Materials Studies of Processes in Internal Oxidation Nb_3Sn wires: TU Bergakademie Freiberg Collaboration

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With thanks to A. Leineweber, J. Lachmann and S. Waschull (TU Bergakademie Freiberg)

Introduction

- Magnet designs for proposed future energy-frontier hadron colliders impose challenging performance targets for Nb_3Sn wire, including:
  - non-Cu $J_c \geq 1500$ A/mm^2 (16 T and 4.2 K)
  - $d_{eff} \leq 20$ µm
- Internal oxidation methods show considerable potential to achieve these targets
- Collaborations in the context of the High Field Magnets (HFM) programme are developing the understanding needed to establish a scalable wire technology, and optimise wire designs and heat treatments
  - UNIGE (KE4663) is working towards a rod-in-tube internal oxidation wire design, producing and characterising trial wires
  - This presentation concerns a new collaboration agreement with TU Bergakademie Freiberg (KE5963) addressing the mechanisms of this process with fundamental materials studies

A. Ballarino et al., *IEEE Trans. Appl. Supercond.* 29 (5) 6001709, 10.1109/TASC.2019.2896469

TU Bergakademie Freiberg

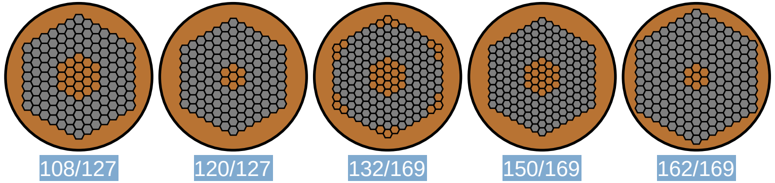
- Prof. Andreas Leineweber, Institute of Materials Science (IWW)
  - Particular expertise in phase equilibria and crystallographic analysis; intermetallics (e.g. solder systems, Nb_3Sn superconductors); XRD and Rietveld analysis
  - Equipment for alloy production, sintering, PVD and galvanic deposition
  - Characterisation by XRD, TEM and SEM (with EBSD), thermal analysis
- Also access to relevant methods in other departments:
  - Institute of Experimental Physics: semiconductor deposition
  - Materials Technology: Institute of Metal Forming

Nb_3Sn Wire Technology

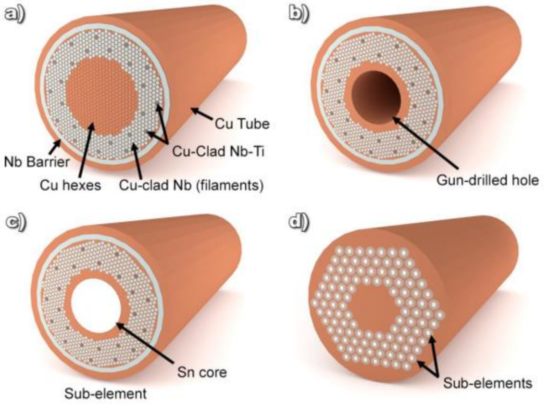
1954-2024

YEARS / ANS CERN

- 2024 marks the 70th anniversary both of CERN and Nb_3Sn, now finally being united for HL-LHC in accelerator magnets
  - Key challenge: Nb_3Sn is **brittle**, and multifilamentary wires with a large fraction of stoichiometric, fine-grained Nb_3Sn are needed
- Our present baseline wire type is a variant of the internal tin process (1974):
  - Nb filaments are distributed in a Cu matrix containing a Sn core
  - Nb_3Sn grows by solid state reaction-diffusion
- The Restacked Rod Process (RRP®, ~2001) was developed by Oxford in Carteret (NJ, USA), now Bruker OST
  - Subelements are produced from an assembly of Nb rods in Cu contained within a Nb diffusion barrier, stacked, and drawn to produce the wire
  - Wires are now Ti-doped (increases B_{c2})
  - Flexible configuration to customise Cu/non-Cu and effective filament size, and optimise J_c and RRR for the application


108/127 120/127 132/169 150/169 162/169

Selected RRP® wire designs (schematic)

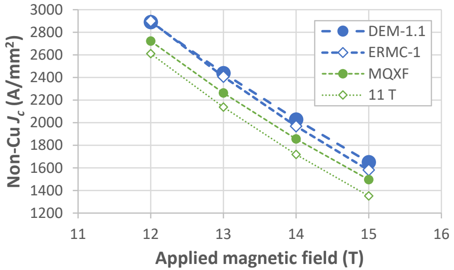


RRP® assembly sequence

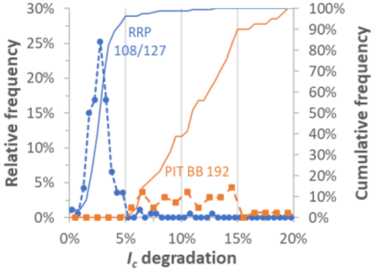
C. Sanabria, *A new understanding of the heat treatment of Nb-Sn superconducting wires*, PhD thesis, FSU 2017

Limits on Nb_3Sn Wire Performance

- RRP® has been extremely successful as a magnet conductor:
  - High J_c and RRR
  - Long piece length production
  - Low degradation on Rutherford cabling
- …but J_c performance has not advanced in recent years:
  - J_c decreases with smaller subelements (d_s < ~50 µm)
  - Flux pinning is mostly by grain boundaries, so layer $J_c(B)$ is limited by grain size (~100 nm) and B_{c2}
  - Influenced by Sn stoichiometry and heat treatment – but a compromise between many parameters
    (grain size, B_{c2}, RRR, stability, mechanical properties)

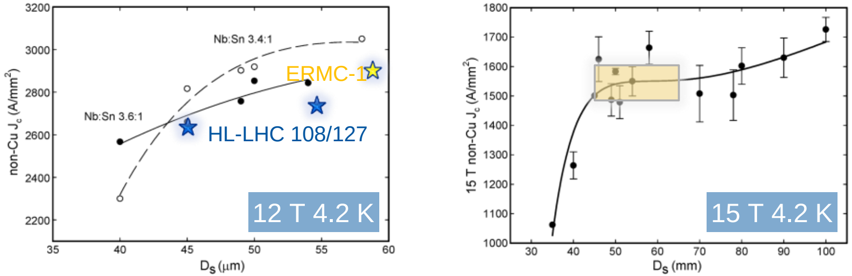


Non-Cu J_c at 4.3 K for several RRP® wires (no corrections)



Degradation on cabling for two RRP® and PIT wires

S. C. Hopkins *et al.*, *IEEE Trans. Appl. Supercond.* **33** (5) 6000609 (2023), 10.1109/TASC.2023.3254497
S. C. Hopkins *et al.*, *IEEE Trans. Appl. Supercond.* **34** (3) 6001308 (2024), 10.1109/TASC.2024.3375274

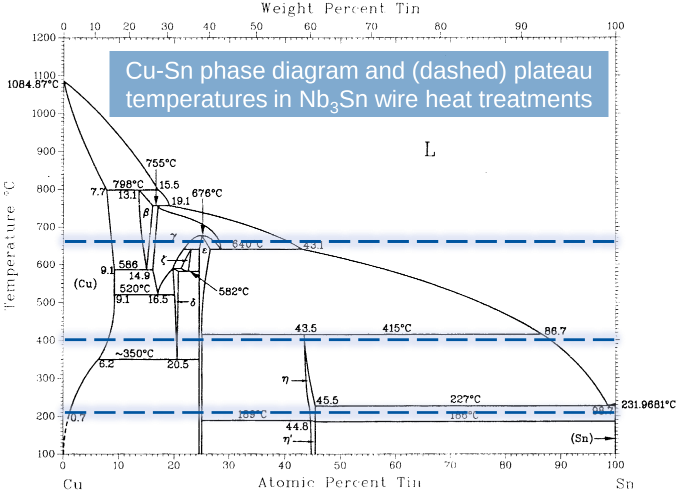


Non-Cu J_c vs. d_s for RRP® wires of different Nb:Sn stoichiometry
M. Field et al., *IEEE Trans. Appl. Supercond.* **24** (3) 6001105 (2014), 10.1109/TASC.2013.2285314

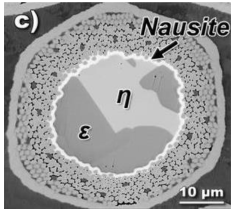
Advancing Nb_3Sn: Nausite (1)

- During heat treatment, Nb_3Sn grows at the surface of Nb filaments – basic approximation:
    - Sn diffuses through Cu-Sn and the Nb_3Sn layer to the Nb interface, where Nb_3Sn is formed
    - For internal tin wires, we pass through all phases of the complex binary Cu-Sn phase diagram, but interactions with Nb (and Ti…) not explicitly considered
- …but far from the full picture
    - Rely on Cu favouring the formation of stoichiometric Nb_3Sn
    - Early reports of inward Cu diffusion and of Nb dissolution
    - Extensive intragranular Cu found in high resolution microscopy
- A ternary Cu-Nb-Sn phase was eventually identified (‘nausite’) (M. Naus *et al.*, 2001)
    - Forms a ‘membrane’ at the interface between the Nb filament bundle and the Sn-rich core, influencing Cu/Sn transport
    - Associated with Nb dissolution and formation of coarse/disconnected Nb_3Sn at CERN (I. Pong *et al.*, 2011)

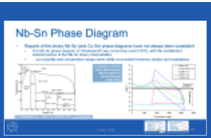
M. T. Naus *et al.*, *IEEE Trans. Appl. Supercond.* **11** (1) 3569–3572 (2001), 10.1109/77.919835
I. Pong *et al.*, *IEEE Trans. Appl. Supercond.* **21** (3) 2537-2540 (2011), 10.1109/TASC.2011.2106473



Cu-Sn phase diagram and (dashed) plateau temperatures in Nb_3Sn wire heat treatments



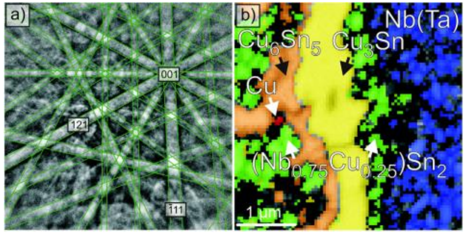
RRP® subelement after the 400 °C heat treatment step
C. Sanabria, PhD thesis, FSU 2017



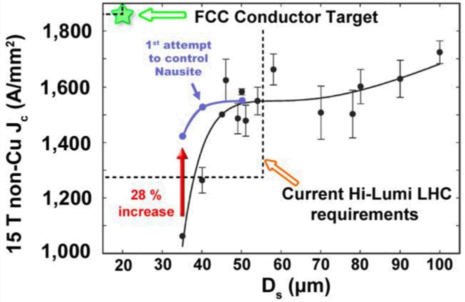
Advancing Nb_3Sn: Nausite (2)

- Work between CERN and TUBAF began following an internship of their student Alexander Walnsch (2015)
- TUBAF identified the crystal structure of nausite $(Nb_{0.75}Cu_{0.25})Sn_2$ in 2016
- Meanwhile, Sanabria (at FSU) had found that optimisation of the heat treatment step at 350–400 °C could regulate nausite thickness (‘nausite control’) and improve J_c for small d_s wires
- The observations that:
  - Heat treatment optimisation – even before Nb_3Sn forms – could achieve progress towards performance targets defined for FCC
  - Knowledge of the ternary Cu-Nb-Sn diagram was remarkably incomplete, but necessary for optimisation

motivated the formulation of a collaboration agreement in 2017 (KE3985)



(a) Kikuchi pattern and (b) distribution of nausite in a PIT wire sample
S. Martin *et al.*, *Intermetallics* **80** 16-21 (2017)
10.1016/J.INTERMET.2016.09.008

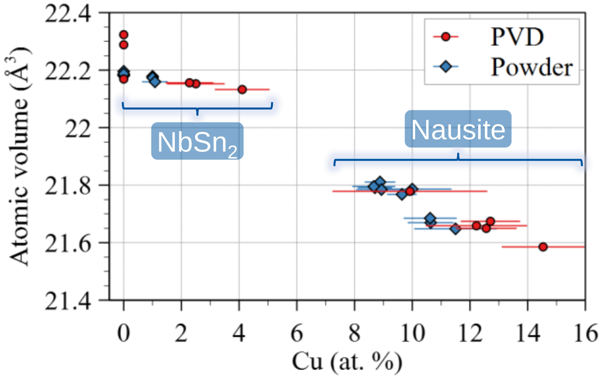


Improvements in $J_c(d_s)$ dependence for nausite control heat treatments
C. Sanabria, PhD thesis, FSU 2017

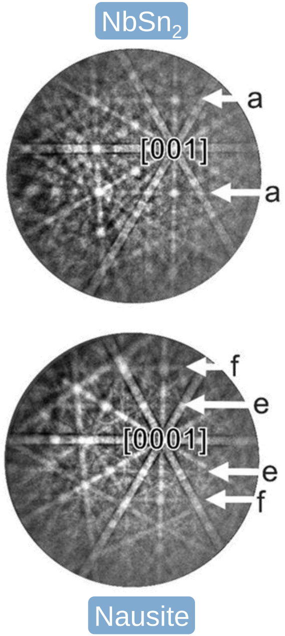
$NbSn_2$ and Nausite

- TUBAF optimised techniques (EBSD etc.) to distinguish $NbSn_2$ and Nausite, and clarified their structural relationships
  - Nausite is derived from $NbSn_2$ by partial substitution of Nb for Cu
  - Similar layered structures along [001]: lattice parameters are within ~1%, and the phase transition can be described by a change in stacking sequence
  - Both phases form with {001} faceted interfaces to a Sn-rich melt, and grow perpendicular to [001], but with differences in morphology vs. temperature

J. Lachmann *et al.*, *Mater. Charact.* **168** 110563 (2020), 10.1016/j.matchar.2020.110563



Atomic volume over the Cu solubility range of $NbSn_2$ and nausite obtained from EDX and XRD of powder mixtures and diffusion couples

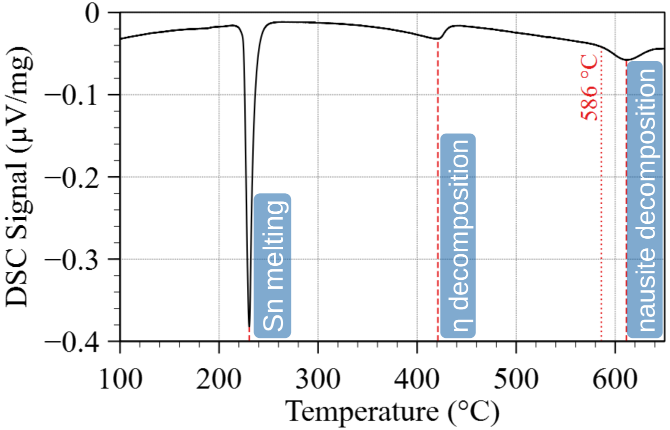


Examples of experimental Kikuchi patterns around [001] showing the characteristic bands with which the phases can be distinguished
$NbSn_2$ – a {022}; nausite – e {111}, f {112}

Nausite Decomposition

- Thermal analysis of powder samples was used to analyse the decomposition of nausite

S. C. Hopkins *et al.*, *IEEE Trans. Appl. Supercond.* **31** (5) 6000706 (2021), 10.1109/TASC.2021.3063675



Analysis of phase transformations during heating of a nausite-containing powder sample

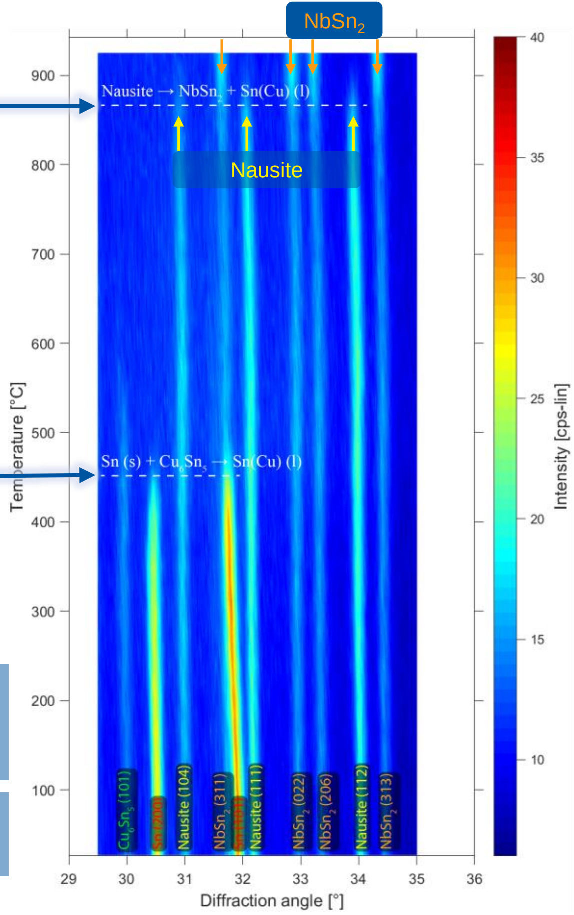
← Left
DSC

Right →
In situ XRD (Cu-Kα)

~586 °C

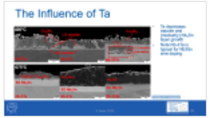
Corrected sample temperatures from DSC

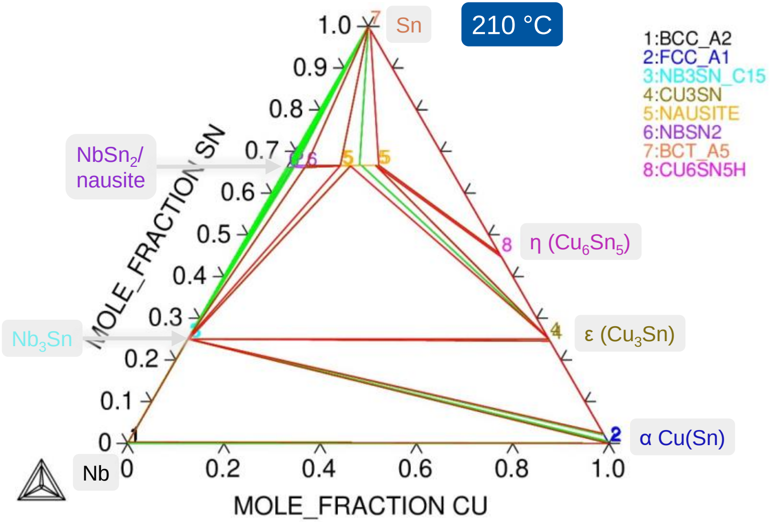
~230 °C



Cu-Nb-Sn Phase Diagram

- Phase equilibria were studied by microscopy and thermal analysis of Nb-Sn and Cu-Nb-Sn samples:
  - Powder pellets
  - Diffusion couples: Cu and Sn sputtered on Nb
- CALPHAD re-evaluation of Cu-Nb-Sn phase diagram, including nausite
- Later collaboration (KE5074) extended this to consider the effects of Ta and O
  - (Ta,Cu)Sn$_2$ identified
  - First steps towards analysing internal oxidation


The Influence of Ta

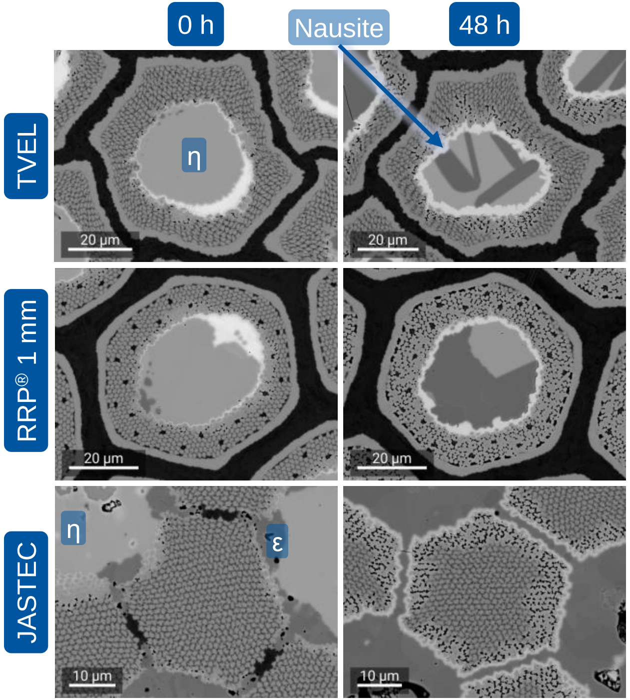


J. Lachmann *et al.*, Thermodynamic re-modelling of the Cu–Nb–Sn system: Integrating the nausite phase, *CALPHAD* **77** 102409 (2022), 10.1016/J.CALPHAD.2022.102409

Phase Transformations in Wires

- CERN and TUBAF also conducted a joint study of phase transformations in wire samples
  - Tested generality of Sanabria’s observations of RRP® for other RRP® designs, and for R&D distributed barrier and distributed tin wires

S. C. Hopkins *et al.*, Phase Evolution During Heat Treatment of Nb_3Sn Wires Under Development for the FCC Study,
IEEE Trans. Appl. Supercond. **31** (5) 6000706 (2021), 10.1109/TASC.2021.3063675



BEI of samples quenched from 400 °C

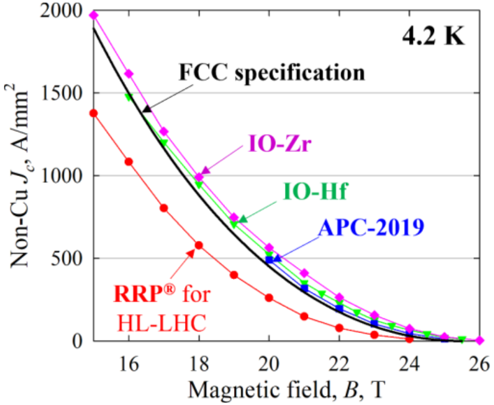
Advancing Nb_3Sn: Internal Oxidation

- Flux pinning in conventional Nb_3Sn wires is mostly on grain boundaries:
  - Enhancing grain boundary pinning → refining grain size
    (compromise with Nb_3Sn area, B_{c2}, heat treatment duration)
  - Adding point pinning → adding or growing precipitates
    (strengthening may impede wire drawing)
- ‘Internal oxidation’ has been proposed by Xu *et al.* (2014) as the solution:
  - Add a readily oxidised solute element (Hf or Zr) to the Nb alloy (e.g. Nb-Ta-Hf)
  - Embed a source of oxygen (e.g. SnO_2)
  - Precipitates (e.g. HfO_2) form only on heat treatment, in Nb_3Sn, and:
    - Impede Nb_3Sn grain growth *and/or*
    - Provide point pinning

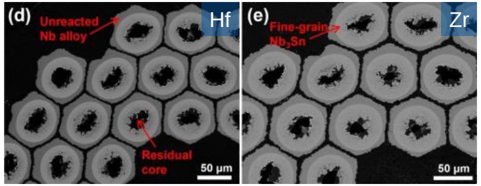
X. Xu *et al.*, *Appl. Phys. Lett.* **104** 082602 (2014), 10.1063/1.4866865

Advancing Nb_3Sn: Internal Oxidation

- Implemented in Hyper Tech Research (Columbus, USA) in collaboration with Ohio State University and Fermilab
  - Nb_3Sn grain sizes reduced to < 50 nm
  - Non-Cu J_c exceeds FCC-hh target of 1500 A/cm^2 at 4.2 K, 16 T
  - Shifts pinning peak towards higher reduced field (B / B_{irr})

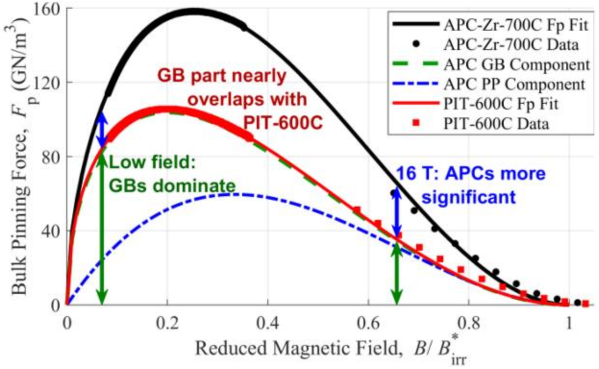


Non-Cu J_c (4.2 K) of internal oxidised wires compared to HL-LHC wire and FCC target



SEM cross-sections of reacted Hyper Tech Hf- and Zr- alloyed internal oxidation PIT wires

X. Xu *et al.*, *Supercond. Sci. Technol.* **36** 035012 (2023), 10.1088/1361-6668/ACB17A



Grain boundary and point pinning contributions in APC wire

J. Rochester *et al.*, *IEEE Trans. Appl. Supercond.* **31** (5) 8000205 (2021), 10.1109/TASC.2021.3057560

- Very promising, but not yet an industrialised wire technology validated for accelerator magnet applications
  - Still to be demonstrated: long length production, degradation on cabling, magnetothermal stability…

Internal Oxidation: Next Steps

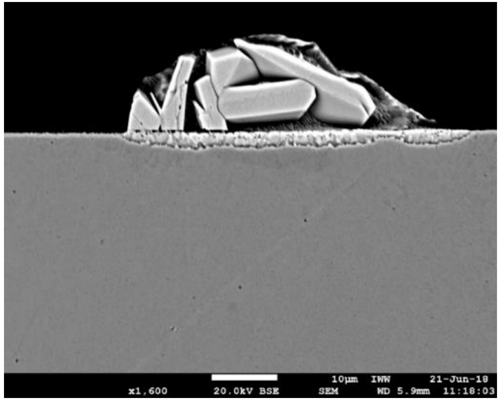
- Considerable progress with building understanding – e.g. at UNIGE (KE4663):
  - Alternative oxygen source configurations have been evaluated
  - Established by XANES that HfO_2 precipitates form at the Nb_3Sn growth front
- but significant questions remain, e.g.:
  - Detailed understanding of oxide decomposition, oxygen transport, and interactions with Cu/Cu-Sn
  - Effects of Zr/Hf alloying on Cu-Nb-Sn thermodynamics and diffusion kinetics
  - Effects of Nb alloy microstructure on Nb_3Sn growth
- Addressing fundamental questions is challenging in wire studies:
  - Long lag between wire trials
  - Complex geometry
  - All processes coupled – e.g. Cu-Sn phase transformations, Nb_3Sn growth, oxygen transport
- Key motivation for new TUBAF collaboration:
  - Use diffusion couples to **decouple** processes and better understand their mechanisms
    (SnO_2 decomposition, O transport, HfO_2 precipitation, influence of Hf/Ta/O on Cu-Nb-Sn, Nb_3Sn formation and grain coarsening)
  - Analyse wire samples to identify relevant model systems and validate applicability of conclusions
- 3-year collaboration (KE5963) signed in March 2024

Methods: Lessons Learnt

- Diffusion couple design
  - Sn dewetting: use higher-melting Cu-Sn alloys and structured films
  - Tune thicknesses and compositions to achieve representative Hf and O atomic fractions
- Purity
  - Characterisation of substrate materials and purity control during deposition to avoid the influence of other oxygen sources
    - cf. wire studies with Hf alloying and without an oxygen source in which HfO_2 precipitates were found

C. Tarantini *et al.*, *Sci. Rep.* **11** 17845 (2021), 10.1038/s41598-021-97353-w

- Superconducting characterisation of diffusion couple samples to close the loop with wire samples
  - Prepare some samples in a form suitable for VSM at CERN
- Grain size determination of very fine-grained regions challenging: multiple methods needed



Dewetting of Sn plated on Nb

Nb_3Sn SRF Cavities

- Cavities: transfer energy from an EM wave to the beam
- Current technology at CERN: Nb/Cu (LHC, HIE-ISOLDE)
- Objective: decrease by 10× the surface resistance at 4.5 K

FCC mid-term report, cds.cern.ch/record/2887249/

- Proposal: Replace Nb by Nb_3Sn
- Material validated on bulk Nb cavities (expensive, high flux sensitivity)

T_c	Nb ~ 9.2 K
	Nb_3Sn ~ 18.3 K
R_{BCS} @4.2K and 500MHz	Nb ~ 45nΩ
	Nb_3Sn ~ 0.4nΩ
H_{SH}	Nb ~ 220mT
	Nb_3Sn ~ 425mT

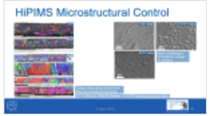
Nb_3Sn SRF Cavities: A Comparison

- Targets:
  - High E_{acc} → high peak field
  - High quality factor → low surface resistance (~0.4 nΩ), high T_c (~18.3 K)
- Compared to wires:
  - Many of the same parameters are influential, but the desired condition is different
  - Operation in full **Meissner state** – flux penetration to be avoided at all costs!
  - Detailed knowledge and control required of phase diagram, interdiffusion, purity/alloying, microstructure
  - Temperature budget: Max 800 °C (cavity material integrity/flange brazing)

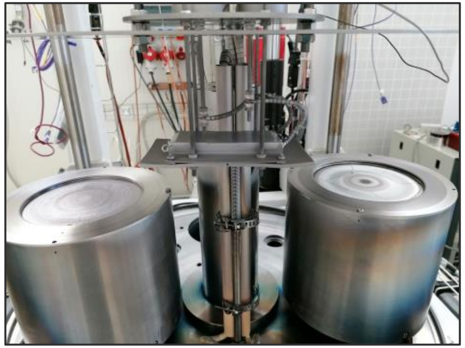
	Wire	Cavity
Key Aim	**Maximise flux pinning, optimise $F_p(B)$**	**Minimise resistance, avoid defects**
Defects	Point pinning increases J_c at high field	Increase residual resistance
Refined microstructure	Fine grains (<100 nm) increase F_p and J_c	Typically ~1 μm (gb losses possible)
Alloying	Ti/Ta increase B_{c2} → increase J_c at high field	Increase residual resistance
Presence of Cu	Favours Nb_3Sn growth	Surface Cu contamination
Stoichiometry	Optimise T_c and B_{c2}	Maximise T_c, avoid secondary phases

Methods Transferrable from SRF

- High Power Impulse Magnetron Sputtering (HiPIMS)
  - Nb and Nb alloy/composite targets (e.g. for Nb_3Sn)
  - Purity, cleanliness, UHV good practices (control O_2 sources)
  - Macrostructure control: porosity
  - Microstructure control e.g. by ion bombardment energy
  - Nb surface preparation (electropolishing, Buffered Chemical Polish, etc.)
- Thin film characterisation:
  - XPS profiling
  - XRD (EN-MME)
  - SHPM, VSM etc.
- Materials
  - RRR 300 Nb
  - Microstructural control by cold work – rolling studies (EN-MME)


HiPIMS Microstructural Control

UHV coating setup



HiPIMS glow discharge during a quadrupolar sample coating

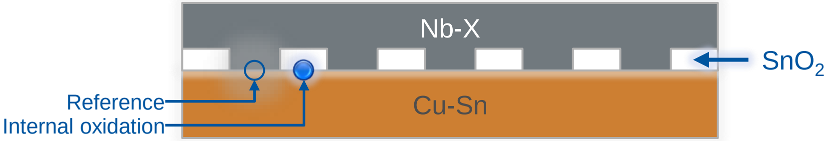
Diffusion Couples: Basic Approach

- Produce layered structures of:
  - Nb and its alloys (‘Nb-X’: Nb, Nb-1Hf, Nb-4Ta-1Hf)
  - Cu-Sn
  - SnO_2 (oxygen source)
  - ‘Inert’ substrates (e.g. Y_2O_3, sapphire)

  using Nb-X sheets and sputtered films
- Perform heat treatments for different temperatures and durations, and analyse the resulting microstructures by:
  - Optical microscopy
  - Scanning Electron Microscopy (SEM; cross-section and top-view)
  - X-ray diffraction
  - Analyse grain sizes by Electron Backscatter Diffraction (EBSD) and/or Transmission Kikuchi Diffraction (TKD)
  - For selected samples:
    - Transmission Electron Microscopy (TEM) – e.g. for precipitate analysis
    - Vibrating Sample Magnetometry (VSM) at CERN – comparative study of J_c, T_c

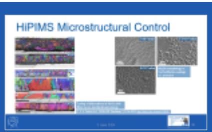
New Approaches: Cu-Sn and SnO_2

- High-melting Cu-Sn substrates:
  - Prepare < 25 at.% Sn **substrates** by arc melting for heat treatments above 400 °C without melting
  - Intermetallics (e.g. Cu_3Sn) and Cu(Sn) solid solutions
- SnO_2 patterned films:
  - Optimise sputter deposition of SnO_2
  - Create laterally structured SnO_2 coatings, e.g. by photolithography:
    - Mitigate dewetting (additional metal interfaces)
    - Provide internal reference away from without oxygen source



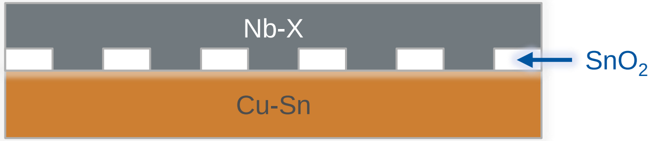
New Approaches: Nb-X

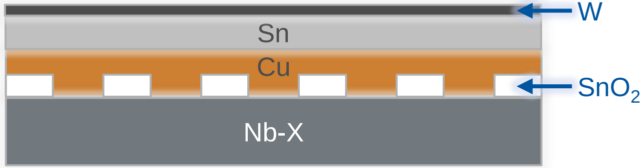
- Nb-X sheets
  - Plates/foils ~1 mm thick
  - Assess effect of microstructure with annealing and different degrees of cold work
  - Tests with RRR 300 Nb (certified purity) and different rolling reductions
- Nb-X sputtered films
  - Coatings ~10 µm thick on ‘inert’ substrates (e.g. Y_2O_3 or sapphire)
  - Produced at TUBAF
  - Produced at CERN by HiPIMS:
    - Benchmarking for purity and defect populations
    - Control of microstructure

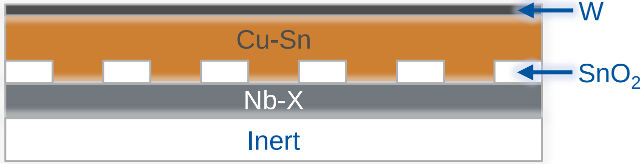

HiPIMS Microstructural Control

Diffusion Couple Configurations

- Expected configurations are shown schematically below
- Designs will be finalised after trials in the first year







- These configurations are flexible enough to allow:
  - Cu-rich (Cu-Sn substrate) and Sn-rich (Cu/Sn coatings) compositions
  - SnO_2 decomposition and O transport with (Nb-Ta-Hf) and without (Nb) Hf oxide precipitation
  - Behaviour with and without an intentionally added oxygen source:
    - As shown – internal reference between SnO_2 patterned strips
    - Samples produced with and without SnO_2 layer
- All with control of starting Nb alloy microstructure

Wire Studies

- Analysis of wire samples provided by CERN:
  - Consistent comparison of microstructures (e.g. Nb_3Sn grain sizes) in wires from different sources
  - Comparison with diffusion couples to identify inconsistencies or interesting cases for further study
  - Correlations with I_c measured at CERN → understanding of microstructural effects and heat treatment optimisation
- Supported by complementary studies in TE-MSC-LSC:
  - Ejection furnace: microscopy, VSM and RRR measurements of samples at different stages of the heat treatment
  - Studies of rolled wire samples and cables when sufficient internal oxidation wire is available
- Supports development of wire activities e.g. in UNIGE

Work Plan

Activity			24				25				26				27
			Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1
D1	**M1.1**	Cu-Sn substrate preparation	■	■	■	■									
D2	**M2.1**	Patterning of SnO_2 layers	■	■	■	■									
	M2.2	Interaction of SnO_2 with Nb/Nb alloys			■	■	■								
D3	**M3.1**	Definition of diffusion couple designs					■								
	M3.2	Trial samples for magnetisation measurement						■	■	■					
	M3.3	Interim report: diffusion couple preparation and analysis						■	■	■					
	M3.4	Samples for CERN characterisation (e.g. VSM)								■	■	■			
	M3.5	Final report: diffusion couple preparation and analysis									■	■	■	■	■
D4	**M4.1**	Analysis of wire samples (batch 1)			■	■	■	■	■	■					
	M4.2	Analysis of wire samples (batch 2)									■	■	■	■	■

Current Status

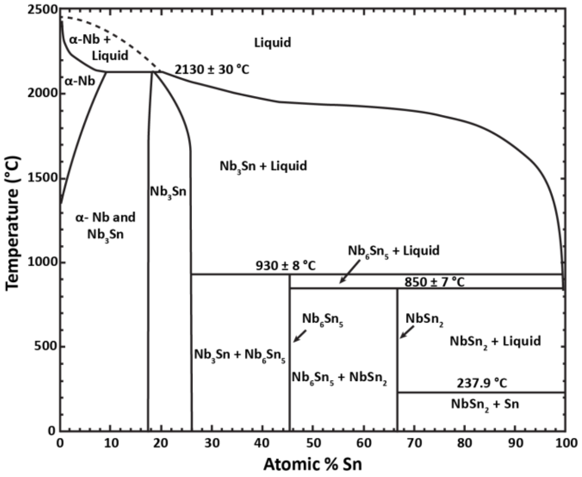
- Visit to TUBAF in January 2024 to visit experimental facilities and discuss the planned work
- Agreement signature completed 18 March 2024
- Kick-off meeting by Zoom in April 2024
- TUBAF hired a PhD student, Simon Waschull, who visited CERN (22-31 May) for:
  - UHV system training in TE-VSC
    - Sample preparation and handling
    - Materials compatibility (UHV)
    - Bakeout procedure
    - He leak testing
    - Residual Gas Analysis
  - Familiarisation with superconducting wire and magnet technologies in TE-MSC
    - Nb_3Sn wire metallography and microscopy (103, 288)
    - Nb_3Sn cabling (103)
    - Superconducting tests (I_c, RRR, VSM, magnetothermal stability in 163)
    - Visit to UNIGE for TEM of internal oxidation sample produced for KE4663 (FIB lamella prepared by EN-MME)
    - Visits to LMF (180) and the polymer lab
  - Discussions with EN-MME
    - Visit of microscopy facilities (112)
    - Discussion of cold worked microstructures in RRR Nb

CERN

Additional Slides

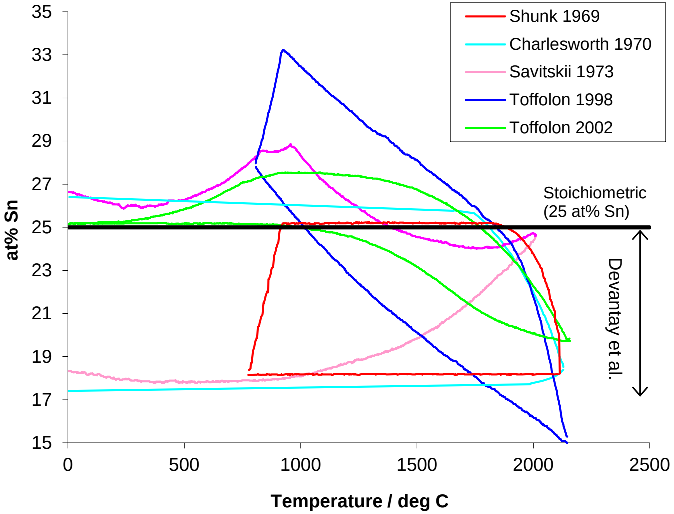
Nb-Sn Phase Diagram

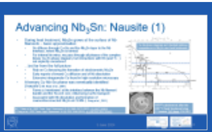
- Reports of the binary Nb-Sn (and Cu-Sn) phase diagrams have not always been consistent
  - The Nb-Sn phase diagram of Charlesworth was commonly used (1970), with the established stoichiometries of the Nb-Sn binary intermetallics
  - …but solubility and composition ranges were wildly inconsistent between studies and evaluations

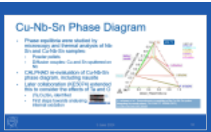


J.P. Charlesworth *et al.*, *J. Mater. Sci.* **5** 580-603 (1970), 10.1007/BF00554367

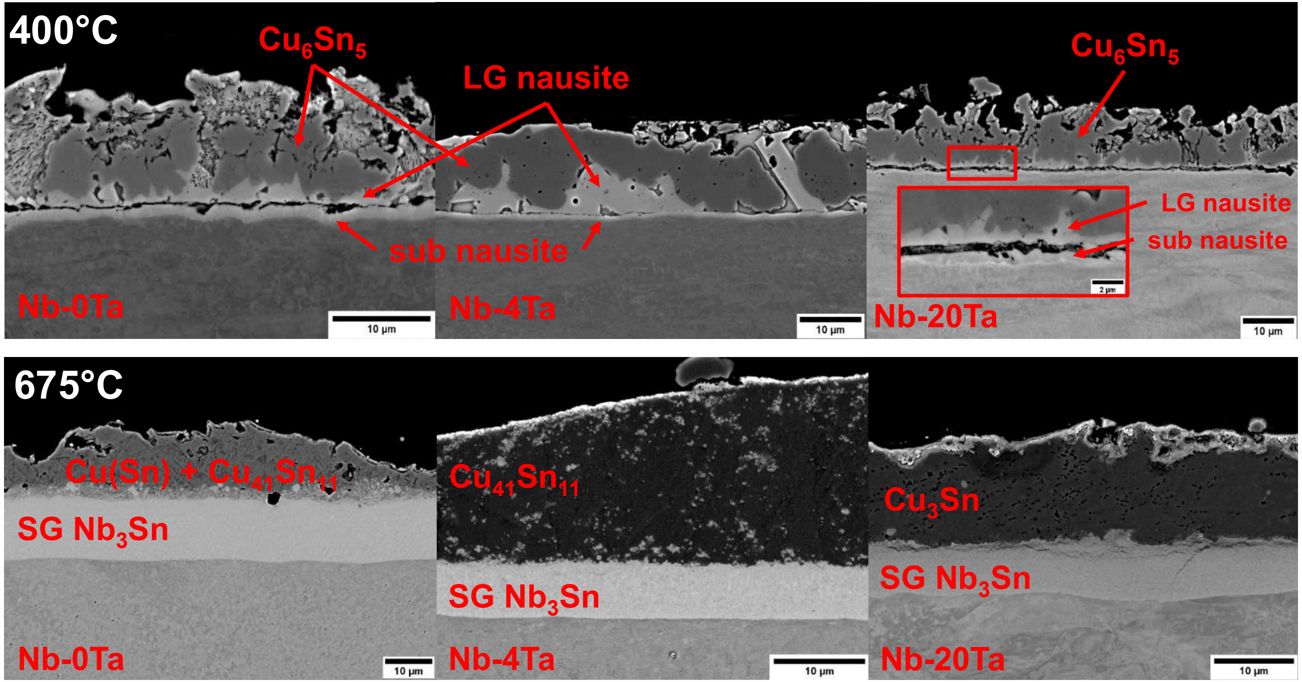
Comparison of Nb_3Sn phase fields between different published phase diagrams (1969–2002)





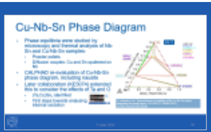


The Influence of Ta

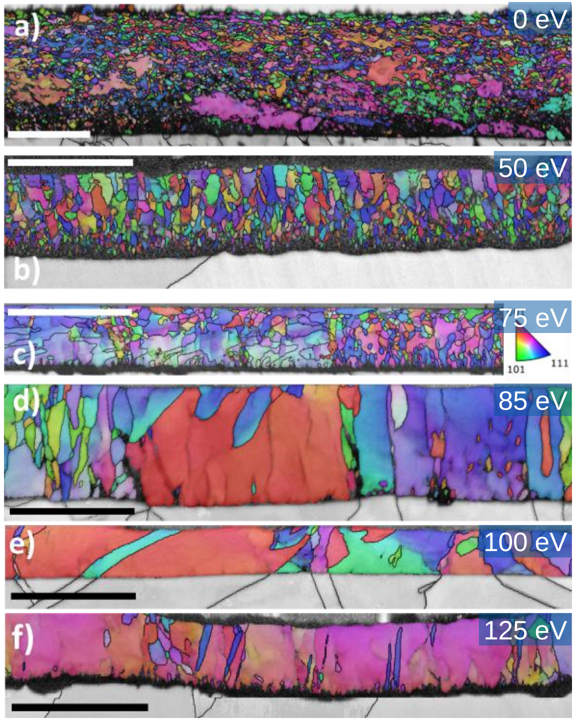


- Ta decreases nausite and (modestly) Nb_3Sn layer growth
- Note Nb-4Ta is typical for Nb3Sn wire doping

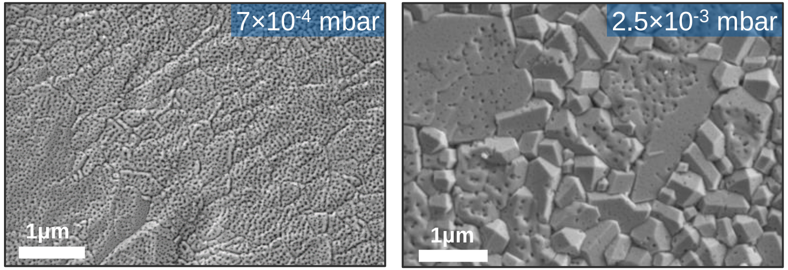
Courtesy of A. Leineweber

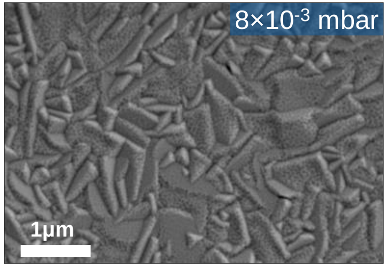

Cu-Nb-Sn Phase Diagram

HiPIMS Microstructural Control



Tuning of dislocations in Nb/Cu thin films by ion bombardment energy





Nb$_3$Sn morphology in Cu/Ta/Nb$_3$Sn coatings vs. pressure

C. P. A. Carlos *et al.*, CERN SRF Workshop, 2-3 Feb 2023, https://indico.cern.ch/event/1235920/


Methods Transferrable from SRF