DE LA RECHERCHE À L'INDUSTRIE

27TH INTERNATIONAL CONFERENCE ON
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NOV 15 – 19, 2021, FUKUOKA/JAPAN

MODELLING PHASE TRANSFORMATION AND DIFFUSION PHENOMENA INSIDE Nb_3Sn SUPERCONDUCTING STRANDS

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Motivation

Particle accelerators for high-energy physics

Present: Large Hadron Collider (LHC) (< 10 T)

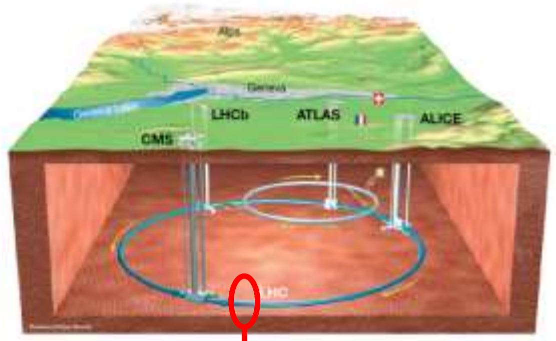
Objectives: HC-LHC upgrade, Future Circular Collider (> 10 T)

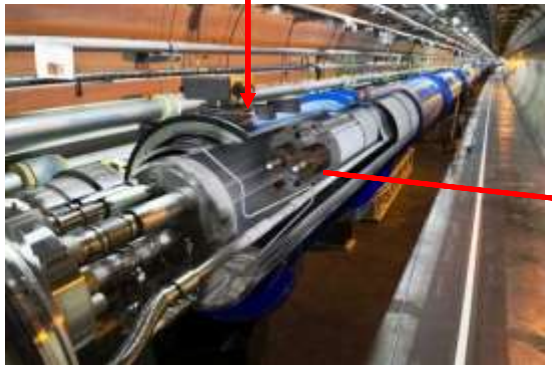
Superconductors are used in high-field accelerators electromagnets

- No resistance at cryogenic temperatures
- High currents, large magnetic fields

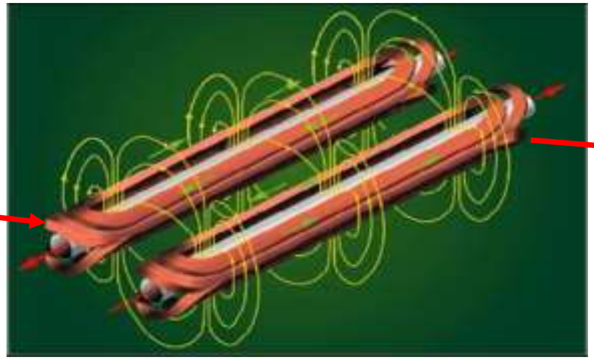
Cables are based on superconducting materials

- Nb-Ti limited behavior (LHC)
- Nb3Sn is a perspective for the future high-field electromagnets (HC-LHC)

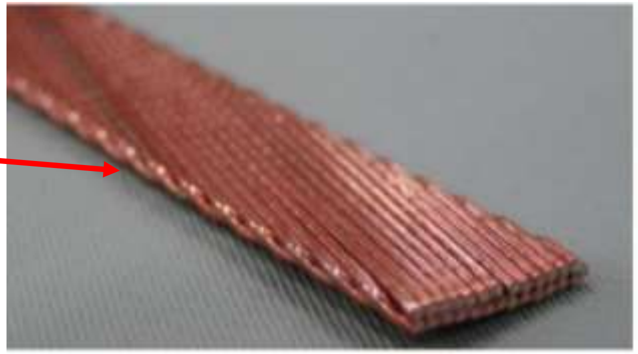




Circular particle accelerators magnet
[https://home.cern]



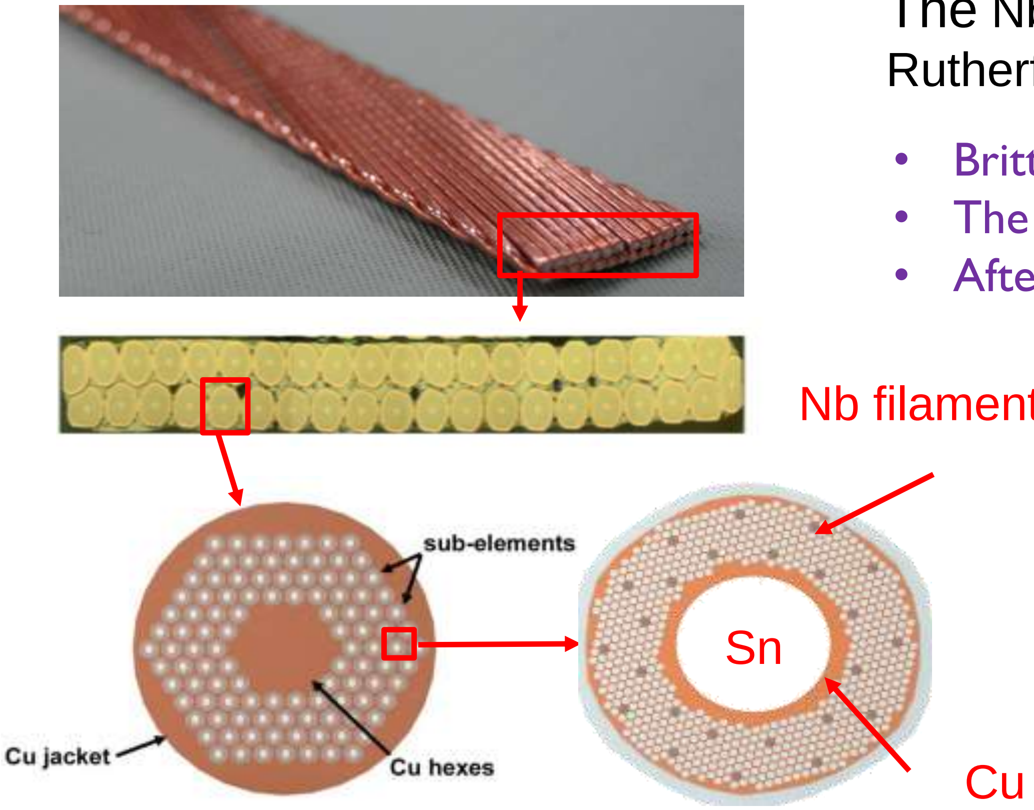
Superconducting coils
[https://www.lhc-closer.es]



Rutherford cables
[Fermilab, https://td.fnal.gov]

Nb3Sn superconductors design (RRP)

Rutherford cable



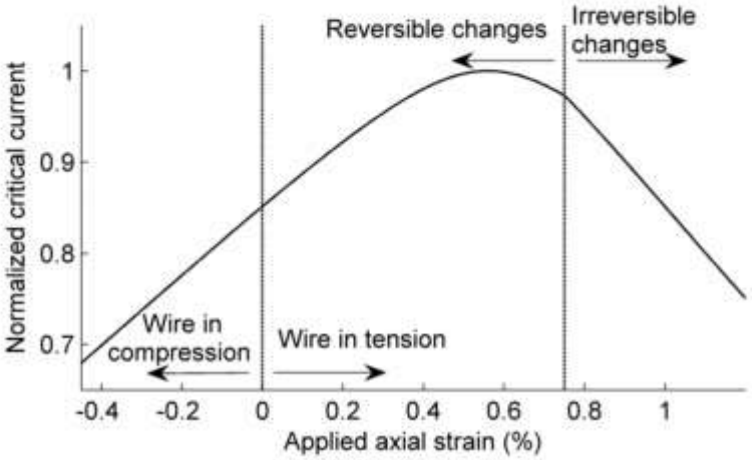
RRP strand cross-section

RRP sub-element cross-section

The Nb3Sn-based conductor is produced in rectangular Rutherford type cables, braided from RRP strands

- Brittleness of Nb3Sn
- The strands are first made from distinct ductile components (Cu, Sn, Nb)
- After, braided into cables and wounded into coils.

After the winding, the conductor requires a 3 step heat treatment (HT) up to 650°C that lead to the formation of the Nb3Sn superconducting phase in sub-elements



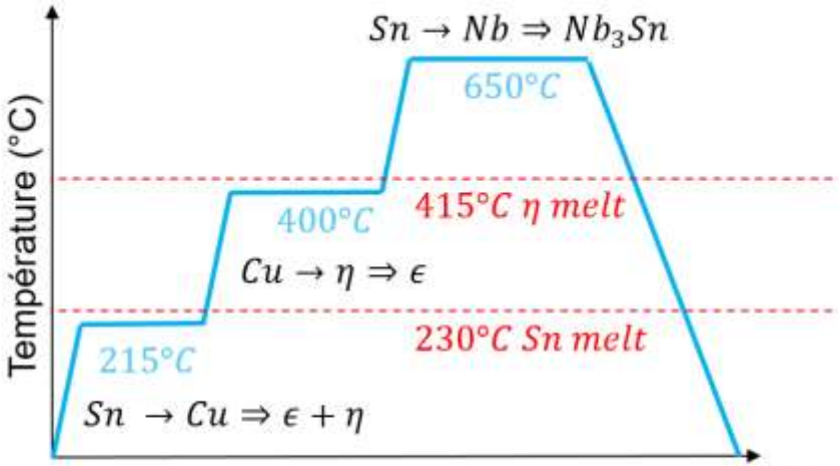
Critical current in Nb3Sn strand under uniaxial tension [Ahoranta, M. (2008)]

- Thermal loading → Accumulate stresses inside conductor
- Nb3Sn is strain-sensitive → May degrade the performance
- Mechanical state of Nb3Sn during HT?
- Dynamics of phase transformation inside sub-elements?

Problem of phase transformation dynamics inside RRP strands

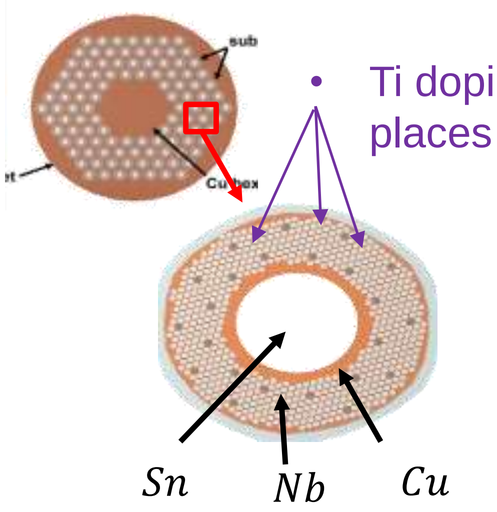
During 3 steps of HT:

1. Cu and Sn interdiffusion. Formation of intermetallics (IMCs) **ε** (Cu3Sn) and **η** (Cu6Sn5)
2. All Sn and Cu transformed into **ε + η**. Formation of Nausite membrane.
3. Sn diffusion into Nb. Formation of Nb3Sn superconducting phase.



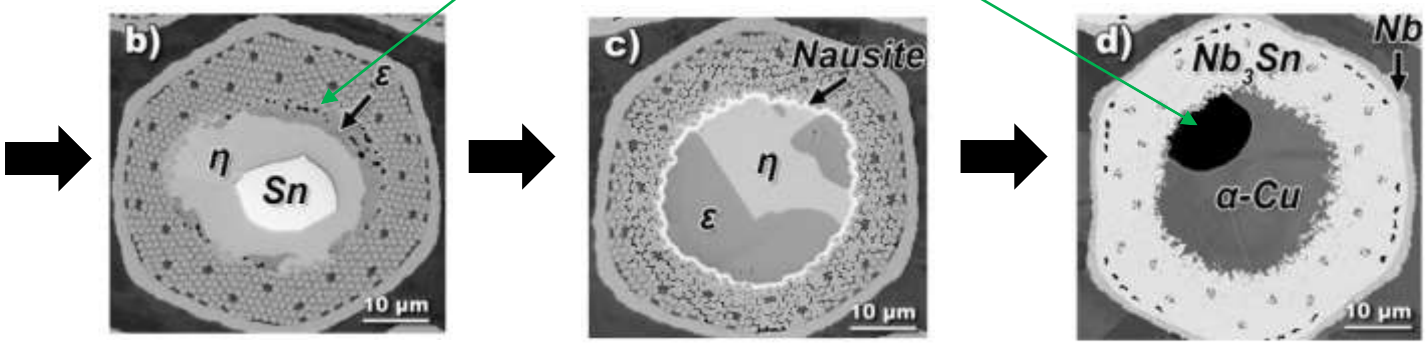
3 steps HT scheme

- Ti doping in places
- Kirkendall voids



Sub-element

1. 48h. 215C.
2. 48h. 400C.
3. 48h. 650C.



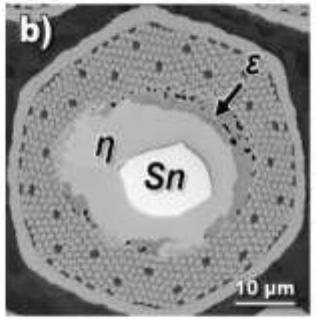
C. Sanabria et al., 2019, IEEE, VOL. 29, NO. 5 I. Pong, 2013 et al., Supercond. Sci. Technol. 26

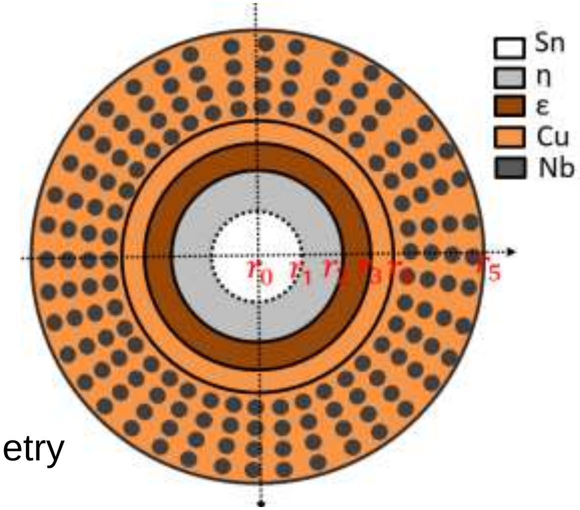
How to estimate dynamics of phase transformations during HT?
Mathematical model is to be constructed

Diffusion based growth model: assumptions

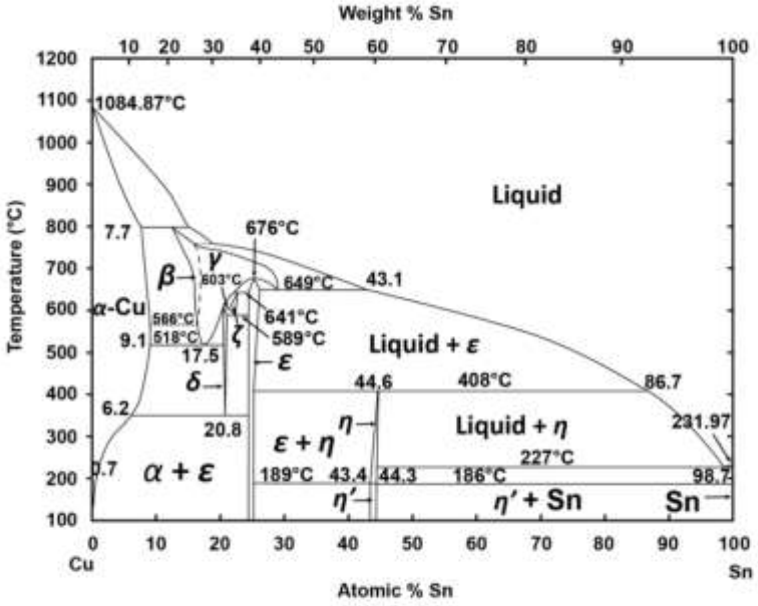
Main assumptions

1. Axisymmetric geometry of sub-element
2. Diffusion controlled growth of **ε, η** phases
3. Thin intermetallic layers are assumed to be presented from the beginning
4. Local chemical equilibrium exists at the interfaces between phases (fast chemical reactions compared to diffusion)
5. Quasi-stationary diffusion (flux is not changing with time)
6. The formation of Kirkendall voids is neglected
7. Formation of Nausite is neglected





Simplified sub-element geometry



Cu-Sn phase diagram

Diffusion based growth model: mathematical formulation

2nd Fick’s law inside each region

$$
\begin{cases}
\dfrac{\partial w^{Sn}}{\partial t} = D^{Sn}\dfrac{1}{r}\dfrac{\partial}{\partial r}\left(r\dfrac{\partial w^{Sn}}{\partial r}\right), \quad r \in [r_0, r_1(t)], \\
\dfrac{\partial w^{\eta}}{\partial t} = D^{\eta}\dfrac{1}{r}\dfrac{\partial}{\partial r}\left(r\dfrac{\partial w^{\eta}}{\partial r}\right), \quad r \in [r_1(t), r_2(t)], \\
\dfrac{\partial w^{\varepsilon}}{\partial t} = D^{\varepsilon}\dfrac{1}{r}\dfrac{\partial}{\partial r}\left(r\dfrac{\partial w^{\varepsilon}}{\partial r}\right), \quad r \in [r_2(t), r_3(t)], \\
\dfrac{\partial w^{Cu}}{\partial t} = D^{Cu}\dfrac{1}{r}\dfrac{\partial}{\partial r}\left(r\dfrac{\partial w^{Cu}}{\partial r}\right), \quad r \in [r_3(t), r_4],
\end{cases}
$$

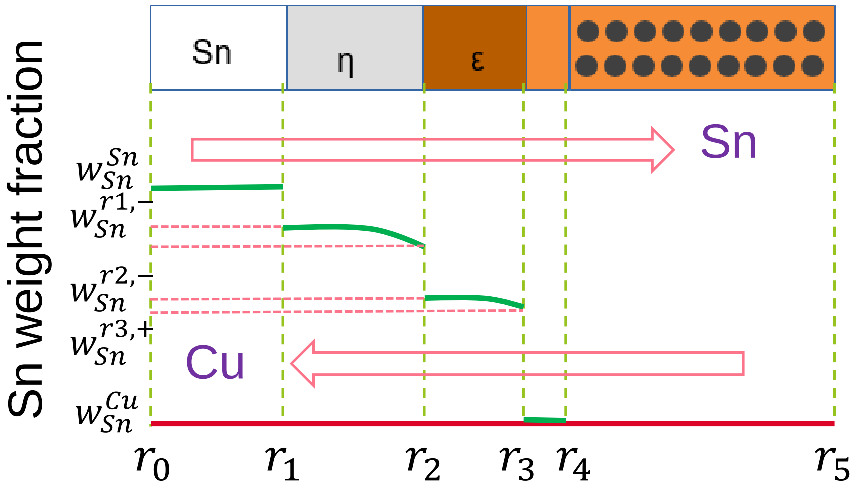
D^{α} – Diffusion coefficient

ρ^{α} – Density

$w^{\alpha}_{Sn} = \rho^{\alpha}\gamma^{Sn}_{\alpha}$ – Weight fraction

$\alpha \in \{Sn, \eta, \varepsilon, Cu\}$,

Weight fractions are constant at the interfaces (known from the phase diagram)



Quasi-stationary diffusion

logarithmic Sn profile

$$0 = D\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial w}{\partial r}\right), -> \quad w = A\, lnr + B,$$

Mass balance at the interface

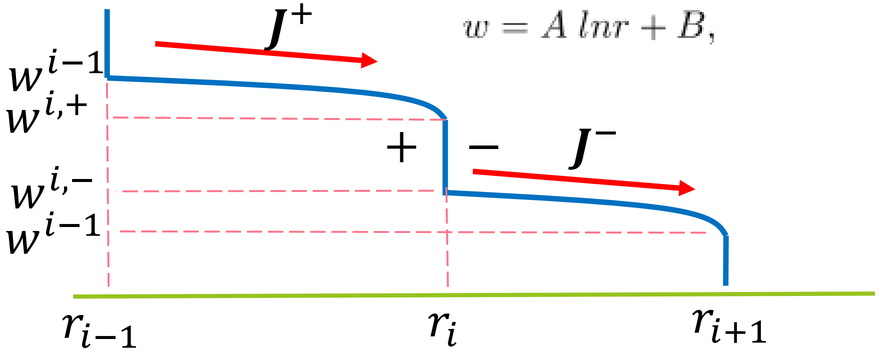
$$(\rho^{+}w^{+} - \rho^{-}w^{-})\frac{dr_i}{dt} = J^{+} - J^{-},$$

$$J^{+} = -D^{+}\rho^{+}\frac{\partial w}{\partial r} = -D^{+}\rho^{+}\frac{1}{r^{i}}\,\frac{w^{i,+} - w^{i-1}}{ln\, r^{i} - ln\, r^{i-1}},$$

$$J^{-} = -D^{-}\rho^{-}\frac{\partial w}{\partial r} = -D^{-}\rho^{-}\frac{1}{r^{i}}\,\frac{w^{i+1} - w^{i,-}}{ln\, r^{i+1} - ln\, r^{i}}$$

Mass conservation in system

$$\int_{r_0}^{r_4} \rho(r)w(r)r\, dr = const.$$



$$w = A\, lnr + B,$$

Applying to each interface → ODE system

Algorithm for modelling HT: Step 1 (215C)

Initial system $J^{Sn}, J^{Cu} \ll J^{\eta}, J^{\varepsilon}$

$$\begin{cases} (\rho^{Sn} w^{r_1,-} - \rho^{\eta} w^{r_1,+})\dfrac{dr_1}{dt} = -J^{\eta} \\ (\rho^{\eta} w^{r_2,-} - \rho^{\varepsilon} w^{r_2,+})\dfrac{dr_2}{dt} = (J^{\eta} - J^{\varepsilon}) \\ (\rho^{\varepsilon} w^{r_3,-} - \rho^{Cu} w^{r_3,+})\dfrac{dr_3}{dt} = J^{\varepsilon} \end{cases}$$

Check BCs at the interfaces:

r3 > r4. Diffusion in the interfilamentary region

$$\begin{cases} (\rho^{Sn} w^{r_1,-} - \rho^{\eta} w^{r_1,+})\dfrac{dr_1}{dt} = -k_{nb,cu} \times J^{\eta} \\ (\rho^{\eta} w^{r_2,-} - \rho^{\varepsilon} w^{r_2,+})\dfrac{dr_2}{dt} = k_{nb,cu} \times (J^{\eta} - J^{\varepsilon}) \\ (\rho^{\varepsilon} w^{r_3,-} - \rho^{Cu} w^{r_3,+})\dfrac{dr_3}{dt} = J^{\varepsilon} \end{cases}$$

r0 = r1. Expiration of Sn

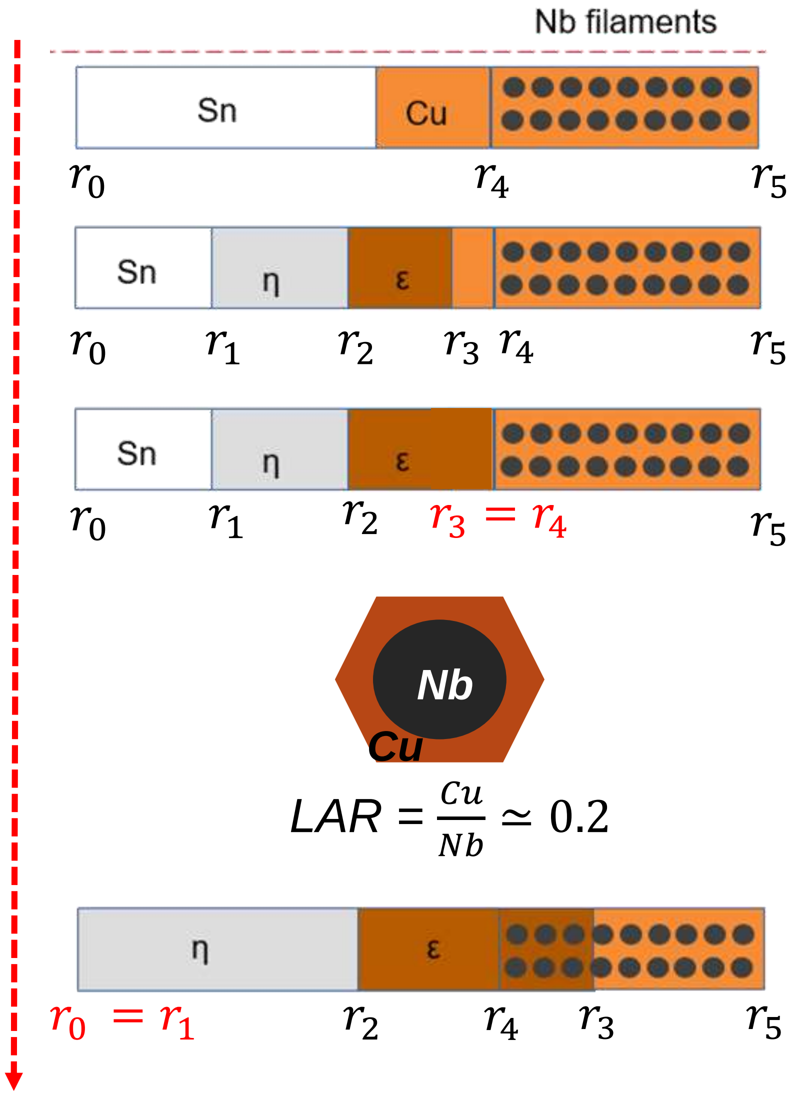
$$\begin{cases} (\rho^{\eta} w^{r_2,-} - \rho^{\varepsilon} w^{r_2,+})\dfrac{dr_2}{dt} = k_{nb,cu} \times (J^{\eta} - J^{\varepsilon}) \\ (\rho^{\varepsilon} w^{r_3,-} - \rho^{Cu} w^{r_3,+})\dfrac{dr_3}{dt} = J^{\varepsilon} \end{cases}$$

Finite difference solver
- Explicit Euler scheme
- Small time step: ~1[s]

Surface reduction factor

$$k_{nb,cu} = \frac{LAR}{LAR+1}.$$

Input parameters?
- Diffusion coefficients
  - Literature
  - Experiments
- Initial geometry



$LAR = \frac{Cu}{Nb} \simeq 0.2$

Algorithm for modelling HT: Step 2 (400C)

215C → 400C

Change of diffusion coefficients

- Ramp not considered
- Nausite formation is neglected
- Tin melting is ignored

The interdiffusion coefficients are taken in the Arrhenius form [Mei, 1992]

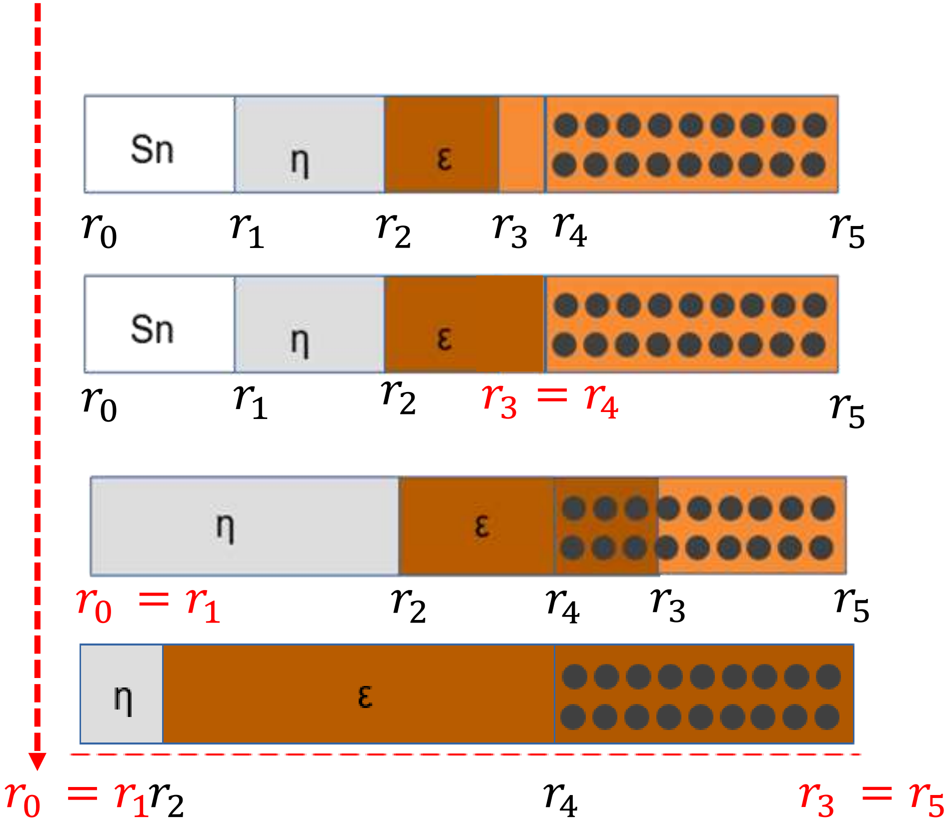
$$D^{\varepsilon} = D_0^{\varepsilon} exp(-\frac{Q^{\varepsilon}}{RT}) = 5.48 \times 10^{-9} exp(\frac{-61.86}{RT}),$$

$$D^{\eta} = D_0^{\eta} exp(-\frac{Q^{\eta}}{RT}) = 1.84 \times 10^{-9} exp(\frac{-53.92}{RT}),$$

Q^{α} — Activation energy

D_0^{α} — Pre-exponential actor

R — Gas constant T — Temperature (K)



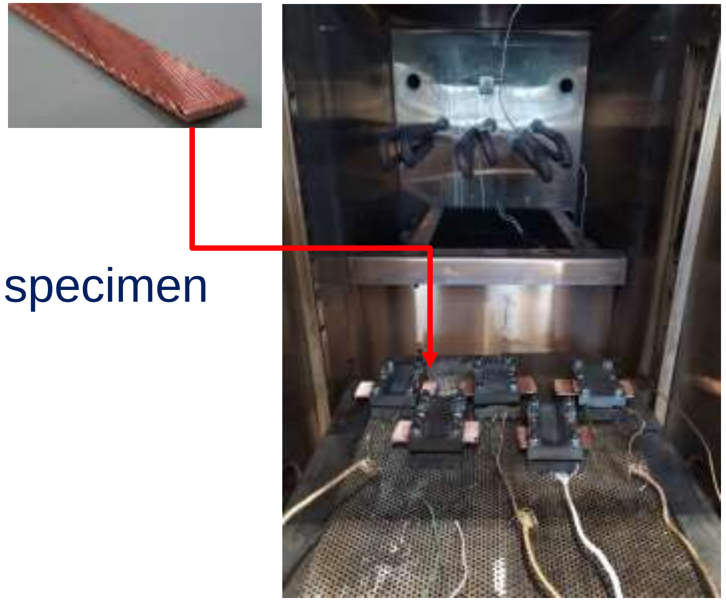
At the end of step 2: No more Sn and Cu

Literature diffusion coefficients: Planar interfaces → Little use

In application to cylindrical system diffusion coefficients should be determined from experiments

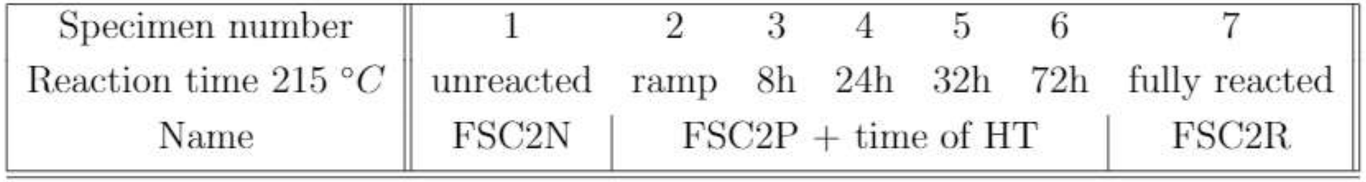
Experimental part: low temperature HT setup

In order to estimate the input parameters for the model (initial geometry, diffusion coefficients), a low temperature heat treatment has been performed on five cable pieces.



- 215 ±5◦C temperature for 72 hours
- no use of argon
- quenched after HT

- Thermocouples connected to each specimen
- Cu brackets to avoid warping
- 7 specimens in total



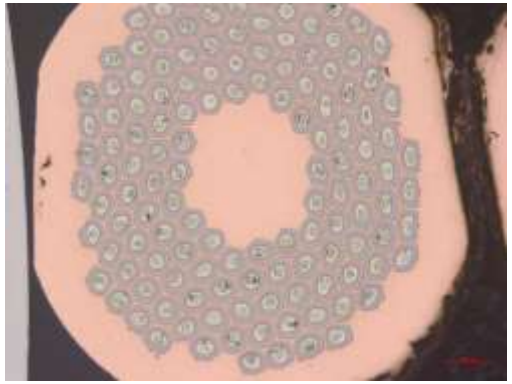
Specimen number	1	2	3	4	5	6	7
Reaction time 215 °C	unreacted	ramp	8h	24h	32h	72h	fully reacted
Name	FSC2N	FSC2P + time of HT					FSC2R

"The conductors were provided by CERN within the collaboration agreement CERN-CEA KE2275/TE"

Scanning electron microscopy (SEM) is used for observations of cross-section of cables

Preparation for SEM:

- Cutting the specimens
- Cold impregnation
- Polishing and grinding
- Sputter coating



Back-scattered electron images analysis

Non-uniform geometry and behavior for each sub-element

Statistical analysis:

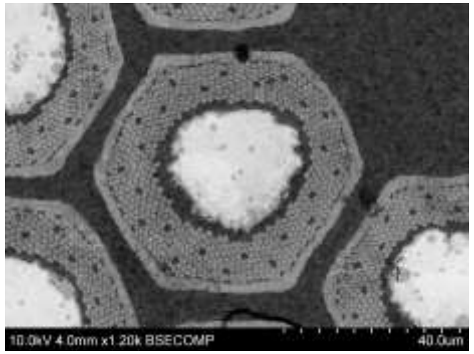
- 7 specimens
- 10-20 BSE images for each specimen
- ~100 images in total

Post processing:

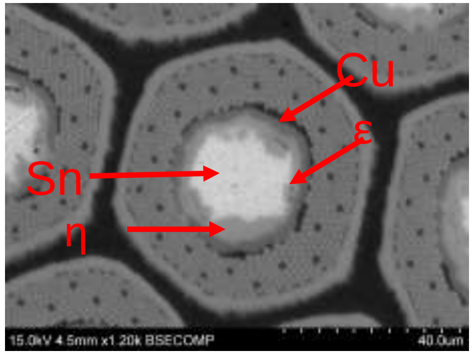
- Threshold adjusting technique (ImageJ)
- Adjusting by eye, manual process

Table 1: Averages of phases during HT, scale: 1 [$inch$] = 21, 1976 [μm].

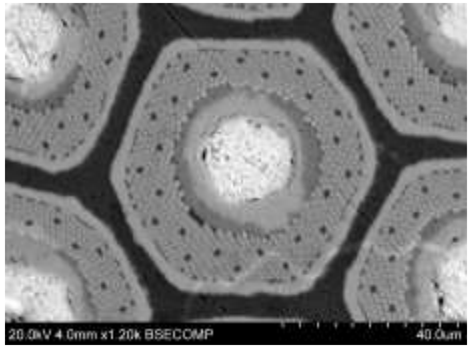
Time of HT	Total area [$inch^2$]	Core area [$inch^2$]	Cu % -	Sn % -	η % -	ε % -
Unreacted	6.04	2.11	29.69	70.73	0.00	0.00
Ramp	6.19	2.16	17.49	51.80	31.32	
8h	6.16	2.17	6.57	37.90	32.65	24.78
24h	6.16	2.17	5.53	26.89	36.25	31.92
32h	5.97	2.10	-	29.20	-	-
72h	6.28	2.21	-	19.69	-	-



Unreacted



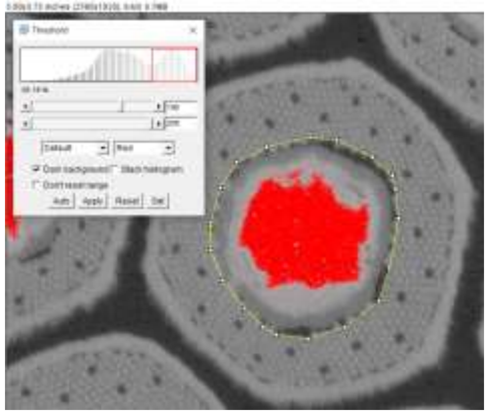
8 hours



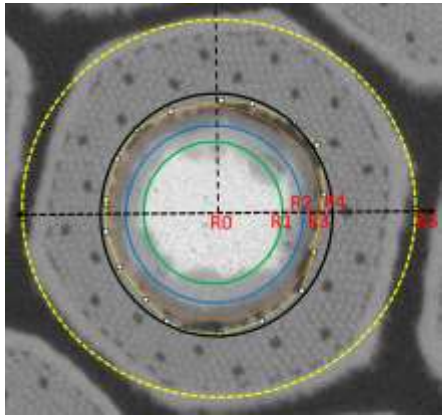
32 hours

BSE sensitive to density. Each phase has it’s own gray level.

To distinct Nb and η: Separation into total sub-element area and core area



Threshold adjustment with ImageJ



Axisymmetric representation of phases

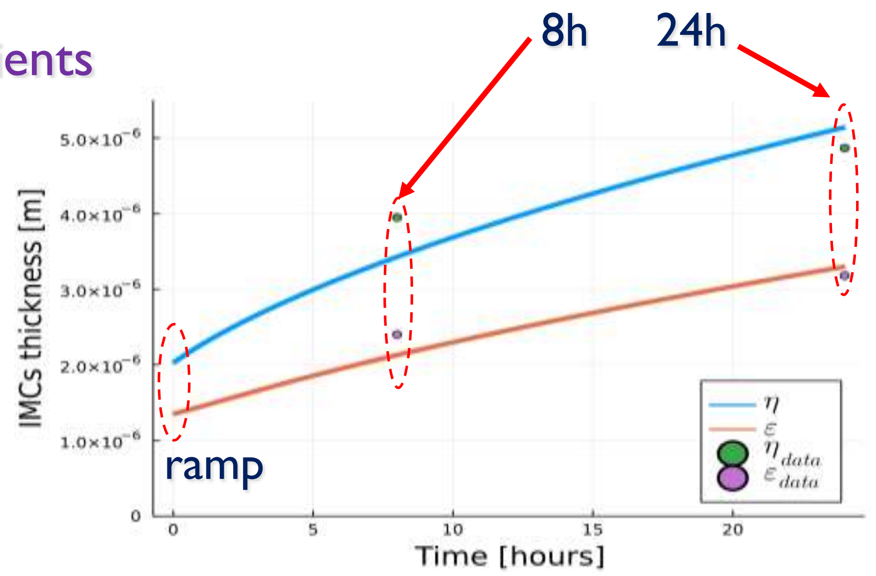
Conversion to characteristic radii for use in the model

Identification of the diffusion coefficients

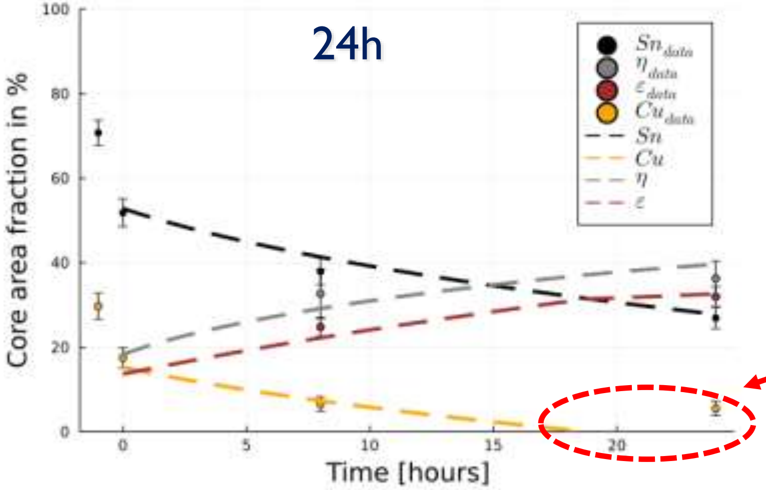
Least squares method was used to determine diffusion coefficients

$$D^{\varepsilon} = D_0^{\varepsilon} exp(-\frac{61.86}{RT}), \quad D^{\eta} = D_0^{\eta} exp(-\frac{53.92}{RT}).$$

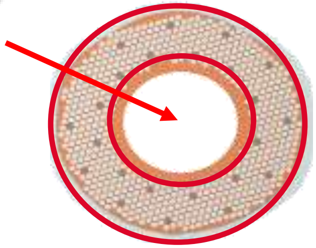
Pre-exponential factor	Literature $[m^2/s]$	Determined $[m^2/s]$
D_0^{η}	5.48×10^{-9}	4.05×10^{-9}
D_0^{ε}	1.84×10^{-9}	1.98×10^{-9}



Comparison with experimental data

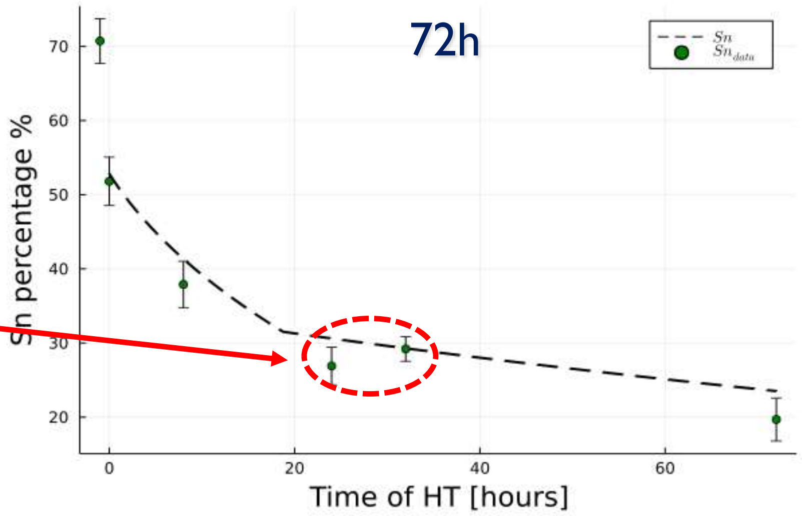


Only core area is considered



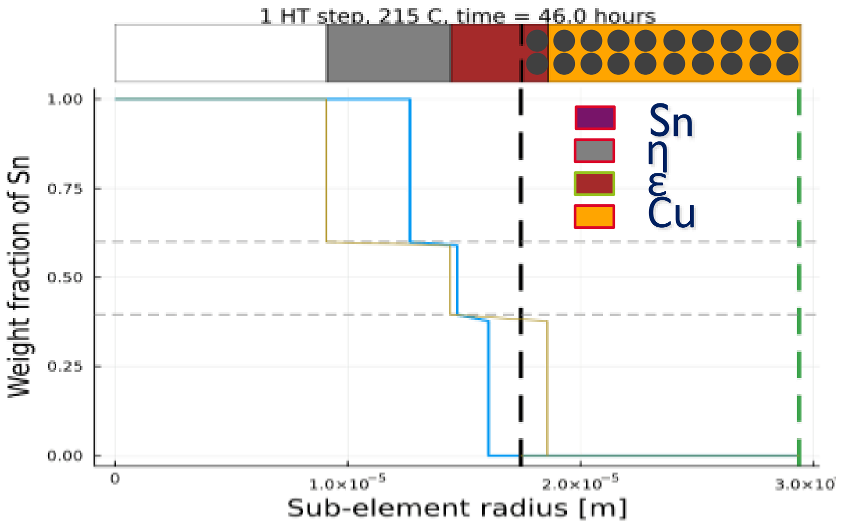
- measurement error
- 72 hours 215 C
- Good agreement

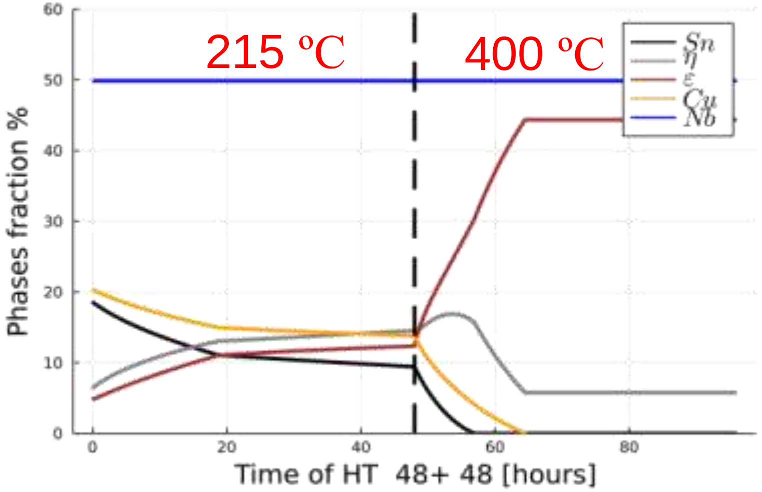
LSQ fit of the model to experimental data

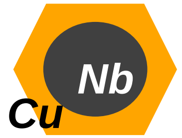


Results: modelling of 1+2 HT steps

Total area is considered



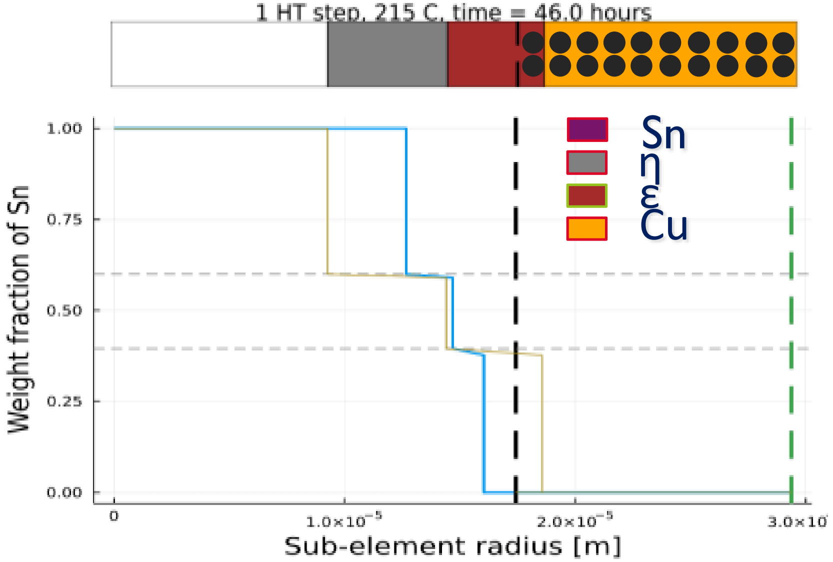




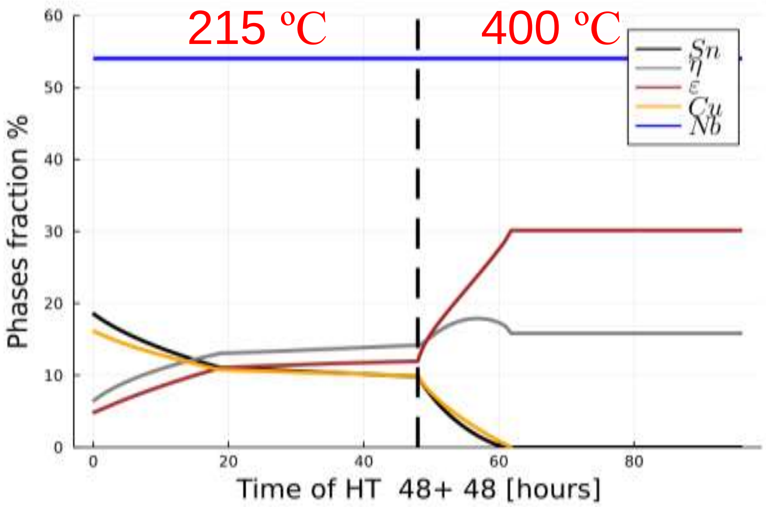
$$LAR = \frac{Cu}{Nb}$$

LAR =0.3

- LAR dependence
- No experimental data



Fraction of Sn, η, ε, Cu in total area

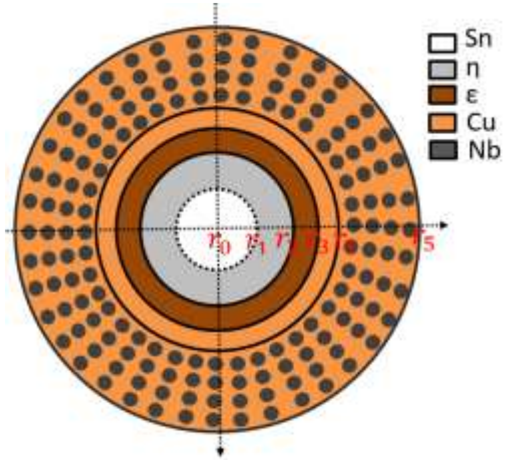


$$LAR = \frac{Cu}{Nb}$$

LAR =0.2

Conclusion

1. A new simplified one-dimensional model was developed
    1. Able to model 1st and 2nd HT steps (Python, Julia codes)
    2. Good agreement with available experimental data
2. A set of observations was performed on cross-sections of Nb3Sn strands
3. Geometrical parameters and diffusion coefficients were determined from experimental observations



Future plans:

- Modelling 3rd step of HT
- Additional experiments at 400 and 650 degrees
- Effect of stresses on diffusion

The model could help:

- Optimize Nb3Sn superconductors
- Modelling mechanical state of Nb3Sn during HT

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THANK YOU FOR YOUR ATTENTION!

Contacting email: a.gorynin@g.nsu.ru

18 NOVEMBER 2021

References

1. Schoerling D., Zlobin A. V., (2019). Nb3Sn Accelerator Magnets: Designs, Technologies and Performance. – Springer Nature.

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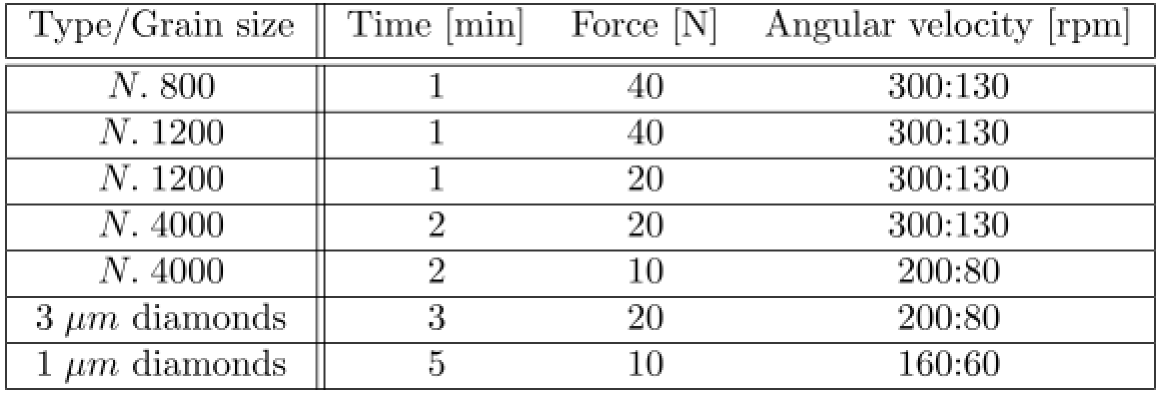
Samples preparation

To proceed with SEM:

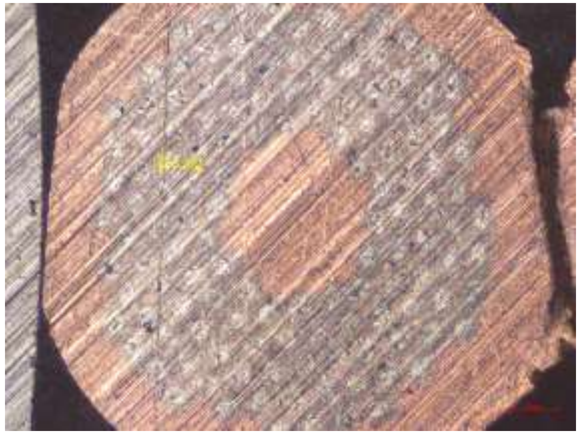
- Cutting the specimens
- Cold impregnation
- Polishing and grinding
- Sputter coating

Impregnated specimens

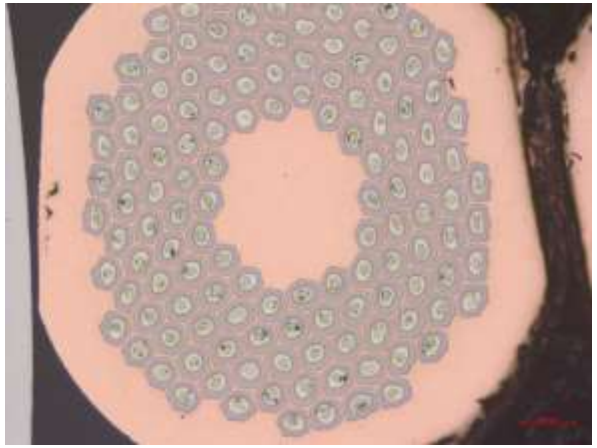


Type/Grain size	Time [min]	Force [N]	Angular velocity [rpm]
N. 800	1	40	300:130
N. 1200	1	40	300:130
N. 1200	1	20	300:130
N. 4000	2	20	300:130
N. 4000	2	10	200:80
3 μm diamonds	3	20	200:80
1 μm diamonds	5	10	160:60

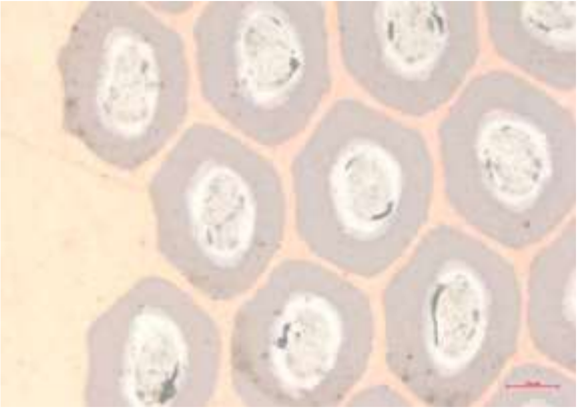
Determined polishing parameters



Surface before polishing, sample FSC2P 72h. Scale: 100μm.



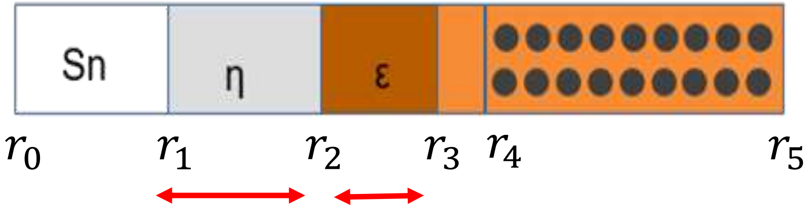
Surface after polishing, sample FSC2P 24h. Scale: 20μm.



Surface after polishing, sample FSC2P 72h. Scale: 100μm.

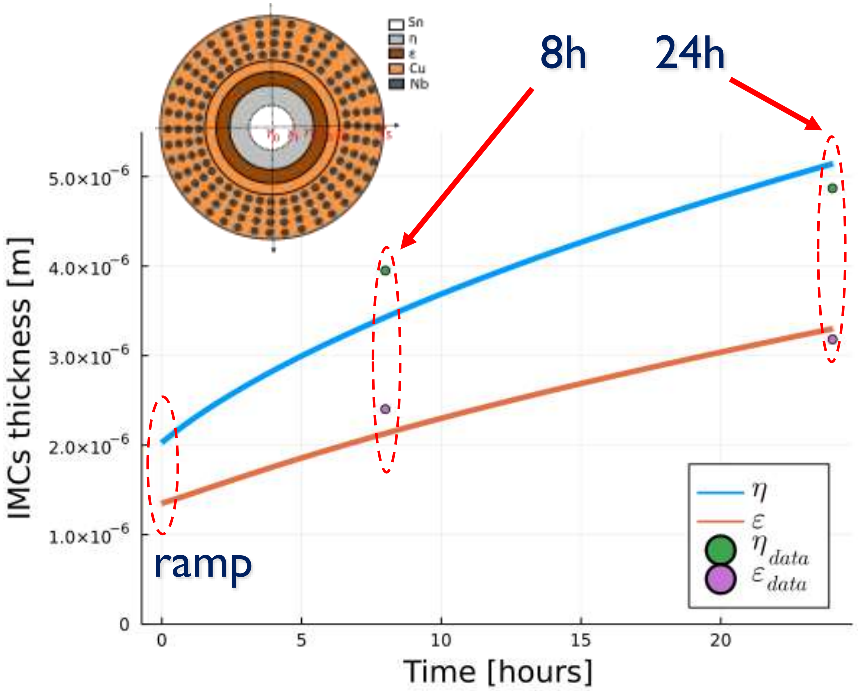
Identification of the diffusion coefficients

Least squares method was used to determine diffusion coefficients



The model gives ε and η layers thickness as function of time

- Estimation of initial thicknesses for ε and η phases (IMCs)
- 215 C temperature
- lack of experimental data



LSQ fit of the model to experimental data

$$D^{\varepsilon} = D_0^{\varepsilon} exp(-\frac{61.86}{RT}), \quad D^{\eta} = D_0^{\eta} exp(-\frac{53.92}{RT}).$$

Pre-exponential factor	Literature $[m^2/s]$	Determined $[m^2/s]$
D_0^{η}	5.48×10^{-9}	4.05×10^{-9}
D_0^{ε}	1.84×10^{-9}	1.98×10^{-9}