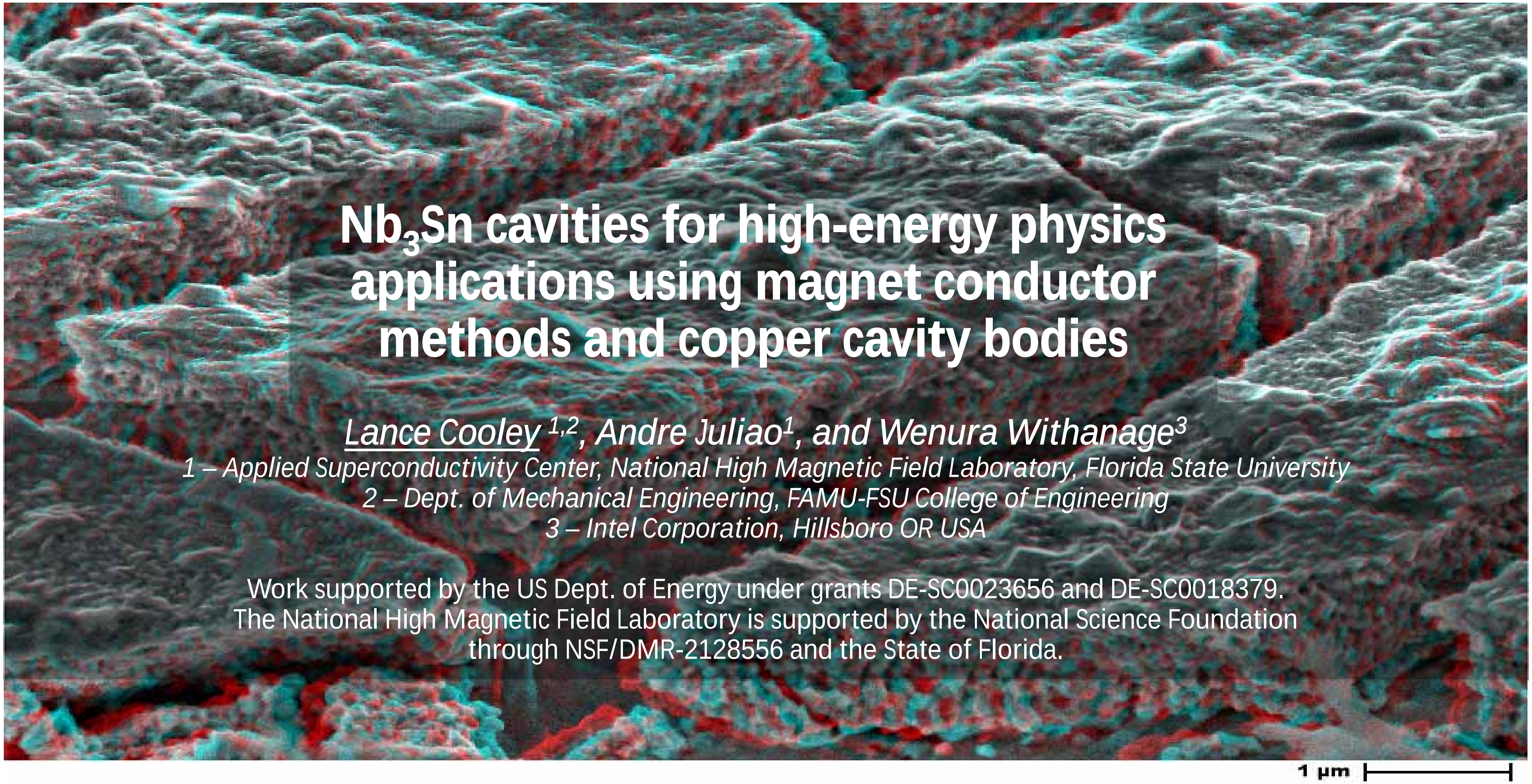


Nb_3Sn cavities for high-energy physics applications using magnet conductor methods and copper cavity bodies

Lance Cooley [1,2], *Andre Juliao*[1], *and Wenura Withanage*[3]
1 – Applied Superconductivity Center, National High Magnetic Field Laboratory, Florida State University
2 – Dept. of Mechanical Engineering, FAMU-FSU College of Engineering
3 – Intel Corporation, Hillsboro OR USA

Work supported by the US Dept. of Energy under grants DE-SC0023656 and DE-SC0018379.
The National High Magnetic Field Laboratory is supported by the National Science Foundation through NSF/DMR-2128556 and the State of Florida.

APPLIED SUPERCONDUCTIVITY CENTER
NATIONAL HIGH MAGNETIC FIELD LABORATORY
FLORIDA STATE UNIVERSITY

Preview

- A quick overview of the Applied Superconductivity Center and some of the work we've been doing in SRF since ~2010
- Nb_3Sn synthesis methods from magnet conductors that could be used to make SRF cavities on copper bodies
  - Challenges from thermodynamics
  - Approaches:
    - Nb onto hot bronze with spontaneous *in-situ* Nb_3Sn formation
    - Cu substrates with diffusion barriers and thermal contraction management
    - High-Sn Cu-Sn phases vs low-Sn bronze (α phase up to Cu 14 wt.% Sn)
    - Cu-Sn onto Nb followed by reaction and etching
    - Healing seams: Are clam-shell cavities possible?
- Prospects for scalability

The Applied Superconductivity Center

- ASC is 42 years old !! Founded in 1981 by Roger Boom
- ASC moved from the University of Wisconsin to NHMFL / FSU in 2005
- Director: Prof. Lance Cooley (since 2018)
- Mech. Eng. Faculty: Profs. Eric Hellstrom, David Larbalestier*, Fumitake Kametani, Simone Hruda, (vacant – S. Hahn)

  *MagLab Chief Scientist, ASC director from 1988-2018
- 14 research faculty + specialists
- 2 postdocs, 13 graduate students, 25 undergraduates
- 10 support + professional staff

ASC's mission

ASC will be a leading organization to help the world realize significant transformational opportunities of superconductors and magnets

- Define the *limits of magnet conductors* and other critical materials *(Nb)* for applications
  - There is a natural transition from ASC to the missions of DOE labs, and magnet manufacturers
- Develop unique, world-class *characterizations of structure and properties* that definitively connect processing with performance. Uncover processing and material *root causes of performance shortfalls*
  - There is a natural pathway for collaboration with conductor manufacturers
- Extend the boundaries of knowledge in materials, conductors, and magnets via leveraging a portfolio of high-impact research *grants, collaborations, and partnerships*
- *Propagate ASC's knowledge and training* via support of MS, PhD, and post-doctoral work, interactions with industry and federal agencies, participation in review panels and oversight committees, and support of publications, conferences, and learned societies.

ASC Capabilities

50-bar Furnaces

Wire Fabrication Laboratory

Hot Isostatic Press

New Rigaku high resolution XRD

1 nm resolution FESEM/FIB

Scanning Laser Confocal Microscope

Magneto-Optical

Hydrostatic Extrusion Press

9 T PPMS

14 T Vibrating Sample Magnetometer

15 T Conductor testing

Frank Shaw Building 1st Floor 20,000 ft²

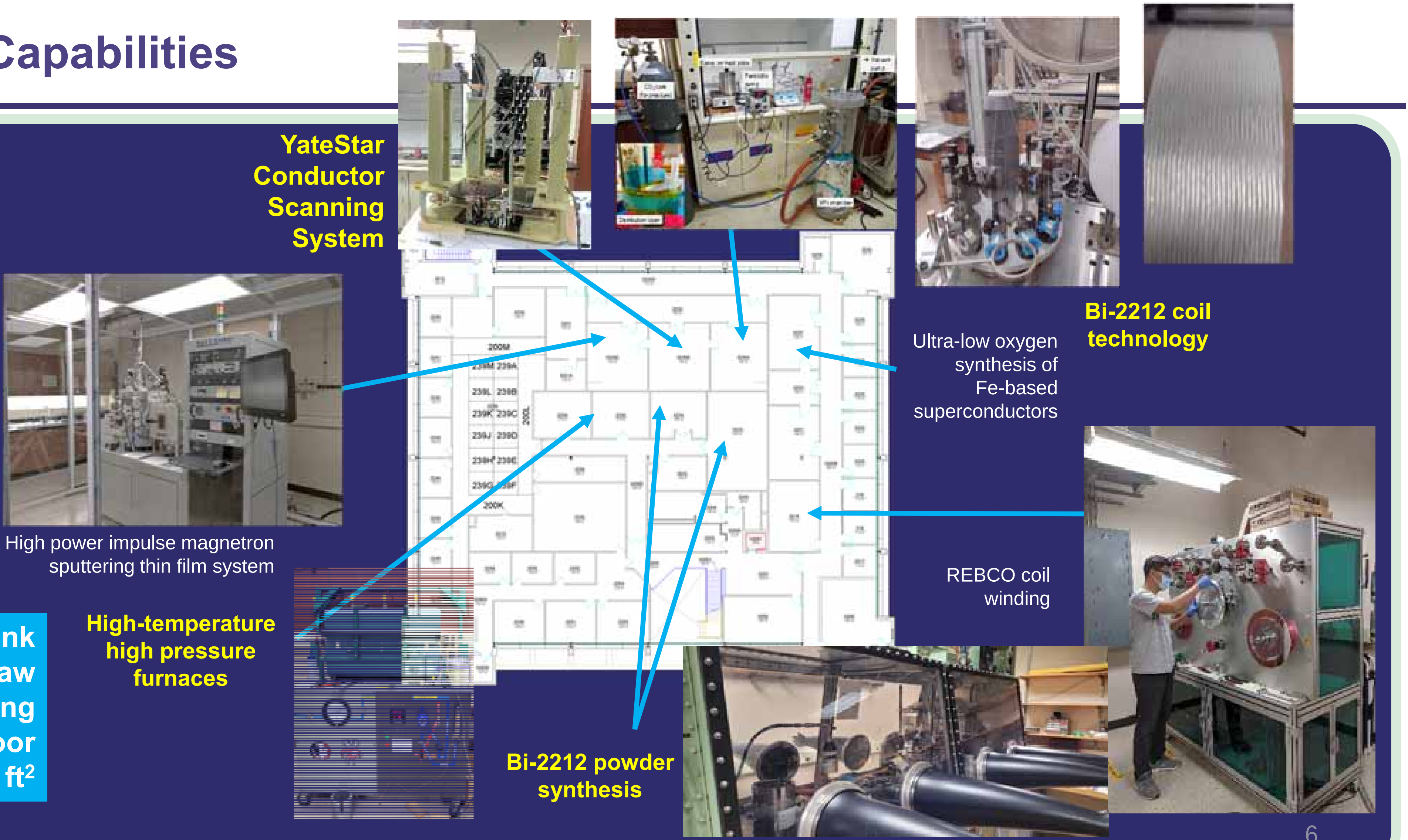
16 T PPMS

5·5T MPMS SQUID

14 T Large Bore

16 T Electo-mechanical Properties Magnet Test System from NIST

ASC Capabilities



YateStar Conductor Scanning System

High power impulse magnetron sputtering thin film system

Bi-2212 coil technology

Ultra-low oxygen synthesis of Fe-based superconductors

REBCO coil winding

High-temperature high pressure furnaces

Bi-2212 powder synthesis

Frank Shaw Building 2nd Floor 20,000 ft^2

Thin film system used for our SRF program

Custom-built system for transition metals using lessons learned from Nb SRF cavity activities

- Cryopumping to efficiently remove H2 and O2, < 10^{-9} torr base
- Baked high-vacuum load lock
- 5 sources, 1 with HiPIMS + z-kick and pulsed DC option
- Plasma clean pre-sputtering
- Deposition to 800 °C

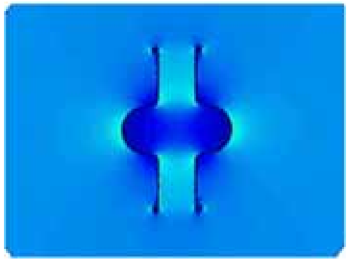
(Not shown) thermal evaporator for Cu-Sn and other metals

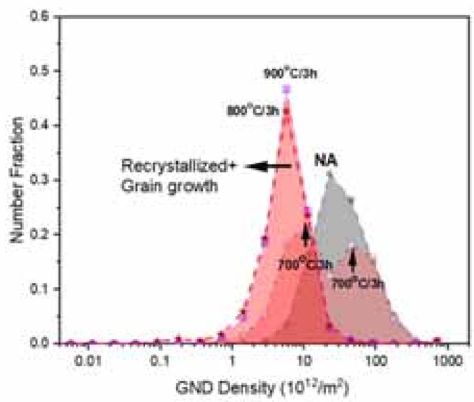
ASC has been working in superconducting radio-frequency cavities (SRF) since 1990

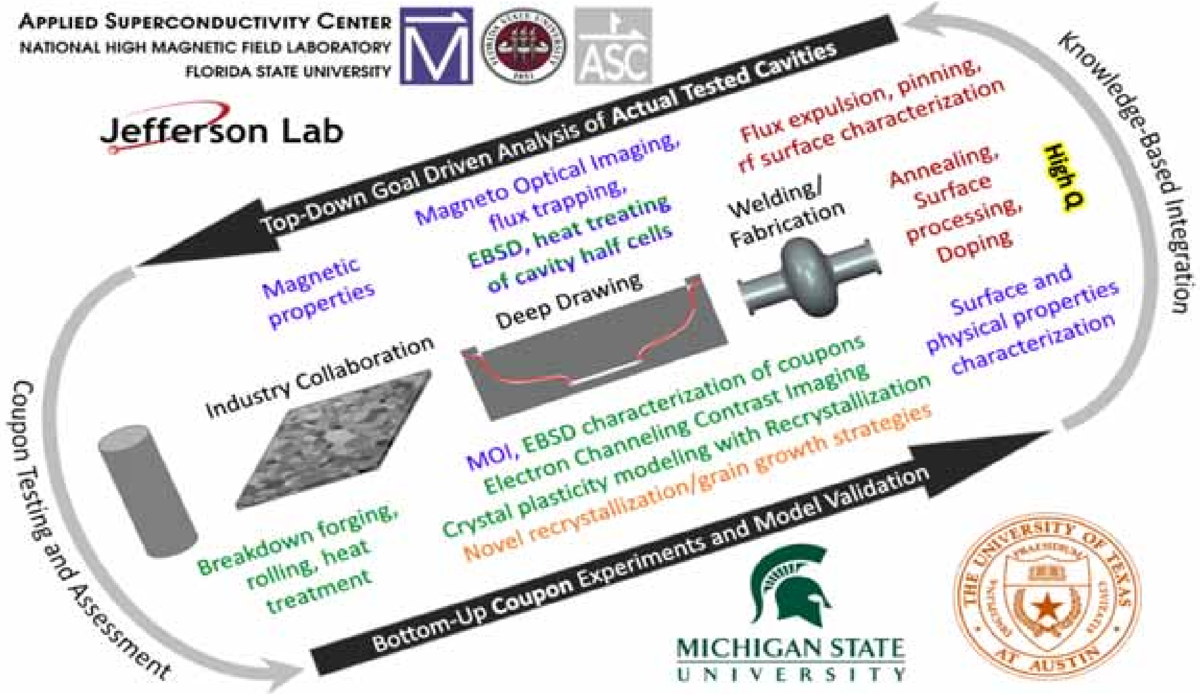
- Measurement of RRR for Fansteel who supplied to CEBAF c. 1990
- Long-standing work to understand the physical metallurgy of niobium (Peter Lee – FSU and Tom Bieler – MSU co PIs)
- DOE-HEP Accelerator Stewardship grant to explore possibilities for Nb_3Sn on copper
  - Nb_3Sn: $T_c \approx 18$ K, $\mu_0 H_c(0) \approx 0.4$ T   Nb: 9 K, 0.2 T
- DOE-HEP Cosmic Frontier grant to explore Nb_3Sn as a detector material for axion searches
- Context and driving questions for this presentation:
  - High-energy linear accelerators for FRIB, SNS, ILC, XFEL, LCLS-II, and beyond: *How should the manufacturing process, starting from Nb ingot through final cavity HPR, serve the development of an optimum final macro-, micro-, and nano-structure for best performance?*
  - High-power accelerators for e-beam applications: *Are there feasible approaches that are cheap (e.g. reduce Nb), compatible with compact portable refrigeration (e.g. no LHe, cryocooled), and capable of delivering high CW power?*
  - Cavities that operate in magnetic fields for ADMX, muon cooling channels, etc.: *Are there feasible materials that can produce high quality factor in a background of high magnetic field (e.g. 10 T)?*

A Metallurgical Approach to Improving Nb SRF Cavity Performance

- Lead PI: Peter J. Lee (FSU). Co-PIs: Lance Cooley (FSU), Thomas R. Bieler (MSU), Philip Eisenlohr (MSU), Pashupati Dhakal (JLab), Shreyas Balachandran (JLab), Eric Taleff (U-Texas-Austin).
- Postdocs: Santosh Chetri (FSU)
- Graduate Students: Andre Juliao (FSU), Zackery Thune (MSU), Cathy Bing (MSU), Bashu Khanal (JLab/ODU), Thomas Bennett (U-Texas-Austin)







Applied Superconductivity Center
National High Magnetic Field Laboratory
Florida State University

Jefferson Lab

Top-Down Goal Driven Analysis of Actual Tested Cavities

Knowledge-Based Integration

Flux expulsion, pinning, rf surface characterization

Magneto Optical Imaging, flux trapping, EBSD, heat treating of cavity half cells

Welding/ Fabrication

Annealing, Surface processing, Doping

High Q

Magnetic properties

Deep Drawing

Surface and physical properties characterization

Industry Collaboration

MOI, EBSD characterization of coupons
Electron Channeling Contrast Imaging
Crystal plasticity modeling with Recrystallization
Novel recrystallization/grain growth strategies

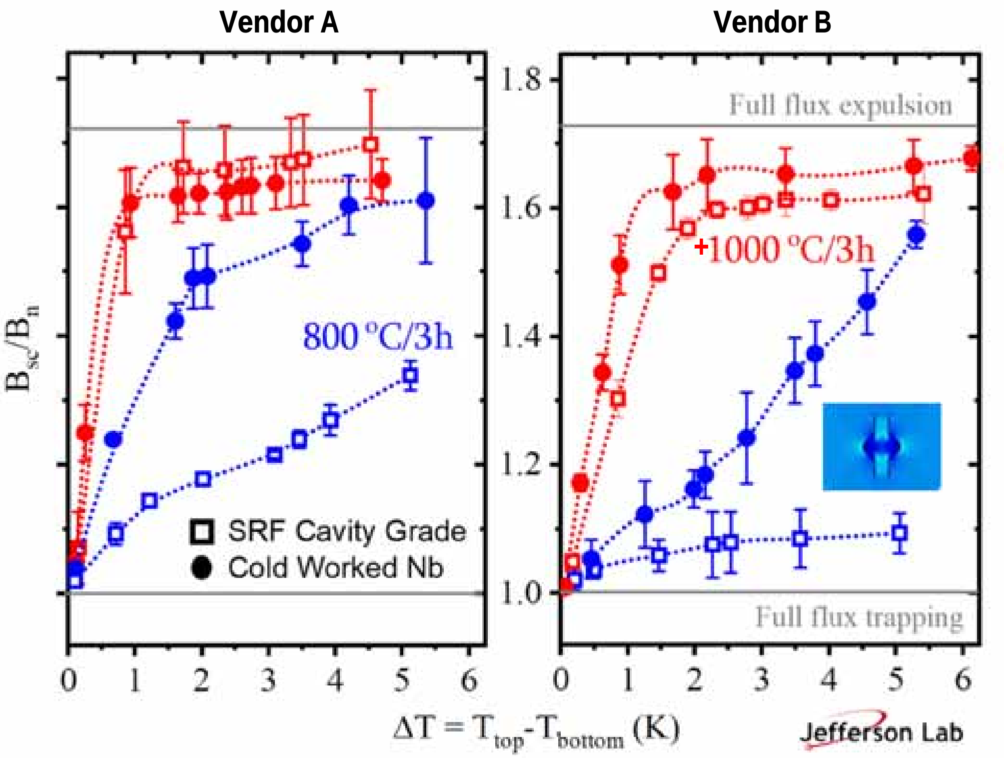
Breakdown forging, rolling, heat treatment

Coupon Testing and Assessment

Bottom-Up Coupon Experiments and Model Validation

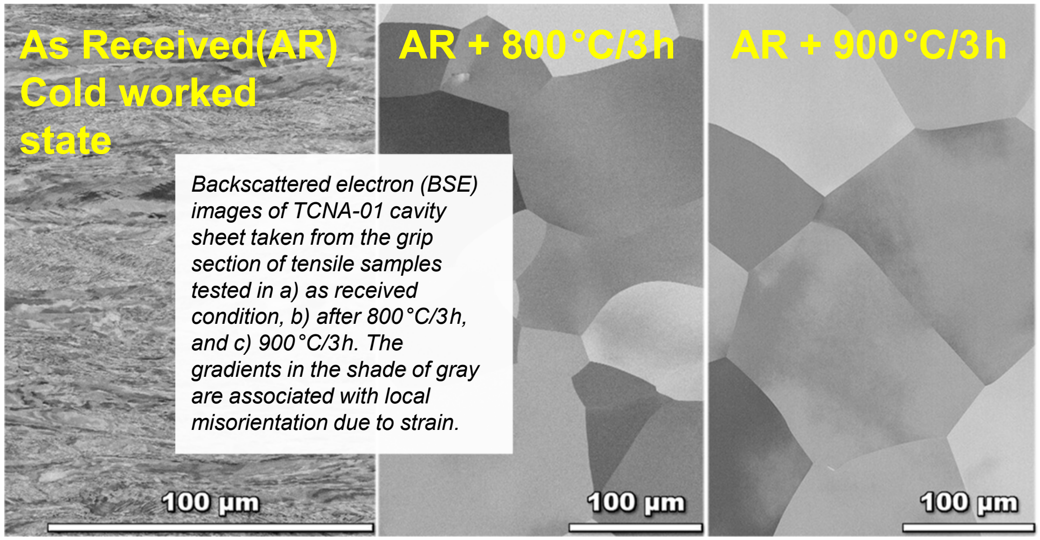
Michigan State University

JLab/FSU: Improving flux-expulsion by using cold-worked Nb



Comparison of Flux expulsion as a function of temperature differential in cavities from traditional sheet from two vendors (squares) versus novel non-annealed cold worked sheet at JLab (circles) with 800 °C/3h and 800 °C + EP + 900 °C + EP + 1000 °C/3h. Note that the flux expulsion is close to complete expulsion with 800 °C/3h heat treatments and ΔT of 2 K for "A" but requires a ΔT of 5 K for "B"

Continuing our investigation of sheets with and without final vendor anneal, we compared the flux expulsion of a Nb cavity made from traditionally specified (TCA-01) and non-annealed as-cold rolled sheet (TCNA-01). Flux expulsion studies support our hypothesis that cold work in the Nb sheet prior to cavity fabrication should improve flux expulsion by producing faster or more complete recrystallization with typical cavity heat treatments (HTs) [DOI: 10.18429/JACoW-NAPAC2022-WEZE5].



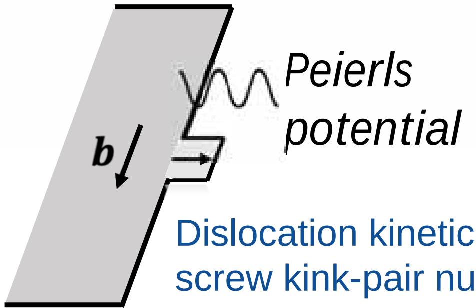
Backscattered electron (BSE) images of TCNA-01 cavity sheet taken from the grip section of tensile samples tested in a) as received condition, b) after 800 °C/3h, and c) 900 °C/3h. The gradients in the shade of gray are associated with local misorientation due to strain.

MSU: Modelling of defects in Nb

Simulation results of the newly implemented crystal plasticity constitutive description are being scrutinized against data from our own deformation experiments (mostly polycrystal tension) as well as literature

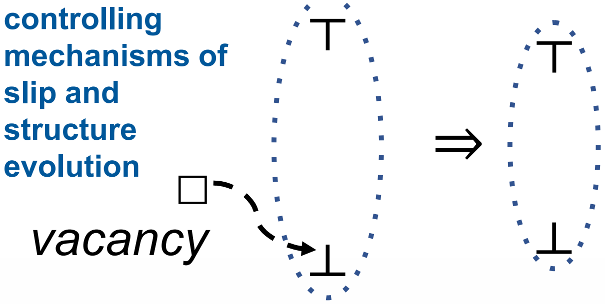
Cathy Bing:
Graduate
Student

Old model



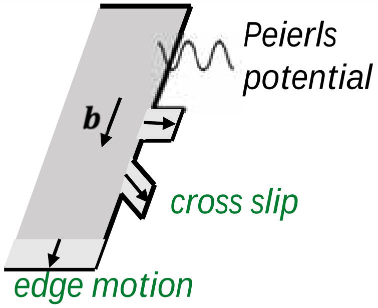
Dislocation kinetics: only screw kink-pair nucleation and lateral expansion

inconsistent state variable for proposed rate-controlling mechanisms of slip and structure evolution



Dislocation annihilation: only vacancy diffusion-assisted edge annihilation

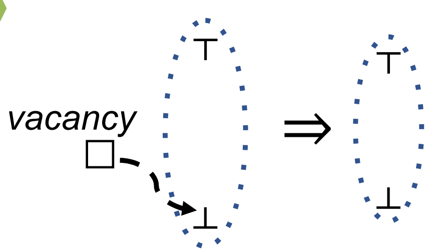
New model completes the separate descriptions of edge and screw



Screw kinetics: kink-pair nucleation and lateral expansion

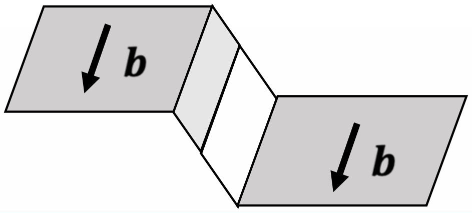
+

Edge kinetics: uniform glide under phonon drag



vacancy diffusion-assisted edge annihilation

+



A newly proposed mechanism for cross-slip and the according annihilation

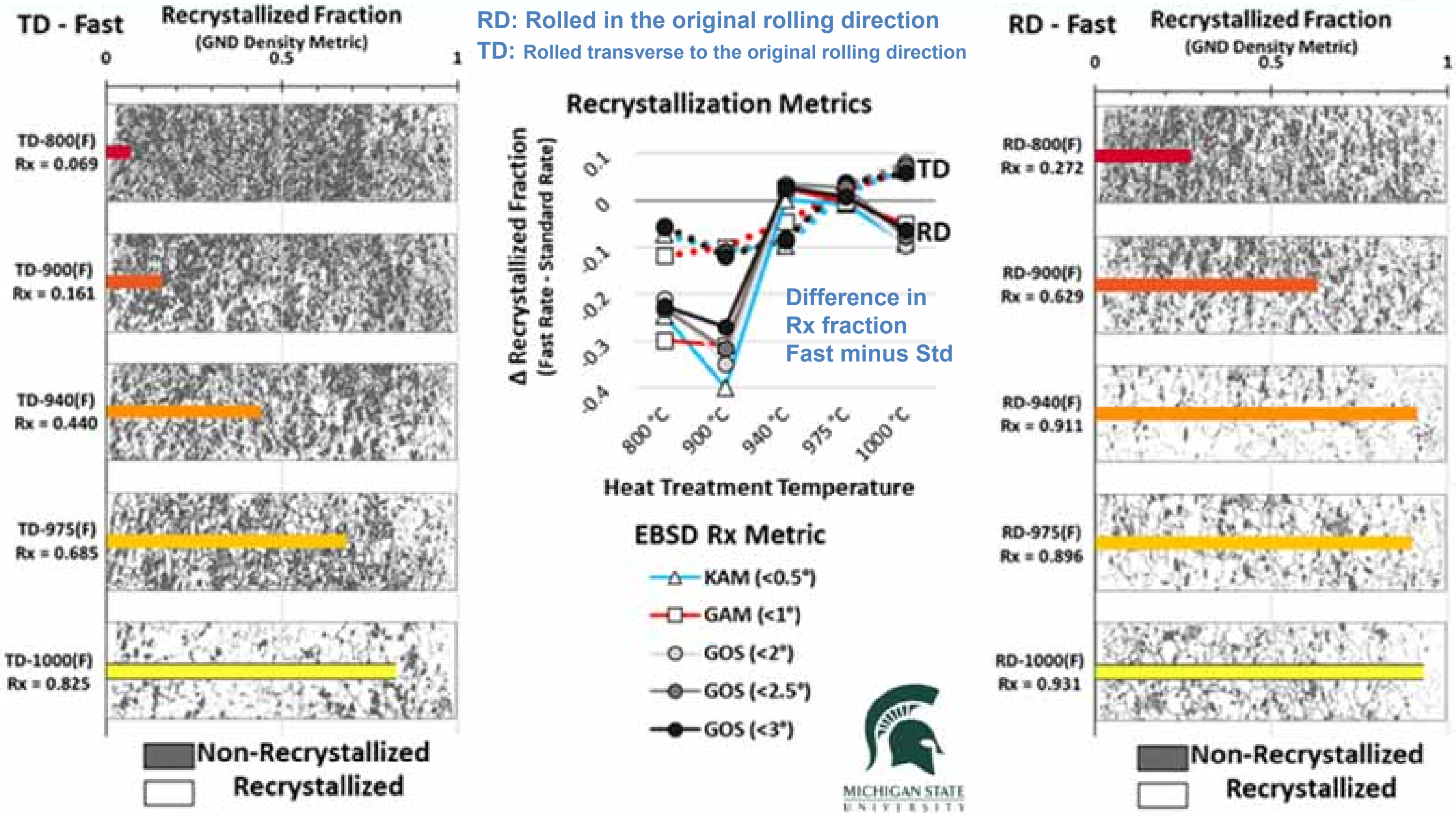
MSU: Novel Strategies and Methods: Fast Heating

The current variability in SRF cavity performance may arise from the known variability in microstructures and microstructure gradients in as-received polycrystalline Nb sheet

Locally different strain paths that occur in different parts of the half-cell as it is formed resulting in spatially variable arrangements of dislocations during forming prior to the heat treatment used to remove hydrogen.

Heat treatment then causes non-homogeneous disappearance or rearrangement of dislocations by *recovery (Rv)* and *recrystallization (Rx)*.

What is the impact of rolling direction and heating rate?



RD: Rolled in the original rolling direction

TD: Rolled transverse to the original rolling direction

Difference in Rx fraction Fast minus Std

10.1109/TASC.2023.3248533

Zack Thune: Graduate Student

*The fraction recrystallized in **TD** samples (left) recrystallized less efficiently than **RD** samples (right). The center graph compares the effect of heating rate (fast = 50°C/min, slow = 5°C/min), indicating a complex relationship that depends on the temperature and deformation path (5 different metrics for measuring the fraction Rx are compared, and they are all essentially equivalent).*

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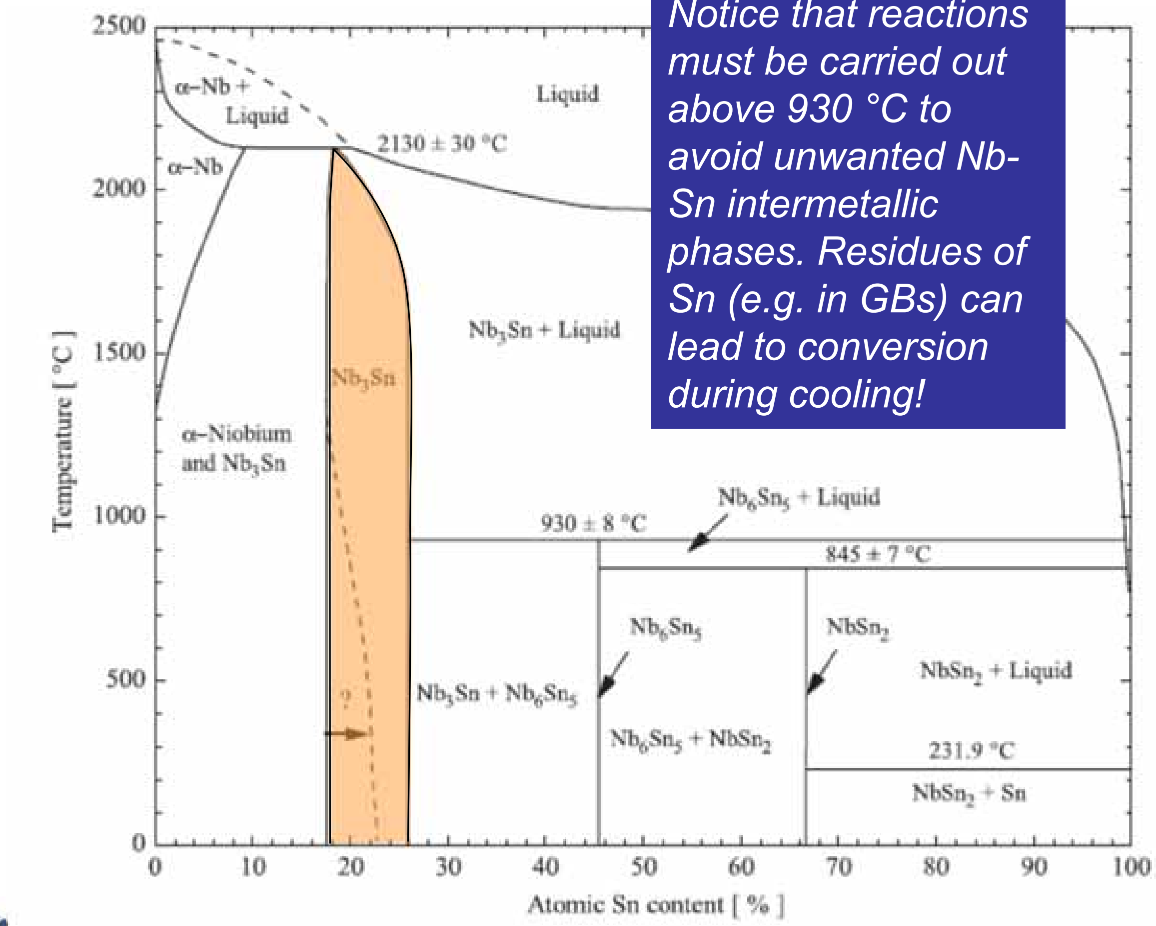
Nb-Sn Phase Diagram

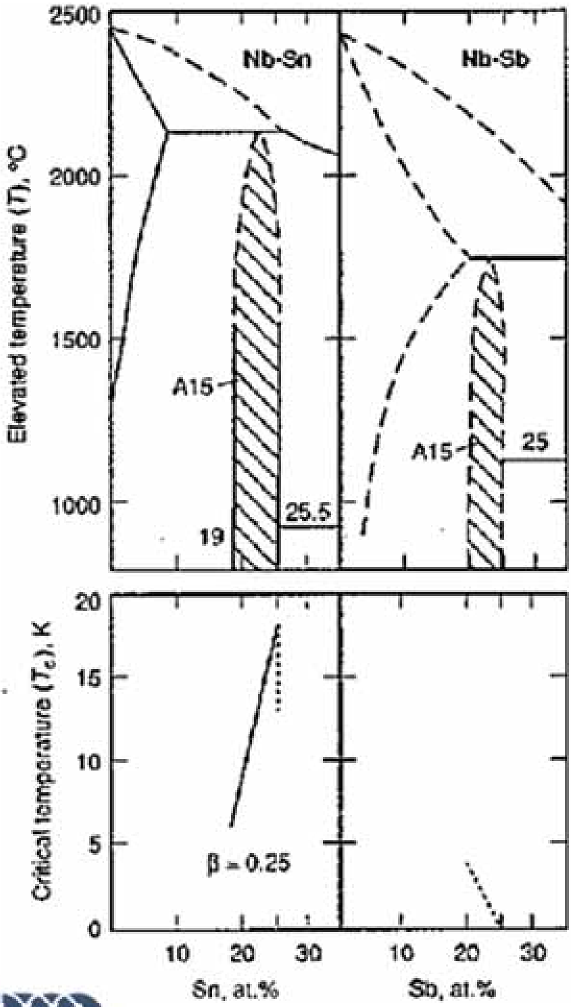


Notice that reactions must be carried out above 930 °C to avoid unwanted Nb-Sn intermetallic phases. Residues of Sn (e.g. in GBs) can lead to conversion during cooling!

Challenges encountered in past work:

- Vapors from toxic and corrosive chlorides
- Vacuum or special environment needed
- Copper melts! How to make a copper-clad conductor?
- Tin does not wet surfaces → balls of Sn produce composition variations
  - Adding a little Cu helps wetting
- Uniform temperature can be difficult to achieve
- Tin liquid and vapor corrode seals and other furnace components
- Formation of a tetragonal phase at cryogenic temperature

Excellent work at Fermilab and Cornell, with traces back to Wuppertal c. 1970



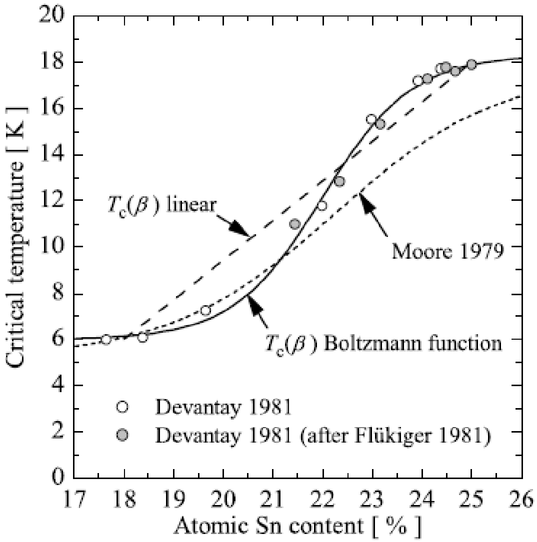
Avoid composition gradients

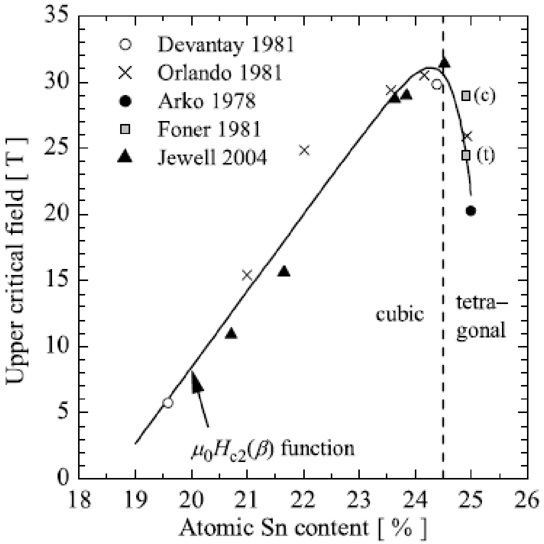
The best superconducting properties occur at the stoichiometric composition

T_c decreases by about 2 K per each at.%Sn less than 25%

Rate of decrease of H_{c2} not well known but certainly large too

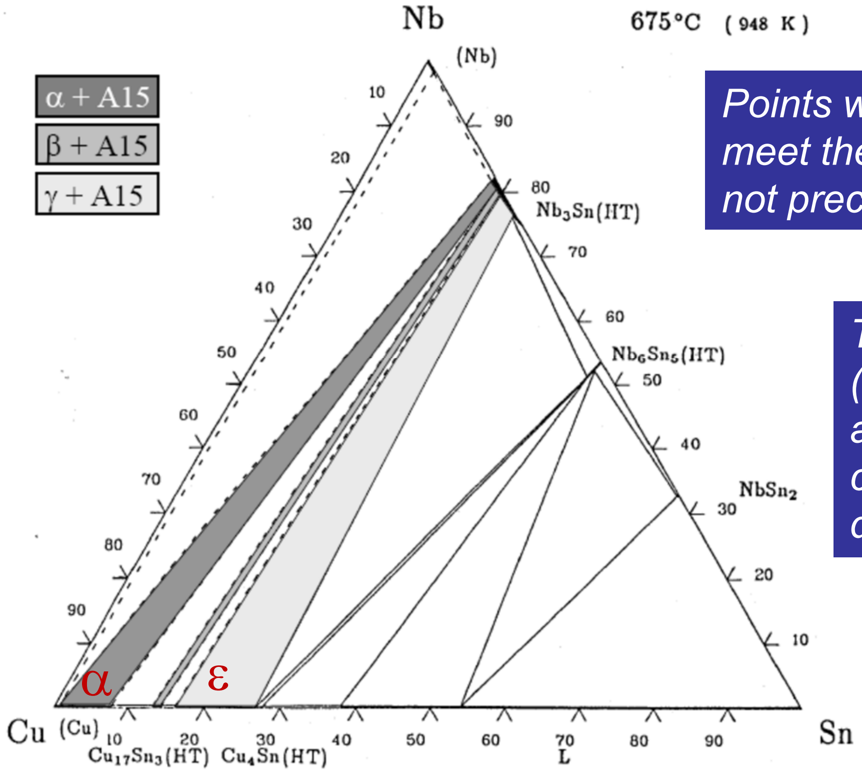
A. Godeke, SuST topical review 2006





Copper avoids the unwanted Nb-Sn intermetallics

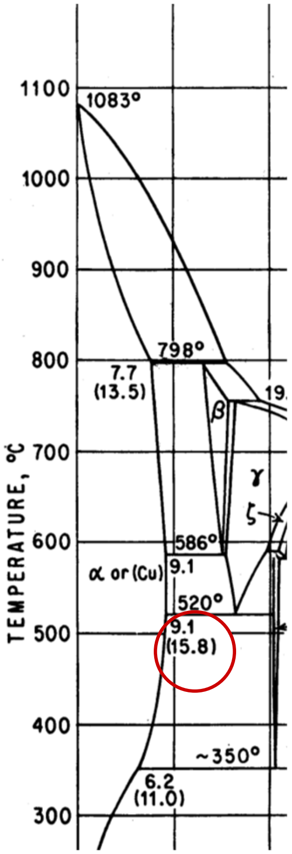
The addition of copper permits solid-state diffusion reactions to occur at temperatures as low as 600 °C and in ranges compatible with copper (m.p. 1085 °C)

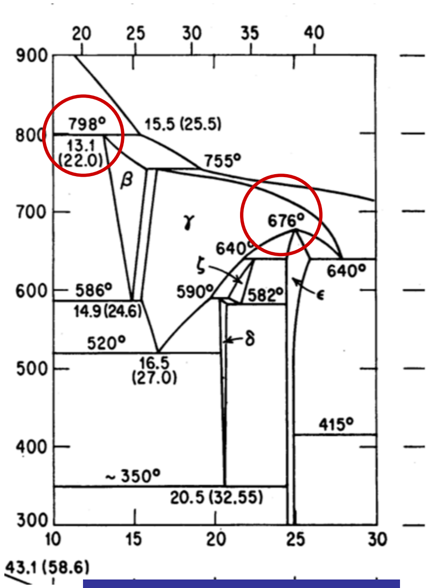


Points where tie-lines meet the Nb_3Sn field are not precisely known

Tin-rich Cu-Sn phases (chiefly ε) increase tin activity and facilitate Nb_3Sn phase composition closer to the desired stoichiometric 25%

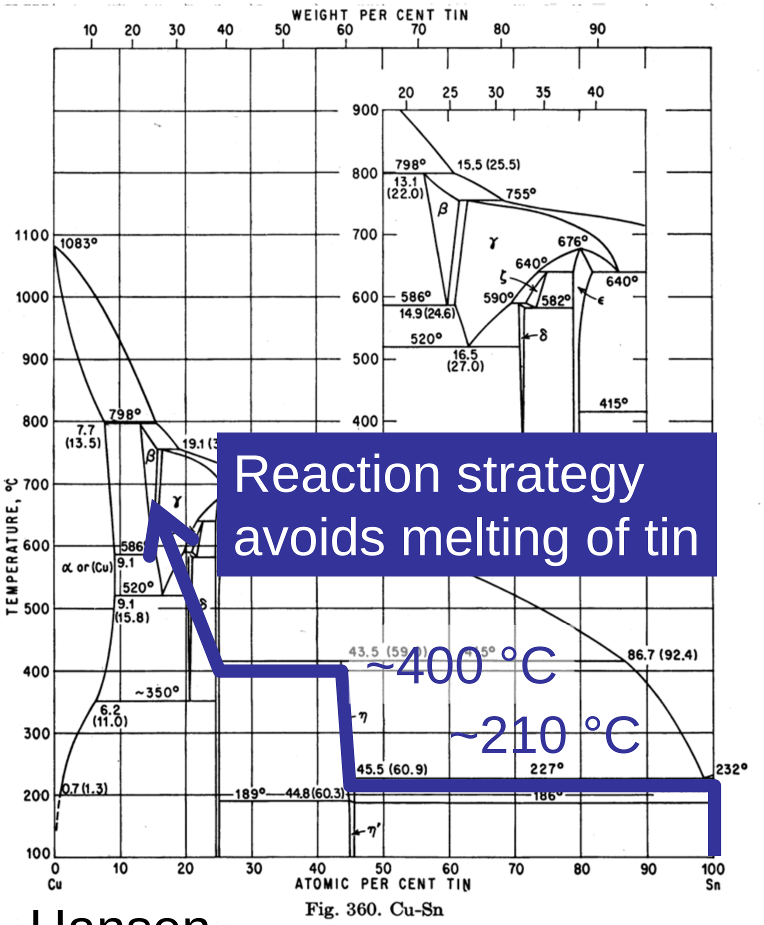
Cu-Sn phase diagram dictates reaction path and wire design strategies





Keep reactions below ~750 °C

9.1 at.% Sn = 15.8 wt% is the highest tin bronze



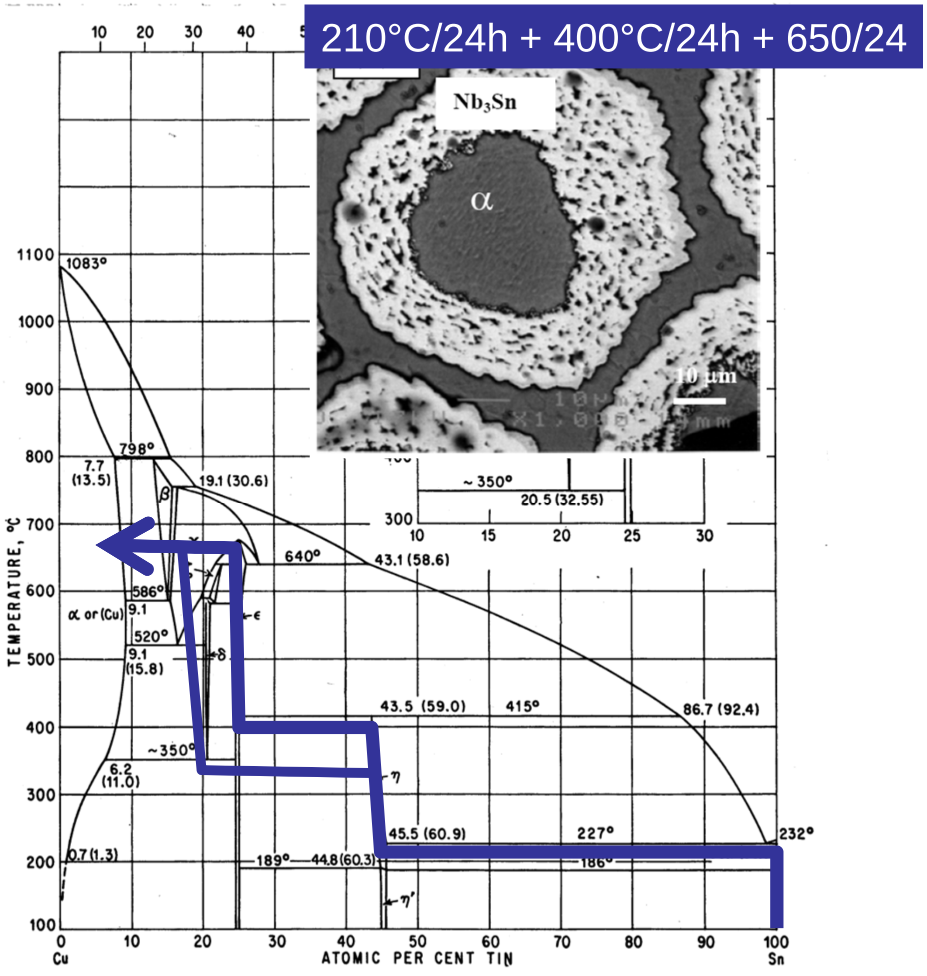
Reaction strategy avoids melting of tin

~400 °C

~210 °C

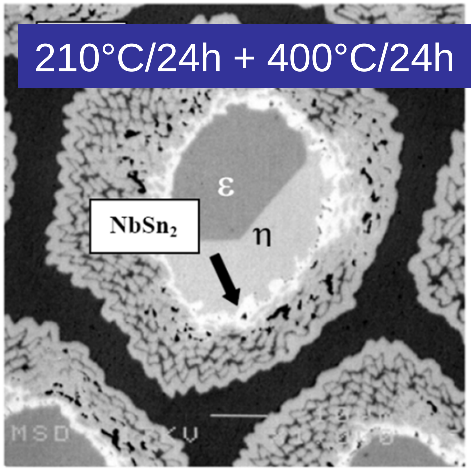
Fig. 360. Cu-Sn

Hansen

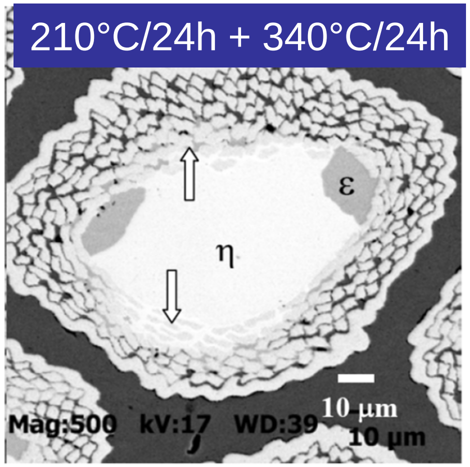


210°C/24h + 400°C/24h + 650/24

Fig. 360. Cu-Sn



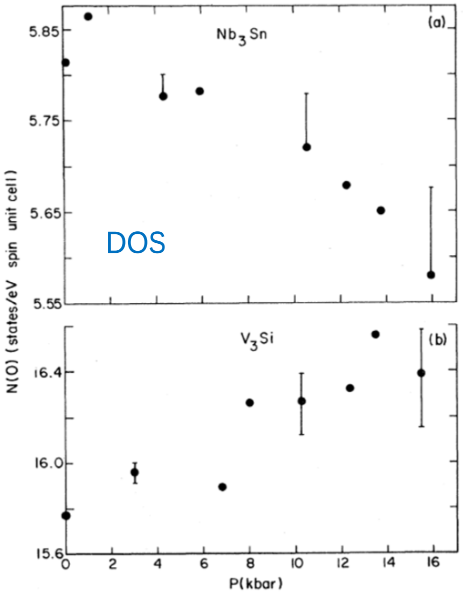
210°C/24h + 400°C/24h

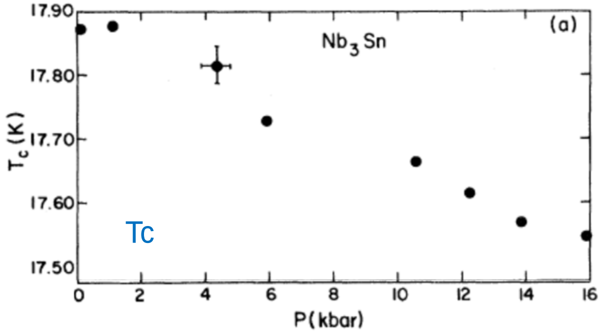


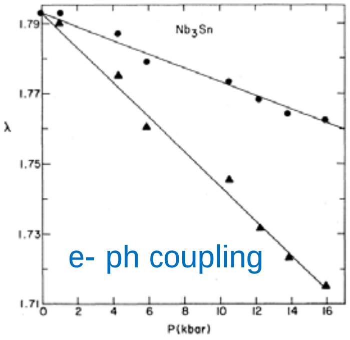
210°C/24h + 340°C/24h

Copper can generate strain effects that reduce Tc

“Electron density of states in Nb_3Sn under pressure”
Lim, Thomson, Webb PRB 1983
Nb_3Sn and V_3Si single crystals



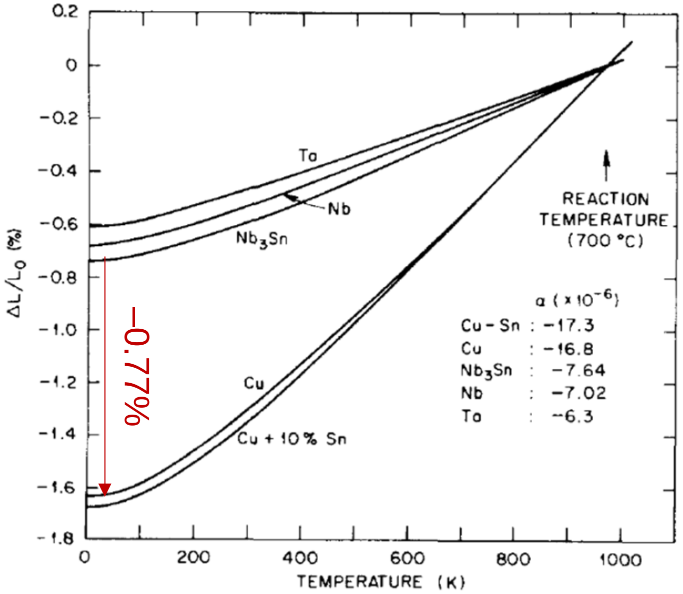




A prediction of the stress state in Nb_3Sn superconducting composites

D. S. Easton, D. M. Kroeger, W. Specking [a], and C. C. Koch
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

JAP 1980



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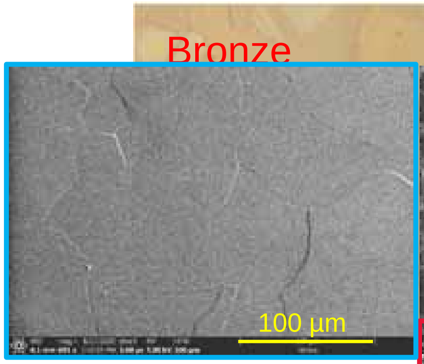
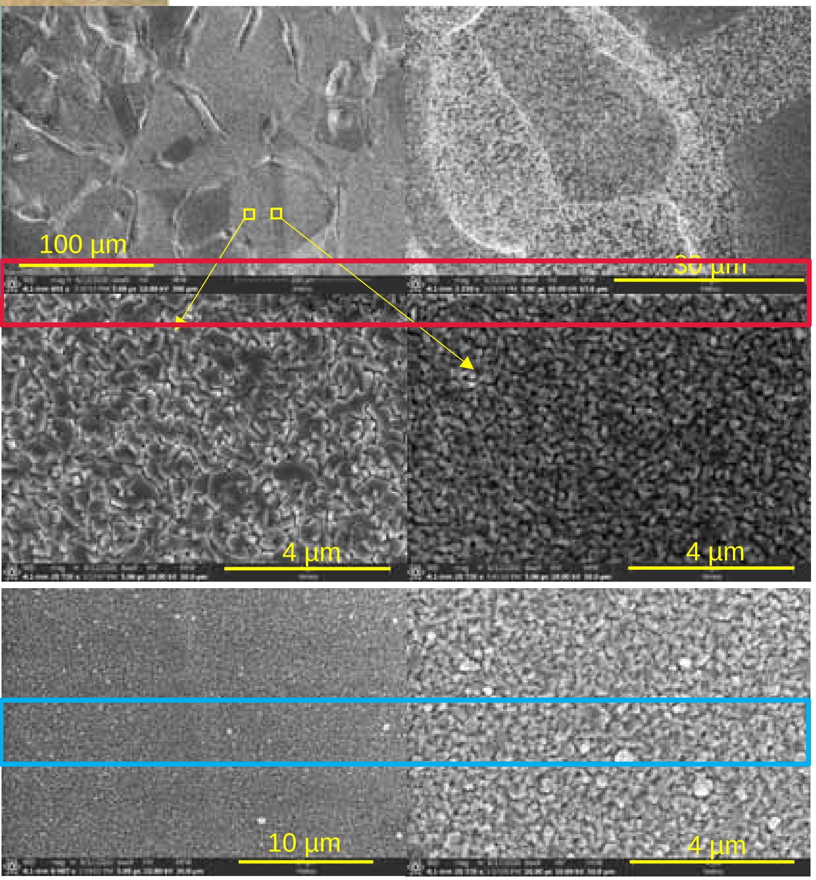
Niobium deposited onto Cu 13.5 wt.% Sn bronze

- In the 1990s, I had success depositing Nb onto Cu 14wt.% Sn bronze to form Nb_3Sn films
  - This process mimics the so-called “bronze route” wires
- Wenura Withanage repeated and perfected this approach 2018-2020

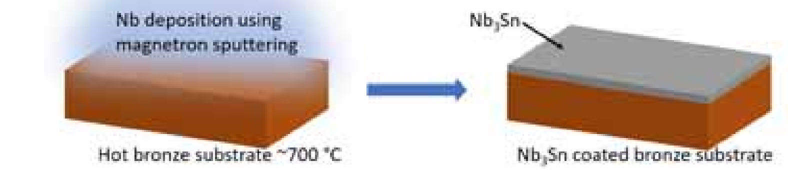


700 nm Nb_3Sn from Nb sputtered on bronze at 200 °C and reacted in vacuum at 715 °C

700 nm Nb_3Sn spontaneously grown on bronze at 715 °C



“Hot bronze”



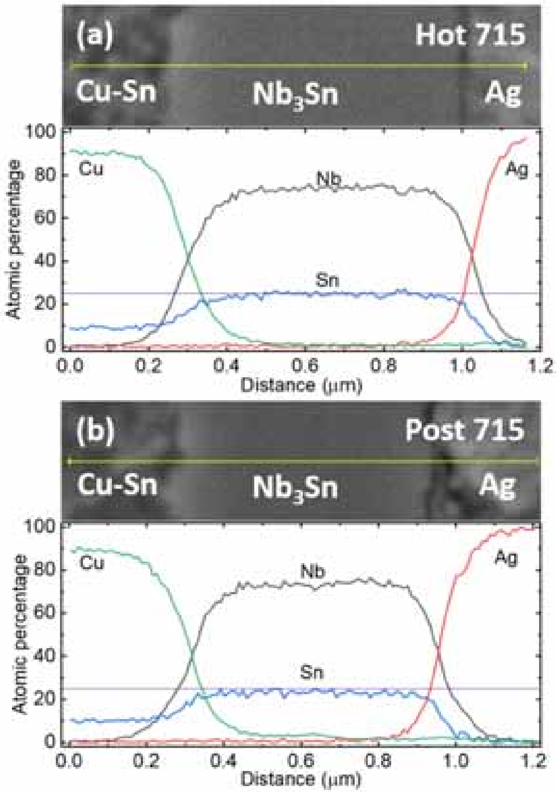
“Post-reaction”

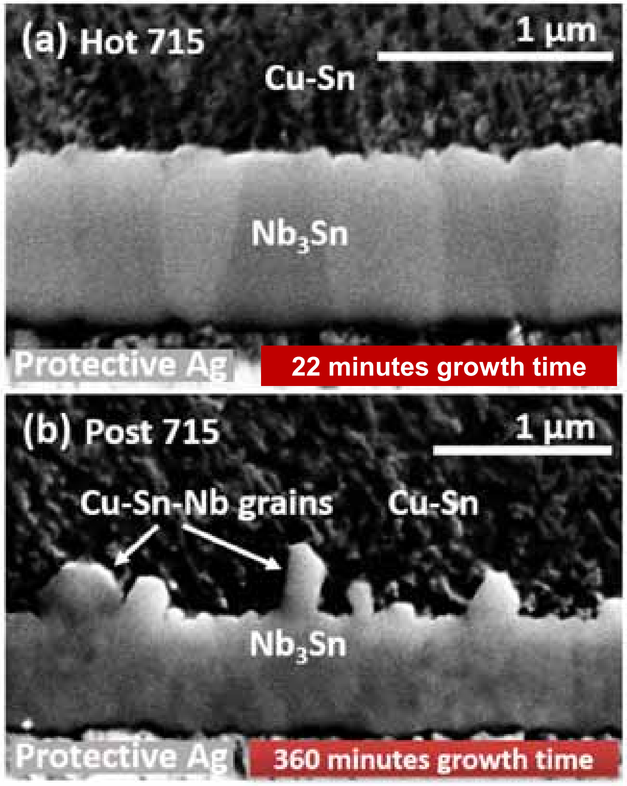
Mechanically polished

Wenura K. Withanage, A. Juliao, S. Balachandran, J. Buttles, C.–U.Kim, P. J. Lee, L. D. Cooley

Deposition of Nb onto “Hot bronze” gives advantages

- The hot bronze method created a nanostructure unlike what has been seen in wires…
- … at 10x faster growth rate
- … with better composition and properties than the post-reaction route
  - Post-reaction is like the method used to make bronze-route wires
- We think the large, columnar grains replicate successful Nb_3Sn microstructures, e.g. Posen et al.
  - RF tests are pending at partner labs





Withanage, Wenura K., Andre Juliao, and Lance D. Cooley. "Rapid Nb3Sn film growth by sputtering Nb on hot bronze." *Superconductor Science and Technology* 34, no. 6 (2021): 06LT01.

Additional results

- CTE mismatch does not explain the full amount of Tc suppression
  - Expect ~15.5 K, now has been verified by work at other labs
- XRD suggests additional strain perhaps near grain boundaries
- Post-reacted film is tin deficient

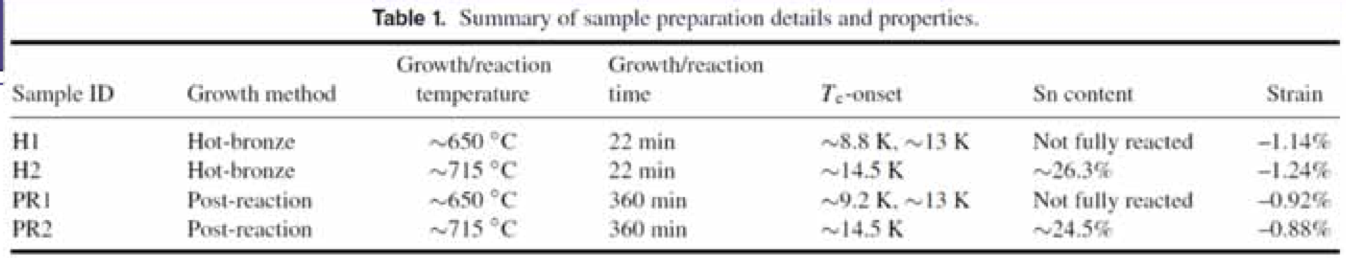
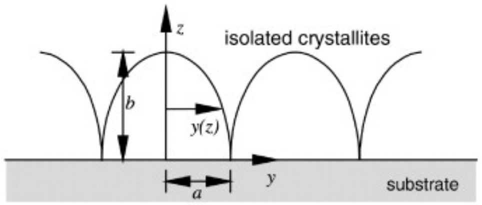
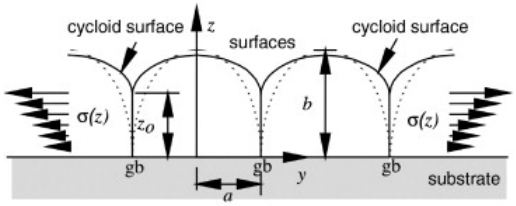


Table 1. Summary of sample preparation details and properties.

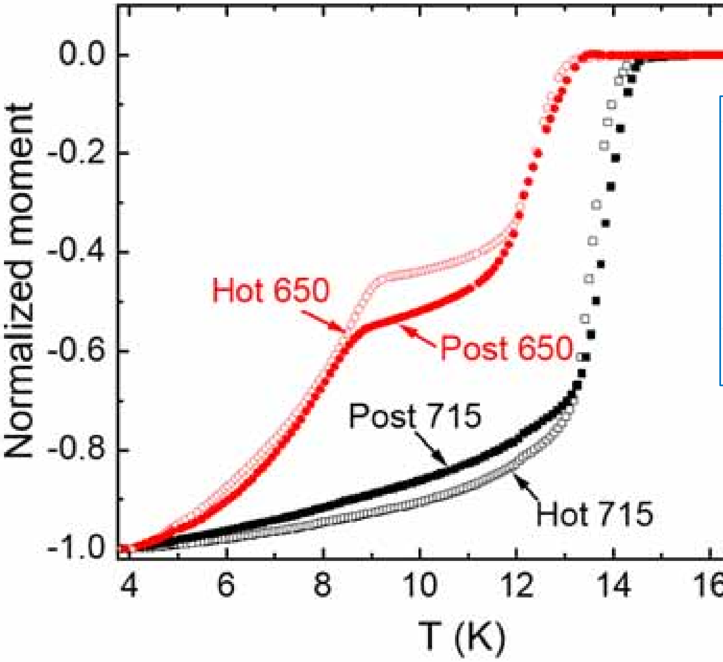
Sample ID	Growth method	Growth/reaction temperature	Growth/reaction time	T_c-onset	Sn content	Strain
H1	Hot-bronze	~650 °C	22 min	~8.8 K, ~13 K	Not fully reacted	–1.14%
H2	Hot-bronze	~715 °C	22 min	~14.5 K	~26.3%	–1.24%
PR1	Post-reaction	~650 °C	360 min	~9.2 K, ~13 K	Not fully reacted	–0.92%
PR2	Post-reaction	~715 °C	360 min	~14.5 K	~24.5%	–0.88%



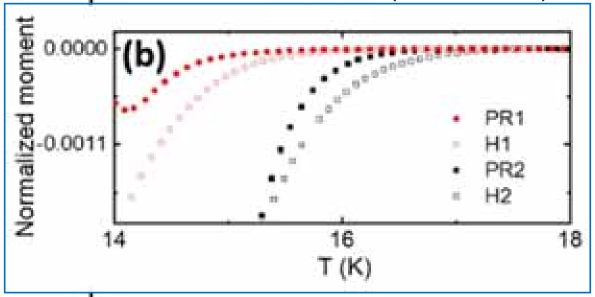
before coalescence

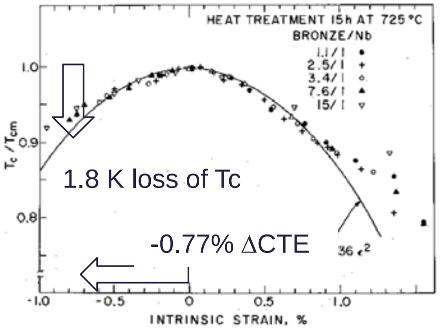


after coalescence



CTE mismatch



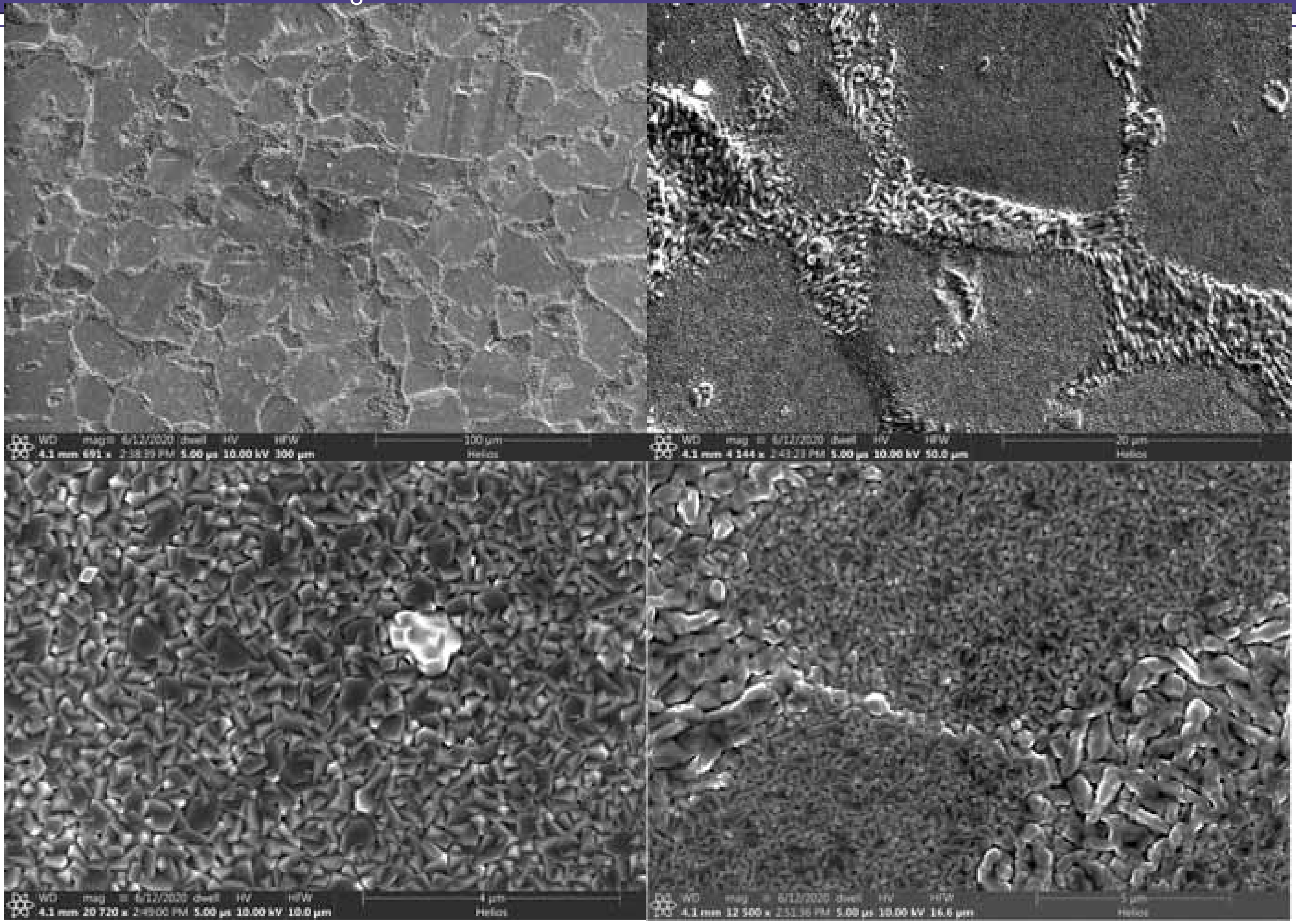


Ternary films

- Adding Ti is known to increase Nb_3Sn layer growth rate and improve properties in wires

- Ti appears to reduce bronze grain size and reduce twinning
  - Ti increases stacking fault energy
- Our bronze sample appears to have excess Ti at grain boundaries at the “hot bronze” conditions, so very large $(Nb,Ti)_3Sn$ grains grow there
  - Different source materials, e.g. “Ospray bronze”, could improve homogeneity

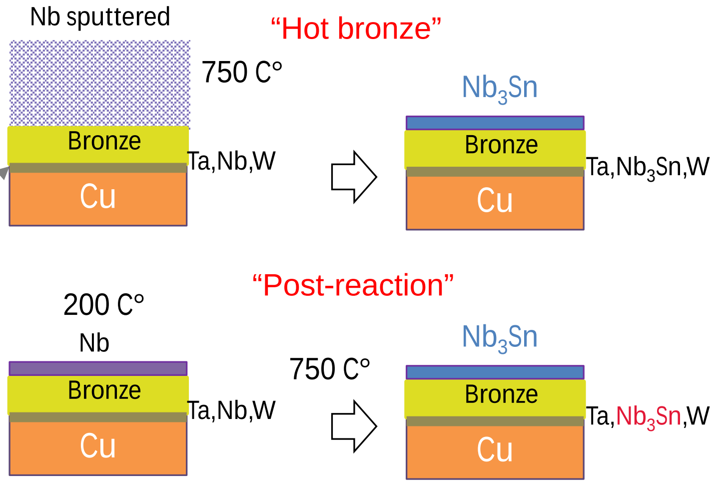
Microstructure – Nb_3Sn on CuSnTi bronze



Withanage, Wenura K., Andre Juliao, and Lance D. Cooley, unpublished

Copper substrates – PhD thesis work of Andre Juliao

- Tin will quickly diffuse into copper and greatly reduce its electrical and thermal conductivity.
  - As little as 0.1 wt.% Sn is sufficient to reduce RRR from 300 to 5.
- Diffusion barriers are standard art in wires.
  - Usually this is a layer of Nb, Ta, or a Nb-Ta mixture because these metals have no solubility for Cu nor any intermetallic compounds.
- All work on copper substrates has used a diffusion barrier of Nb, Ta, or W.
  - Ta and W could also provide offsetting CTE

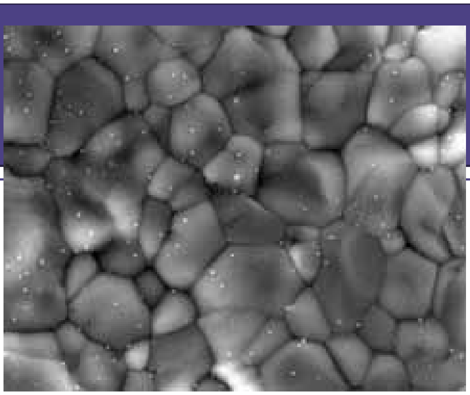


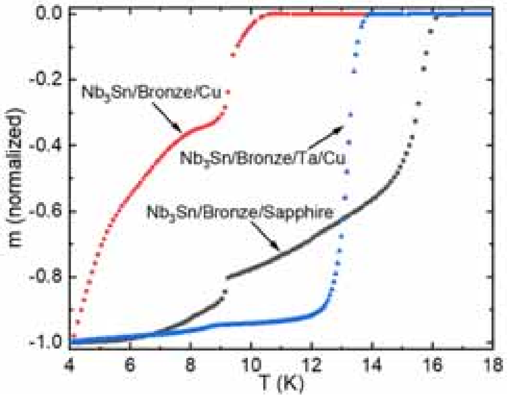
Opportunities:

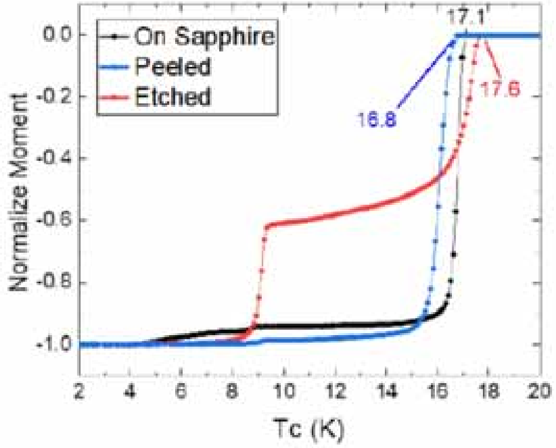
1. *The 10x faster reaction rate for "hot bronze" might facilitate growing a thick Nb_3Sn coating without losing too much Sn to diffusion through or reactions with the diffusion barrier*
2. *Cu-Sn (bronze) composition can be varied to explore Sn-rich layers*

Validating the need for a diffusion barrier and verifying that the Nb_3Sn film itself is of good quality

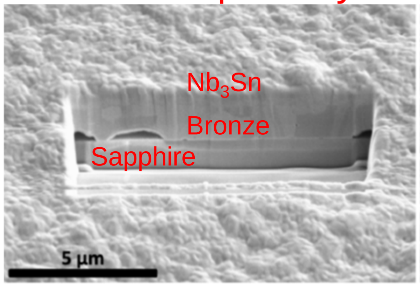
- We chose to evaporate bronze from Cu-Sn sources
  - Other work in community: multilayers, electroplating
- Pre-heat Sapphire/Bronze to 680 °C and hold before Nb deposition (Wenura Withanage)
  - Method used for solid bronze
  - However, the hold resulted in significant loss of Sn as vapor from the bronze prior to the Nb deposition.
- Pre-heat + immediate Nb deposition (Andre Juliao)
  - Low Sn loss, good quality
  - The film was peeled off after low temperature measurements to detach from the CTE of sapphire
  - Then the film was etched to remove bronze and its CTE contribution
  - Interface bubbles revealed – is this Kirkendall porosity?





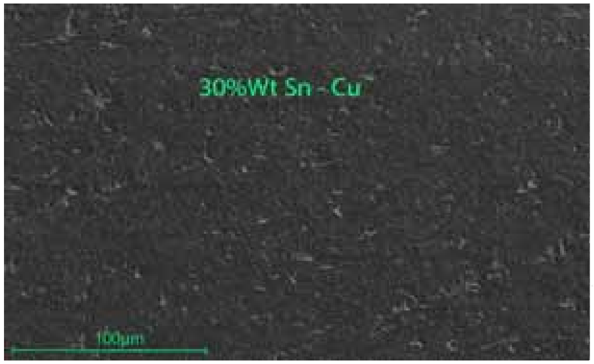


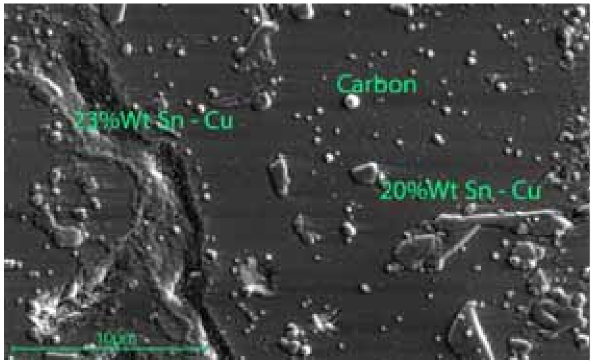
Kirkendall porosity?



Ta barrier, higher Sn activity via Sn-rich Cu-Sn

- We mixed Cu and Sn powders to get Cu-Sn source composition up to Cu40wt%Sn (ε phase)
- Sn content after evaporation was typically higher than Sn content in the source
  - Consistent with Sn vapor pressure
  - Control over composition is more difficult that anticipated initially
- Some compositions gave homogeneous Cu-Sn coatings, while others were multi-phase





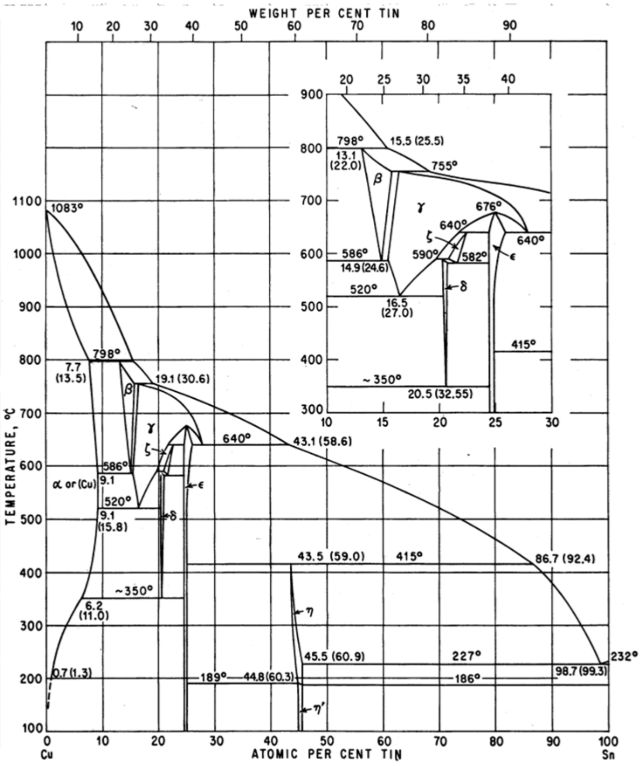
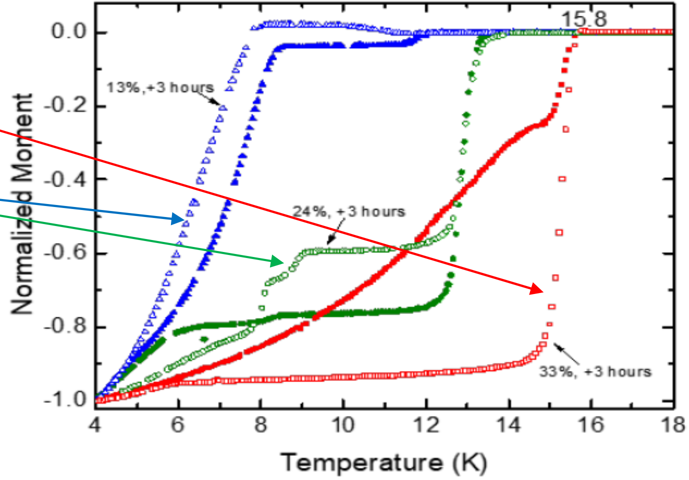


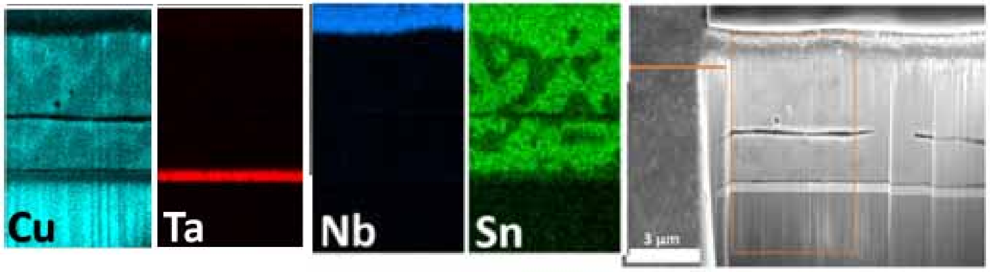
Fig. 360. Cu-Sn

Results for Cu/Ta barrier with high Sn activity

- Hot deposition with follow-on anneal in-situ
  - Anneal can homogenize film composition and reduce structural disorder
  - But anneal can also cause Sn to evaporate from Nb_3Sn, resulting in Sn loss and degraded properties
    - In wires, Sn is continually supplied from a large reservoir. Evidently, 13% and 24% Sn layers deplete before the Nb_3Sn reaction completes
- Post reaction: encouraging Tc results
- Nb_3Sn films are continuous
- Cracks and delamination of Cu-Sn parallel to substrate are seen after reaction
  - Is this related to Cu-Sn phase changes upon heating and after Sn loss to Nb_3Sn?
  - Or is it due to Kirkendall porosity?

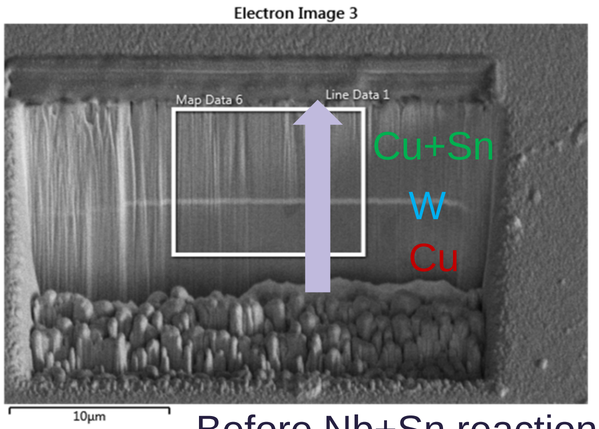


Filled symbols = hot deposition only
Open symbols = hot deposition + 3 hrs anneal

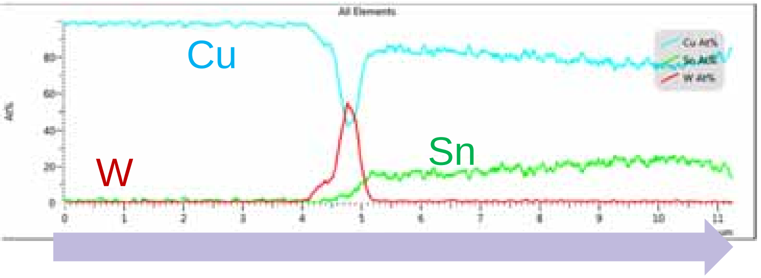


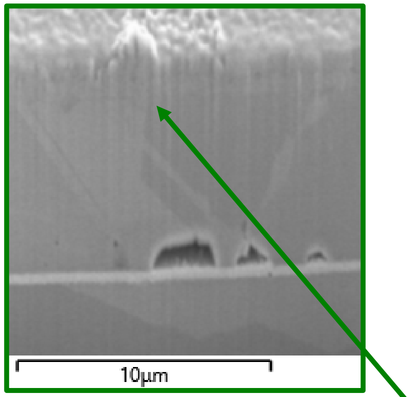
Low CTE diffusion barrier - tungsten

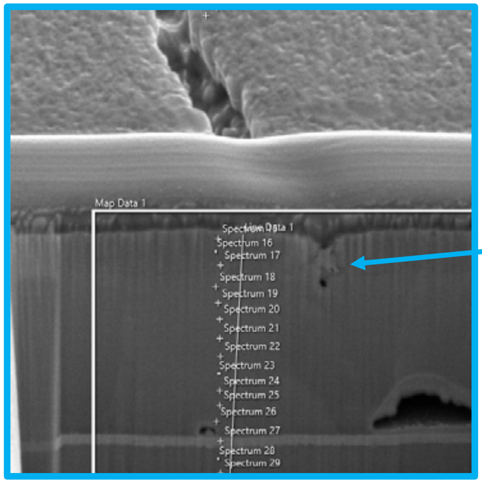
Cracks and delamination observed post-reaction, not fully understood.



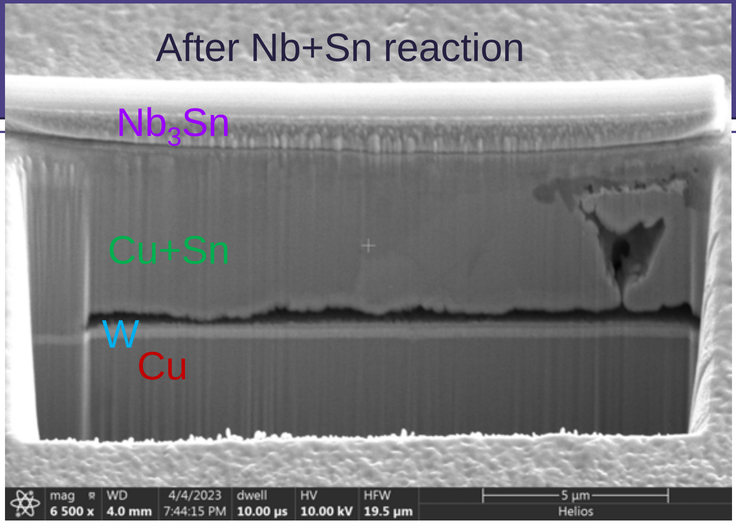
Before Nb+Sn reaction

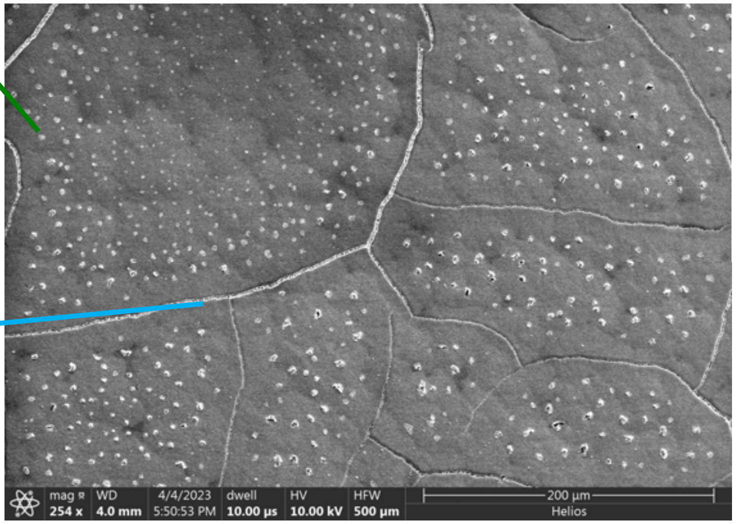






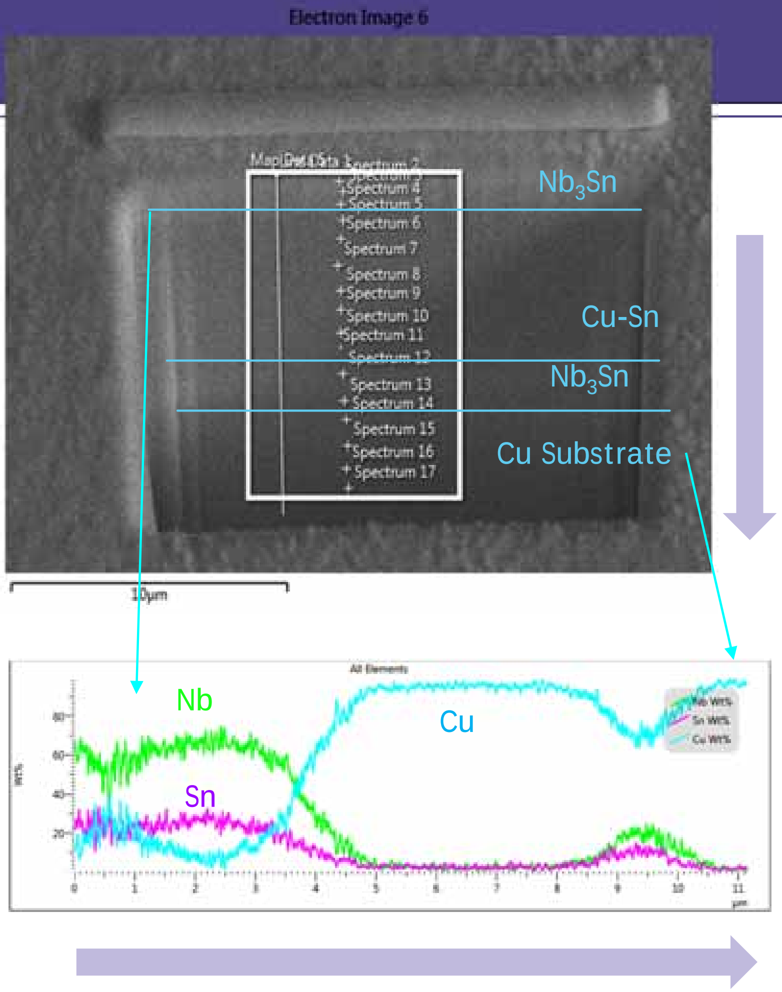
After Nb+Sn reaction

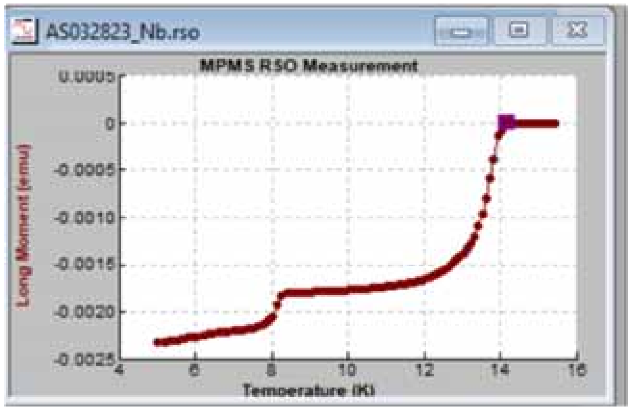


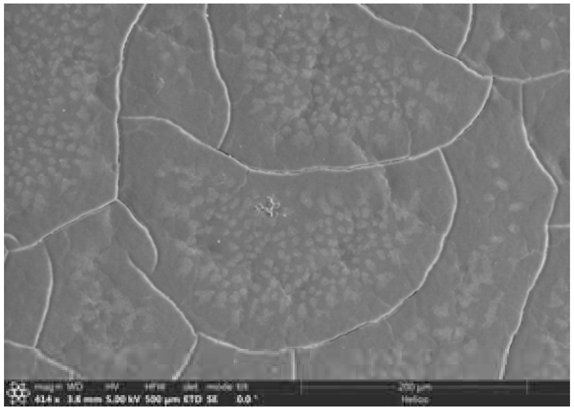


Nb barrier, high tin Cu-Sn

- Wire technologies usually use a Nb barrier
- A Nb diffusion barrier will react with the Cu-Sn and “steal” tin from the supply
- Kirkendall porosity appears to be mitigated
- High “hot bronze” reaction rate facilitates growth of thick Nb_3Sn at the surface by the time a thin Nb_3Sn layers appears at the barrier







Preview

- A quick overview of the Applied Superconductivity Center and some of the work we've been doing in SRF since ~2010
- Nb_3Sn synthesis methods from magnet conductors that could be used to make SRF cavities on copper bodies
  - Challenges from thermodynamics
  - Approaches:
    - Nb onto hot bronze with spontaneous *in-situ* Nb_3Sn formation
    - Cu substrates with diffusion barriers and thermal contraction management
    - High-Sn Cu-Sn phases vs low-Sn bronze (α phase up to Cu 14 wt.% Sn)
    - Cu-Sn onto Nb followed by reaction and etching
    - Healing seams: Are clam-shell cavities possible?
- Prospects for scalability

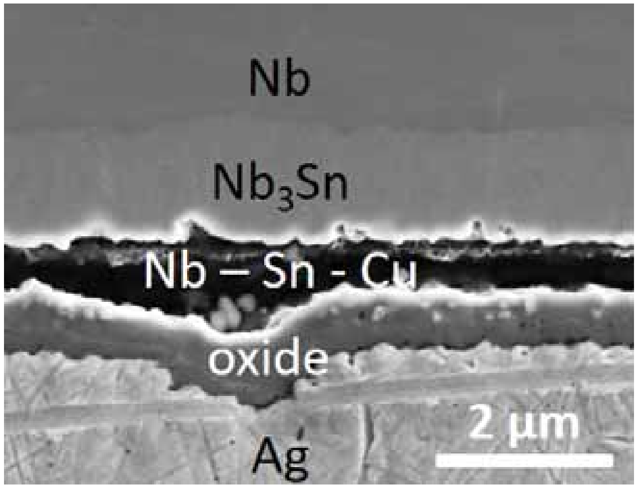
Bronze on niobium

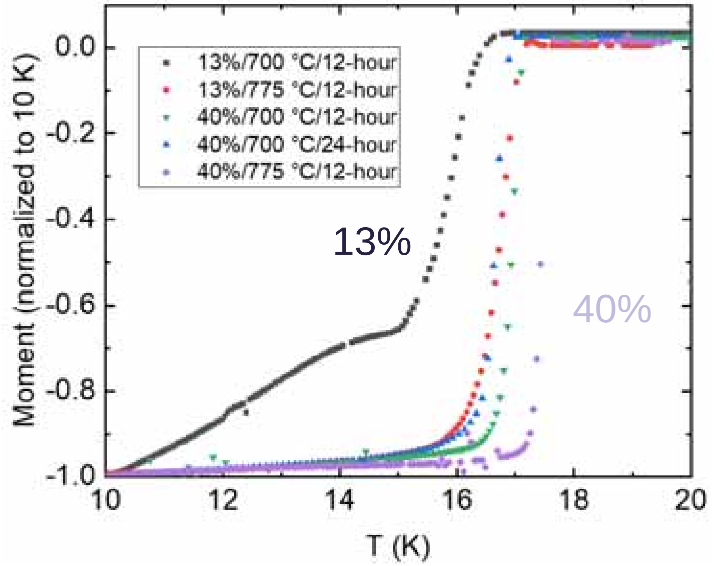
- A plausible path that can be used with existing Nb cavities, as well as Nb films on copper bodies, is to deposit Cu-Sn onto the Nb, give a reaction heat treatment, and then remove the bronze by gentle etching (APS) or electropolishing
  - Excellent work elsewhere by Fermilab / U. Pisa, CAS Lanzhou, IHEP, NIMS/KEK

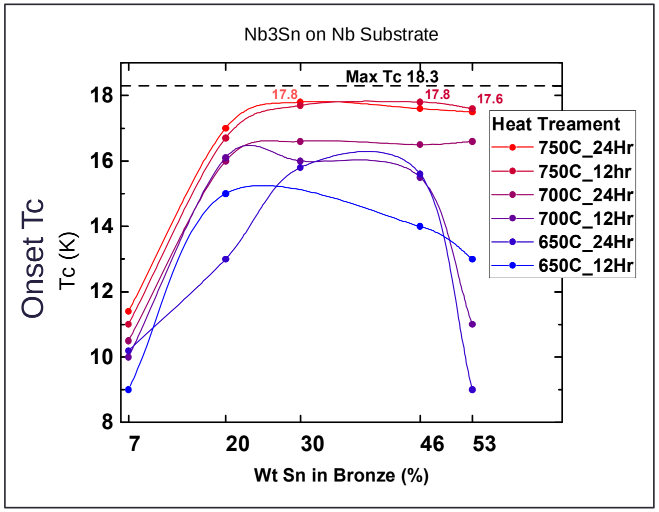
CTE match to Nb mitigates degradation due to strain

Higher tin activity produces better results

Furnace contamination produced oxide artifact

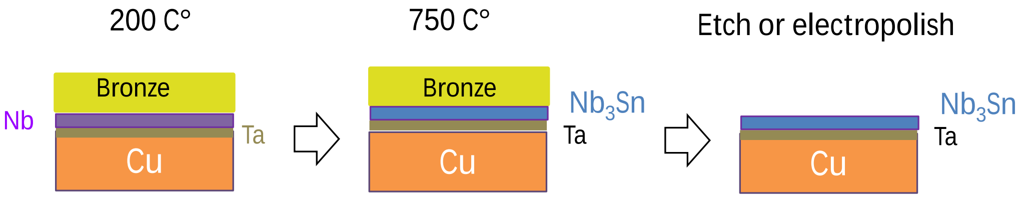


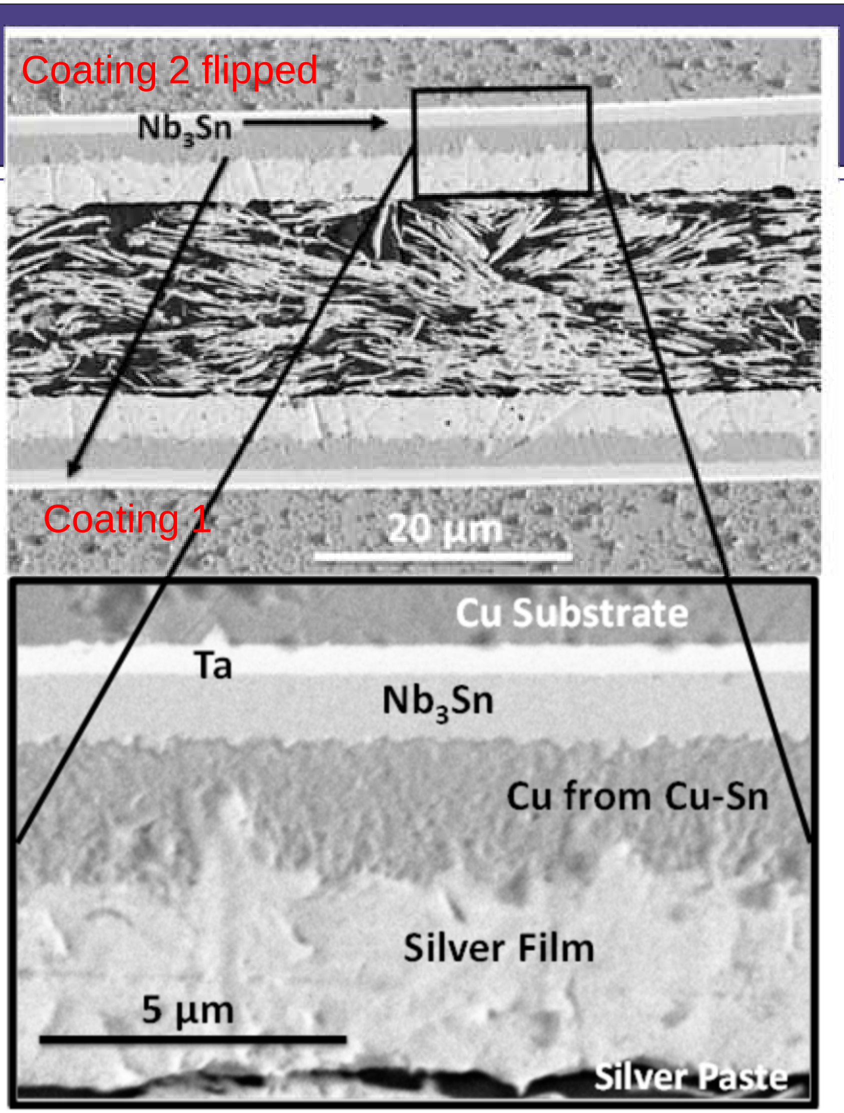




Bronze on Nb with copper substrate

- Ta barrier deposited on mechanically polished copper, then Nb is deposited on the Ta
- The Cu-Sn coating is then evaporated
  - This could also be a sequence of Cu and Sn layers (as Fermilab and Pisa are exploring) or Cu-Sn alloy deposited by other means (as being explored by groups in China and Japan).
- This approach is very promising since there appears to be good adhesion and uniform structure. (Tc data is in progress.)





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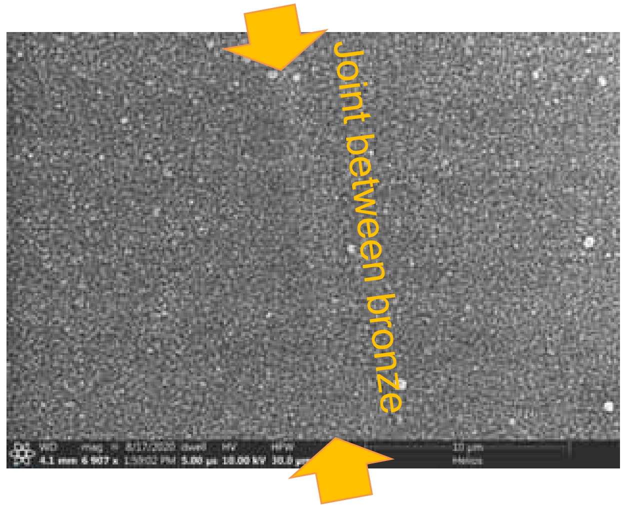
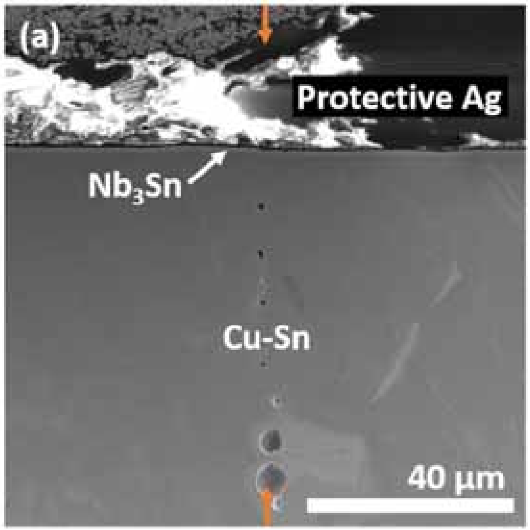
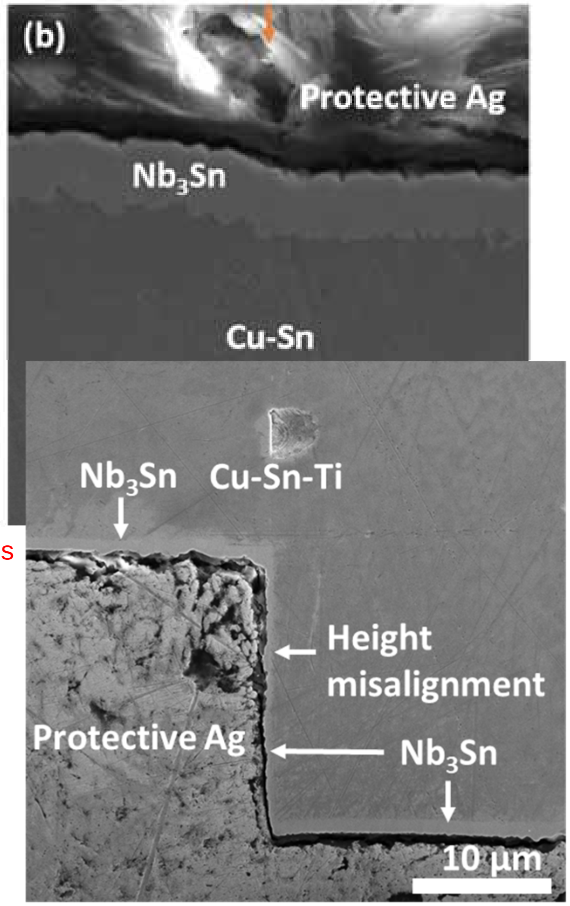
Post-reacted films suggested that seams could be sealed over by the Nb_3Sn

Nb on two bronze pieces, “hot” method





Mechanical strength measurements in progress



- Since Nb expands by 37% when it takes up Sn to form Nb_3Sn, films that cover joints and interfaces can expand to meet up and cover the interface
- Are clam-shell cavities possible, therefore?
  - Enables line-of-sight deposition methods and post-deposition inspection

Z lwkdqdjh/Z hqxud N1/Dqguh Mkdr/dqg Odqfh G1Frrdn|/vxep lwhg

Prospects for scalability (summary)

- RF tests of coatings are needed
  - We have distributed “hot bronze” samples to SLAC, JLab, and LLNL but no results yet
  - Chief concerns: How lossy are grain boundaries? Compared to other Nb_3Sn routes, do Cu-Sn routes always contaminate boundaries with copper and degrade RF performance?
- Interface stress, Cu-Sn delamination, and Kirkendall porosity needs attention
  - Locate the vacancy sink in a safe place, e.g. as the outer surface for Cu-Sn on Nb methods
  - Further opportunities exist to tailor the CTE mismatch by depositing multiple layers, e.g. Cu/Ta/W/Nb with Cu-Sn top coating followed by reaction and etching.
- Better control over the composition and structure of the Cu-Sn coating is needed
  - Evaporation from alloy sources appears to have more difficulty than initially anticipated, e.g. due to imbalance and variation of Cu and Sn vapor pressures during the evaporation run.
  - Evaporation of Cu and Sn layers, followed by heat treatment, could be a viable option
  - Many other methods exist to apply Cu-Sn

Prospects for scalability (2)

- High Sn activity can be facilitated by re-tracing methods used in wire technologies
  - We used evaporation from Cu-Sn alloys with high wt.% Sn
  - Multilayers of pure Cu and pure Sn could be used, as well as other combinations of Cu and Sn particles
  - Densification, management of density changes between different Cu-Sn phases, and avoidance of the (Nb,Cu)Sn_2 intermetallic (so called “Nausite”) will continue to be challenges
- “Hot” methods, when scaled to cavities, could require cylindrical magnetrons to be inserted inside heated cavity bodies that are effectively ovens
  - Andre Anders design at LBNL: Overpower the heat load with cooling water, but this places a heavy premium on plumbing, feed-throughs, magnets, etc.
  - Other exciting methods that are compatible with copper are available, e.g. Ultramet’s CVD process
- “Post reaction” methods are adequate, but they require a lot of time and temperature to achieve microstructures known to have good RF properties
  - Deposition process inherently create a lot of defects that inhibit structural organization and grain growth
  - Fine-grained structures are, therefore, most likely, which could increase RF losses by grain boundaries

Thank you