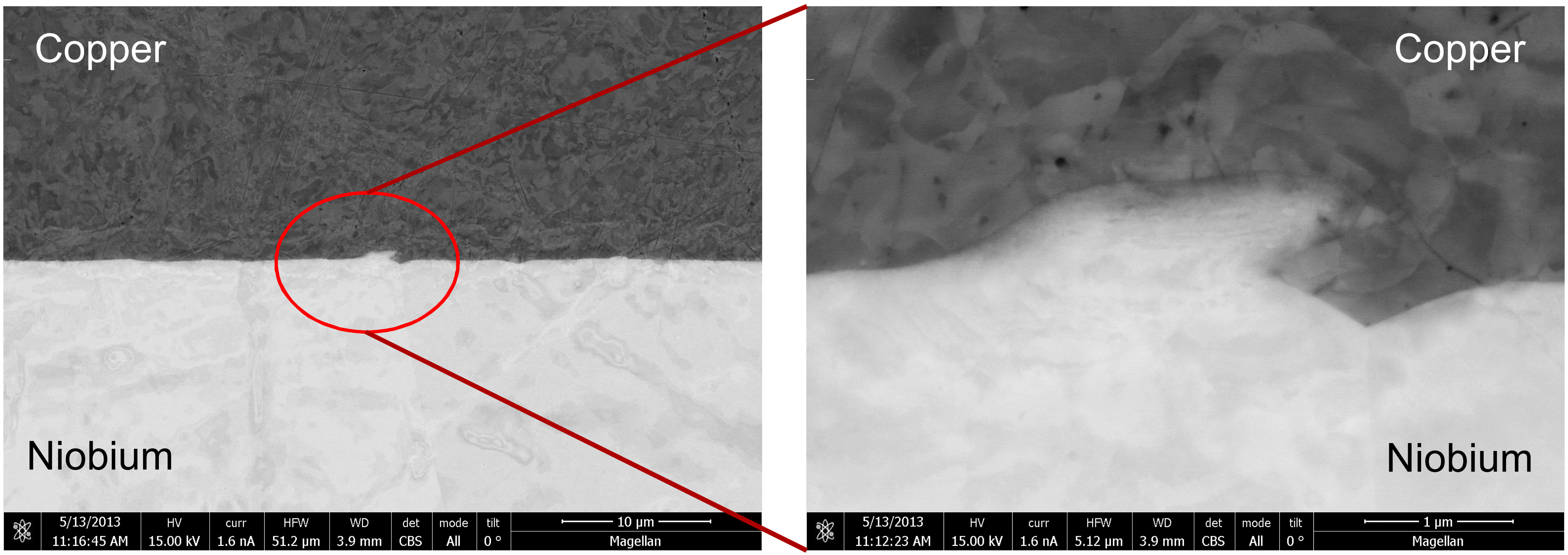
Results: SEM analysis of sample 1

- Cu-Nb diffusion bonded interface.
- Bonding parameters: **1035ºC**, 3 hours, 4.1MPa



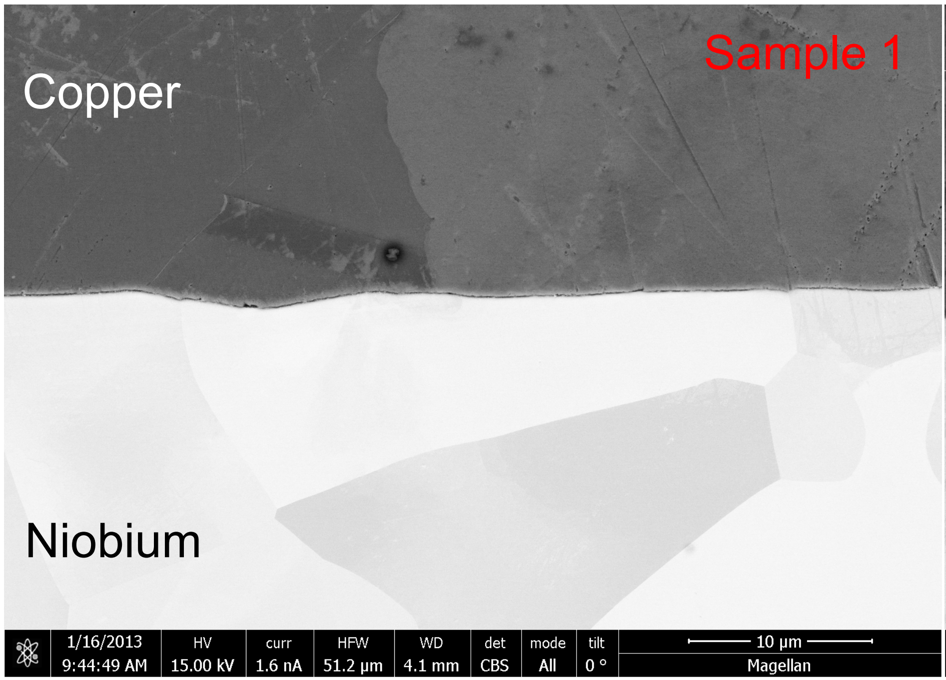
Results: SEM analysis of sample 2

- Cu-Nb diffusion bonded interface.
- Bonding parameters: **<u>1050ºC</u>**, 3 hours, 4.1MPa

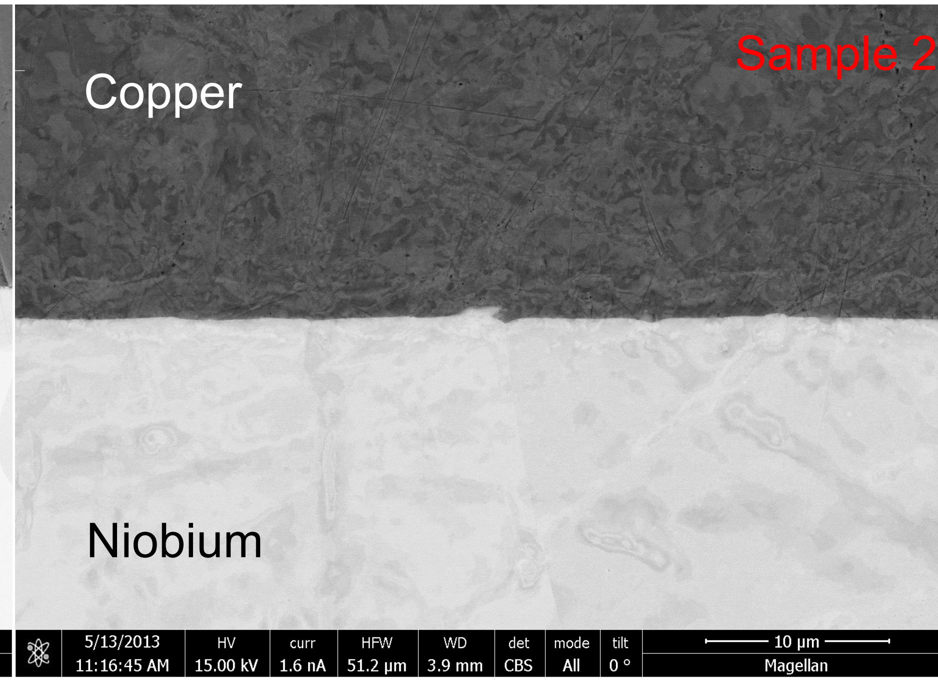


Results: Interface comparison

Bonding temperature: **1035°C**



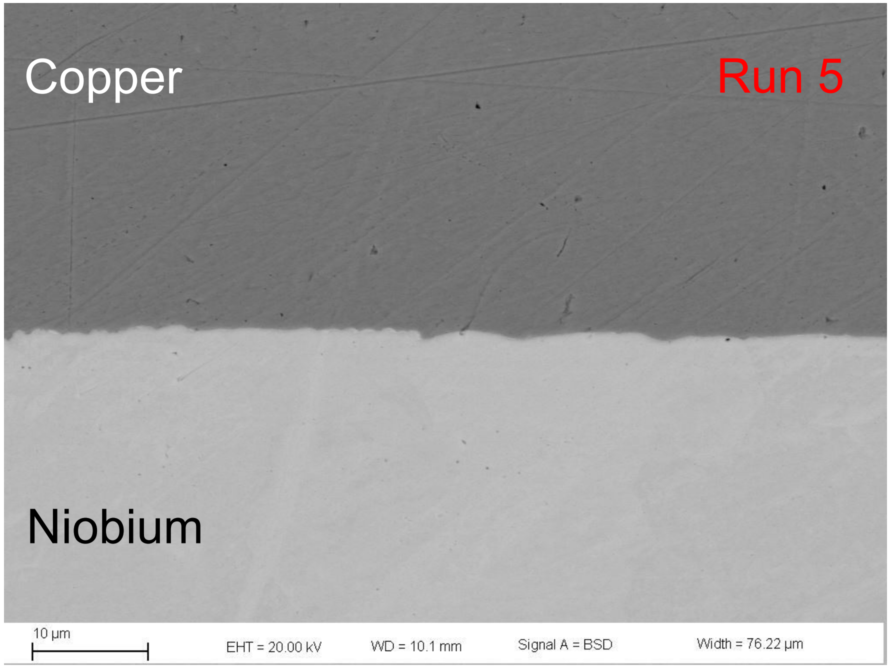
Bonding temperature: **1050°C**



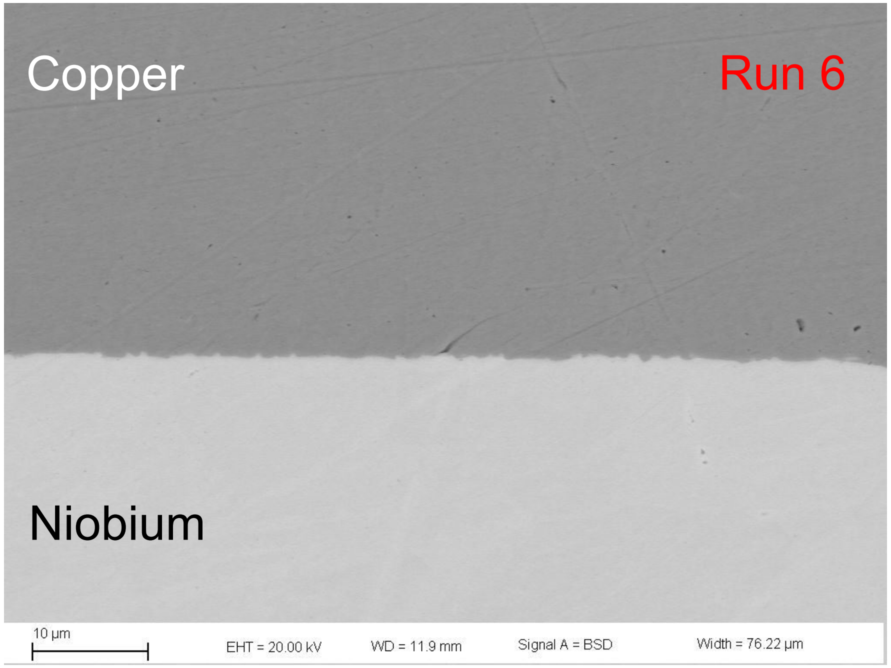
Constant bonding parameters: 3 hours, 4MPa

SEM analysis: Run 5 and 6

No interfacial voids present at Cu-Nb interface



Run 5: 1050^{o}C, 4.1 MPa, 3.0 hours

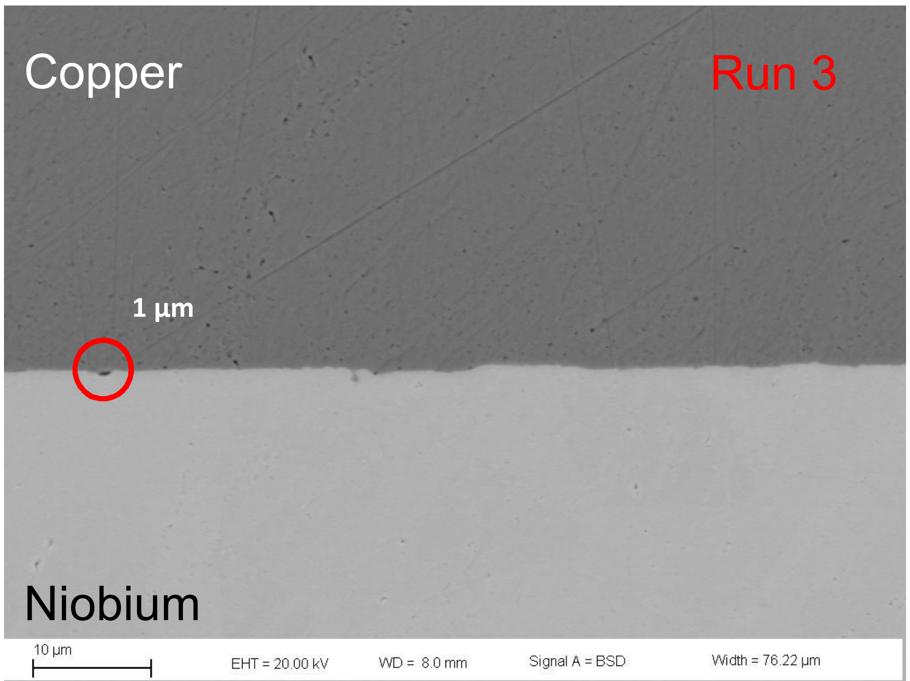


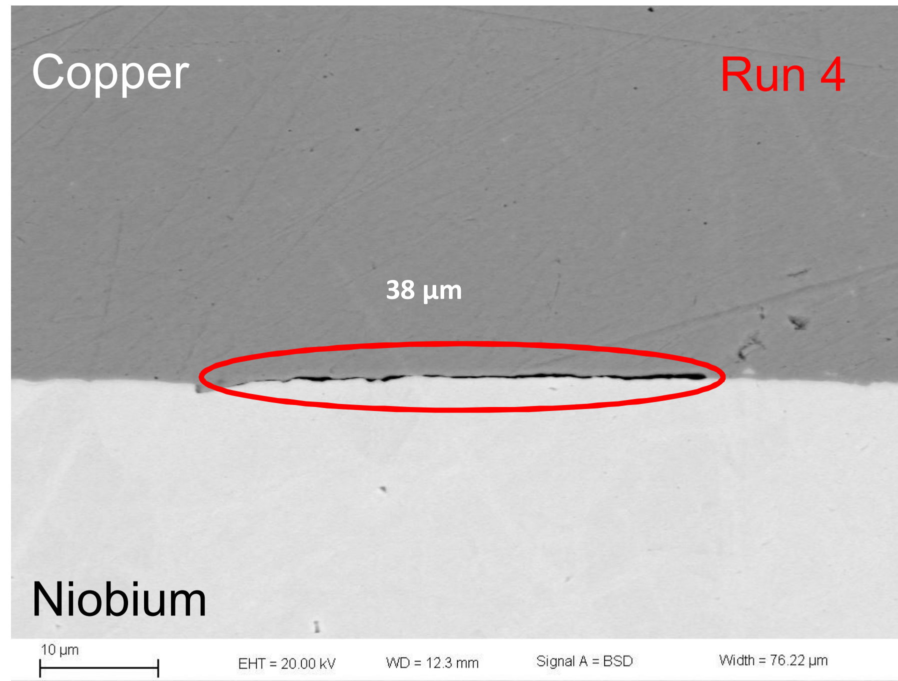
Run 6: 1050^{o}C, 10.3 MPa, 0.5 hours

-Back scatter detection SEM micrographs
-Scratches from polishing

SEM analysis: Run 3 and 4

Interfacial voids present at Cu-Nb interface





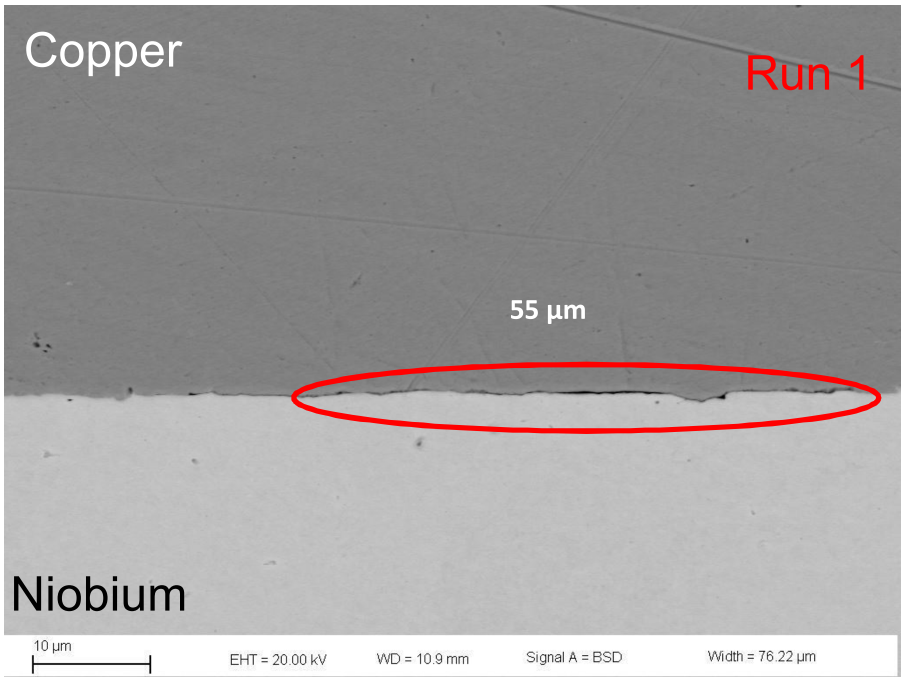
Run 3: 1000^{o}C, 6.9 MPa, 1.5 hours

Run 4: 1035^{o}C, 4.1 MPa, 3.0 hours

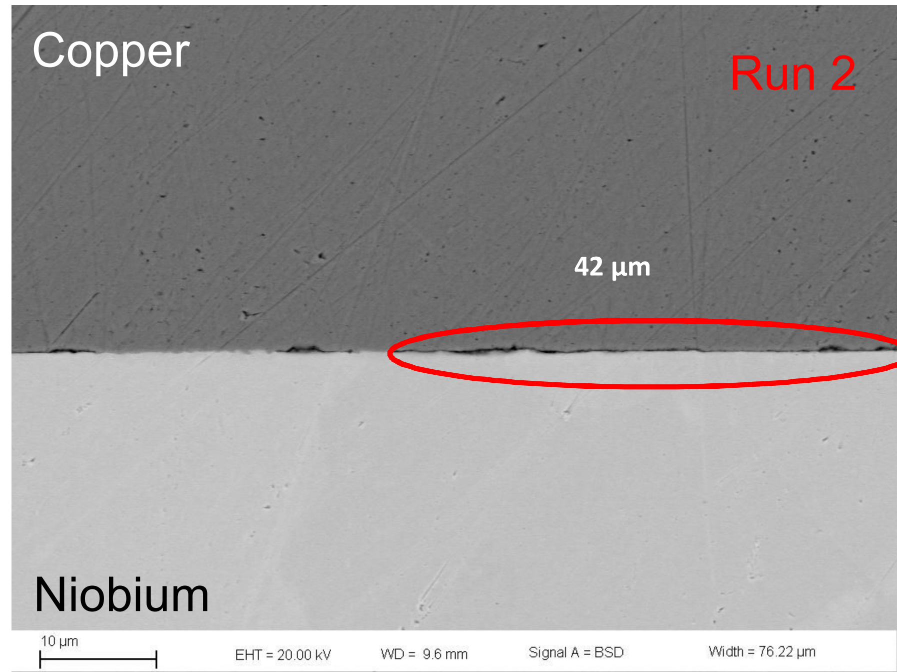
-Back scatter detection SEM micrographs
-Scratches from polishing

SEM analysis: Run 1 and 2

Interfacial voids present at Cu-Nb interface



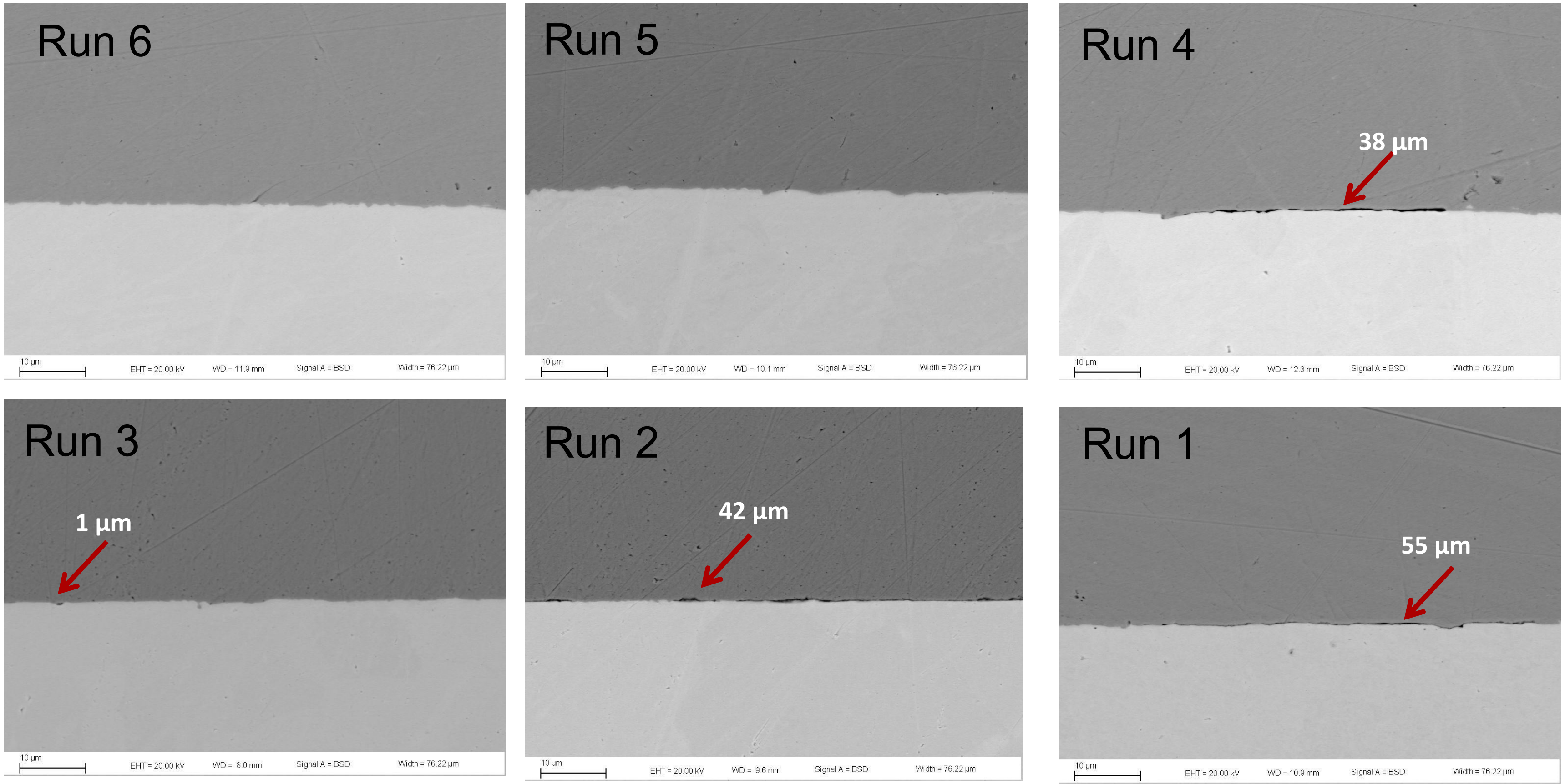
Run 1: 950°C, 10.3 MPa, 0.5 hours



Run 2: 950°C, 4.1 MPa, 3.0 hours

-Back scatter detection SEM micrographs
-Scratches from polishing

Diffusion interface comparison



-No interface voids in Run 5 and 6
-Small 1 to 2 µm interfacial voids in Run 3
-Large 30 to 60 µm interfacial voids in Run 4, 2, and 1

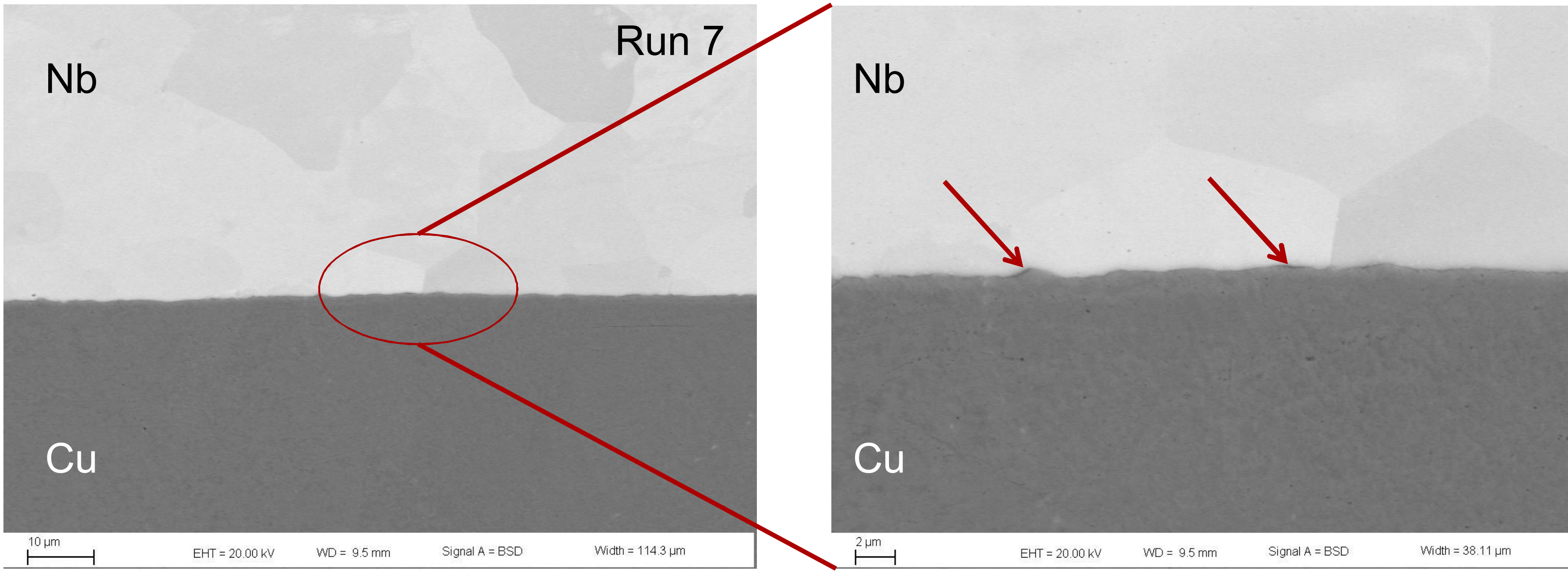
Recap: Optimization experiments

- Experiments to determine optimal bonding parameters
  - Based on SEM results from initial experiments

	Temperature [^oC]	Pressure [Mpa (KSI)]	Time [Hours]	Material thickness		Load applied [^oC]
				Cu [µm]	Nb [µm]	
Run 7	1050	10.3 (1.5)	0.25	127	508	1050
Run 8	1050	4.1 (0.6)	1.5	127	508	1050
Run 9	1050	4.1 (0.6)	0.5	127	508	1050

Run 7, 8, 9: SEM

Optimization experiment results



Run 7: 1050^{o}C, 10.3 MPa, 0.25 hours

- Optimization experiment samples contained interfacial voids from ~1µm to ~40µm.
- Voids indicate the bonding time was insufficient.
- Results from optimization experiments indicate parameters used in Runs 5 and 6 are ideal for bonding Cu to Nb.

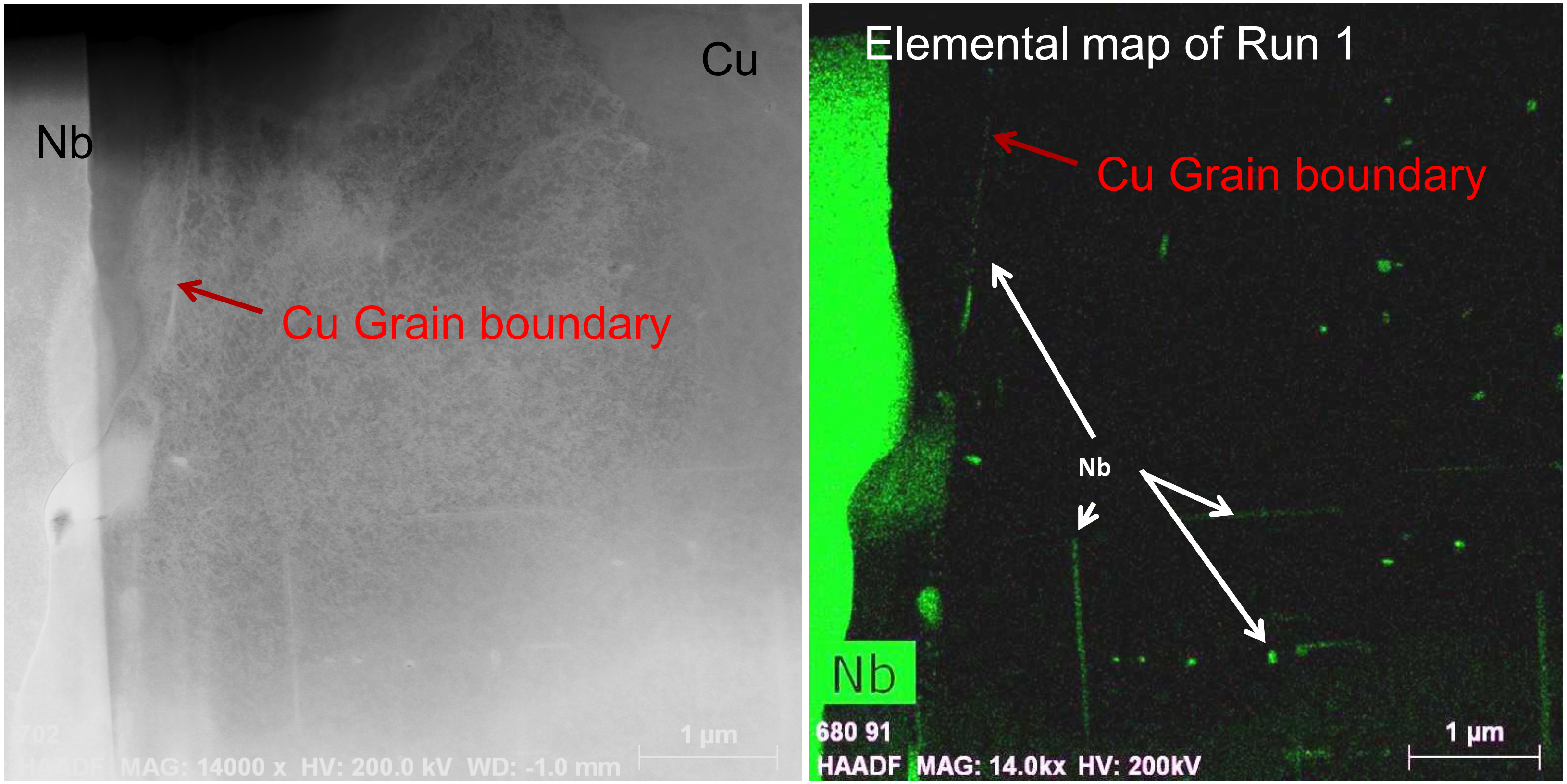
Summary: SEM analysis

- Samples from runs 5 and 6 did not have interfacial voids, while all remaining samples had interfacial voids. Thus parameters used to bond runs 5 and 6 were ideal for bonding Cu to Nb.
  - Run 5: 1050^{o}C, 4.1 Mpa, 3.0 Hrs.
  - Run 6: 1050^{o}C, 10.3 Mpa, 0.5 Hrs.
- Diffusion was not observable using SEM imaging
  - Electron interaction volume was too big
  - TEM was used to observe diffusion

TEM analysis: determine interdiffusion characteristics

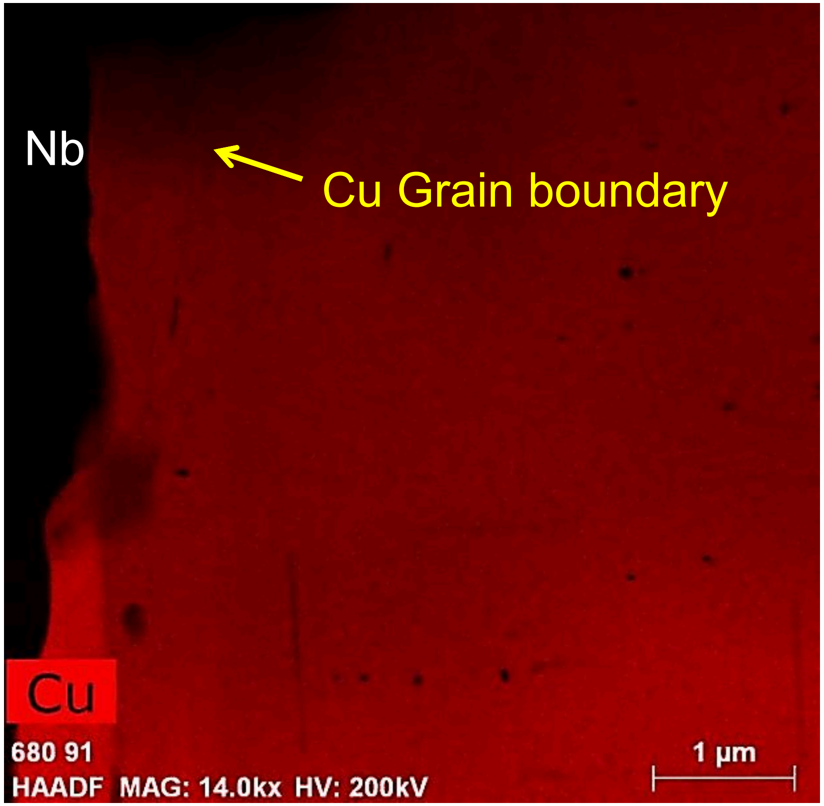
- Interdiffusion coefficients for Cu into Nb and Nb into Cu at 1000°C
  - Cu into Nb: 1.7×10^{-13} cm^2/sec
  - Nb into Cu: 4.57×10^{-9} cm^2/sec
    - Cu into Nb << Nb into Cu
- Diffusion depth estimates {depth=(Dt$)^{1/2}$}:
  - Cu into Nb: 0.17µm
  - Nb into Cu: 30.0µm
- TEM indicated Nb diffusion into Cu and no Cu diffusion into Nb.
  - Nb diffused along grain boundaries and dislocations with in the Cu.
  - Nb diffusion was observed in all the samples subjected to TEM (Run 1, 3, 5, and 6)
  - Nb interdiffusion estimate supported by TEM

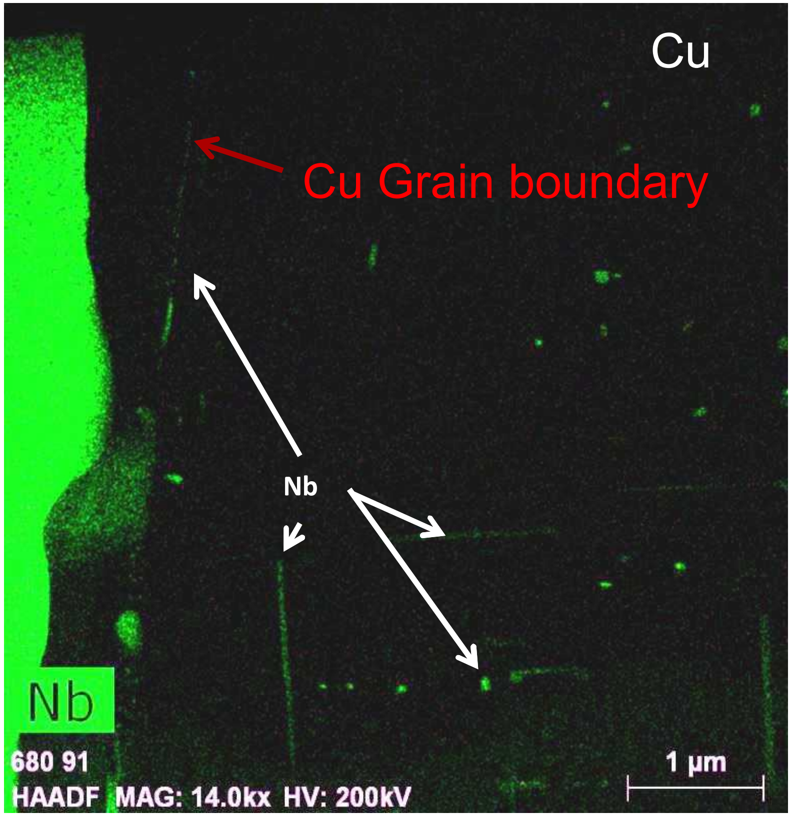
TEM analysis: Run 1(950ºC, 0.5 hrs)



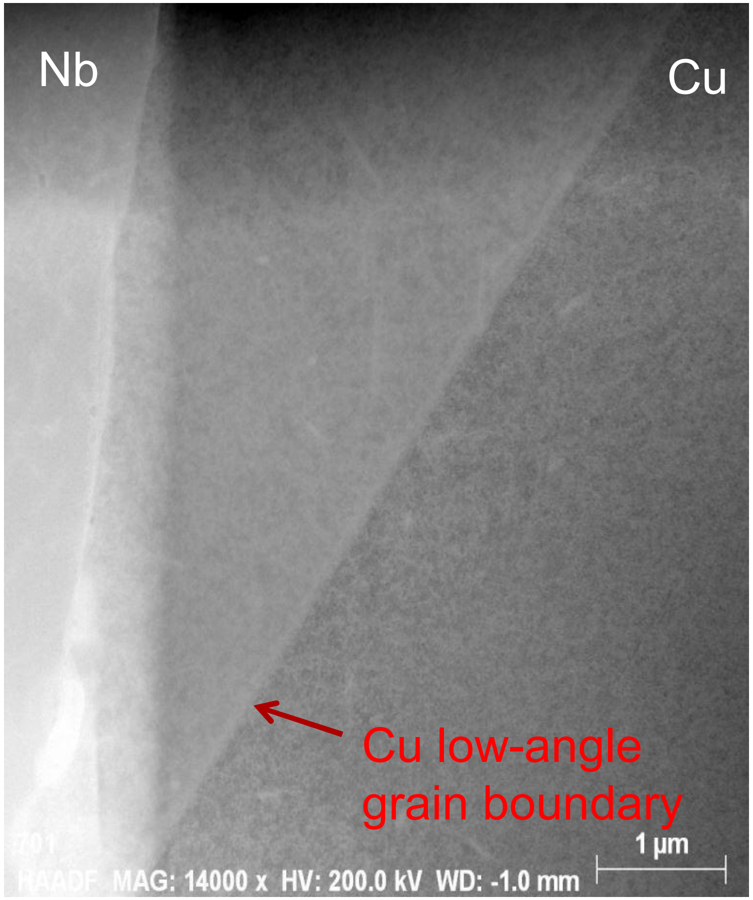
- Nb diffusion along grain boundary
and dislocations, forming needle-like precipitates.
- Nb diffused 5-6µm from interface

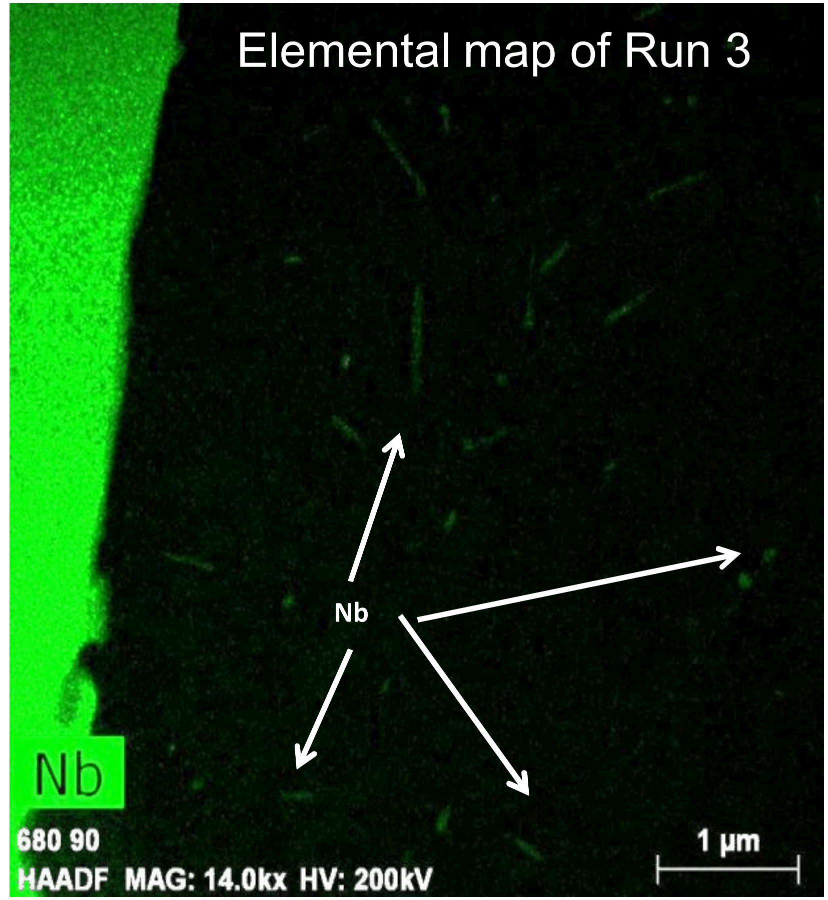
TEM: Elemental map of run 1





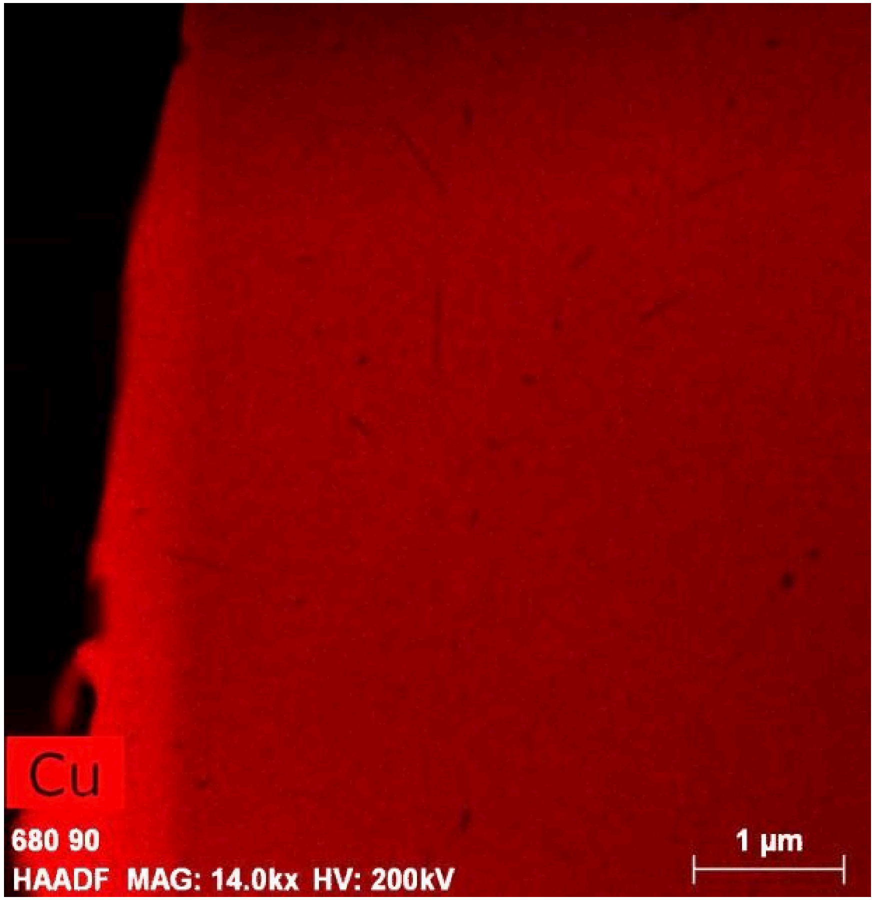
TEM analysis: Run 3(1000ºC, 1.5 hrs)

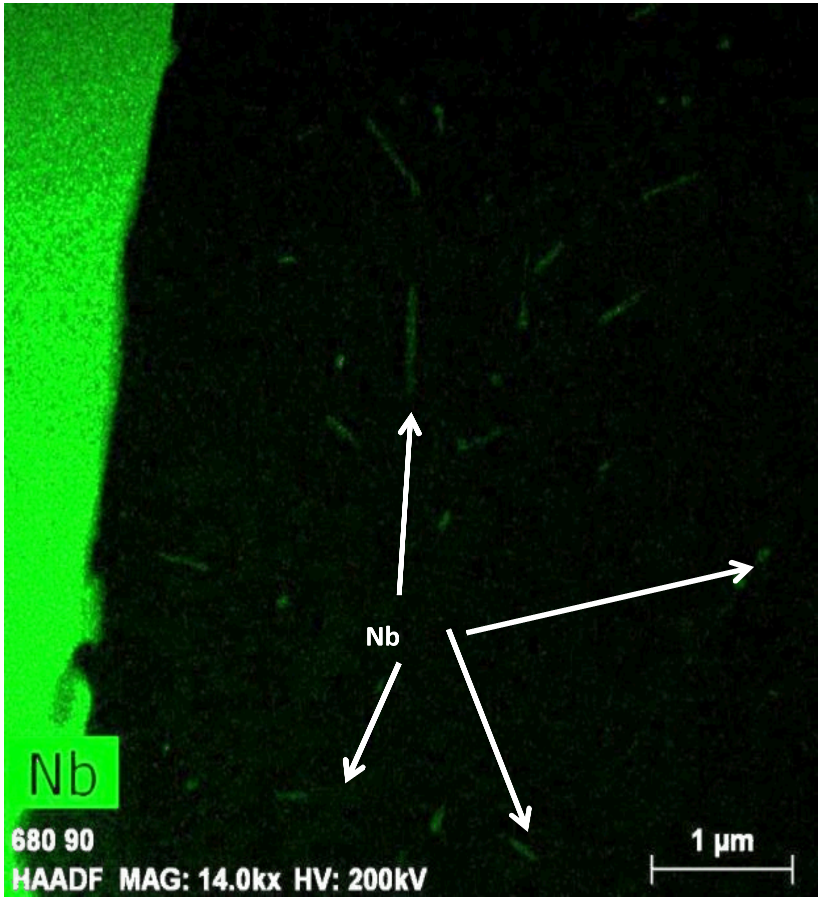




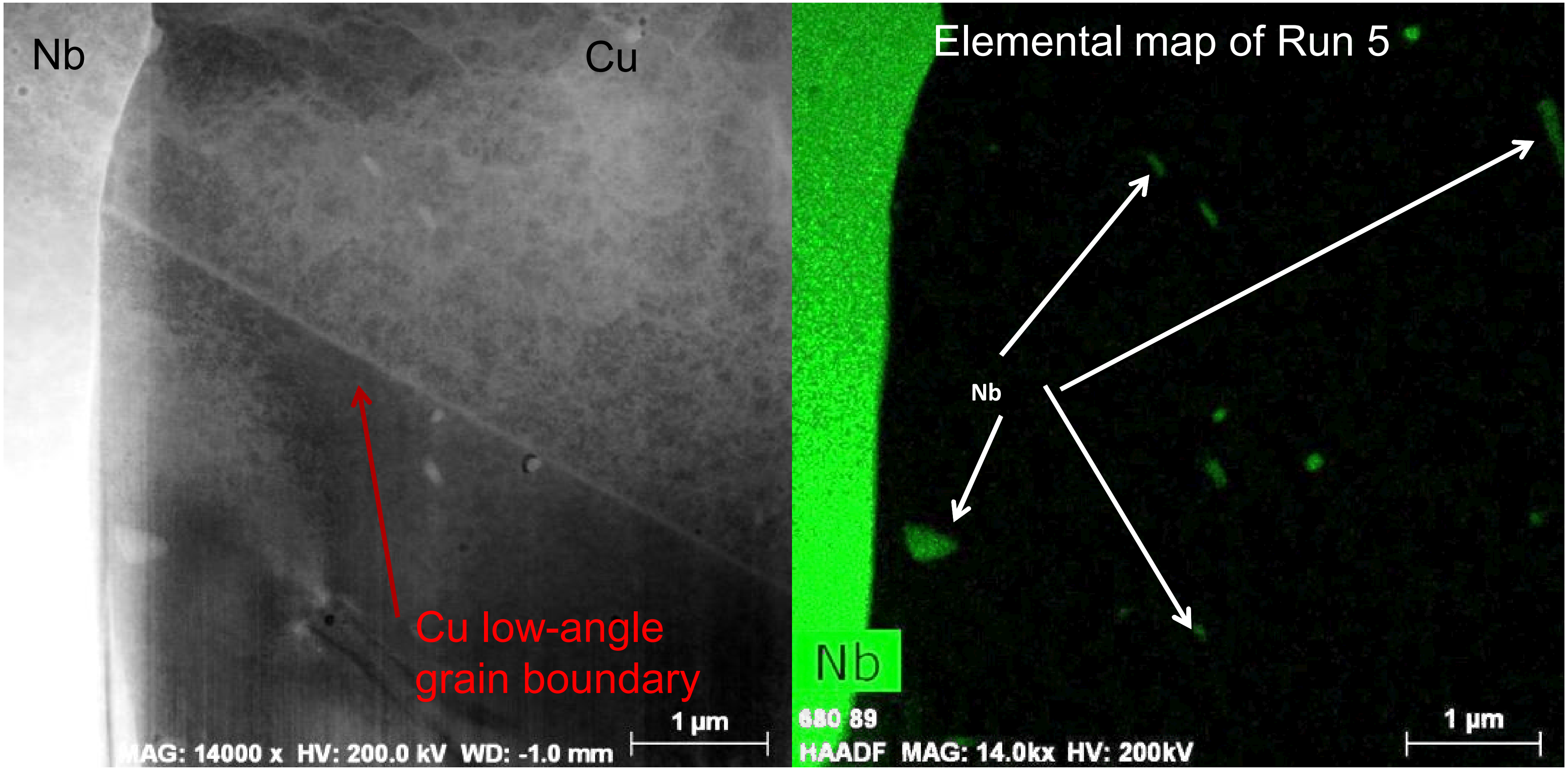
- Nb diffusion along dislocations forming more compact elongated Nb precipitates.
- Nb diffused 5 to 6µm from interface

TEM: Elemental map of run 3



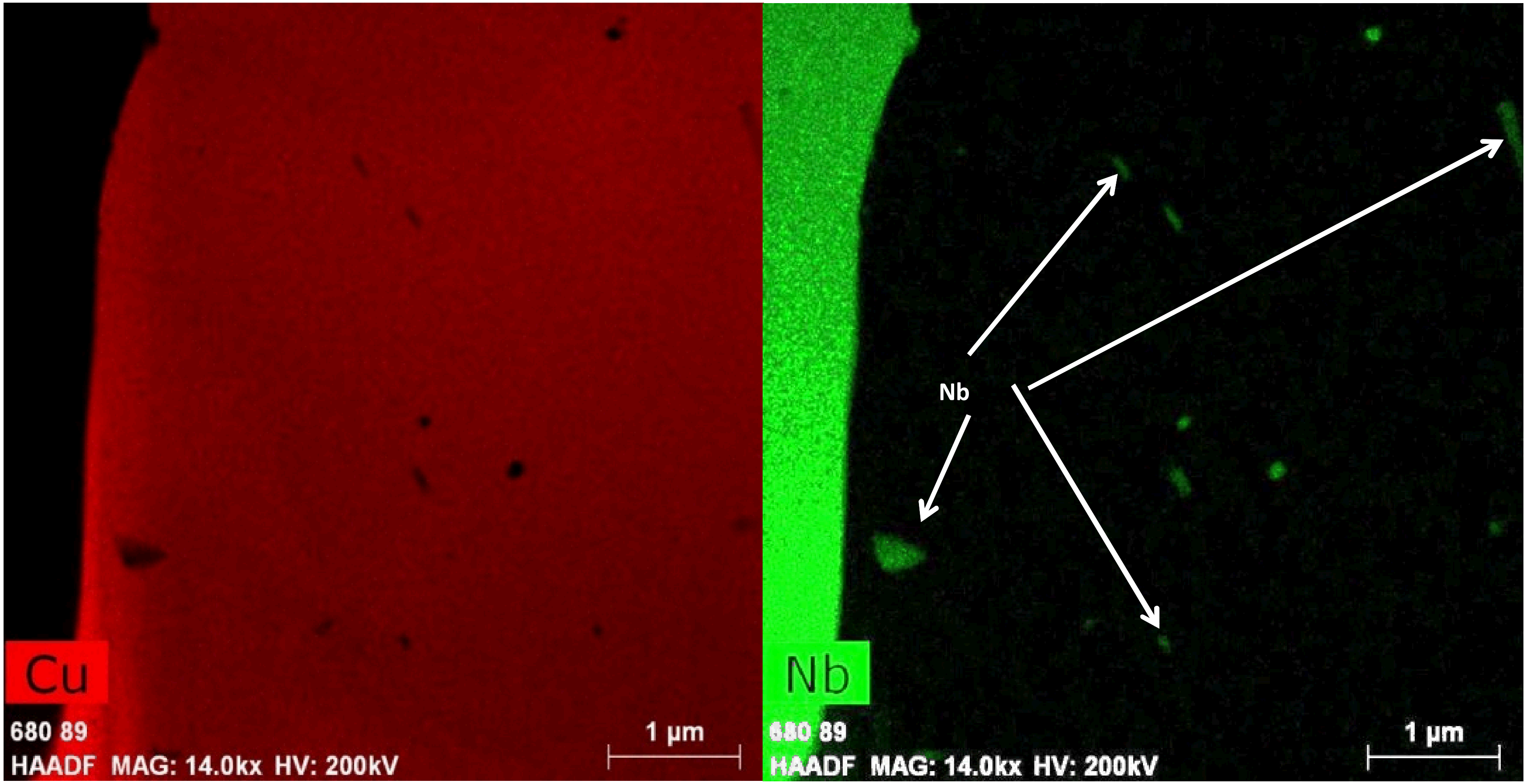


TEM analysis: Run 5(1050ºC, 3.0 hrs)

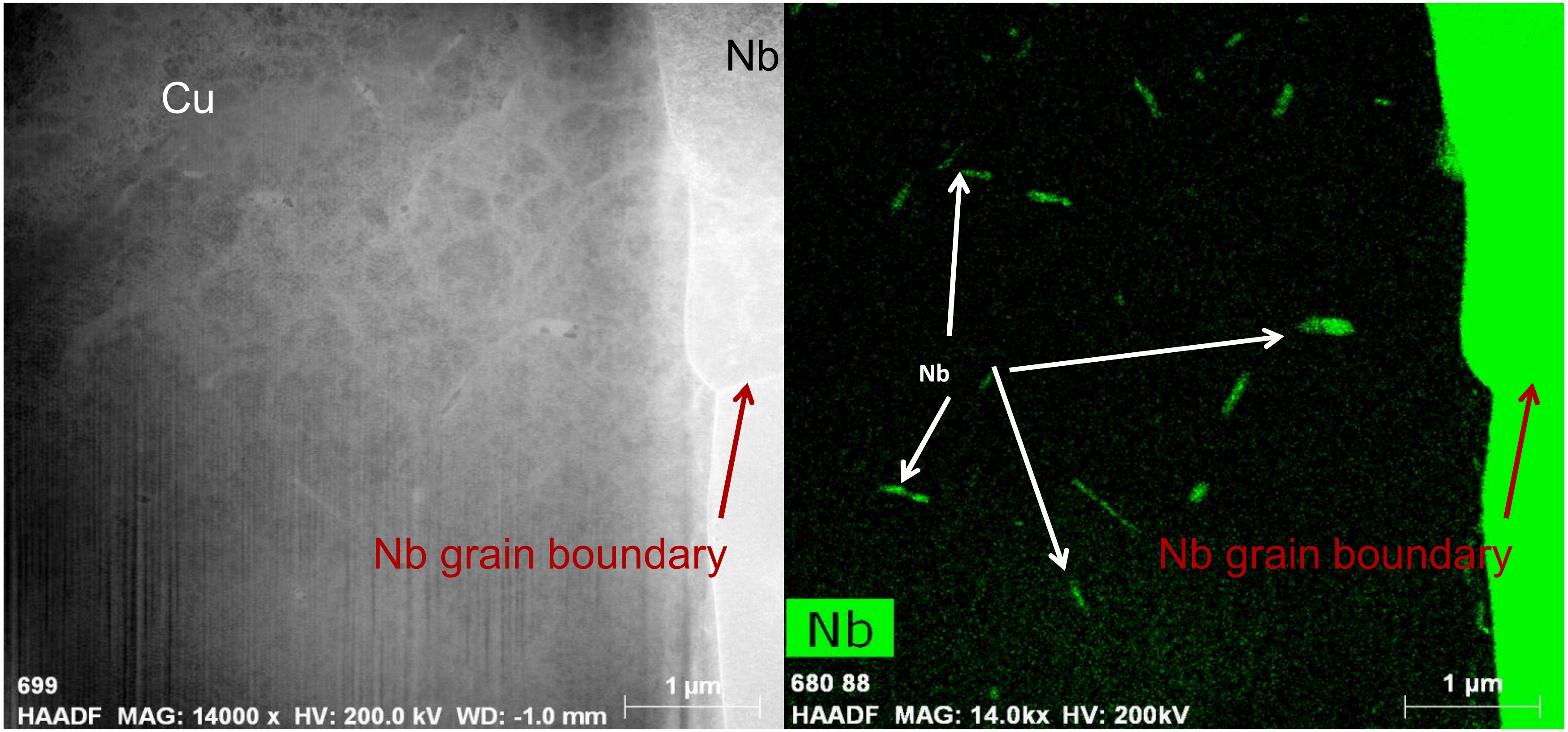


- Nb diffusion along dislocations forming compact Nb precipitates.
- Nb diffused 5 to 6µm from interface

TEM: Elemental map of run 5

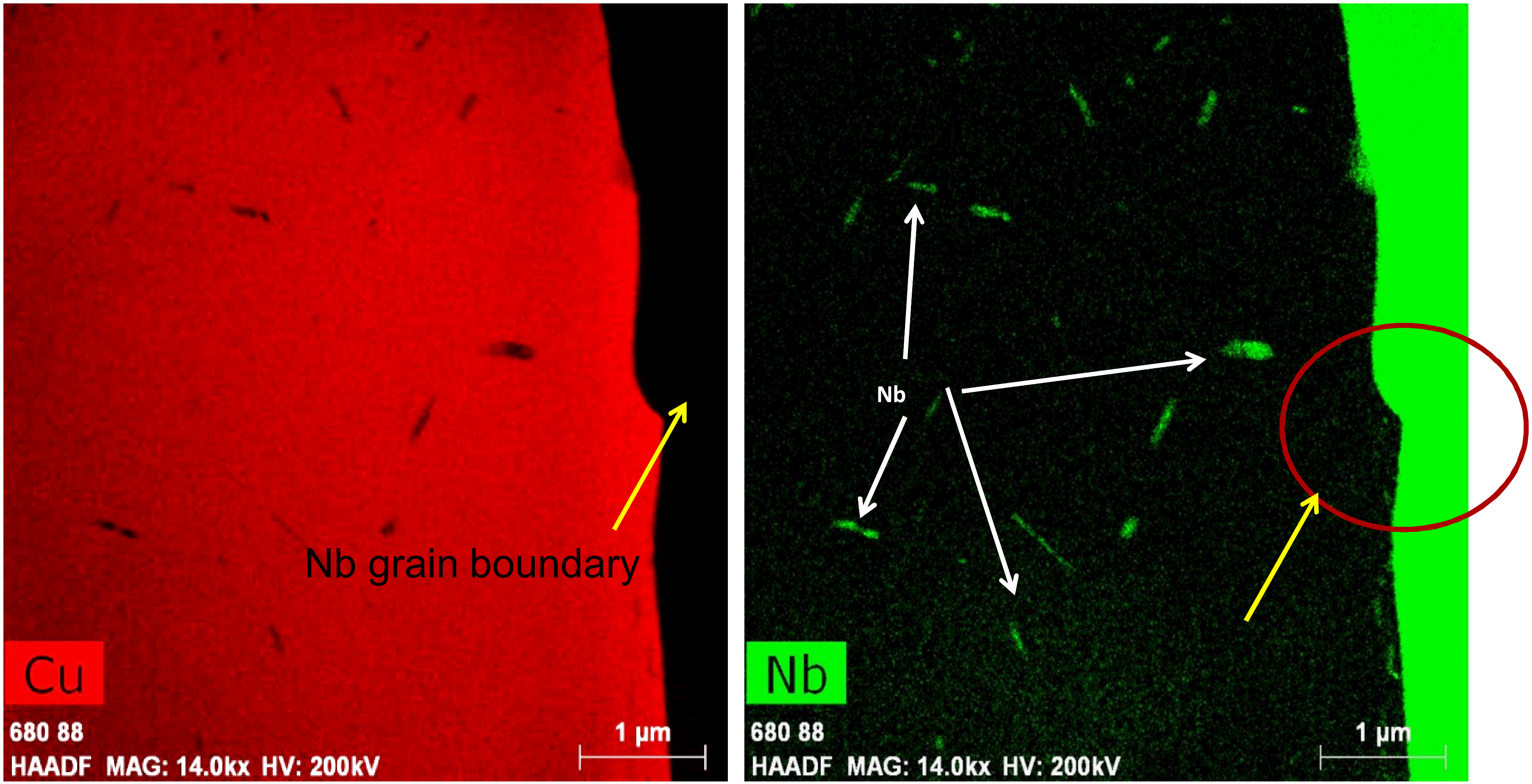


TEM analysis: Run 6(1050^{o}C, 0.5 hrs)

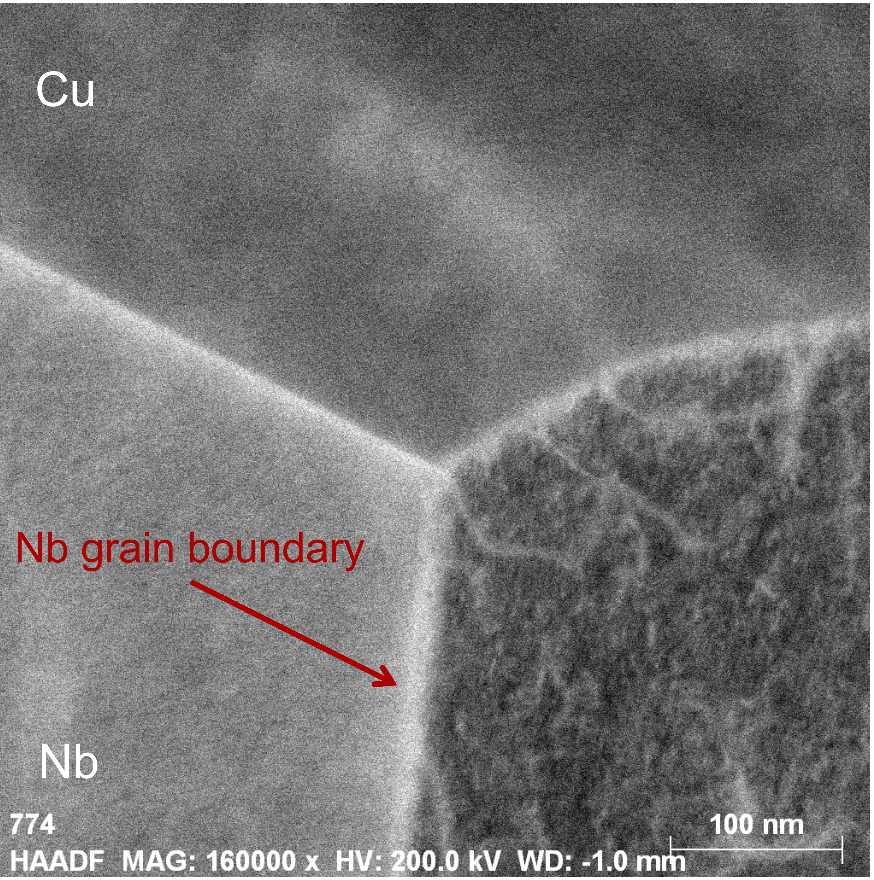


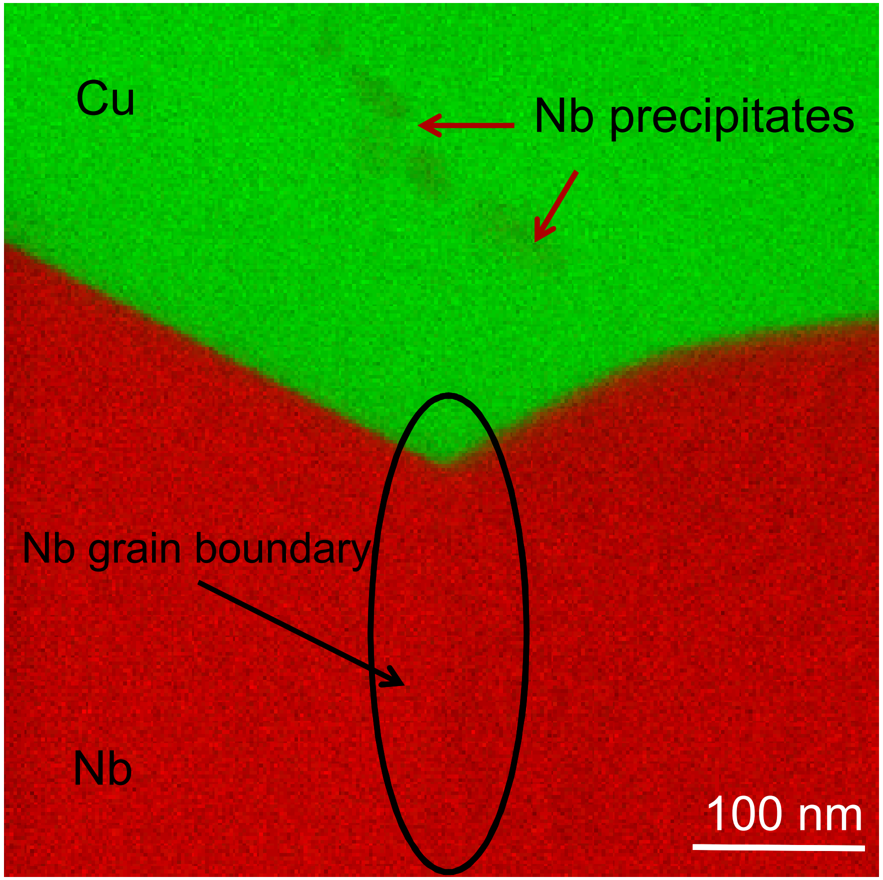
- Nb diffusion along dislocations forming larger Nb precipitates.
- Nb diffused 5 to 6µm from interface

TEM: Elemental map of run 5



TEM analysis: magnified Nb grain boundary, run 6





- No Cu diffusion along Nb grain boundary

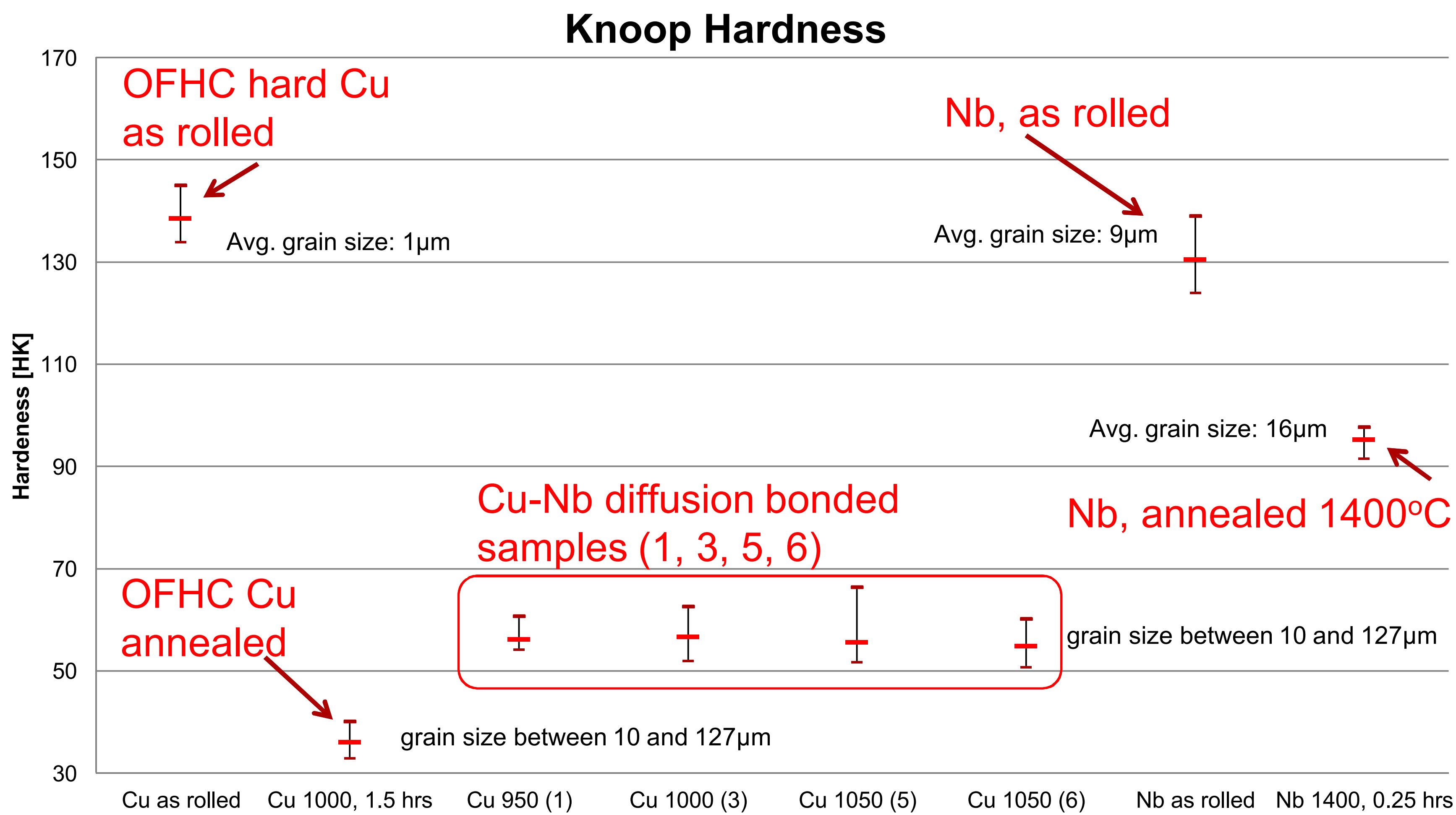
Summary: TEM analysis

- Nb diffusion depth of 5-6 µm into the Cu supports the interdiffusion estimate
  - Nb diffused along fast diffusion paths: Dislocations, and grain boundaries
  - Nb diffusion in Cu was seen in all samples, even when large interfacial voids were present
  - Cu diffusion in Nb was not seen in any samples
    - Does not support interdiffusion estimate

Mechanical testing

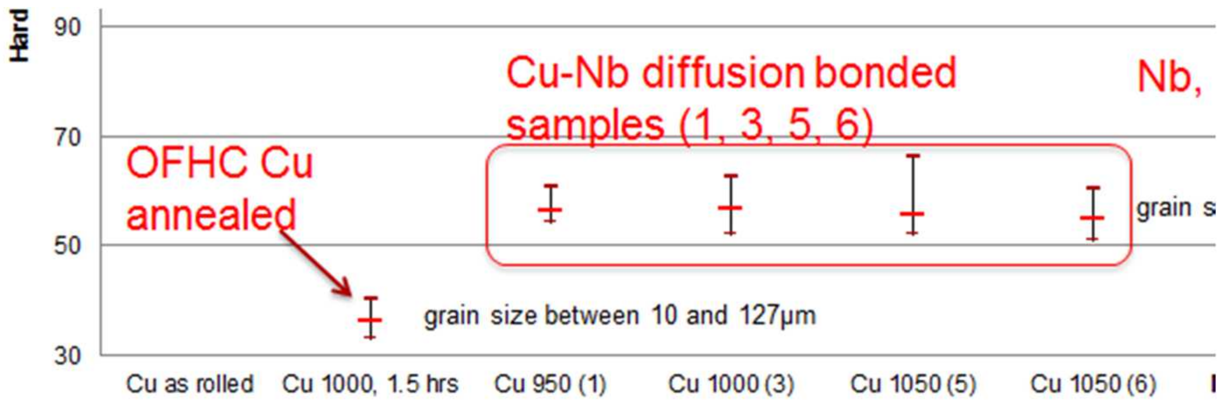
- Knoop hardness test
  - Performed on:
    - As rolled Cu
    - Annealed Cu (1000^{o}C, 1.5 hours, in vacuum)
    - Diffusion bonded samples 1, 3, 5, and 6
    - As rolled Nb
    - Annealed Nb (1400^{o}C, 0.25 hours in vacuum)
    - Test was conducted about 0.5 mm from Cu-Nb interface
- Peel testing
  - Performed on diffusion bonded samples
- Tensile button testing
  - Performed on diffusion bonded samples brazed to alumina

Hardness test: Knoop Hardness



- 100gf used on all samples except 'Cu 1000, 1.5 hrs' where 50gf was used.

Hardness testing

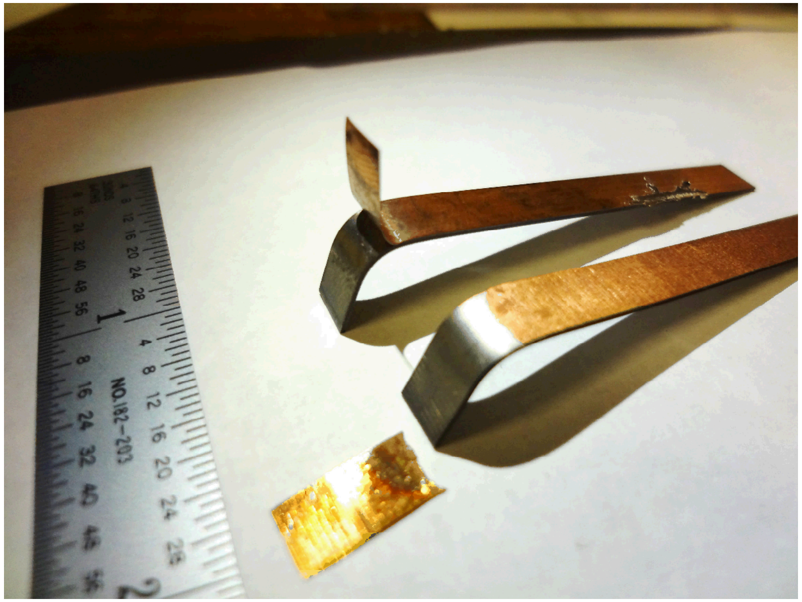


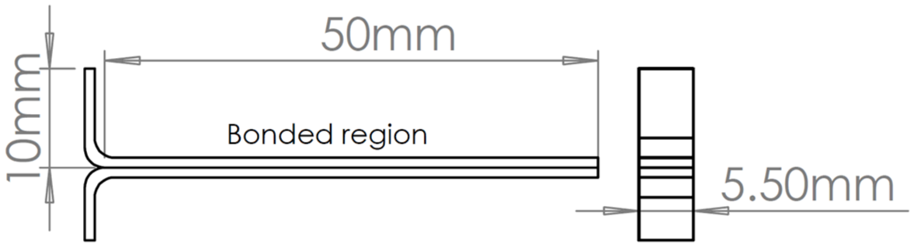
- The difference in hardness between annealed Cu and diffusion bonded Cu indicate the Nb precipitates hardened the Cu

- This increase in hardness supports the Nb interdiffusion depth (~30μm)
  - Test was performed ~0.5mm from Cu-Nb diffusion interface
  - Cu in that area was harder relative to the annealed Cu because of the Nb precipitates
  - This suggest Nb diffused more than 30μm into the Cu

Characterizing diffusion bond strength via peel testing

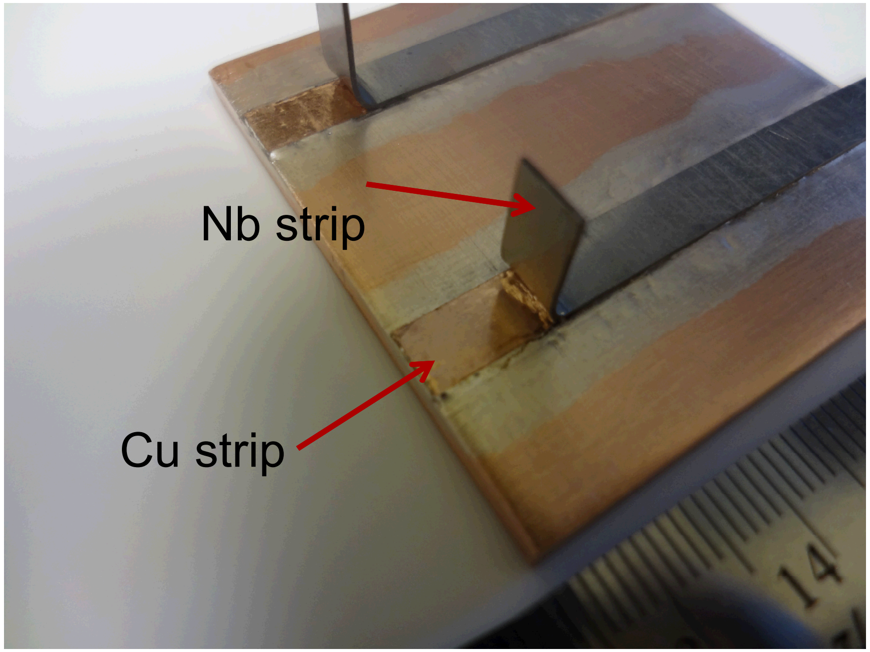
- Failure occurred in Cu between 18 and 20 pounds of force
  - All samples tested with the following orientation failed in the annealed Cu outside the Cu-Nb diffusion bond
  - The diffusion bond did not fail.

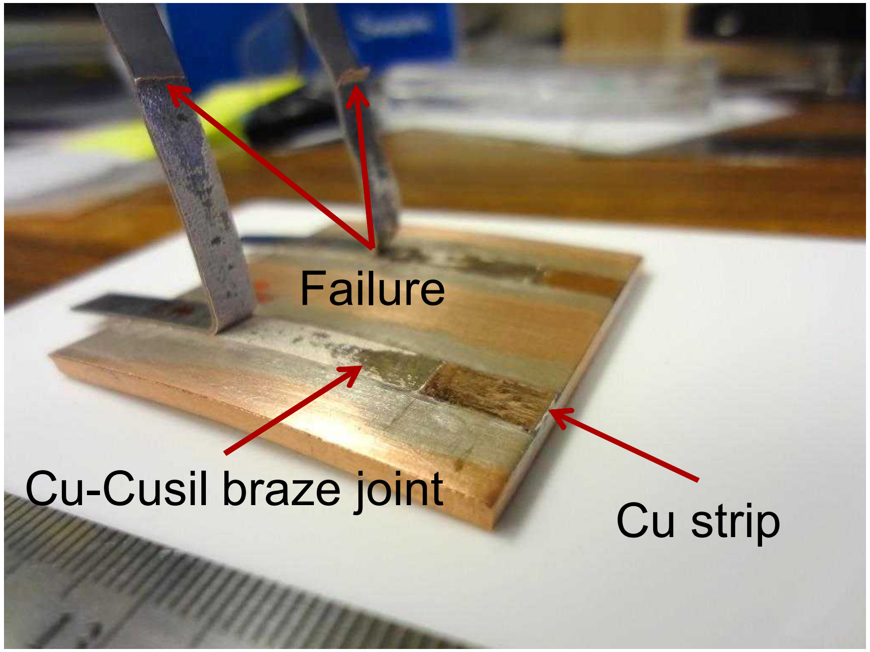




Peel test continued

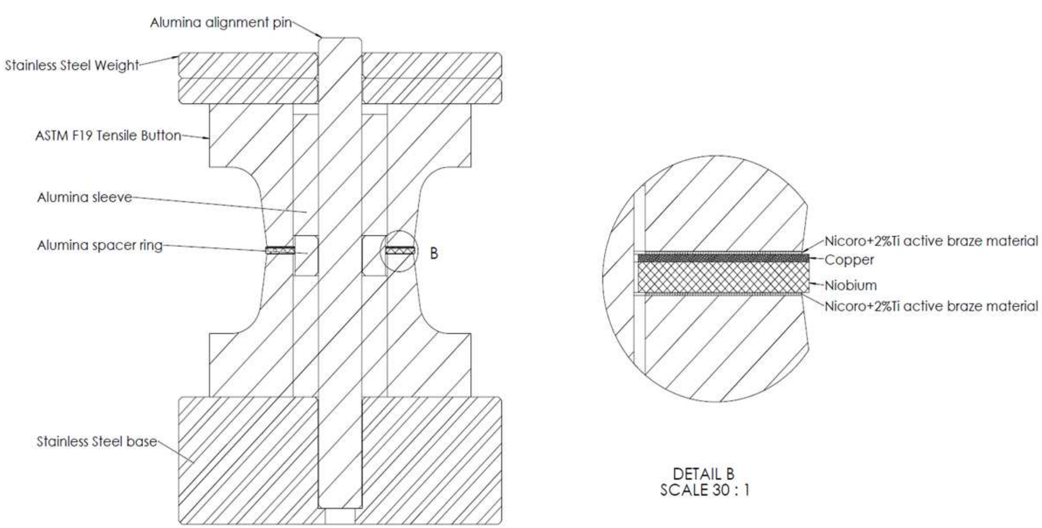
- Additional attempts at testing the bond strength were inconclusive due to the failure in the annealed Cu. Again, the diffusion bond did not fail in any test.
- Cu-Nb strips were brazed to Cu using Cusil™ (brazing temp ~810^{o}C), failure of the braze joint occurred around 50lbs.
- Cu-Nb strips were glued (Gorilla® super glue; JB weld®) to a stainless steel plate; failure occurred around 10lbs.

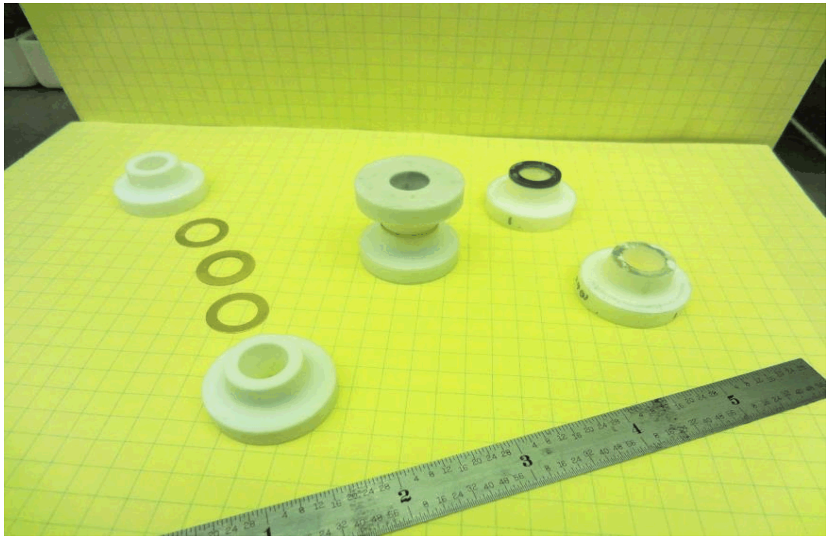




Tensile button test results

- All tensile buttons were hermetic except one, which had a lopsided braze joint
- Roughly 2/3 of samples failed on Cu side with crack initiation in alumina, remaining 1/3 failed on the Nb side
- Failure of tensile buttons initiated at or near braze fillets, due to associated stress concentration

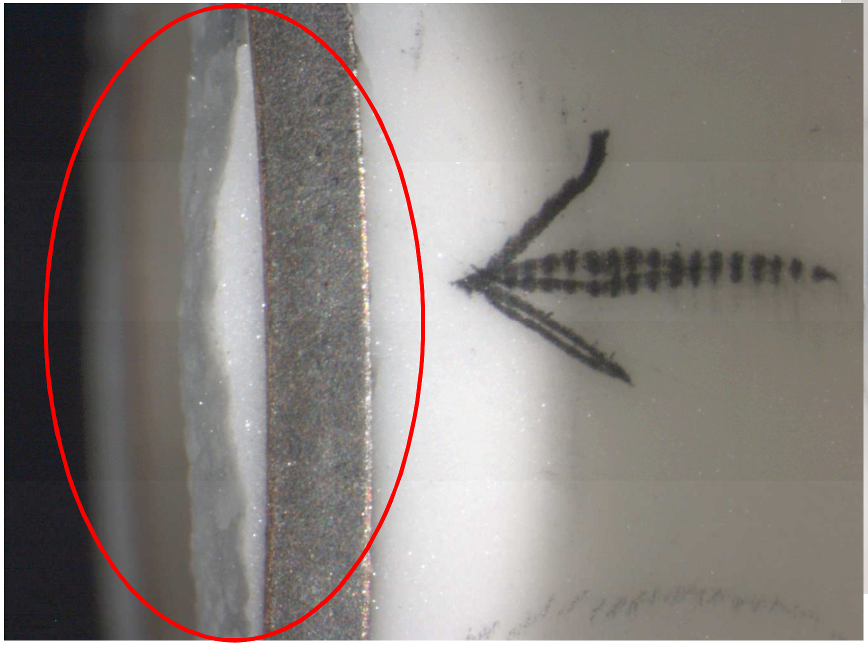


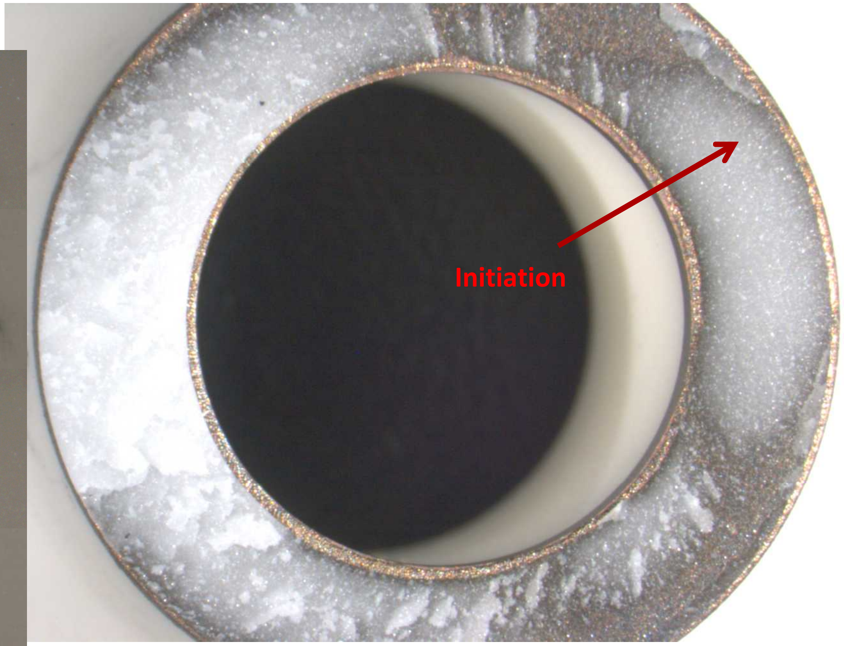


Fracture of tensile button

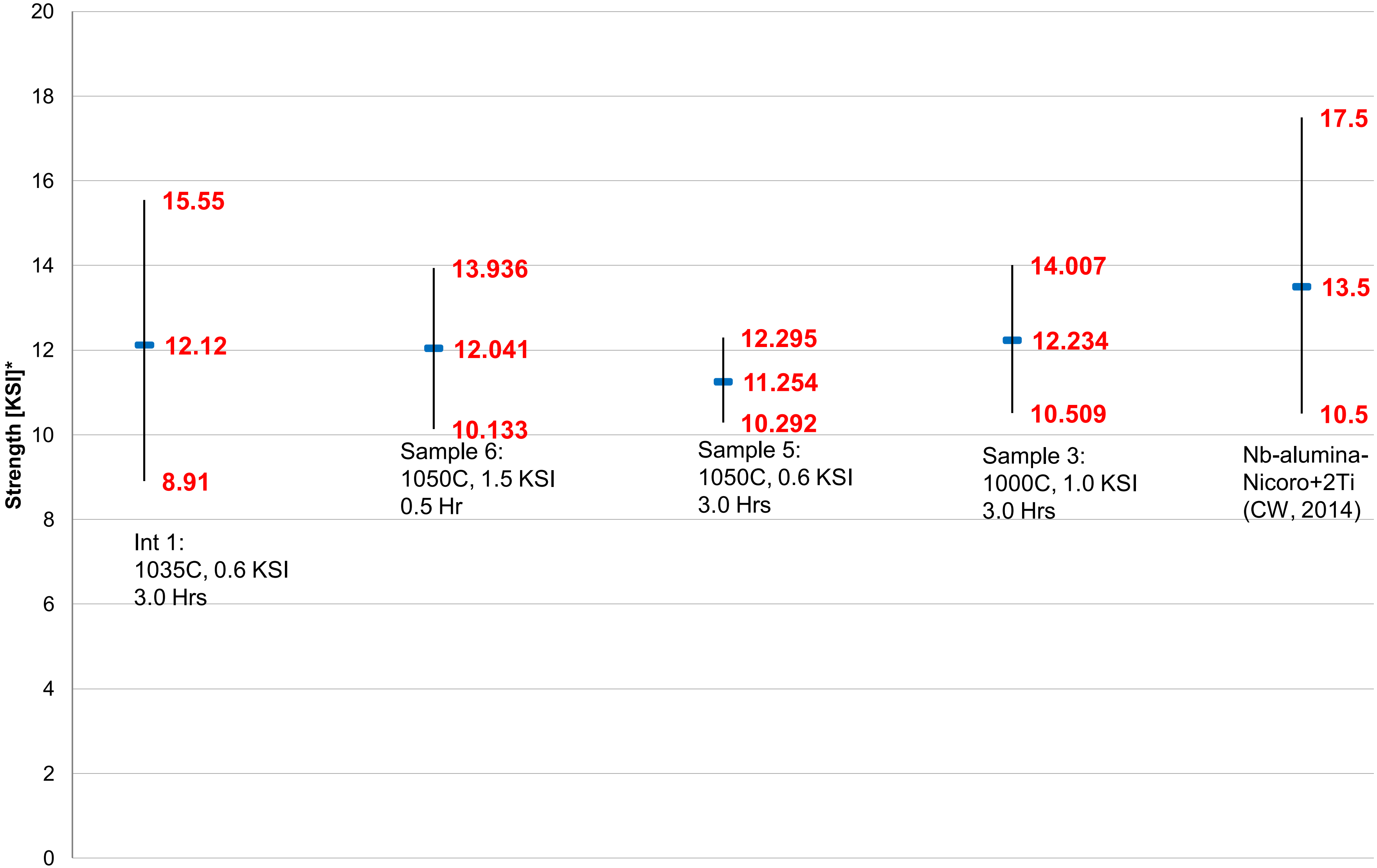
- All tensile buttons had primary failure occur in the alumina
- Samples failed due to the size of braze fillets
  - Braze fillets cause location of high stress

Initial Sample 1





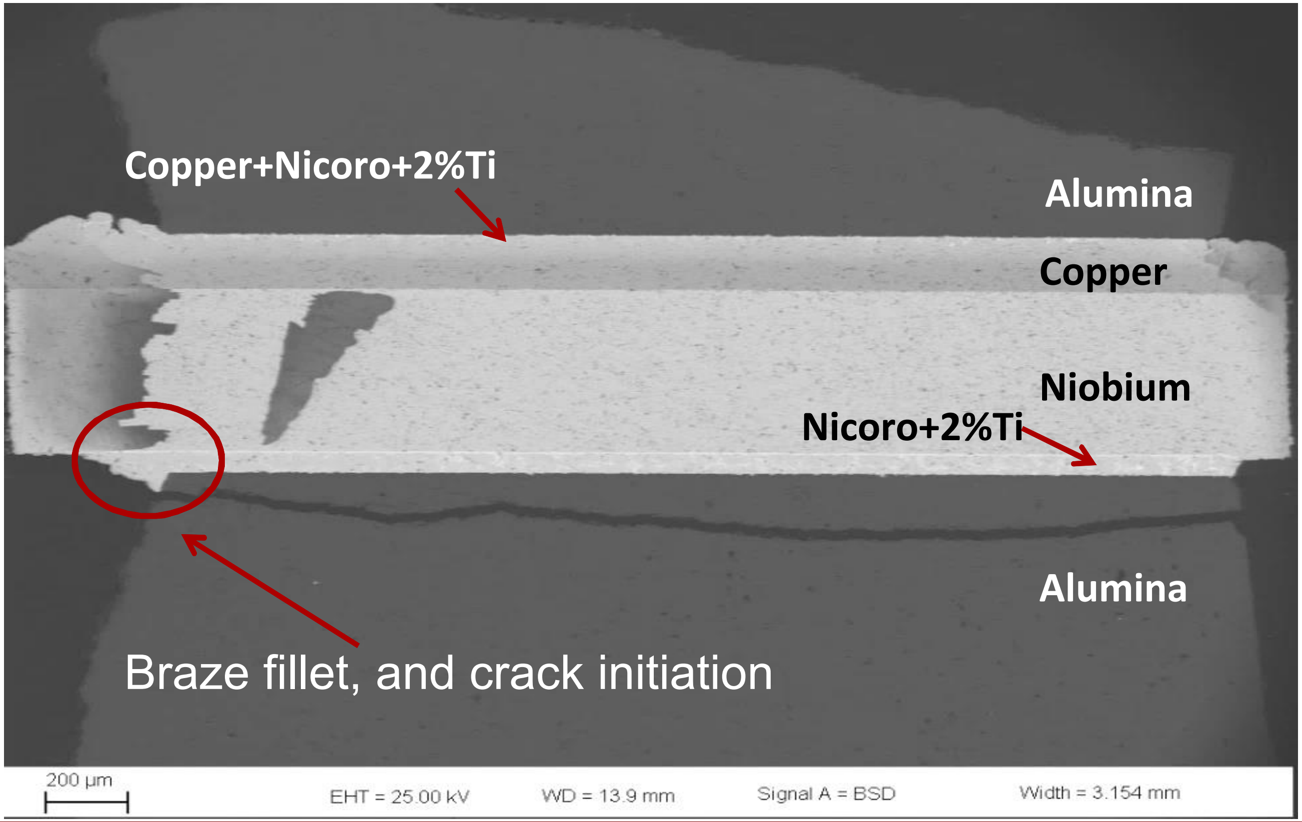
Tensile button test results



*Surface area: 0.179873 sqr in

SEM of tensile button fracture

- Cu-Nb diffusion bonded interface remained voidless after tensile testing
- Tensile buttons failed within the alumina
- Crack initiation occurred at large braze fillets

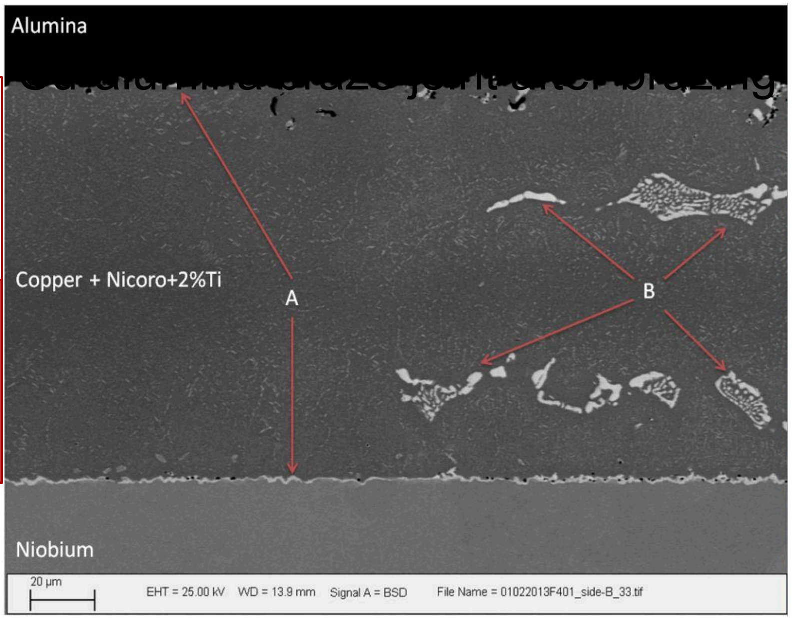


Dissolution of Cu in braze joint

Original thickness

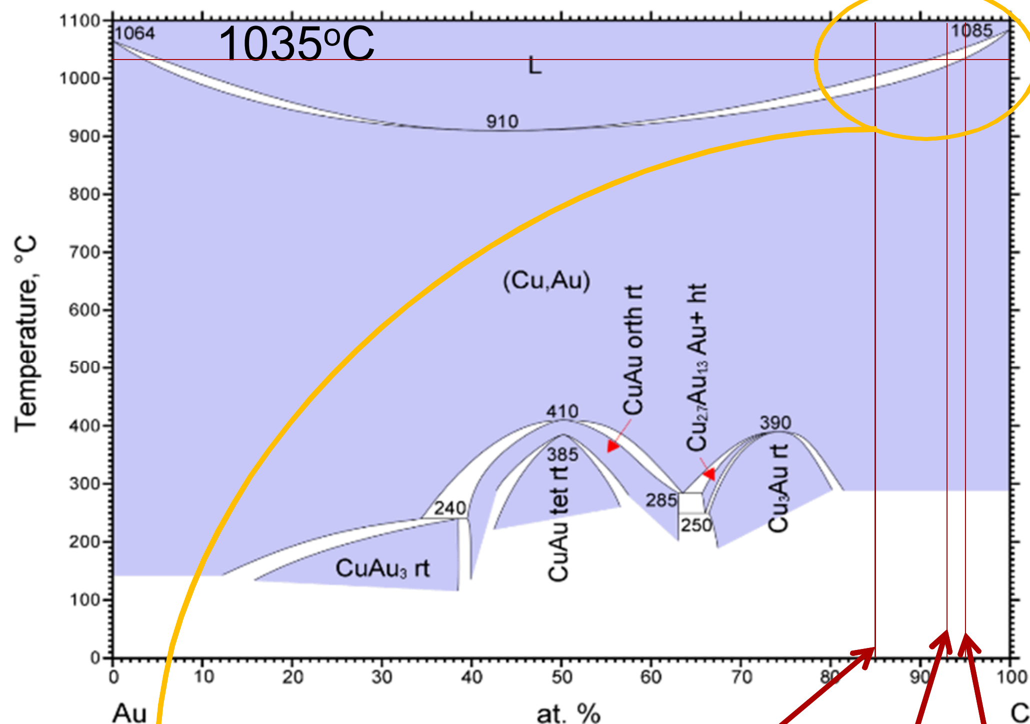
Nicoro+2%Ti 50.8µm

Copper 50.8µm



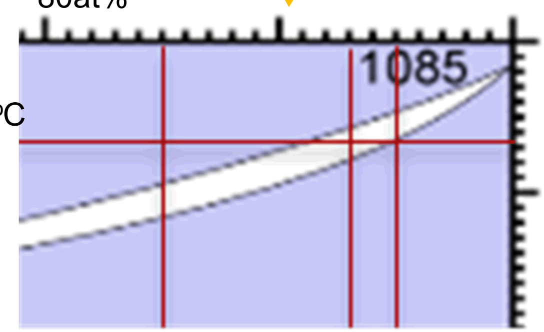
SEM of run int 1-sample 2
Tensile strength: 107.21 Mpa
Original thicknesses:
Cu: 50.8µm
Nb: 1016µm
Nicoro®+2%Ti: 50.8µm

*



80at%

1035°C



Initial composition of braze alloy 85 at %Cu

Final compositions of braze joint 93 at% and 95 at %Cu

*W. T. Zheng, Study on phase diagrams for Ag-Au, Au-Cu binary alloys at high temperature, 36, 75-79, (1991)

Dissolution of Cu:
127µm Cu vs 50µm Cu

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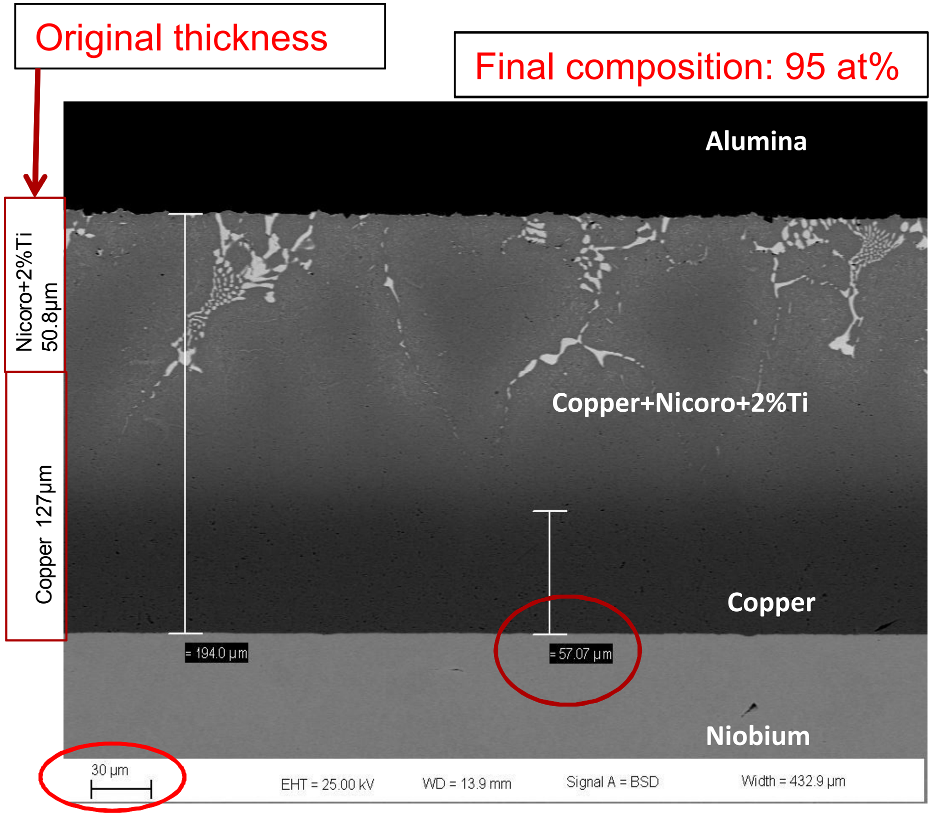
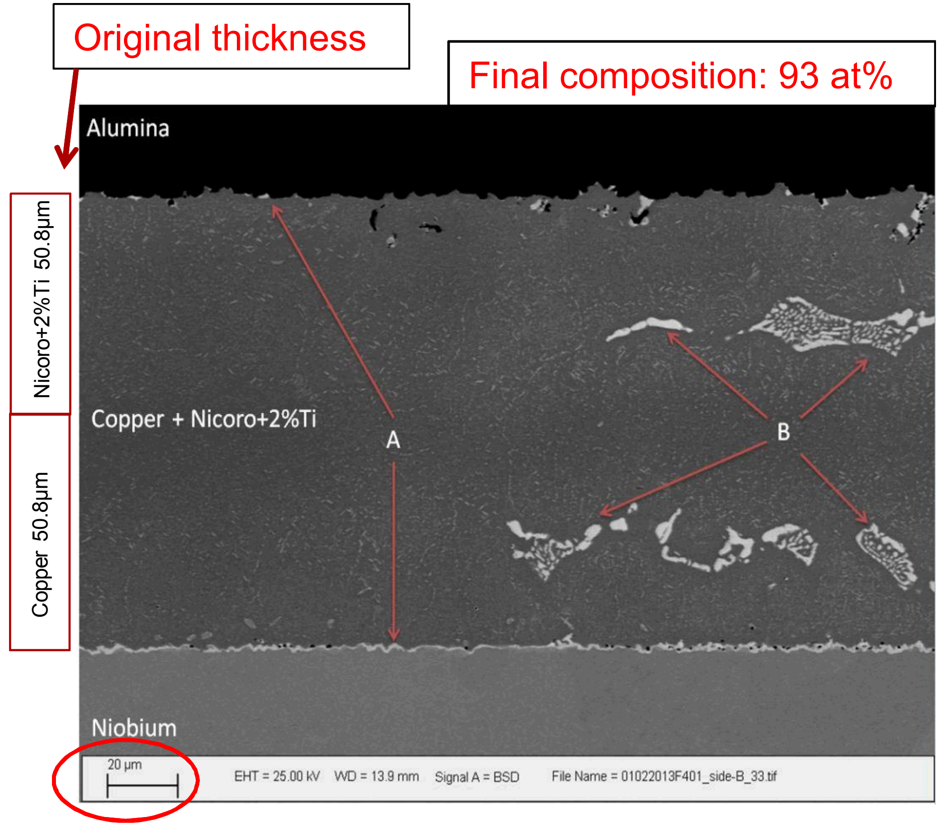


SEM of run 5- sample 2
Tensile strength: 76.9 MPa
Original thicknesses:
- Cu: 127 µm
- Nb: 508 µm
- Nicoro®+2%Ti: 50.8µm



SEM of run int 1-sample 2
Tensile strength: 107.21 MPa
Original thicknesses:
- Cu: 50.8µm
- Nb: 1016µm
- Nicoro®+2%Ti: 50.8µm

Conclusions

Cu-Nb has not been previously researched, nor has Nb diffusion into Cu been observed.

1. The diffusion OFHC Cu to Nb was accomplished using different diffusion bonding parameters, including bonding temperatures less than half the melting temperature of Nb (the highest melting point of the two materials).
2. Nb diffused into Cu along fast diffusion paths, even when large interfacial voids were present, and the processing temperature was at 950^{o}C ($<<0.5T_m$ of Nb).
3. The location of failure during mechanical testing, which did not occur at the diffusion interface, indicated that a strong mechanical bond was formed between the Cu and Nb through Cu-Nb surface diffusion.

Future work

- Cu is soft and has large grains after diffusion bonding
  - Problematic during peel testing
    - All samples failed in the bulk Cu, outside the diffusion bond
- Develop reliable and reproducible testing method to determine the failure strength of Cu-Nb diffusion bonds
  - Start with ASTM standards to determine baseline data for Nb, Cu, and Cu-Nb diffusion bond
    - Compact tension (CT) sample (notch at Cu-Nb interface)
    - Single and double lap shear: Nb bonded to thick Cu
    - Torsional shear test with gauge section centered on Cu-Nb diffusion interface
    - Tensile test using samples with a rectangular cross section and samples with a circular cross section, both with gauge sections centered on the Cu-Nb diffusion interface

Future work continued

- Once baseline data has been established, tests will be modified
  - CT samples: modify stack so that Cu is bonded between two pieces of Nb, with notch at either of the Cu-Nb interfaces.
    - adjust size and location of notch
  - Adjust size and geometry of gauged sections
  - Adjust strain rate
  - Cyclically loading and unloading of samples, while adjusting the cycle rate
- Mode and location of failure will be identified for each test sample, leading to a reliable testing method.

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Questions and Comments