UNIVERSITÉ DE GENÈVE
FACULTÉ DES SCIENCES

LNCMI

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European Magnetic Field Laboratory

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PSI

Influence of Oxygen Source on the High Magnetic Field Behavior of Nb_3Sn Wires Manufactured via Internal Oxidation

CHART
Swiss Accelerator Research and Technology

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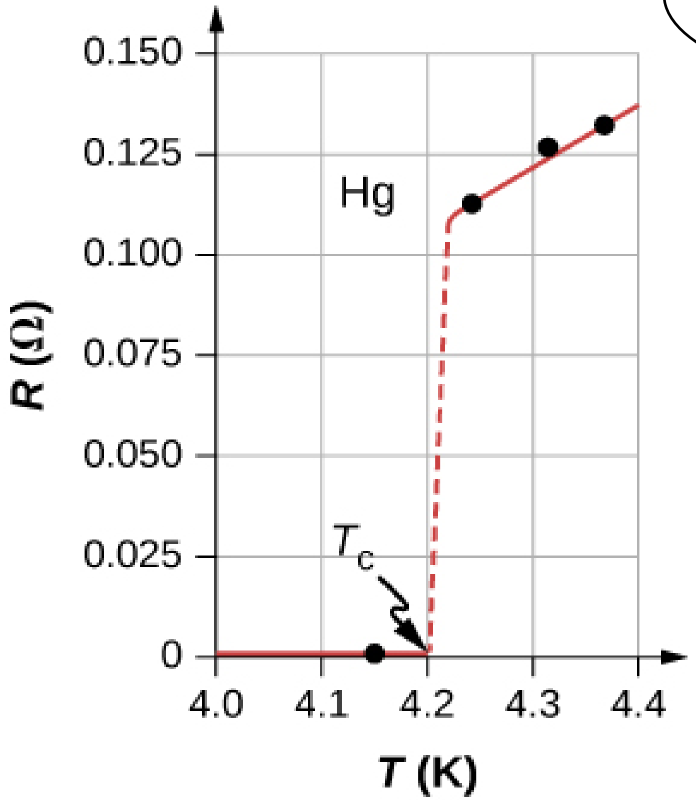
HFM
High Field Magnets

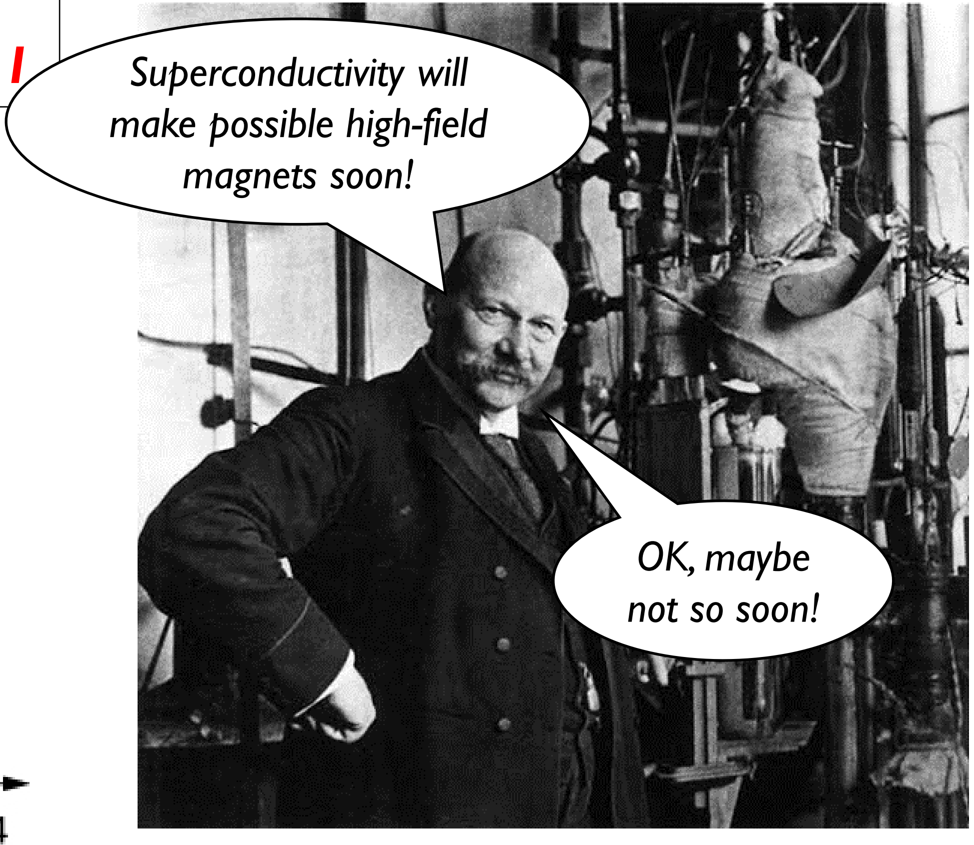
Outline

- *Why low temperature superconductors have still their word to say!*
- *The internal oxidation process*
- *Enhancement of Nb_3Sn superconducting properties*
- *High magnetic field measurements (done and to do)*
- *Morphological overview of Nb_3Sn and precipitates*

Magnetic field for material research and materials for high-magnetic fields

Discovery of superconductivity in 1911





Heike Kamerlingh Onnes

"The solution of the problem of obtaining a field of 100000 Gauss (10 T) could then be obtained by a coil of say 30 cm in diameter and the cooling with a plant which could be realized in Leiden with a relatively modest financial support"
H. K. Onnes, 3rd International Congress on Refrigeration (1913)

TABLE I. Critical constants for superconducting mercury.

Sample	T_c (°K)	H_0 (gauss)	γ millijoules/mole°K²
Hg-1	4.1535±0.0005	415.4+0.5, −1.5	.103+0.01, −0.04
Hg-3	4.153 ±0.001	415.1±0.5	.088±0.01
Hg-4	4.1531±0.000[illegible]	414.9+0.5, −1.5	2.108+0.01, −0.04
Hg-5	4.1532±0.0005	414.4±0.4	2.079±0.01

- Wilson M. N. IEEE TAS (2012) 22 3
- Finnemore D. K. et al. Physical Review 118 1 (1960)

Nb_3Sn: an old material still to be unraveled

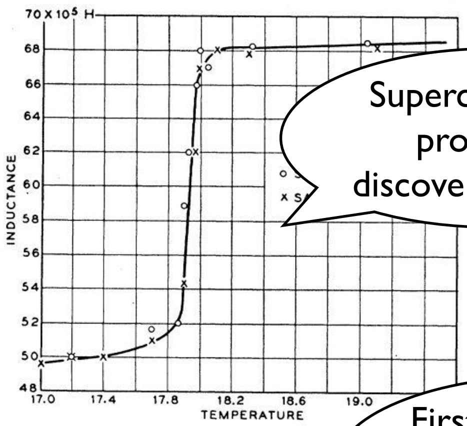
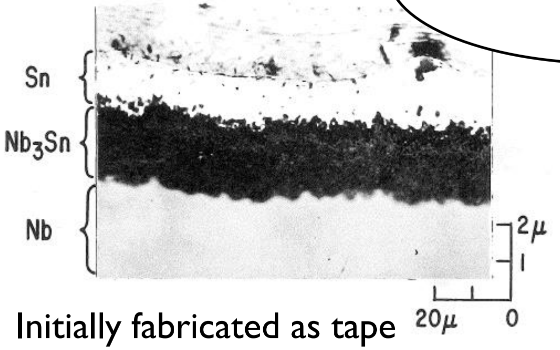
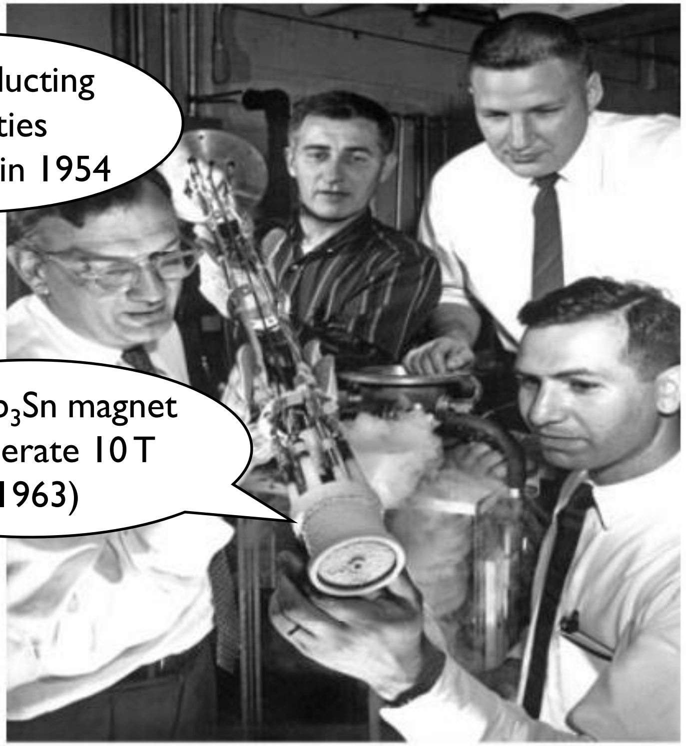


FIG. 1. Variation of susceptibility with temp

Superconducting properties discovered in 1954



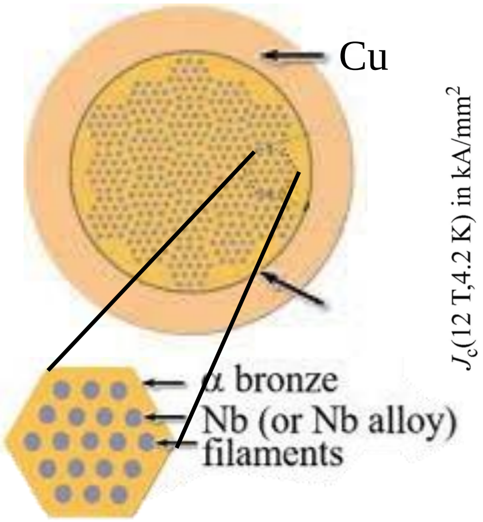
Initially fabricated as tape

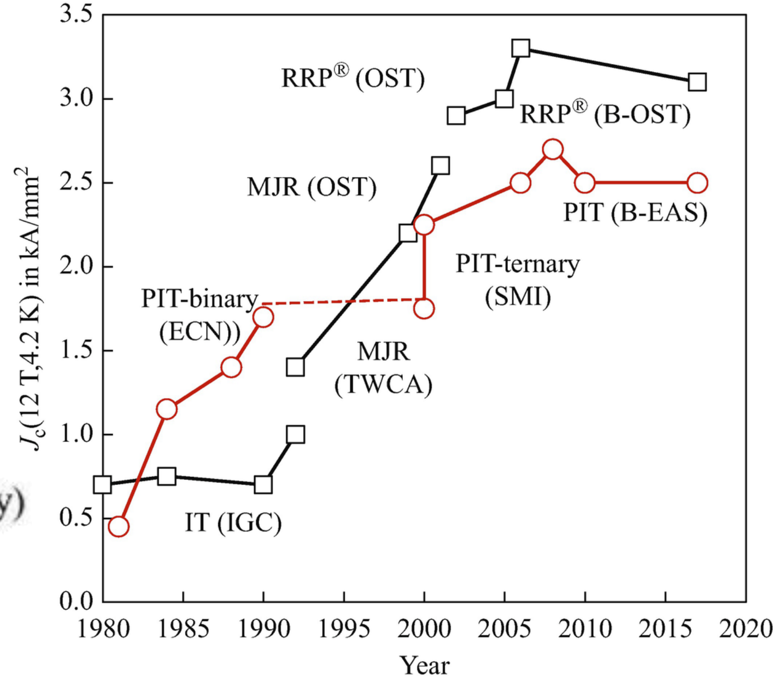


First Nb_3Sn magnet to generate 10 T (1963)

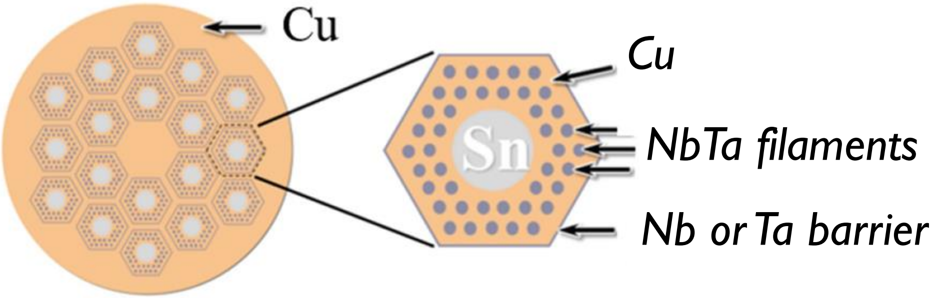
Magnet, fabricated and tested by: L. Martin, C. Bruch, M. Benz and C. Rosner (left to right)

Bronze wire



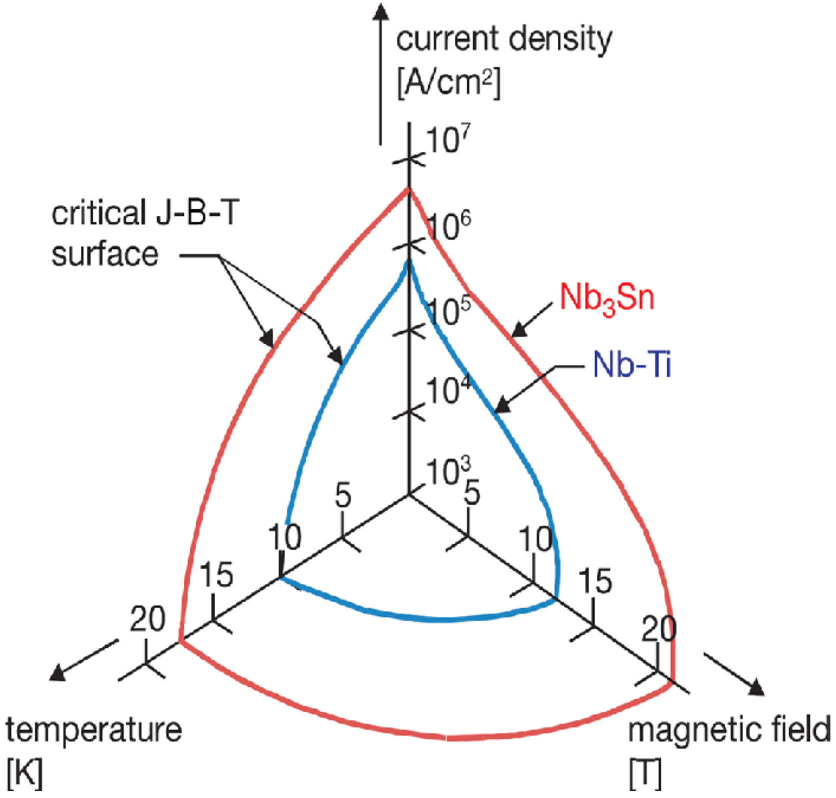


Rod-type wire manufacturing process (e.g. RRP)



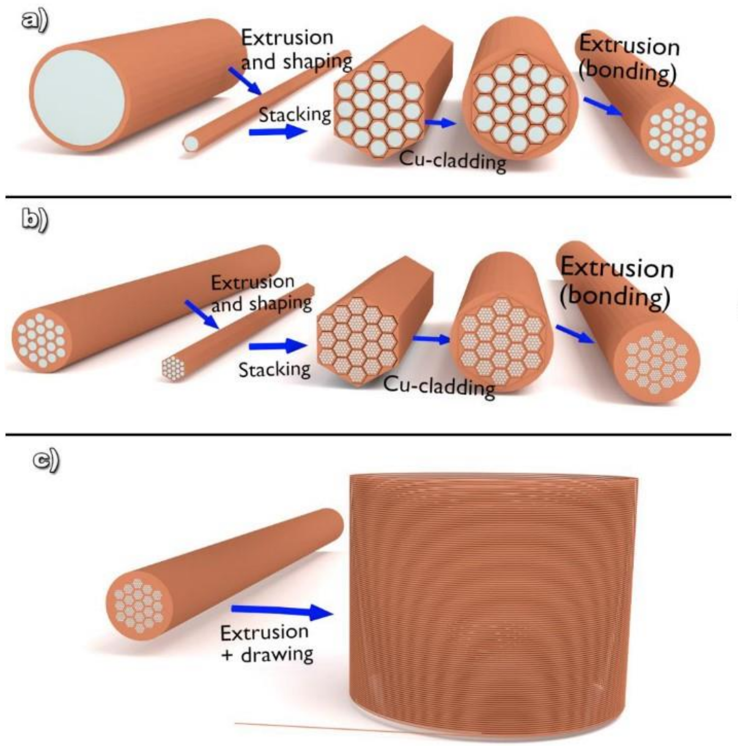
- Matthias B. T. et al. *Physical Review* 95.6 (1954): 1435.
- Rosner H. et al. *IEEE-CSC ESAS Eur. Supercond. News Forum*. No. 9. (2012)
- Barzi E and Zlobin A.V. Nb_3Sn Wires and Cables for High-Field Accelerator Magnets(2019)

The dominion of Low Temperature Superconductors

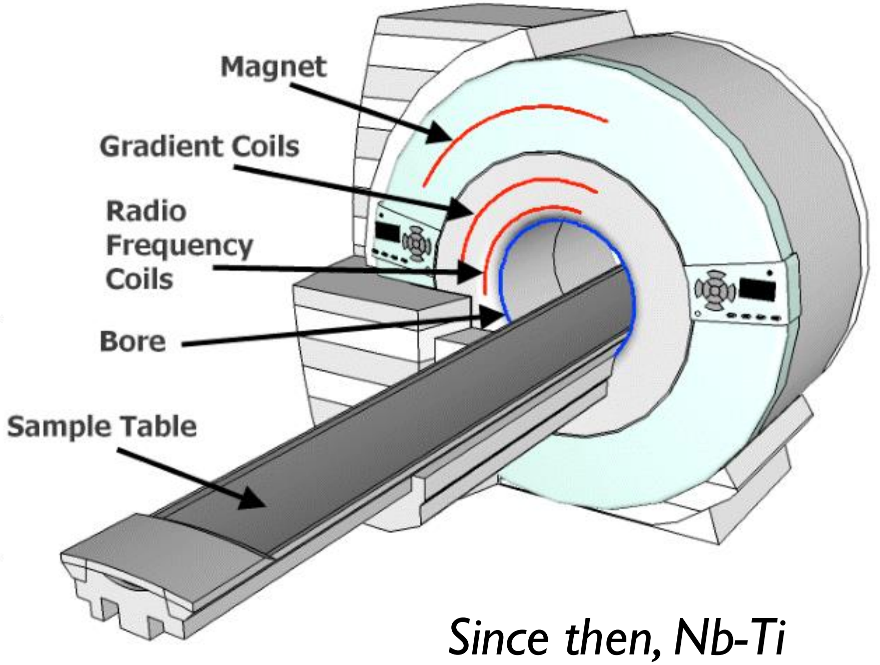


The Niobium-Titanium alloy (Nb-Ti) was discovered to be a superconductor in 1965, two years after the first Nb_3Sn magnet operating at 10 T

Nb-Ti has lower properties compared to Nb_3Sn, but is easier to wind and manufacture



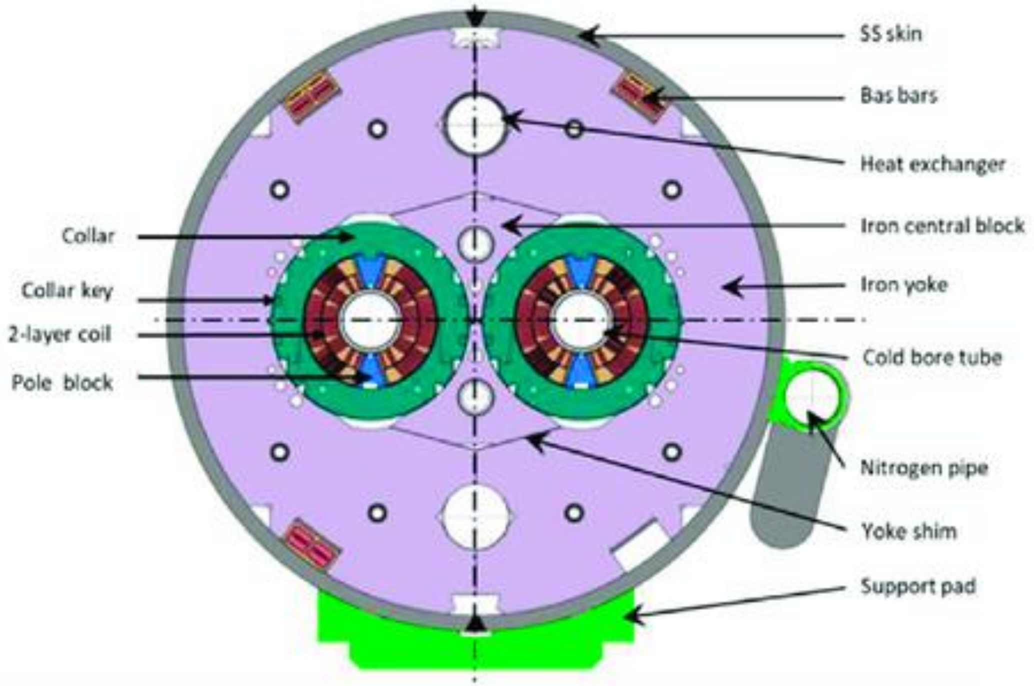
<u>Nb-Ti</u> *is and alloy,* ***<u>ductile</u>***
<u>Nb_3Sn</u> *is an intermetallic compound,* ***<u>brittle</u>***



Since then, Nb-Ti is the backbone of MRI magnets

The dominion of Low Temperature Superconductors

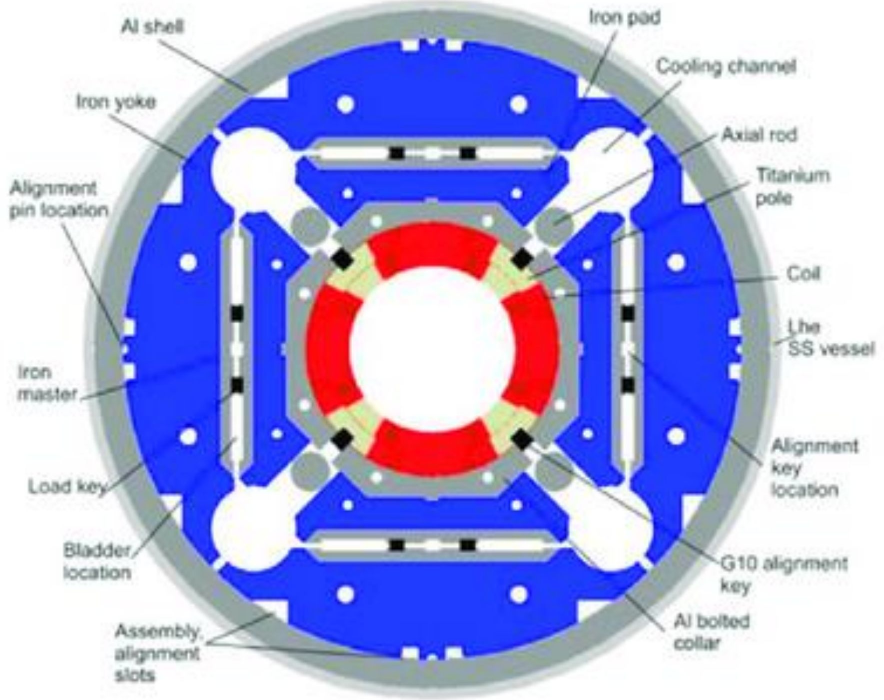
LHC dipole magnet



Fabricated using NbTi wires

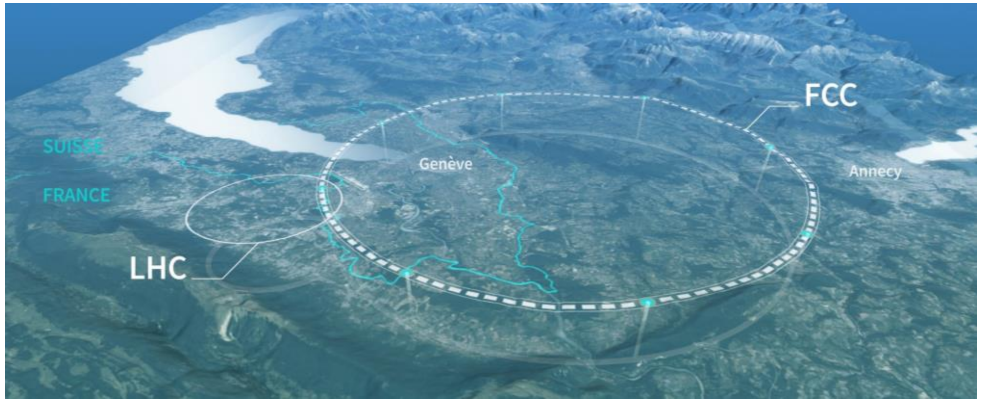
LHC had to be updated using Nb_3Sn magnets to have a higher beam focus and enhance the number of collisions

Hi Luminosity LHC quadrupole magnet



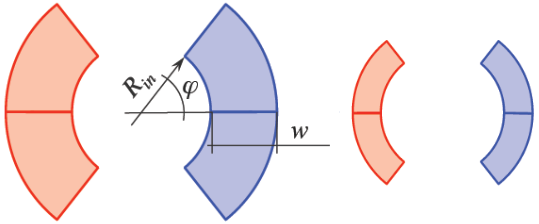
Fabricated using Nb_3Sn wires

The future of Nb_3Sn

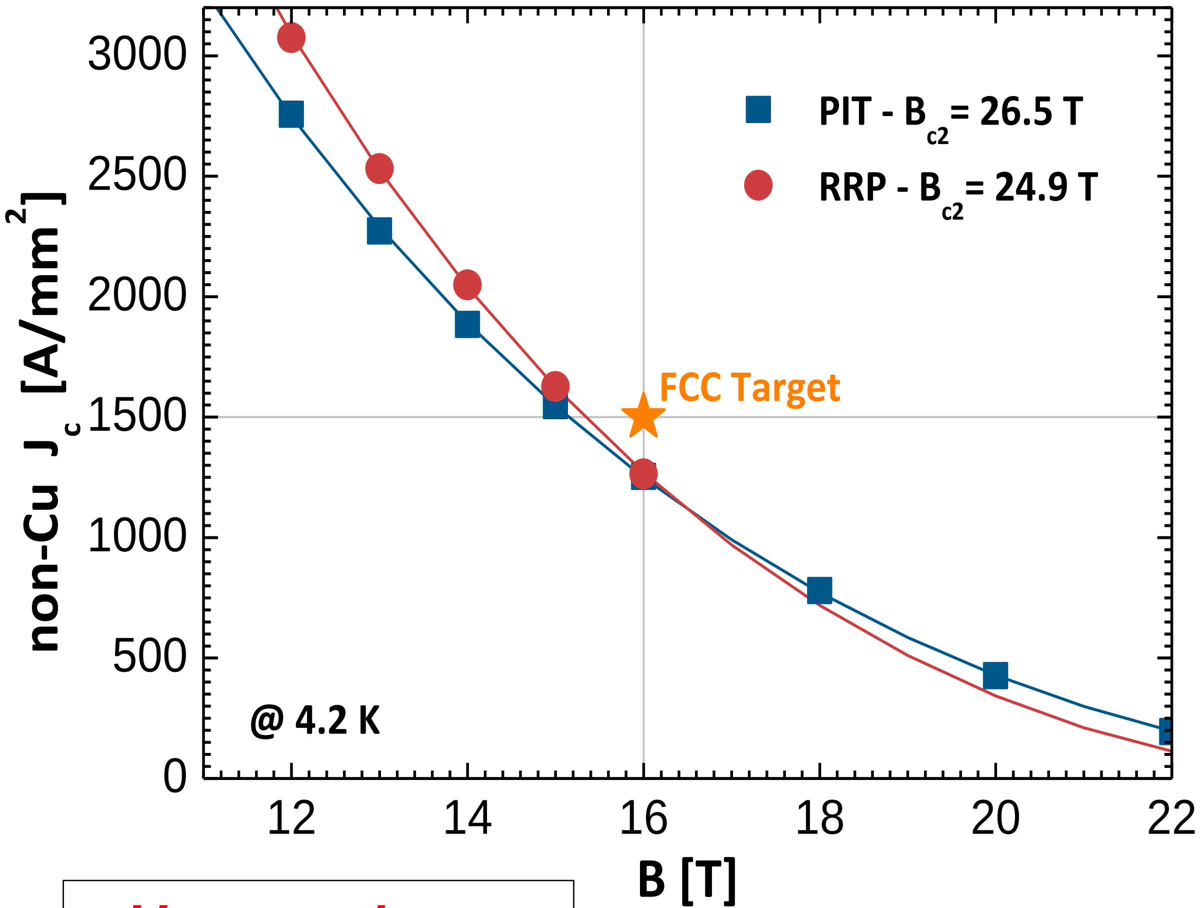


LHC	FCC-hh
27 km, 8.33 T	100 km, 16 T
14 TeV (c.o.m.)	100 TeV (c.o.m.)
1'300 tons NbTi	~10'000 tons Nb_3Sn

B [T]	16	16
J_{op} [A/mm²]	300	600 (2x)
w [mm]	76	38
A_{coil} [mm²]	20'000	7'000



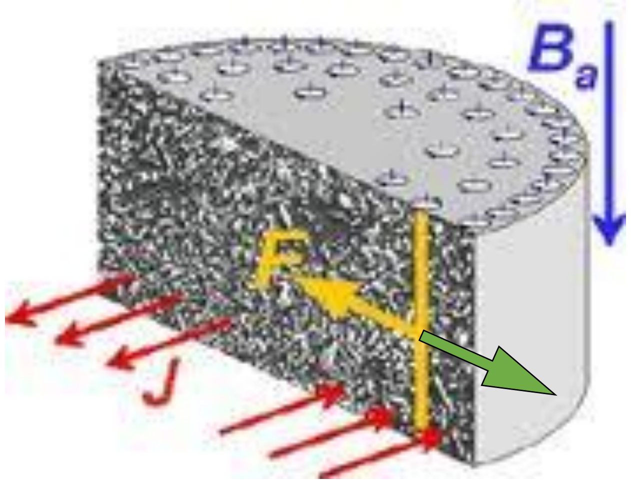
Doubling the operating current density reduces the superconductor area to one-third!

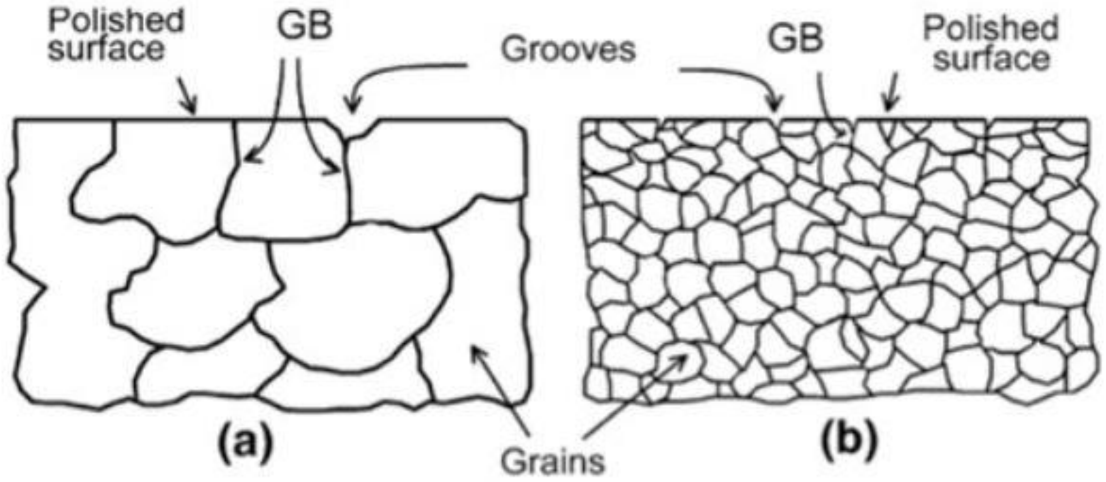


How to enhance the J_c of Nb_3Sn?

- Parrell et al. AIP Conf. Proc. 711 (2004) 369
- Boutboul et al., IEEE TASC 19 (2009) 2564

Nanometrical control of Nb_3Sn grains





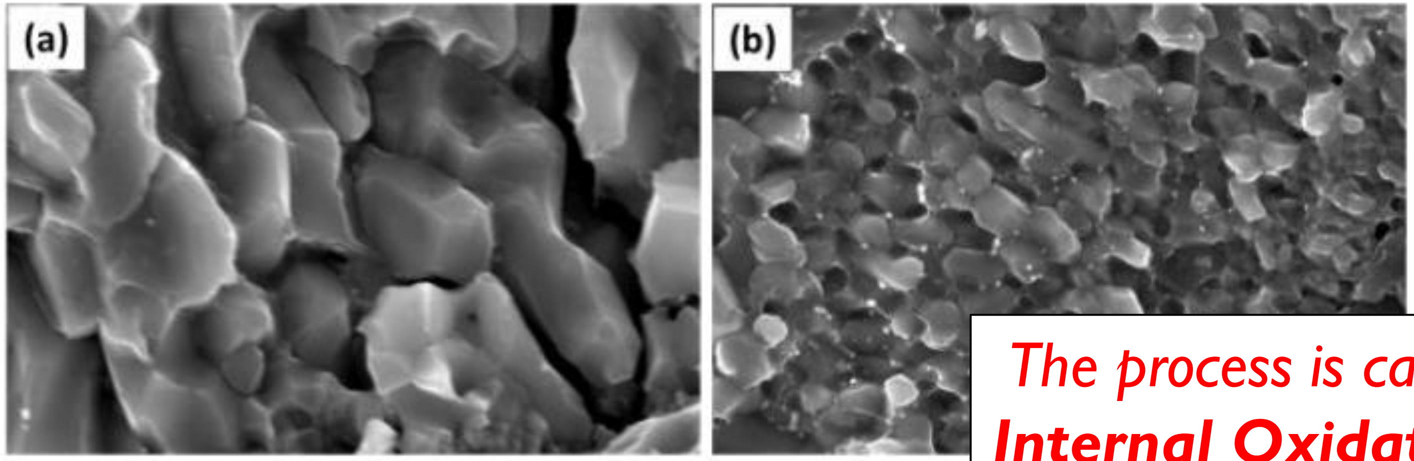
The pinning mechanism in Nb_3Sn is due to grain boundary pinning, and grain refinement can enhance J_c

Movement of flux lines causes dissipation, *detrimental for power applications. The* ***flux line lattice*** *must remain* ***pinned to pinning centers*** *(e.g., grain boundaries, or defects)*

$$J_c = \frac{f_p}{\phi_0}$$

Higher the pinning force, higher the critical current density

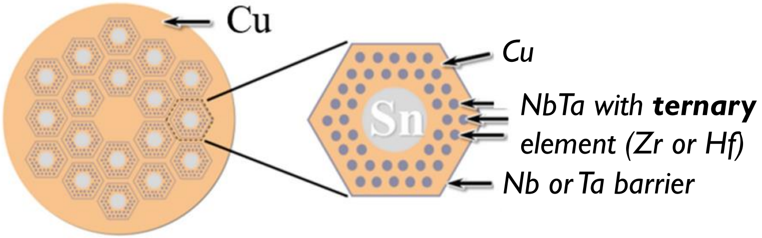
Grain refinement induced by ZrO_2 precipitation

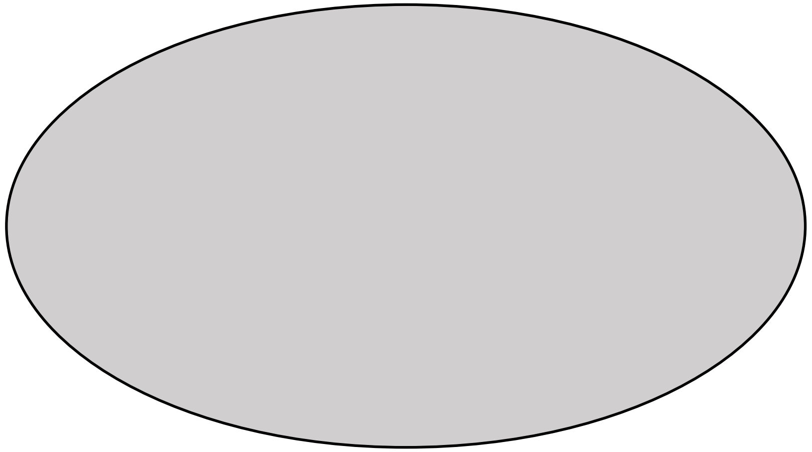


The process is called ***Internal Oxidation***

Internal oxidation process

What happens during heat treatment

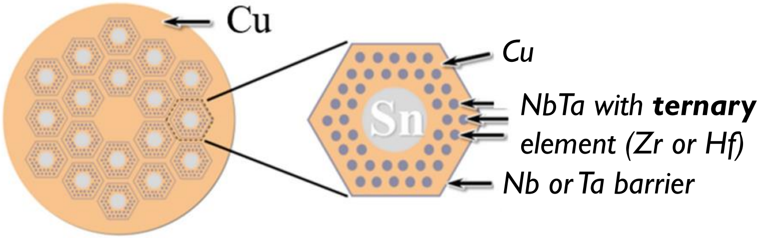


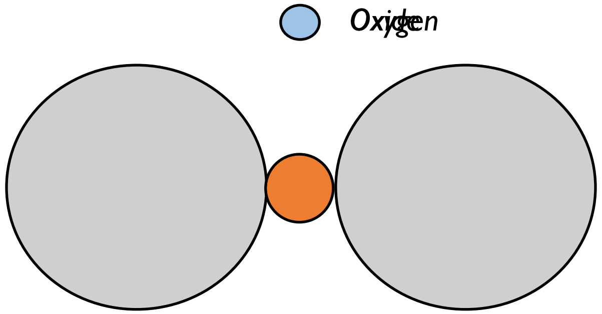


During heat treatment, grains continue to grow and join together when their boundaries are in contact

Internal oxidation process

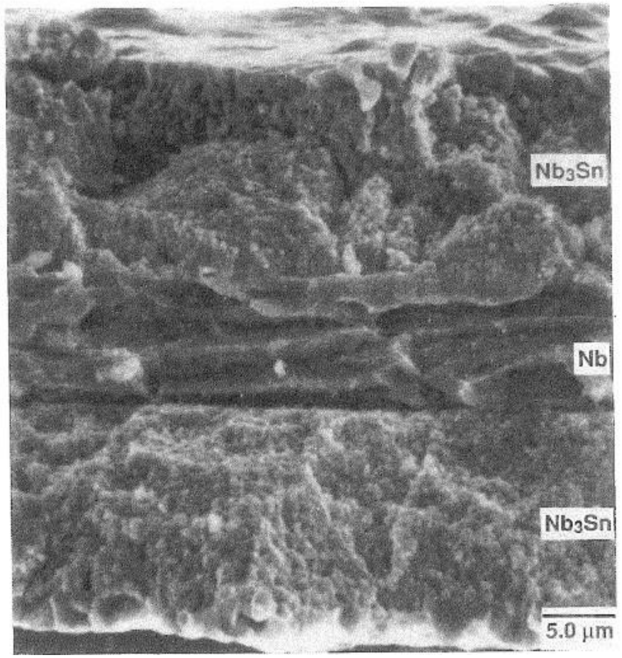
What happens during heat treatment





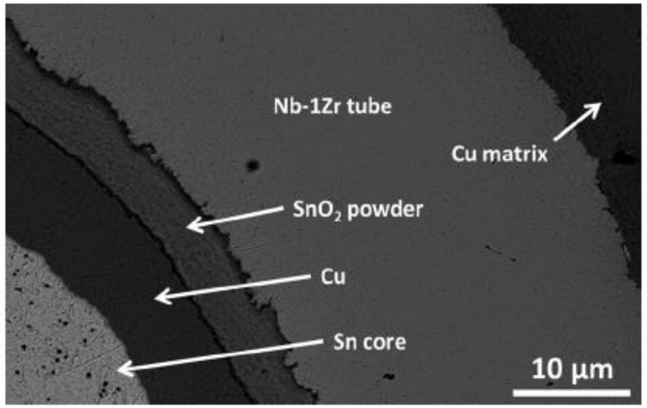
Oxygen reacts with the third element (with a higher affinity for oxidation)

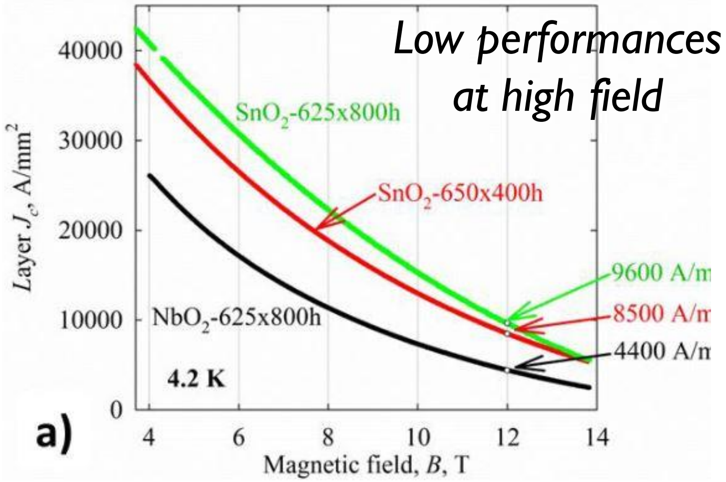
ZrO_2 (or HfO_2) nanoparticles prevent grains from joining together, keeping the grain size small



First proposed in 1968 for tape samples due to the easier introduction of oxygen. It was "impossible" to implement in round conductors: oxygen in alloy is detrimental to wire deformation

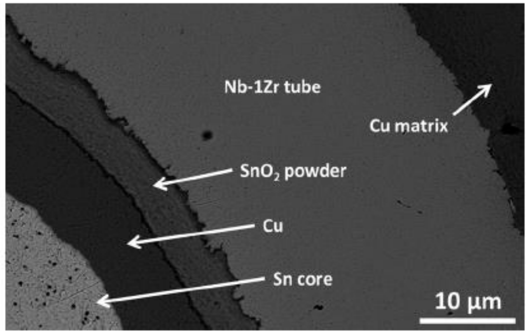
The first wire with internal oxidation was fabricated in 2014, using a separate oxygen source to allow wire deformation

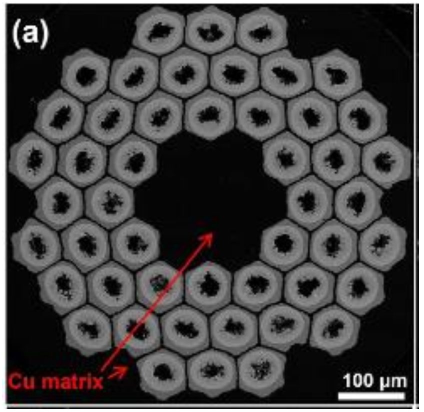


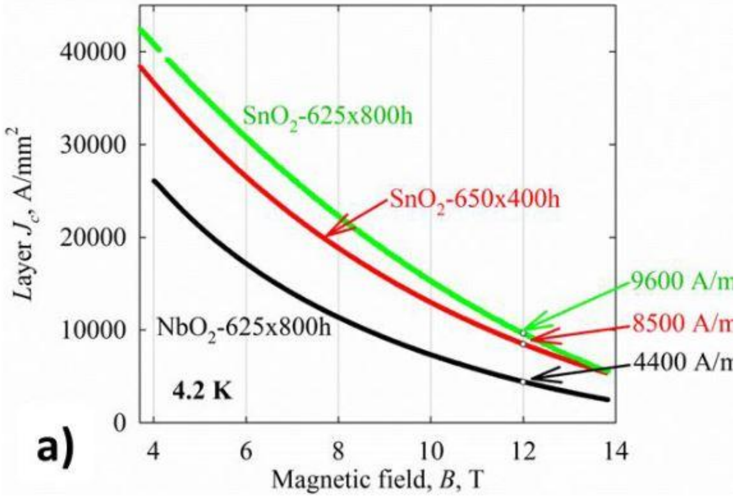


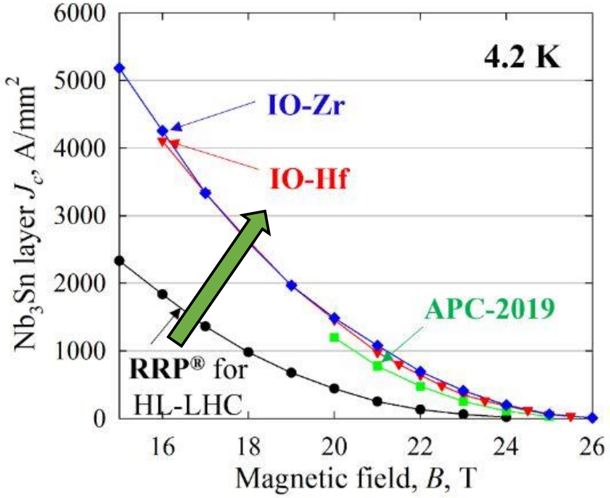
- Benz M. G. *Transaction of the Metal. Soc. of AIME* 242 (1968)
- Xu X. et al. *Applied Physics Letters* 104.8 (2014): 082602)

Evolution of layer J_c at high magnetic field

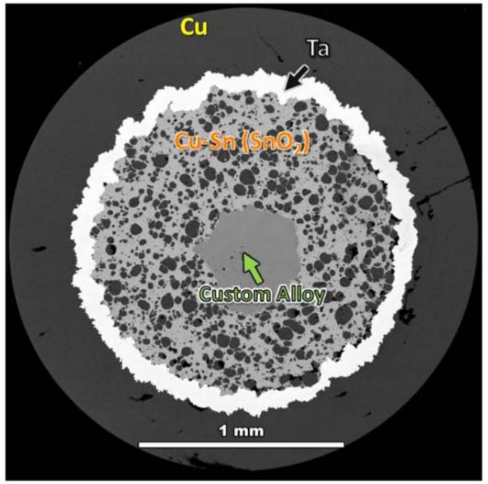


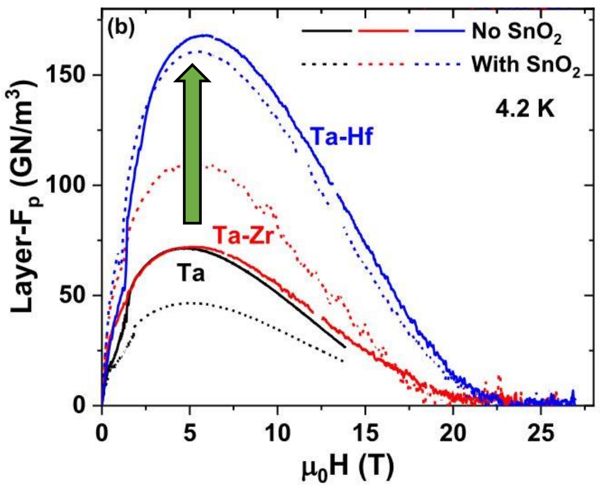


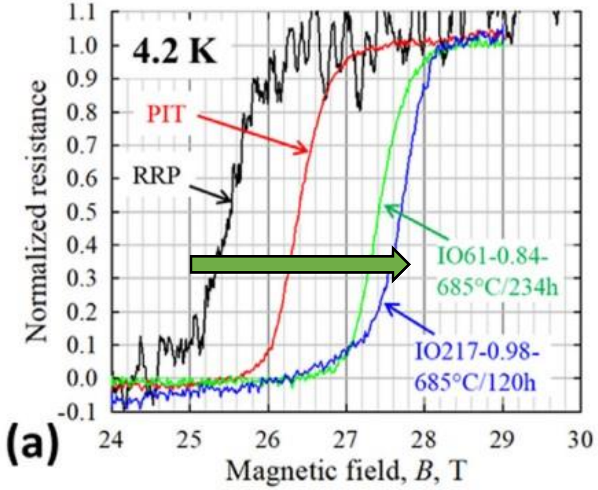




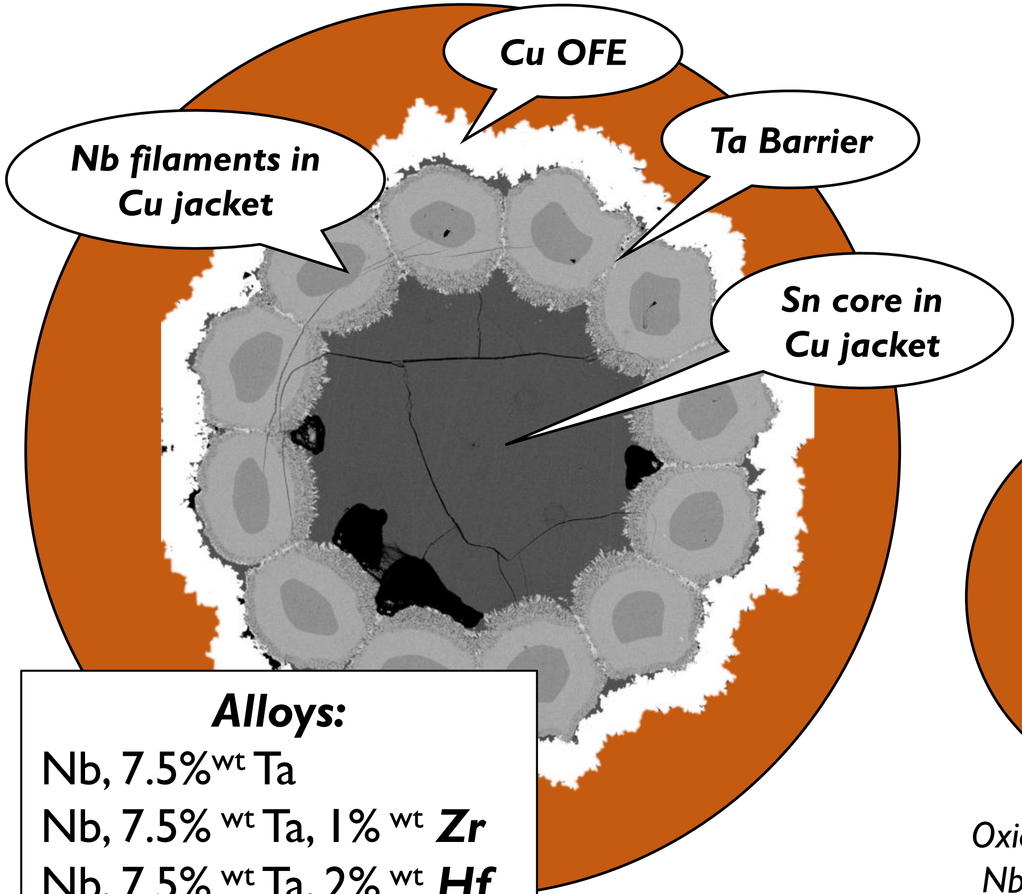
- *New wires designs*
- *Multifilamentary wires*
- *Introduction of Ta in Nb alloy*
- *Enhancement of J_c, F_p (max) and B_{c2}*







Simplified multifilamentary wires layout and fabrication process

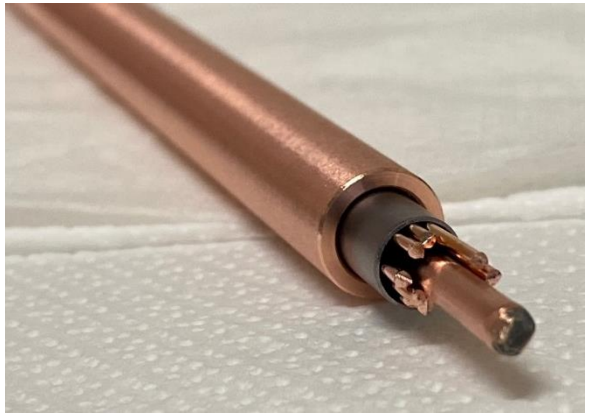


Alloys:

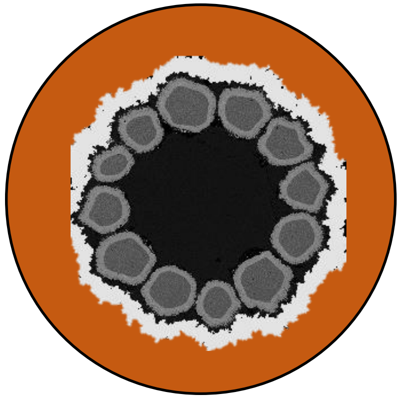
Nb, 7.5%^{wt} Ta

Nb, 7.5% ^{wt} Ta, 1% ^{wt} ***Zr***

Nb, 7.5% ^{wt} Ta, 2% ^{wt} ***Hf***

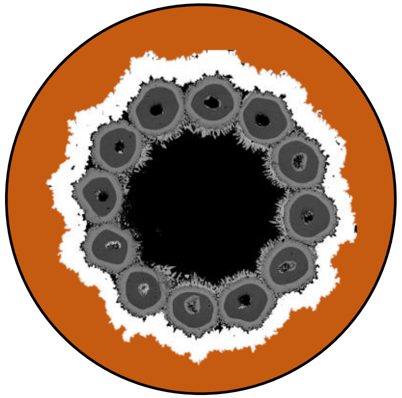


AnnularOS



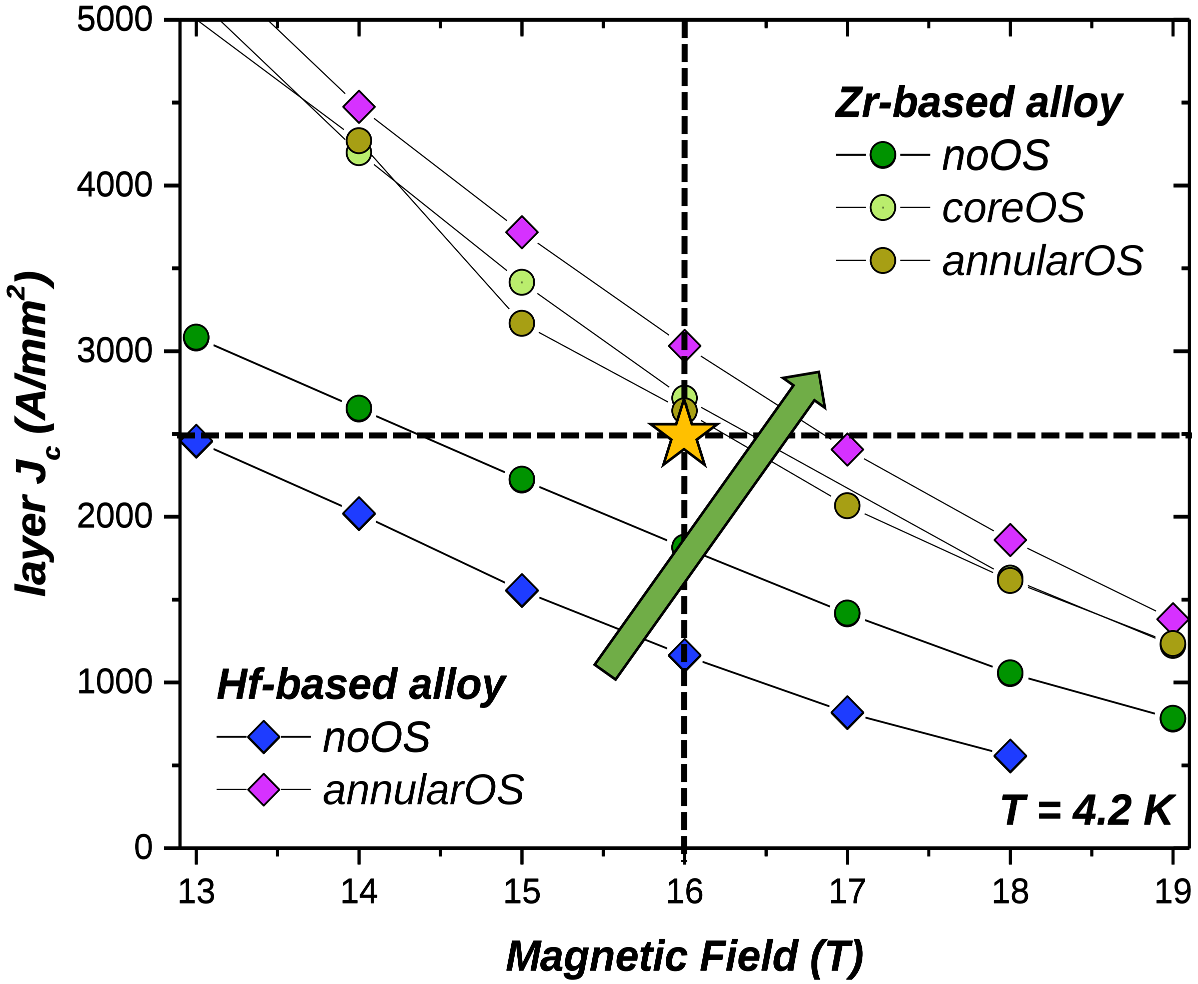
Oxide powder between the Nb-alloy filament and the copper jacket

CoreOS

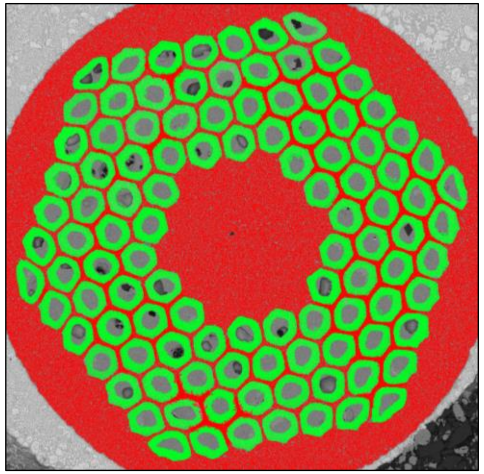


Oxide powder inside the Nb-alloy filaments

Effects of the internal oxidation on the superconducting properties



Layer J_c *above* ***FCC target*** *of* ***2500 A/mm²****,* *at 4.2 K and 16 T*



The FCC target for layer J_c is calculated based on the area fraction of reacted Nb_3Sn in a typical rod-type wire

- Bovone G. et al. *Superconductor Science and Technology* 36.9 (2023): 095018.

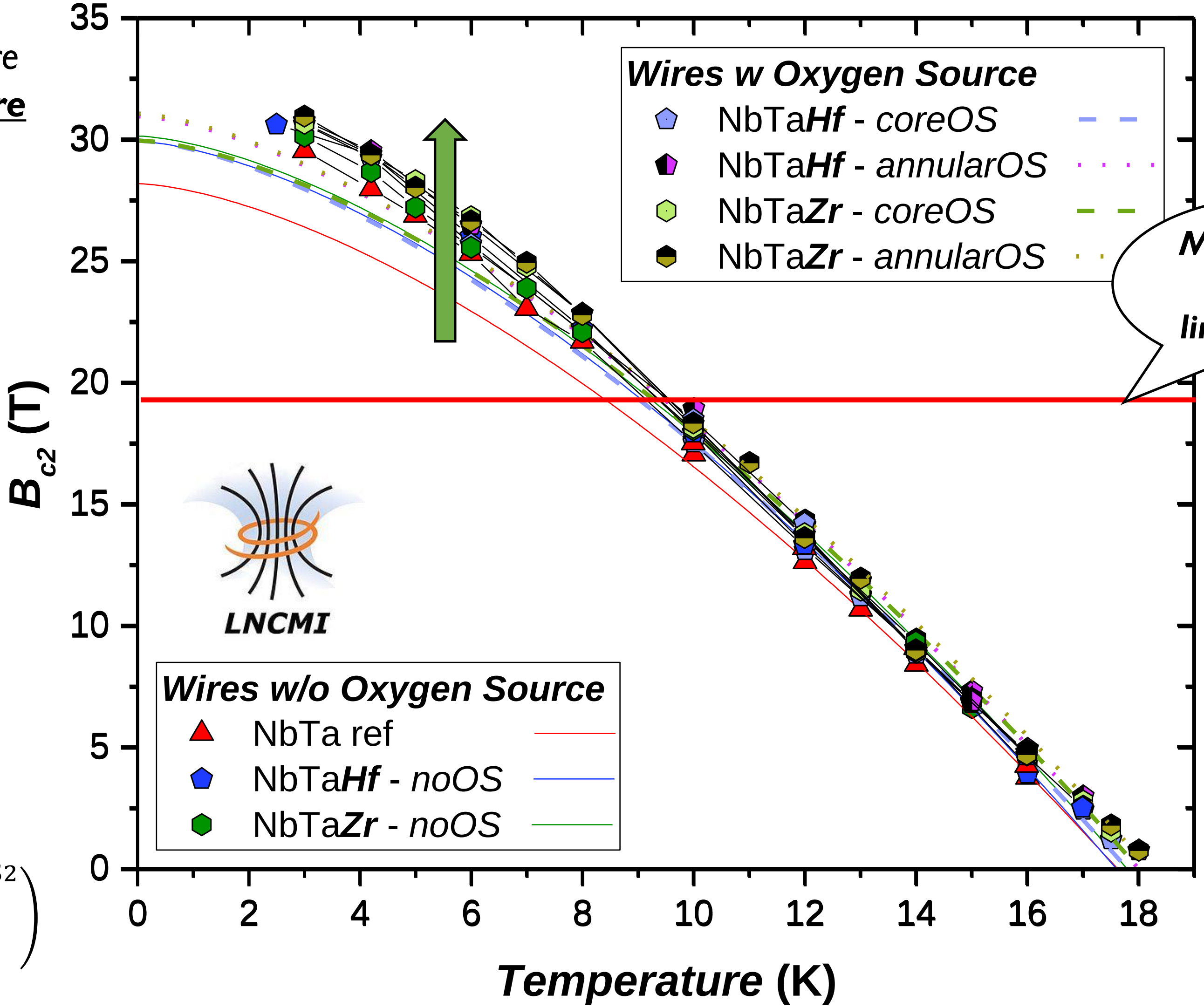
High magnetic field measurements

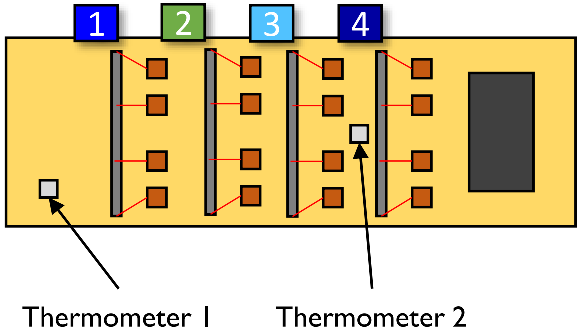
High-field measurements were performed at the ***Laboratoire National des Champs Magnétiques Intenses*** *(LNCMI) in Grenoble*

WHH Model

$$B_{c2}(0) \approx -0.69 \frac{dB_{c2}}{dT}\bigg|_{T_c} T_c^{eff}$$

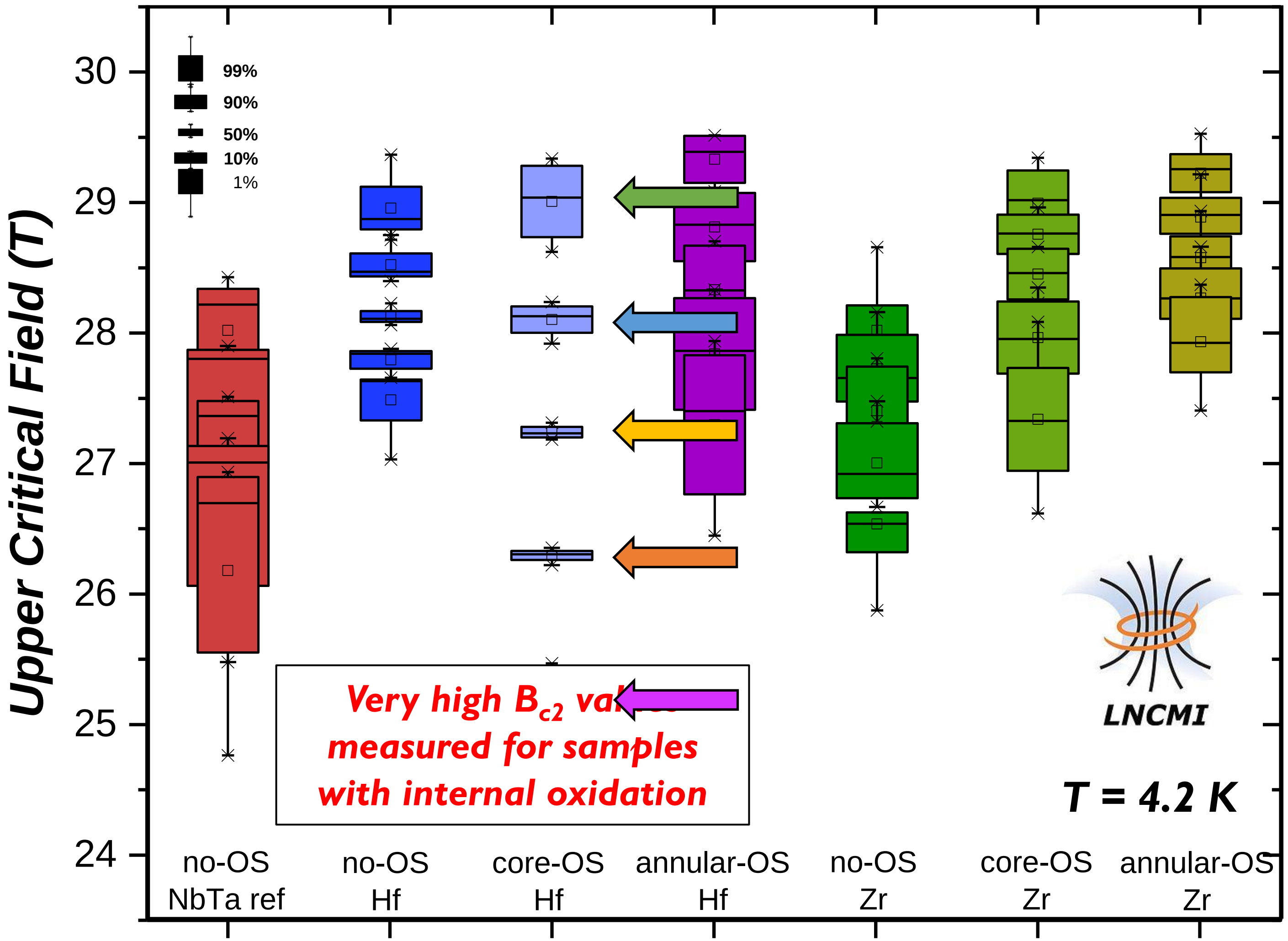
$$B_{c2}(T) = B_{c2}(0)\left(1-\left(\frac{T}{T_c}\right)^{1.52}\right)$$

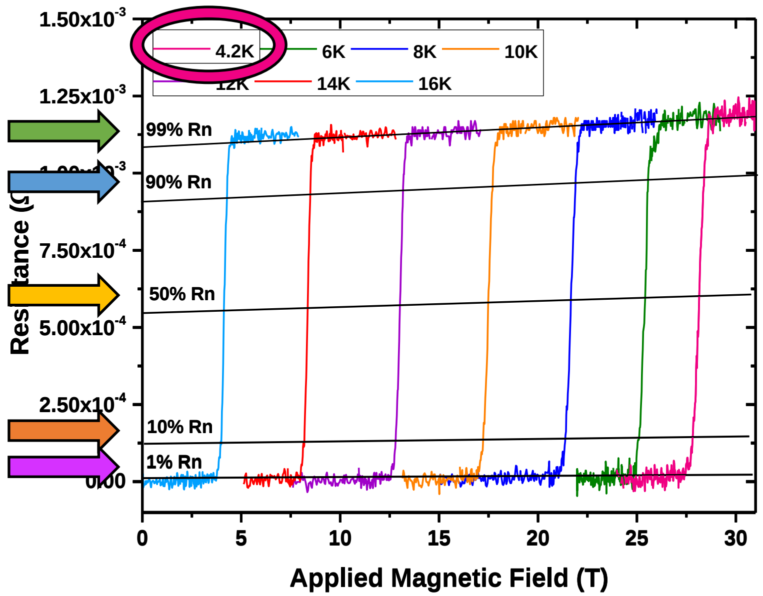




Bc_2 results at low magnetic fields overlap with measurements in Geneva, but high-field results are higher than extrapolated values

B_{c2} enhancement





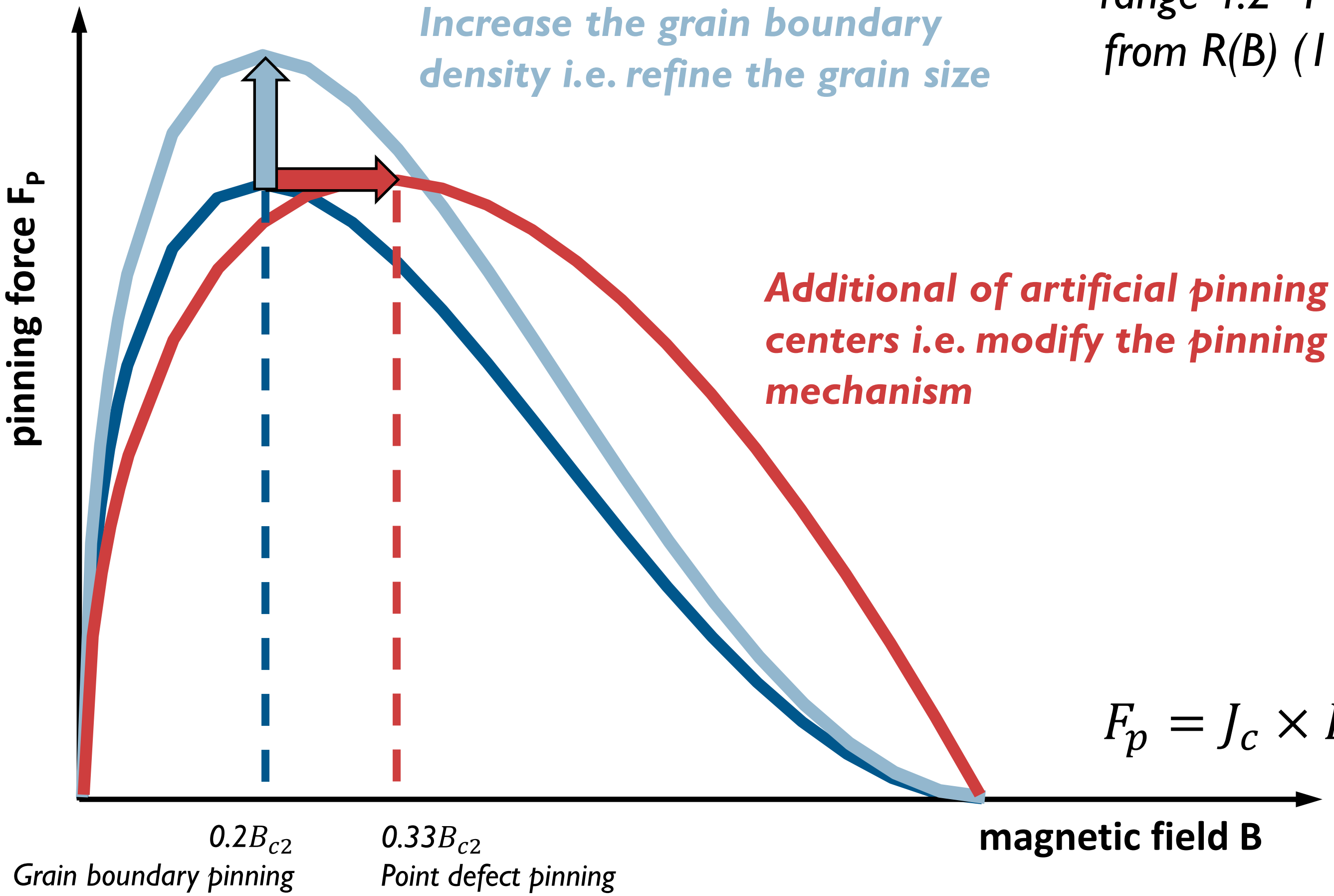
Nb alloy	B_{c2} (T) 4.2 K, 99 % R no-OS	B_{c2} (T) 4.2 K, 99 % R Core-OS	B_{c2} (T) 4.2 K, 99 % R Annular-OS
Nb 7.5%wt Ta 1%wt Zr	28.0 ± 0.60	28.97 ± 0.38	29.20 ± 0.38
Nb 7.5%wt Ta 1%wt Hf	28.9 ± 0.56	29.0 ± 0.36	29.32 ± 0.36
Nb 7.5%wt Ta	28.01 ± 0.85	N/A	

Pinning mechanism

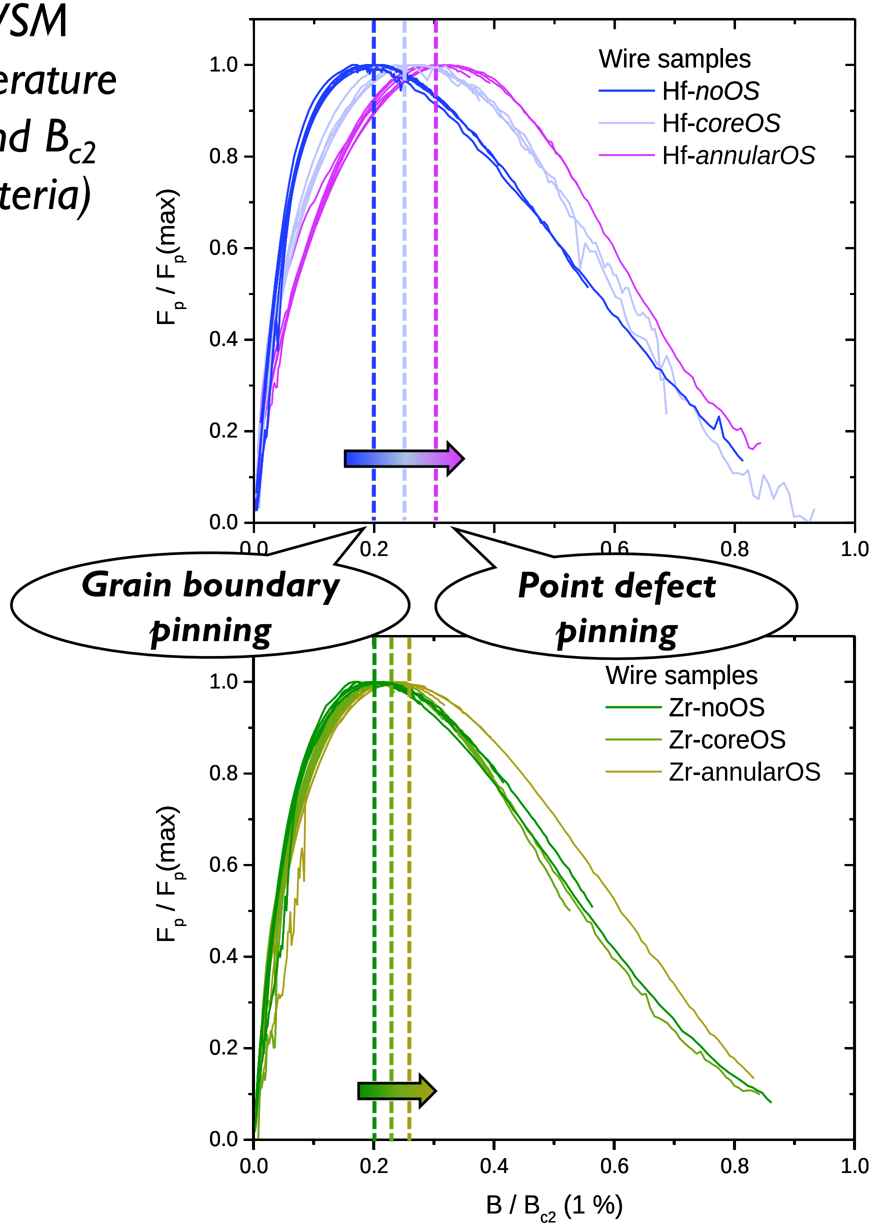
M(H) loop from VSM SQUID in the temperature range 4.2 -14 K and B_{c2} from R(B) (1 % criteria)

Increase the grain boundary density i.e. refine the grain size

Additional of artificial pinning centers i.e. modify the pinning mechanism



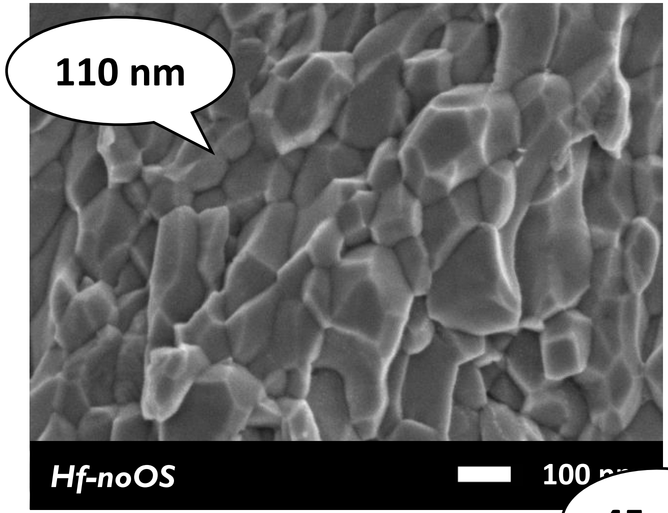
$$F_p = J_c \times B$$

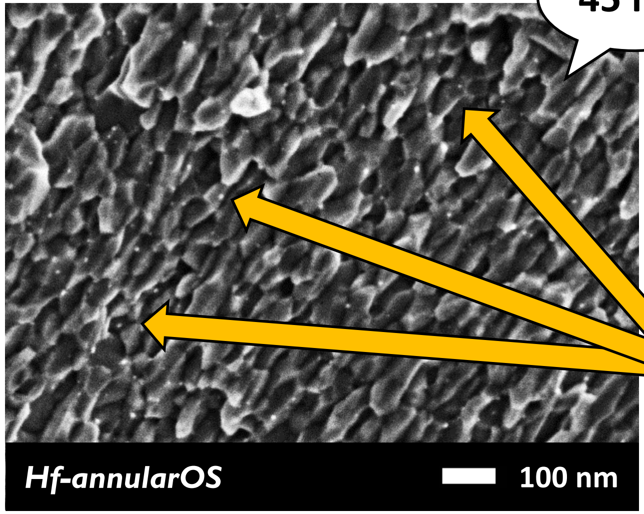


Modification of pinning mechanism when an oxygen source is added in presence of Hf and Zr

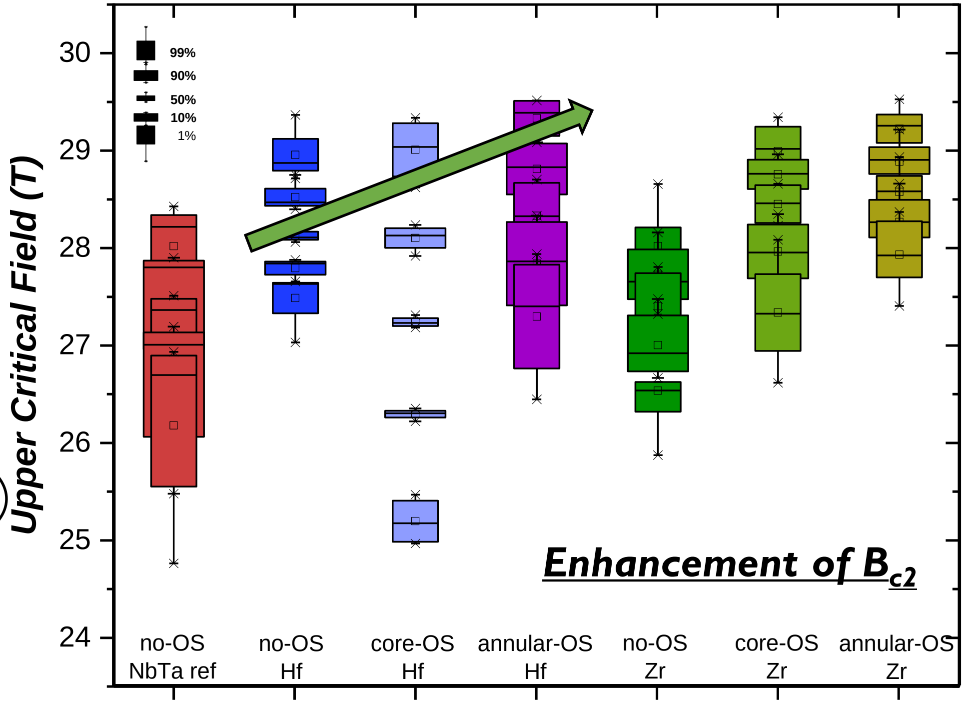
$$F_p = J_c \times B$$

What drives the enhancement?

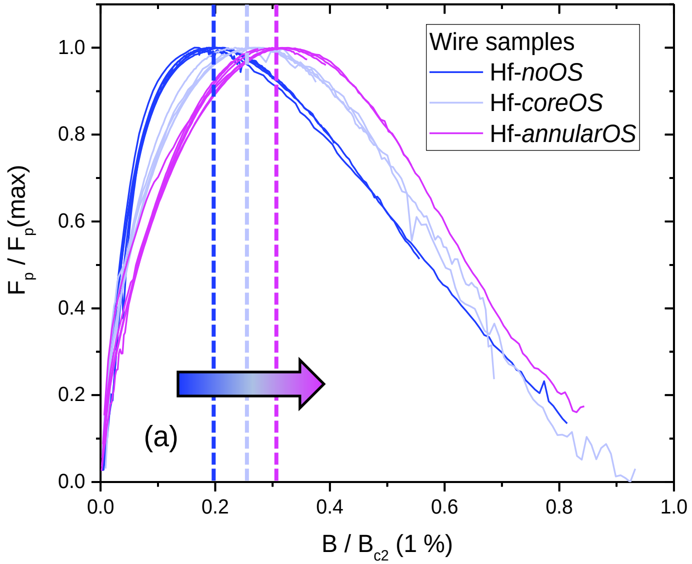


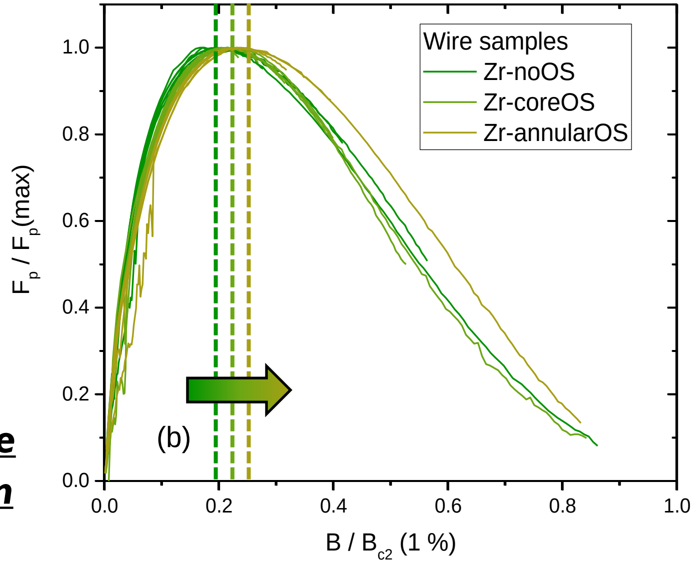


Nb_3Sn **grain size reduction** induced by precipitates (HfO_2)



J_c enhancement due to precipitated oxides

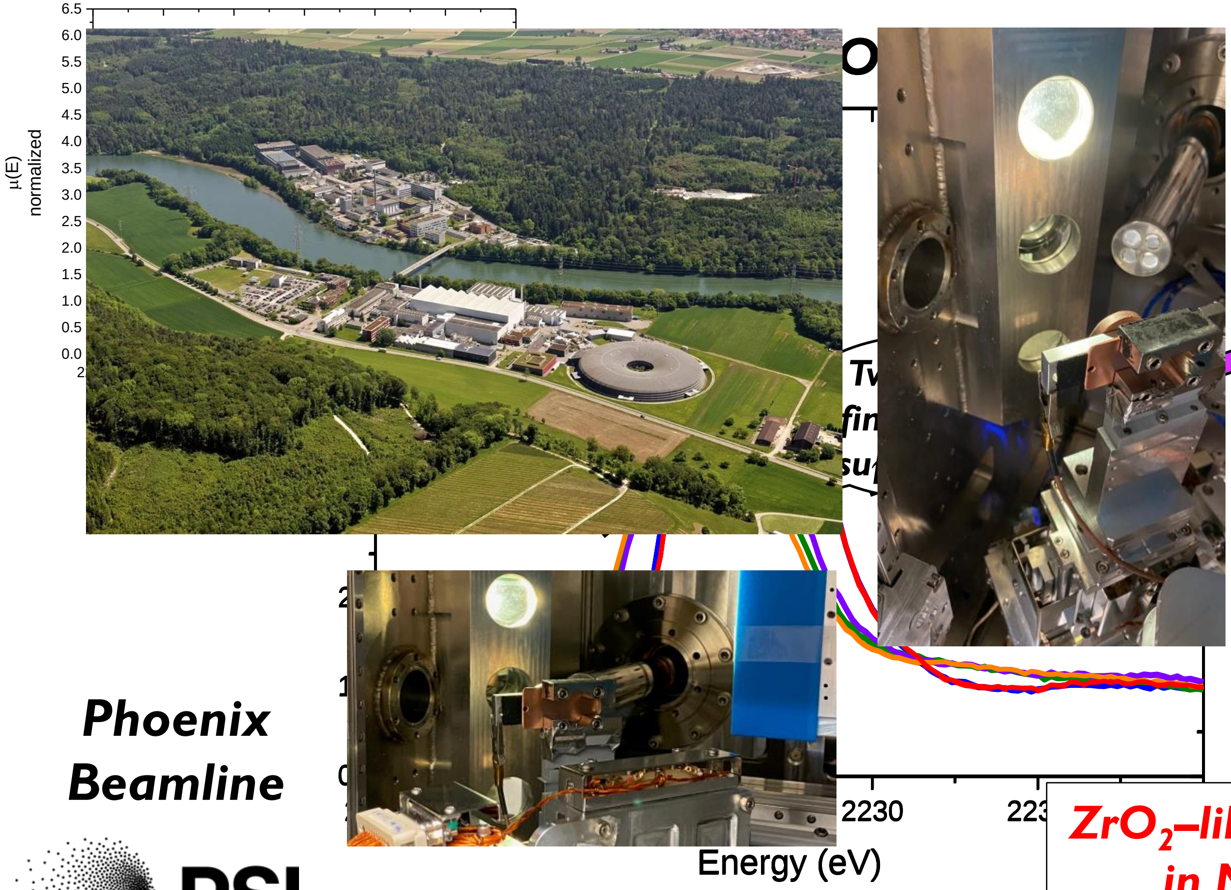




Modification of the pinning mechanism

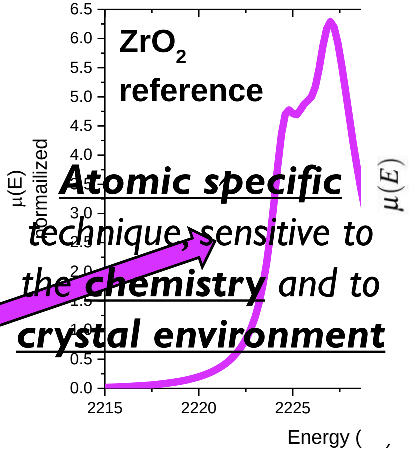
- Bovone G, et al. *Superconductor Science and Technology* 36.9 (2023): 095018

XANES investigation on precipitates

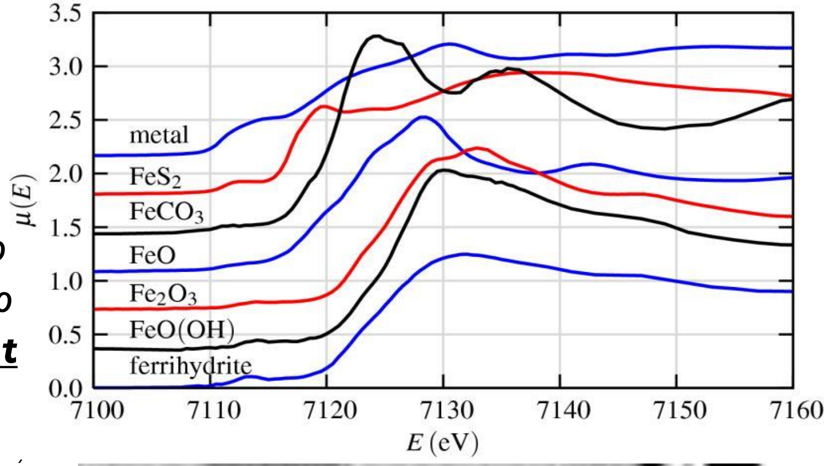


Phoenix Beamline

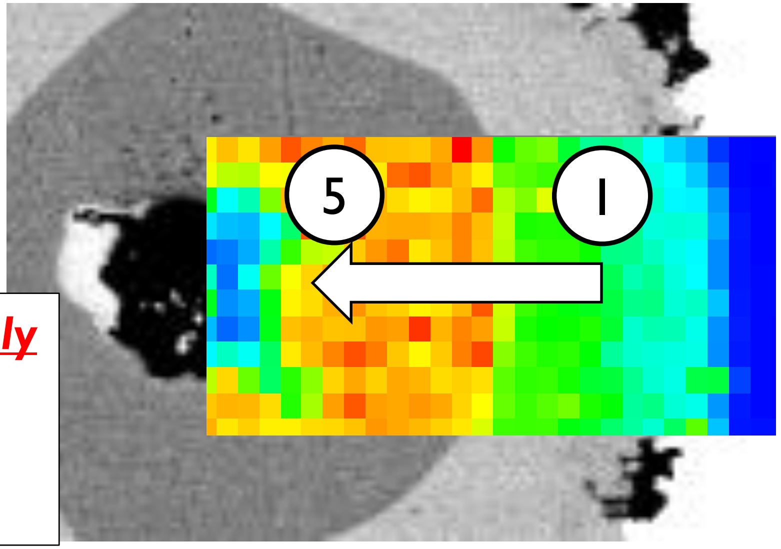
PSI



Atomic specific *technique, sensitive to the* ***chemistry*** *and to* ***crystal environment***



Investigation of ***Zr spectrum*** *in* ***different region*** *of the* ***reacted (and unreacted) wires***

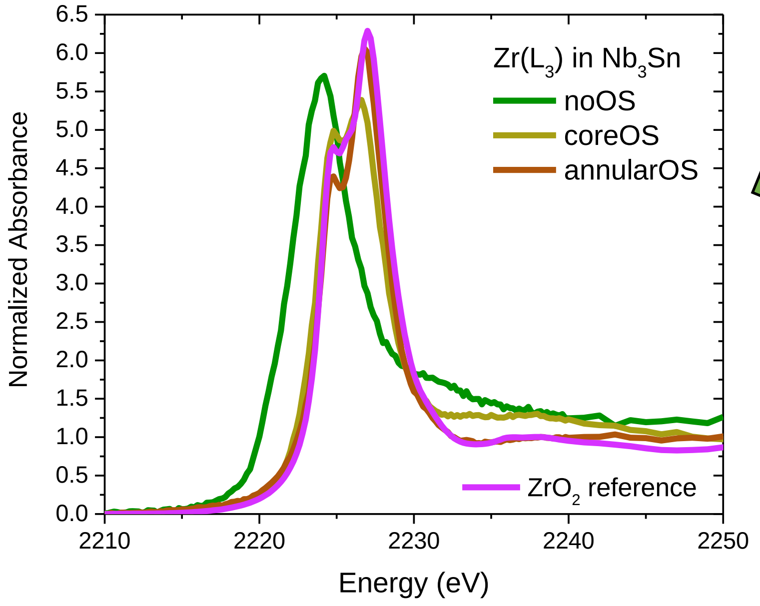


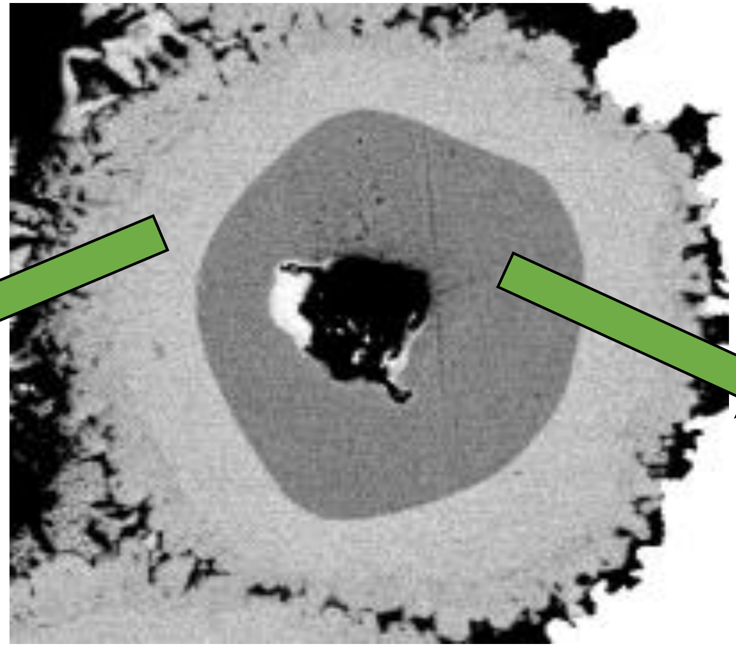
ZrO_2–like spectrum found only in Nb_3Sn! Different Zr spectrum in residual alloy, despite oxygen diffusion

- Bovone G et al. *IEEE Transactions on Applied Superconductivity* 34.3 (2024),6000205.

What did we learn from XANES?

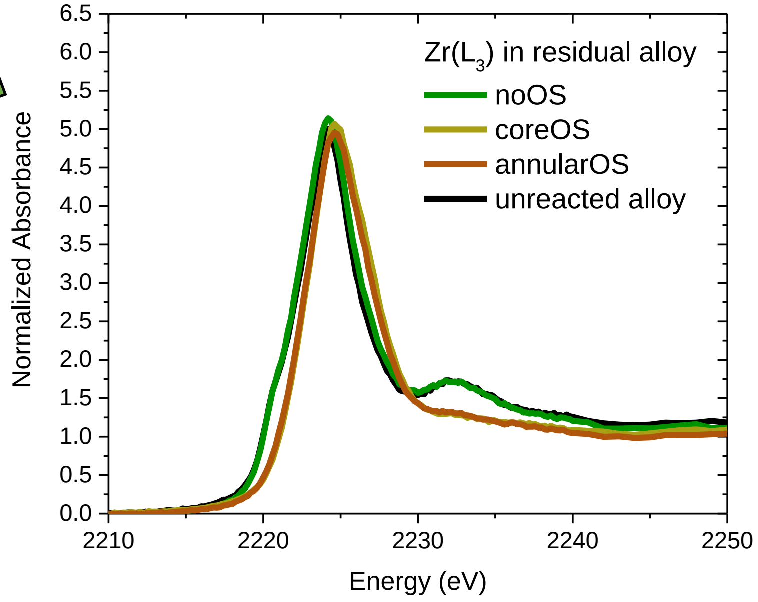
Zr in Nb_3Sn is fully oxidised to ZrO_2



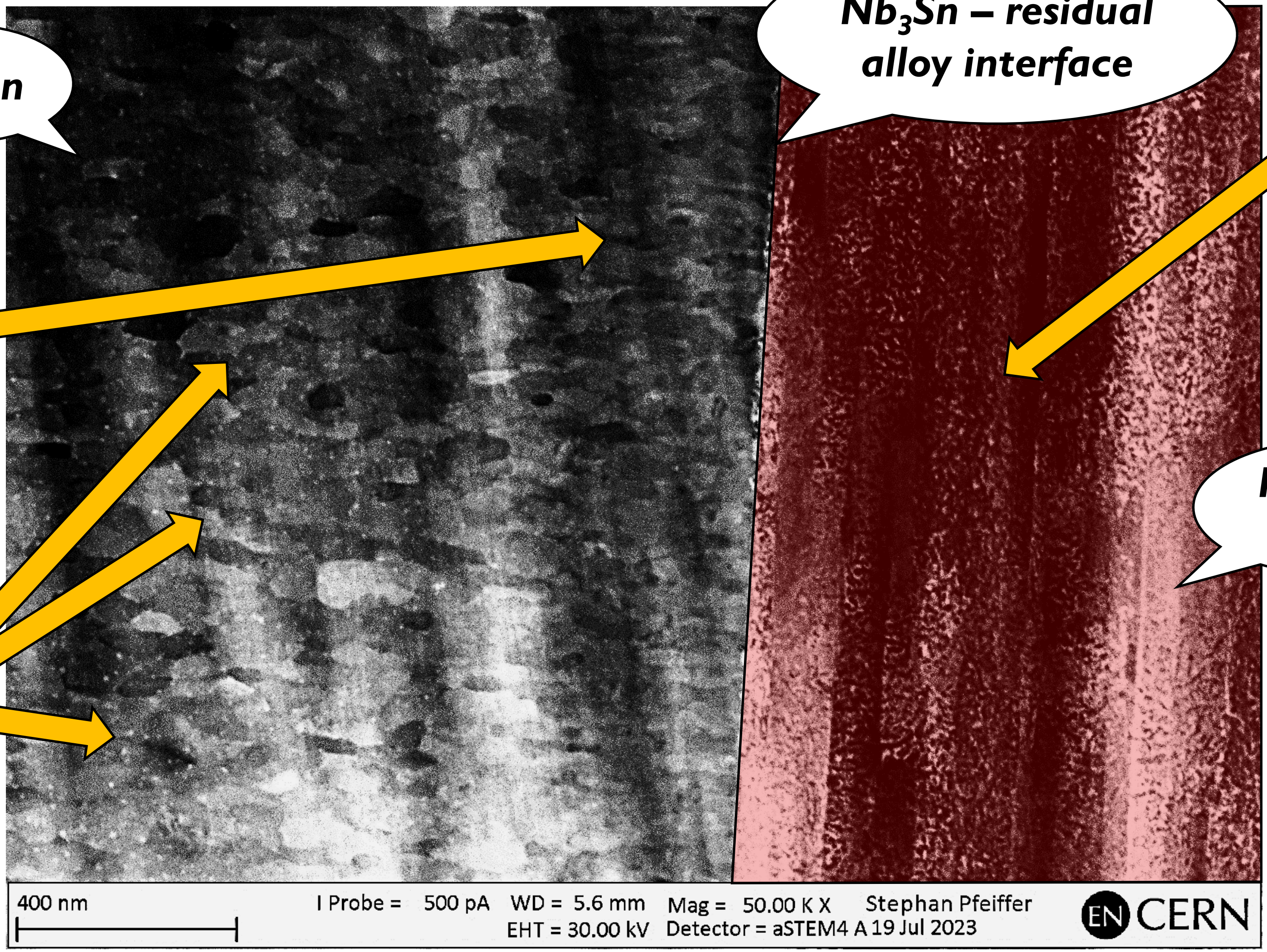


ZrO_2 precipitates due to the lower solubility of Zr and O in Nb_3Sn compared to Nb

Zr in the residual alloy is not in the form of ZrO_2, but changes in the spectra suggest modifications induced by oxygen diffusion. Clusters?



Precipitates at the interface



No observable ZrO_2 in the Nb_3Sn area next to the residual alloy interface. Are the precipitates too small to be detected with the microscope used?

Uniform distribution of ZrO_2 precipitates

No observable precipitates and no ZrO_2 fingerprint from XAS. However, Zr-O clusters may be present

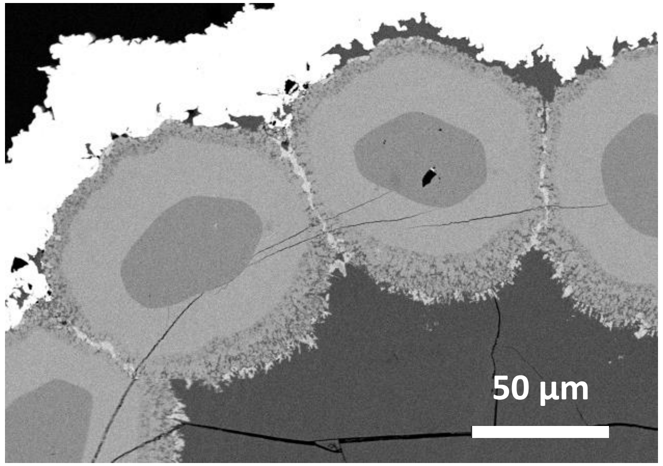
Courtesy of Stephan Pfeiffer, CERN

- Hall, Ernest L., et al. *MRS Online Proceedings Library (OPL)* 205 (1990).

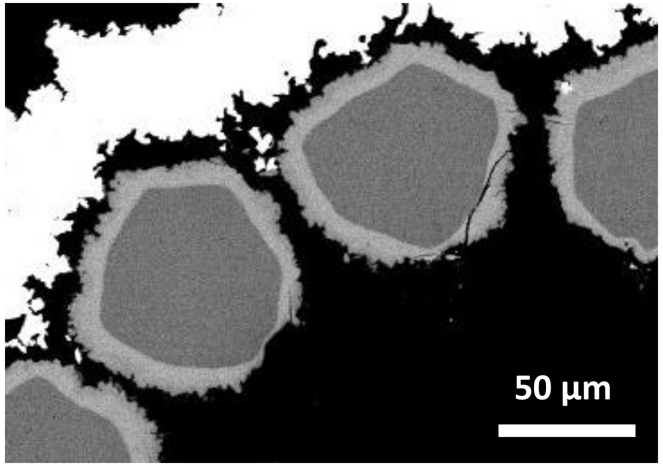
Heat treatment optimization: reaction layer thickness

Heat treatment (HT):
550°C × 100 h + 650°C × 200 h

No OS



With OS



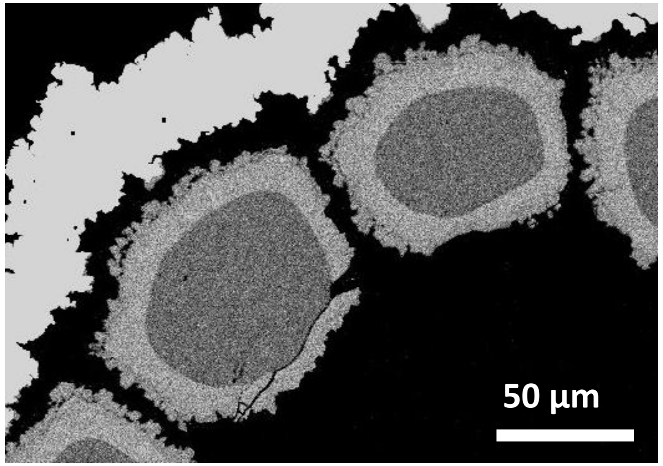
*Drastic reduction of **Nb_3Sn layer thickness** when OS is added*

*Higher temperature to enlarge Nb_3Sn layer thickness keeping **grain size** low*

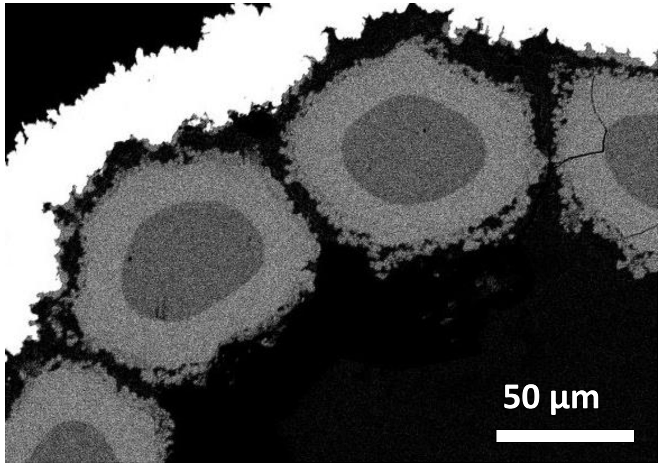
Significant increase of layer thickness at 700 °C

With OS

700 °C × 50 h



700 °C × 100 h

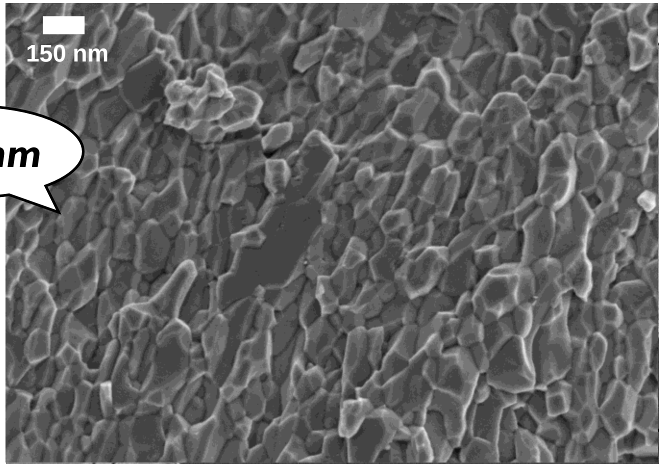


Heat treatment optimization: reaction layer thickness

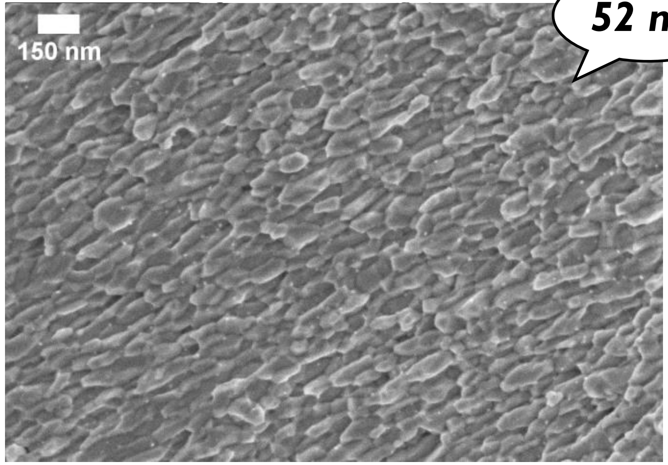
Heat treatment (HT):

550°C × 100 h + 650°C × 200 h

No OS



With OS



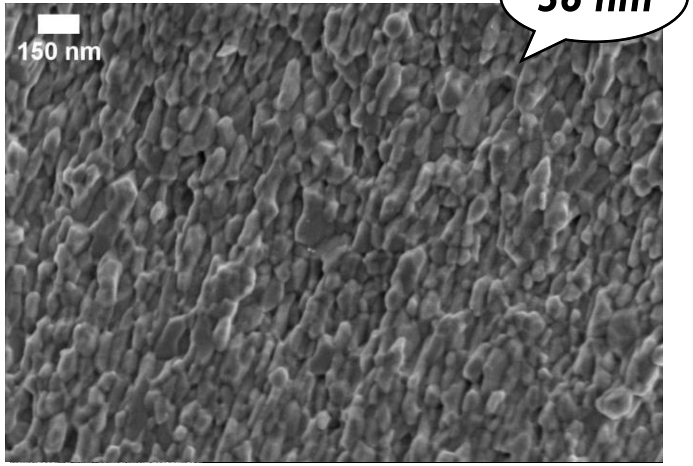
Drastic reduction of ***Nb_3Sn layer thickness*** *when OS is added*

Higher temperature to enlarge
Nb_3Sn layer thickness
keeping ***grain size*** *low*

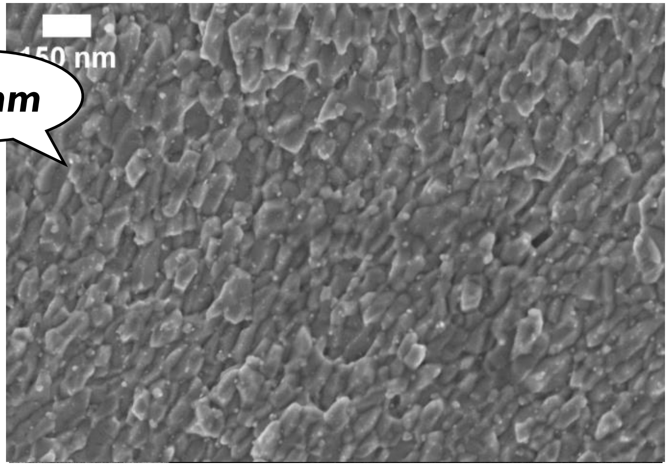
Significant increase of layer thickness at 700 °C, but modest grain growth

With OS

700 °C × 50 h

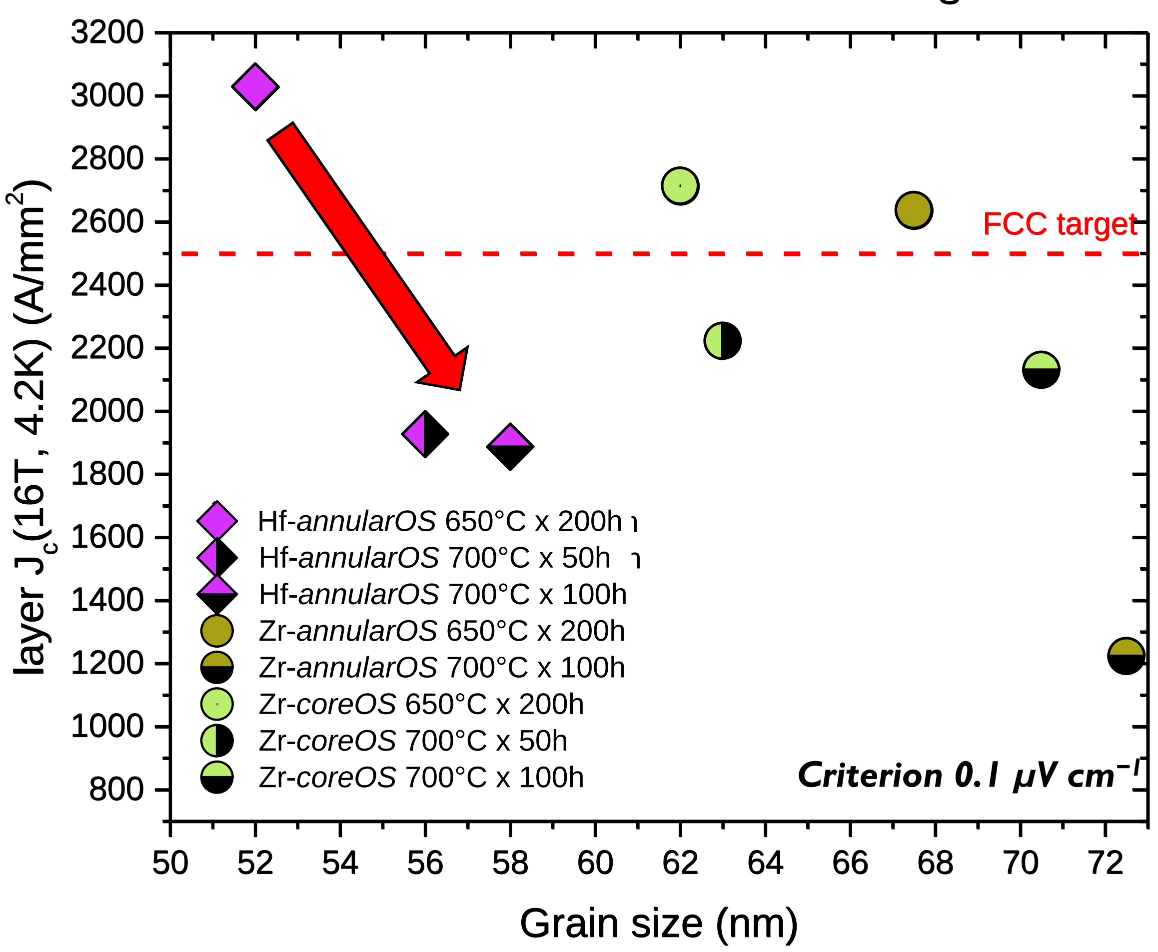


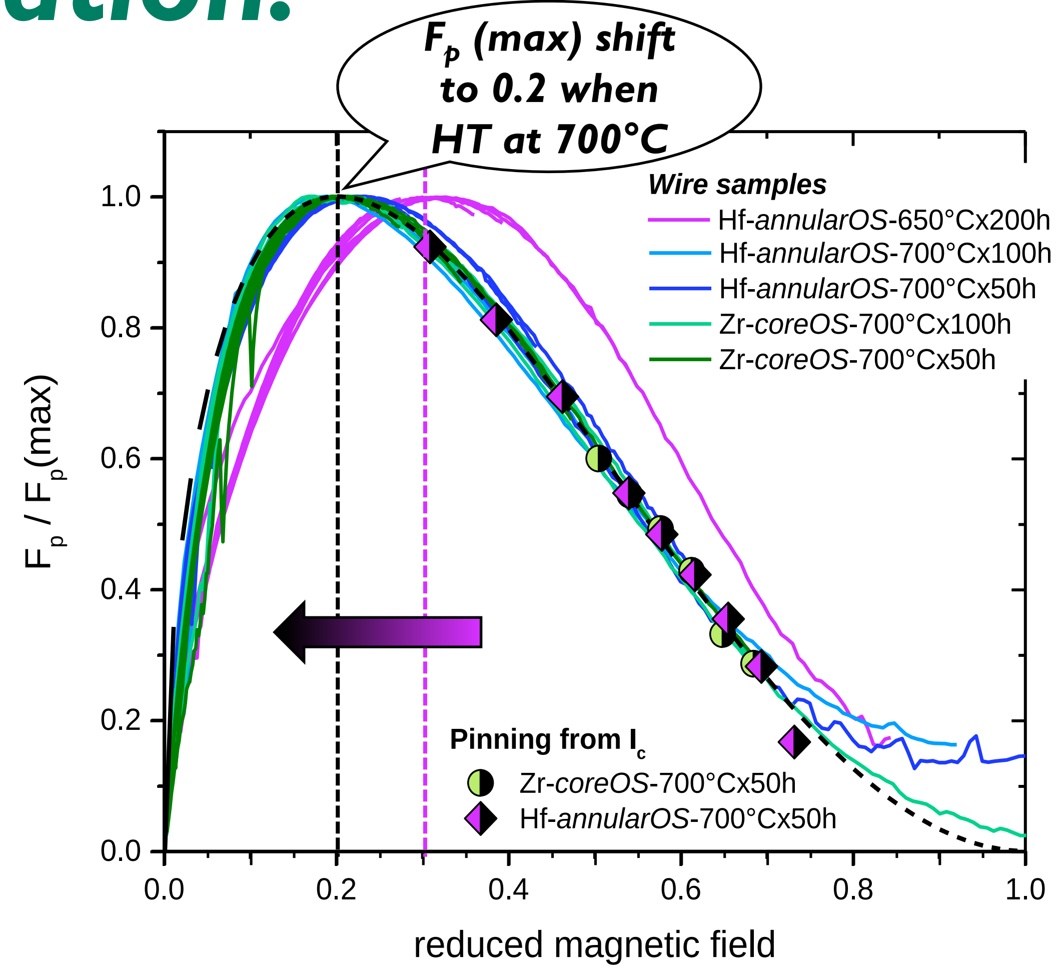
700 °C × 100 h



Heat treatment optimization: layer-J_c

Why J_c is lower despite the small grain size?

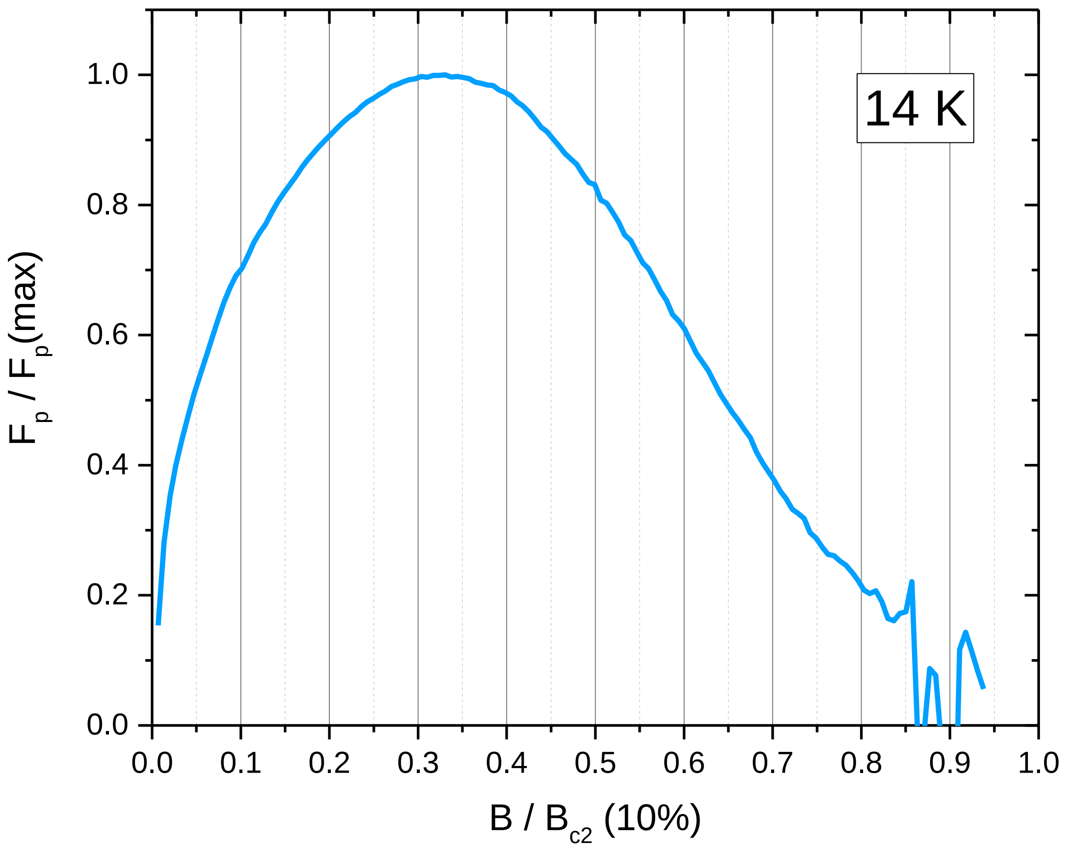




Lower interaction between flux lines and precipitates due to size mismatch

- Lonardo F. et al. IEEE Transactions on Applied Superconductivity 34.5 (2024), 6000305

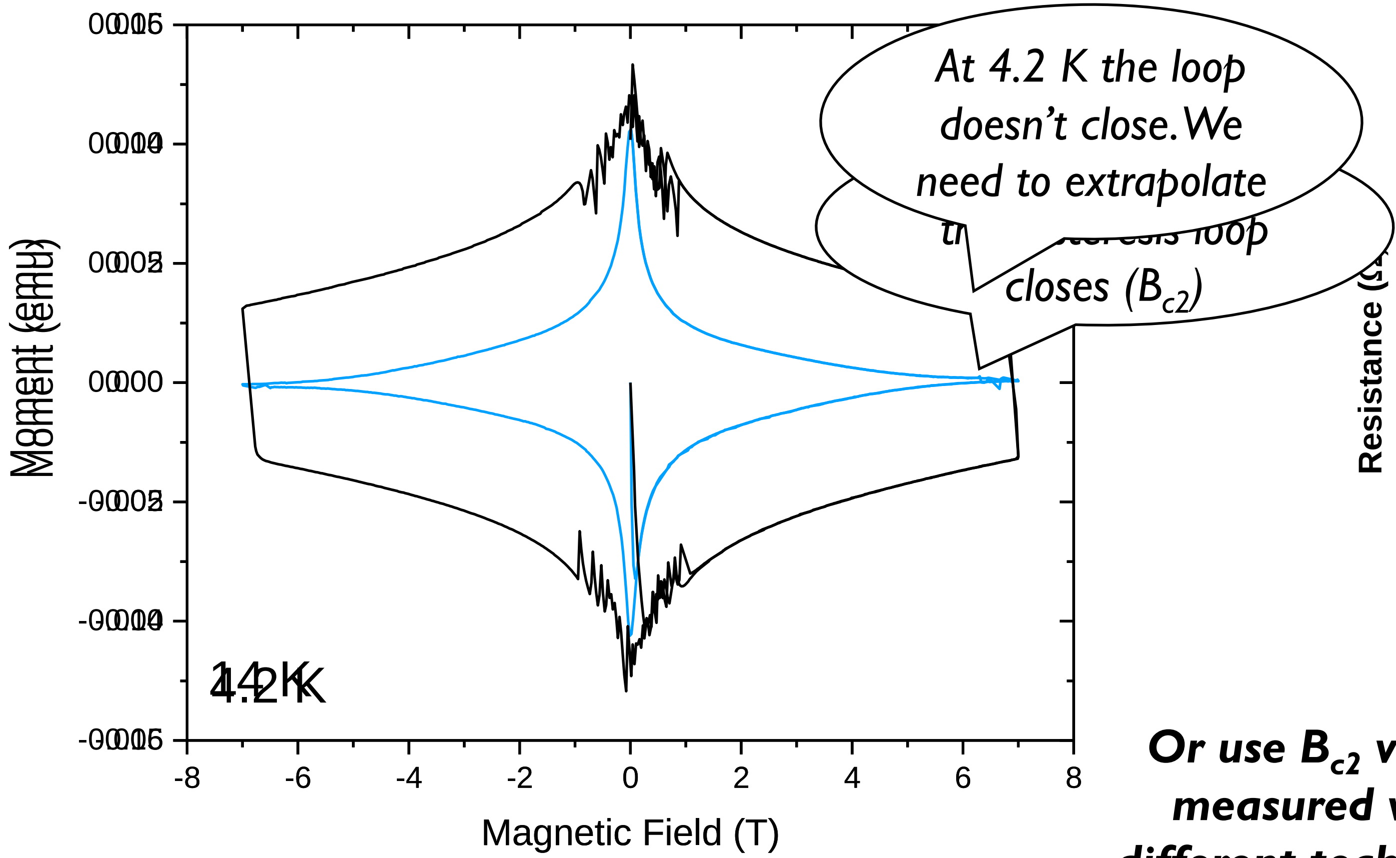
Problems in pinning mechanism analysis

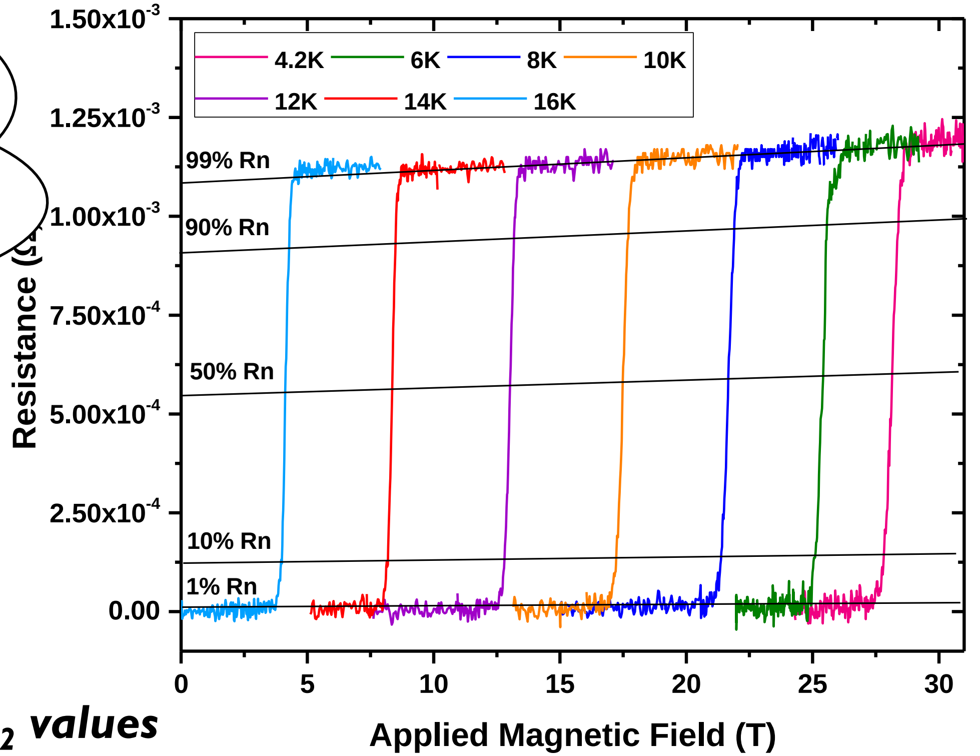


To determine the pinning mechanism, we need to precisely locate the position of the F_p peak in the reduced field (b)

$$b = \frac{B}{B_{c2}}$$

Problems in pinning mechanism analysis





Or use B_{c2} values measured with different techniques

To determine the pinning mechanism, we need to precisely locate the position of the F_p peak in the reduced field (b)

$$b = \frac{B}{B_{c2}}$$

European Magnetic Field Laboratory

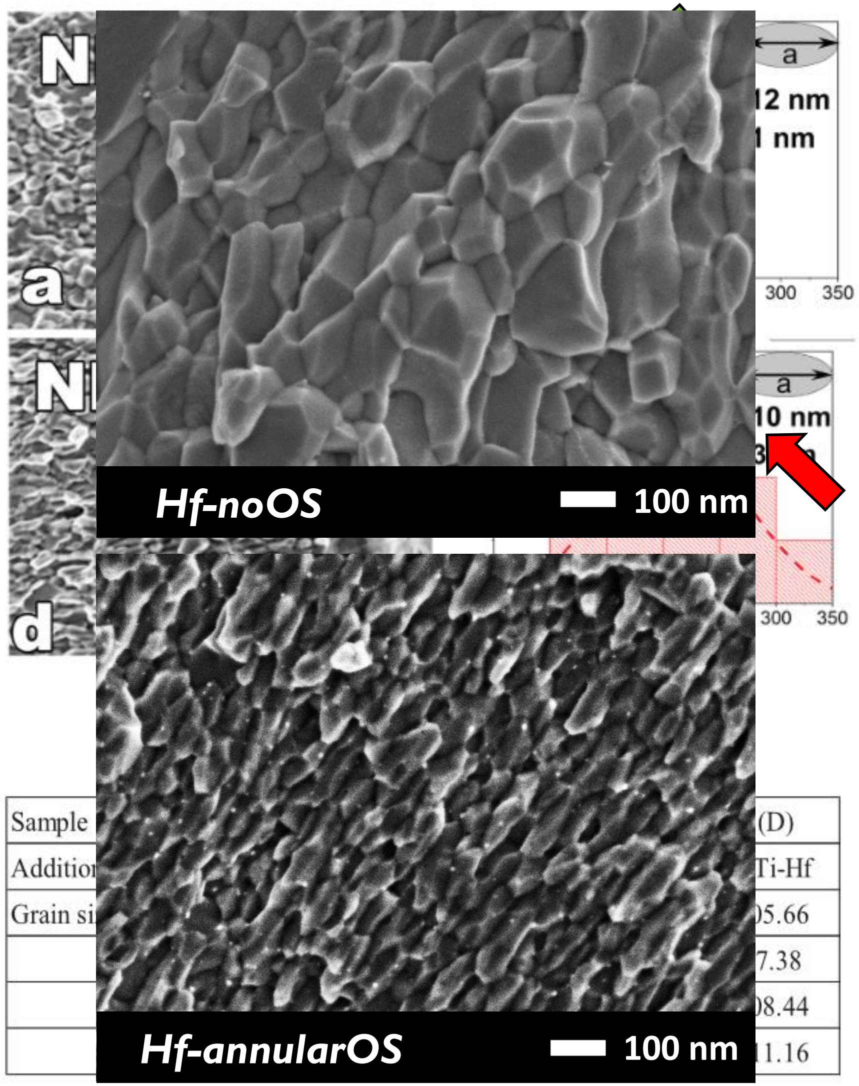
New campaign for VSM measurements up to 30 T at EMFL in Nijmegen

Conclusions

- *We successfully **enhanced the layer J_c** above the **FCC specifications**, **record-high B_{c2}** and change **of pinning mechanism** (**point defect**) when **Oxygen Source** is present, for wires **reacted at 650 °C***
- ***X-Rays Absorption Near Edge Structure (XANES)** on Nb_3Sn wires **with and without OS** show the presence of **ZrO_2 only in the Nb_3Sn layer** and not in the unreacted alloy*
- *The layer **J_c (16 T, 4.2 K)** is strongly **enhanced by the shift of F_p(max)** to a higher magnetic field, due to **B_{c2} enhancement** and/or a **modified pinning mechanism***
- ***Internal oxidation** is the **most effective** way to **reduce grain size, enhance B_{c2} and modify the pinning mechanism***
- *Despite its "age", **Nb_3Sn** can still **play a role** in the future generation of **high magnetic field magnets***

Thank you for
your attention

But are precipitates necessary?



Precipitates reduce Nb_3Sn grain size through the Zener drag effect

$$R = \frac{4r}{3f}$$

R = Maximum Nb_3Sn grain radius
r = precipitates radius
f = precipitates volumetric fraction

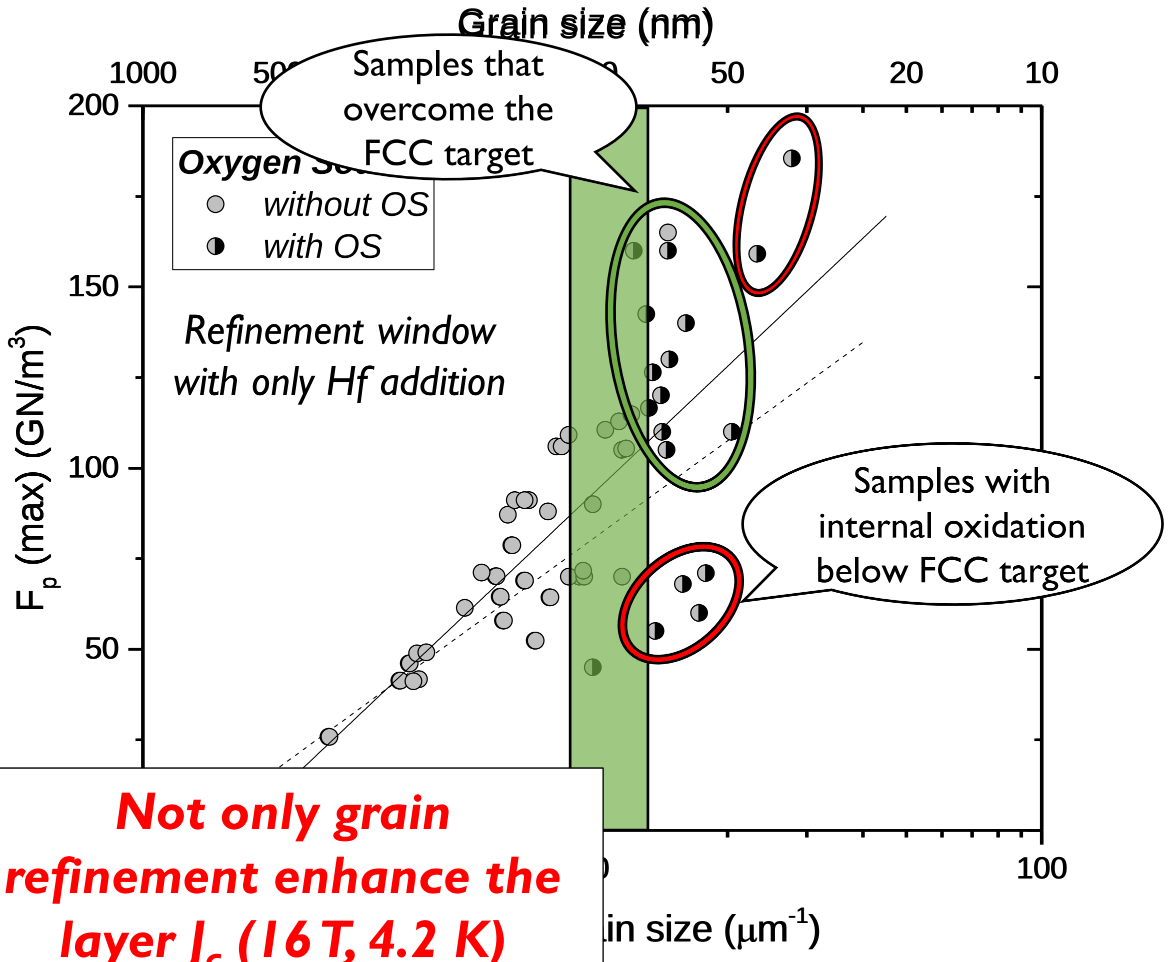
Some groups observed grain refinement without the addition of an oxygen source

Is the refinement observed here enough to reach the FCC target?

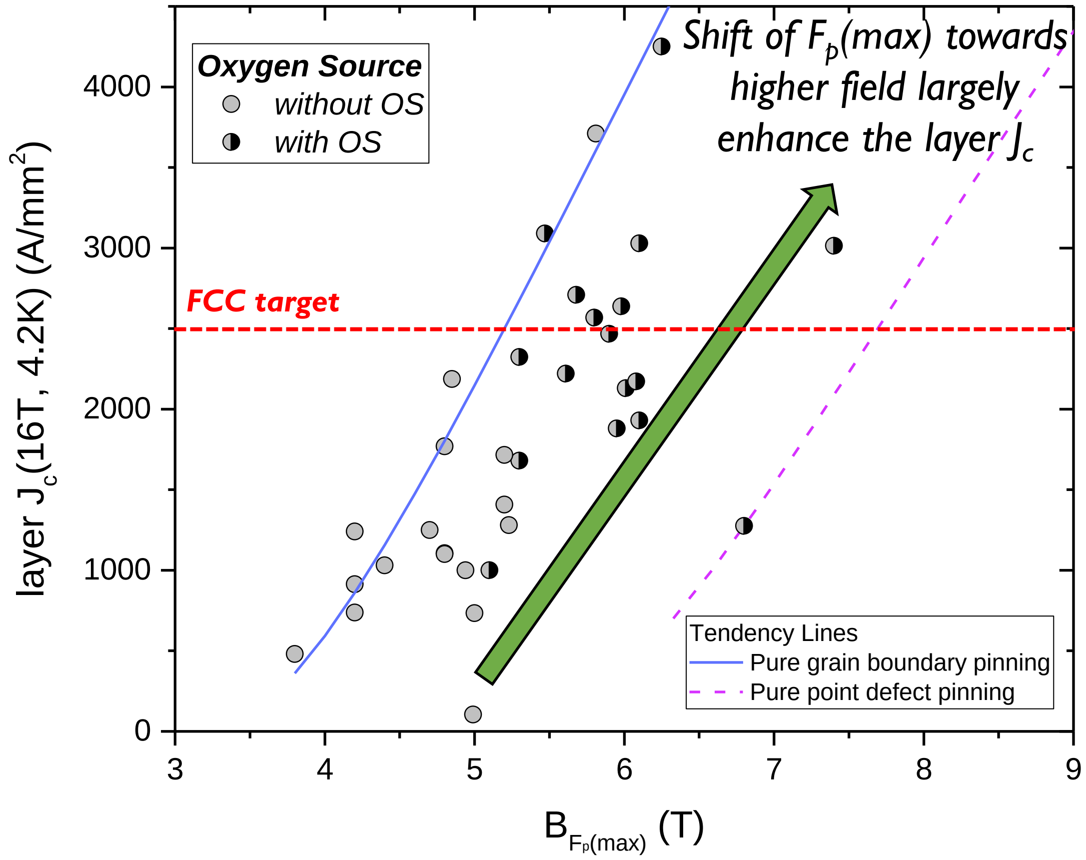
- Bovone G et al. *IEEE Transactions on Applied Superconductivity* 34.3 (2024),6000205.
- Xu X et al. *Scripta Materialia* 186 (2020): 317-320.
- Asai K et al. *IEEE Transactions on Applied Superconductivity 34.5* (2024), 8600105
- Balachandran S et al. *Journal of Alloys and Compounds* 984 (2024): 173985.

How to reach the FCC target

B_{c2} value and pinning mechanism play a role in the enhancement of J_c (16 T, 4.2 K)



Not only grain refinement enhance the layer J_c (16 T, 4.2 K)

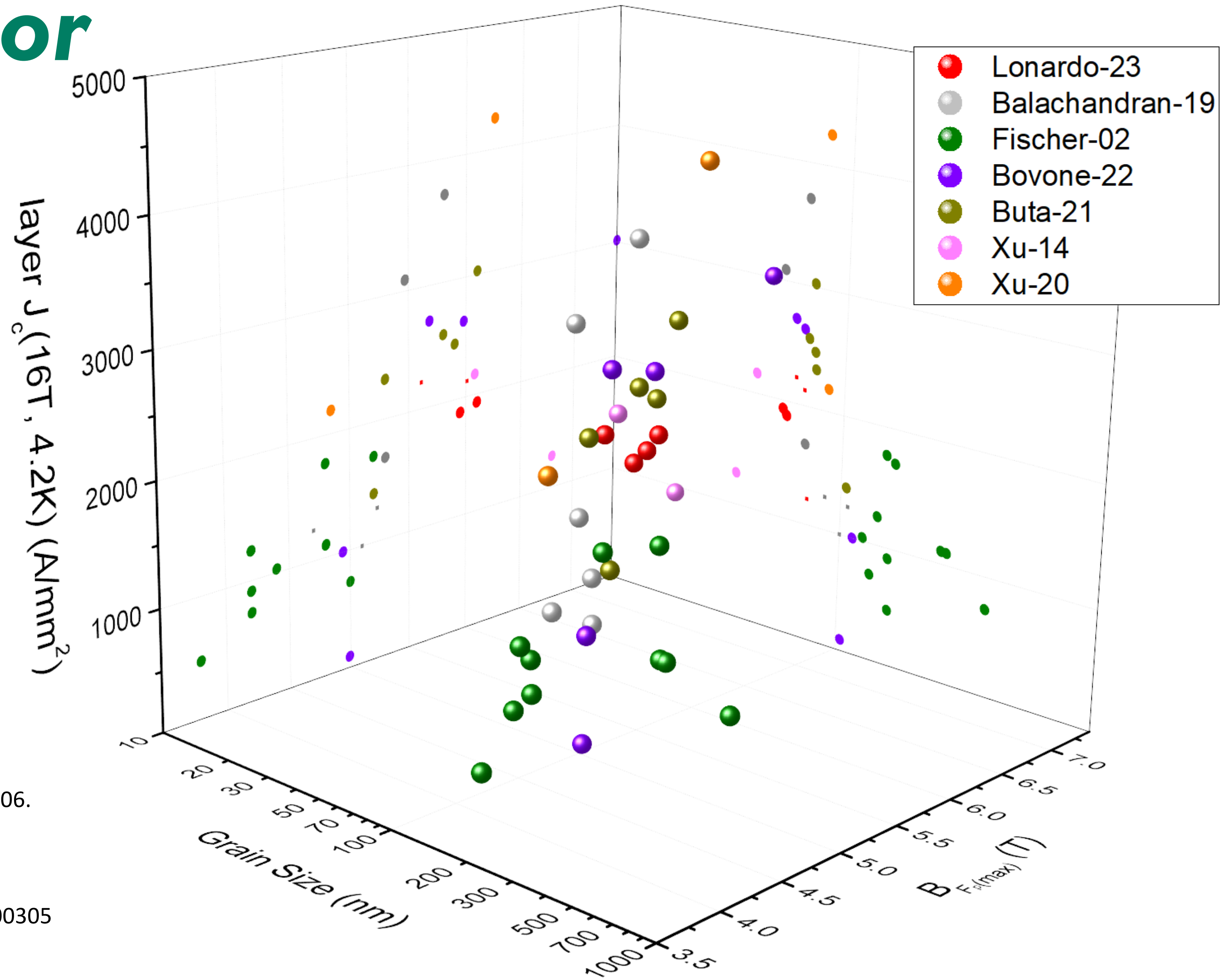


- Godeke A. *Superconductor Science and Technology* 19.8 (2006): R68.
- Fischer C. Master's Thesis Univ. of Wisconsin-Madison (2002).
- Balachandran S et al. *Superconductor Science and Technology* 32.4 (2019): 044006.
- Bovone G et al. *Superconductor Science and Technology* 36.9 (2023): 095018
- Lonardo F et al. *IEEE Transactions on Applied Superconductivity* (2024).
- Xu X et al. *Scripta Materialia* 186 (2020): 317-320.
- Xu X et al. *arXiv preprint arXiv:1411.5397* (2014)

Combined behavior

The FCC target at 16 T and 4.2 K is reached when both grain size is refined and F_p(max) is shifted at higher magnetic field

Internal oxidation is fundamental to reach the FCC target due to grain refinement, B_{c2} enhancement, and modification of pinning mechanism



- Balachandran S et al. *Superconductor Science and Technology* 32.4 (2019): 044006.
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- Xu X et al. *arXiv preprint arXiv:1411.5397* (2014).