Development of APC (ZrO_2) Nb_3Sn Multifilamentary and Ternary Conductor

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This work was supported by the U.S. Department of Energy, Office of Science, Division of High Energy Physics, under SBIR phase I DE-SC0013849 and University Grant DE-SC0011721.

Department of Materials Science and Engineering

Need of FCC for improved Nb_3Sn

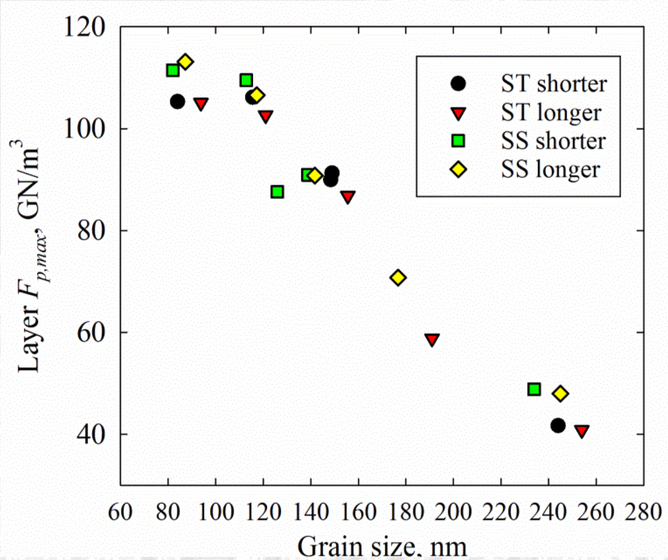
	Internal Sn, RRP	Tube	ITER	PIT	Bronze
12 T Jc, A/mm2	2500-3000	2000-2500	1000-1200	2000-2500	600-800
Stability	Low	medium	high	medium	high
Loss	High	medium	low	medium	low

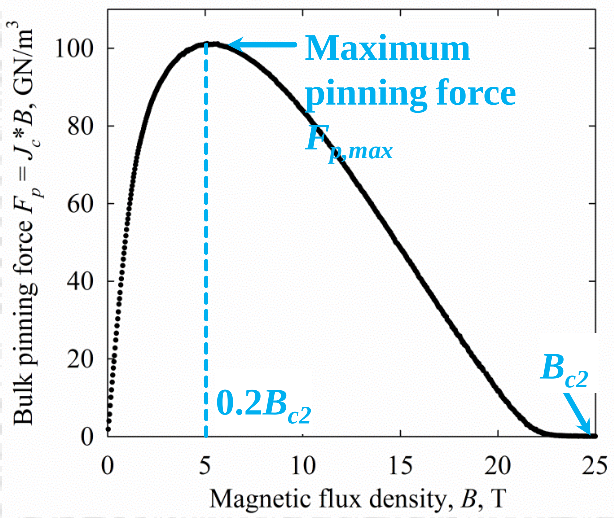
At 15 T J_c is 2700 A/mm^2, J_{nonCu} (RRP) = 1600 A/mm^2, and Tube/PIT 1350 A/mm^2

Needed conductor amount for FCC

- FCC with 16 T magnets: 4,500 tons of Nb_3Sn and 10,000 tons on NbTi
- FCC with 20 T: 1,400 tons HTS, 6,300 tons Nb_3Sn, 11,000 tons NbTi
- Conductor Specifications?
  - Non Cu J_c of 1500 A/mm^2 at 16 T?
- Present conductors do not meet requirements when production limits and margins are taken into account
- HTS options very expensive

Importance of refining Nb_3Sn grain size

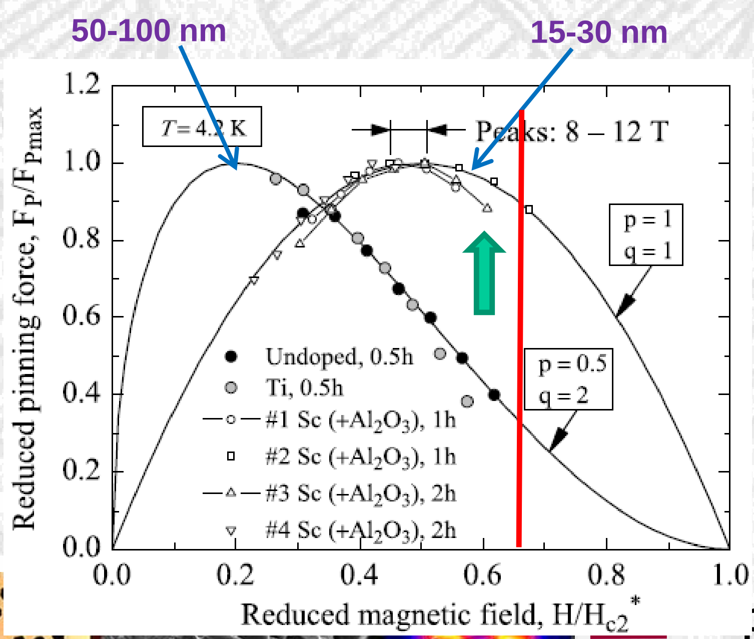




Conventionally -- Reducing grain size leads to increase in $F_{p,max}$, but $F_{p,max}$ is always at $0.2B_{c2}$.

At low grain size F_p is increased both by reduced grain size and shifting $F_{p,max}$ to $0.5B_{c2}$.

(Dietderich, 1997) on films –
For fine grain size, the F_p-B curve peak shifts to $0.5B_{c2}$.



D.R. Dietderich and A. Godeke, Cryogenics 48, 331 (2008)

How to obtain such small grain size in **practical strands**?

- Reducing reaction temperature? Cannot go to < 80 nm, also strain irreversibility cliff limits
- **Adding second phase particles to prevent grain coarsening?**

Internal oxidation of Nb_3Sn to reduce grain size-proof of principle - external oxygen source

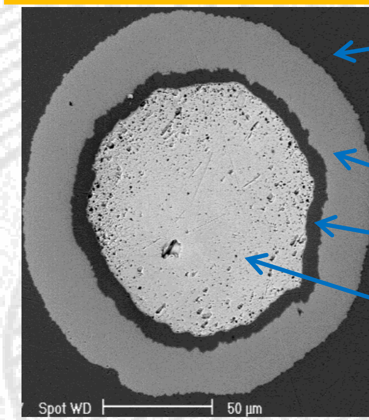
"Internal oxidation": O diffuses in an A-B solid solution, and selectively oxidizes the solute B, forming BO_n particles in matrix A.

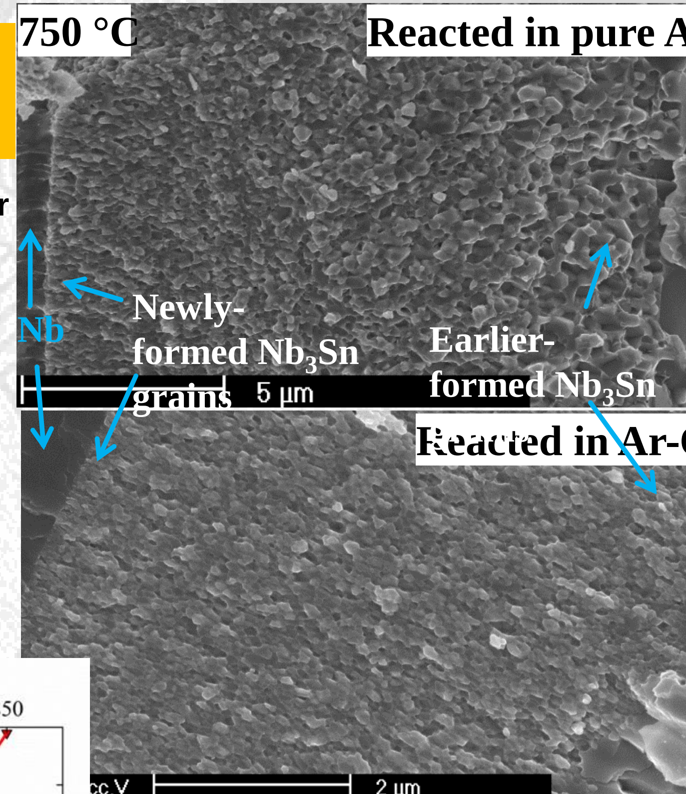
Prerequisites:

- **B is much less noble than A.**
- **O diffuses fast in matrix A.**
- **O partial pressure is only high enough to oxidize B.**

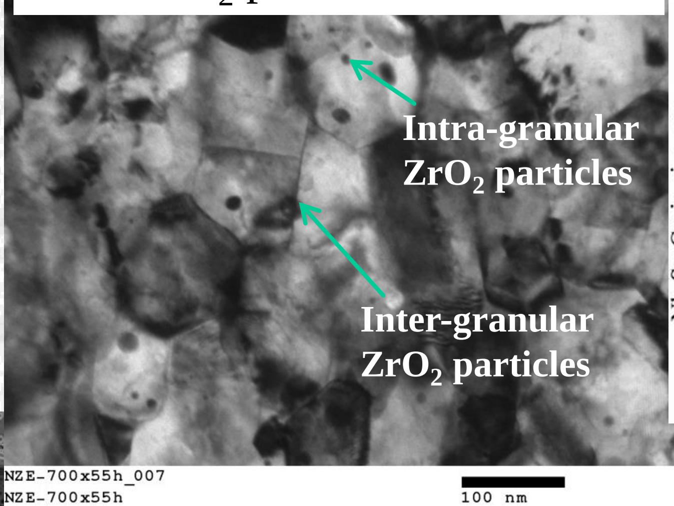
X. Xu et al., Appl. Phys. lett. **104**, 082602 (2014)

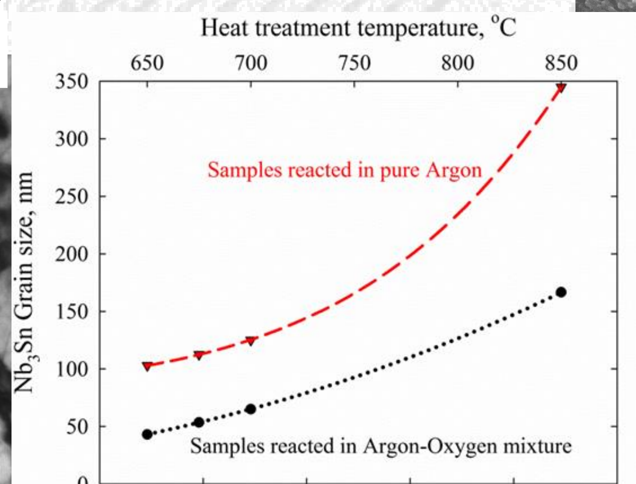
First experiments relied on externally supplied oxygen





Note ZrO_2 particles 10 nm OD

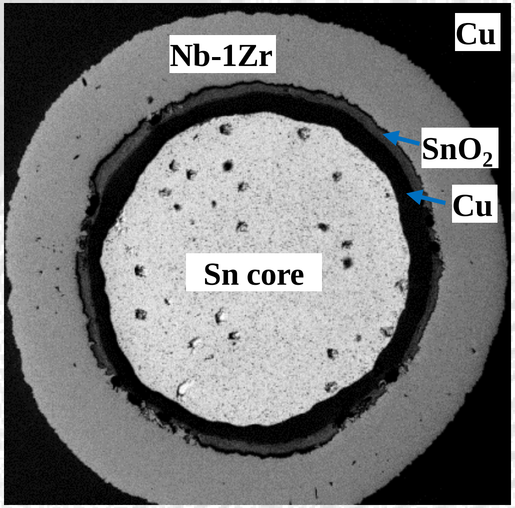




- **Experiment worked – grain sizes less than 50 nm achieved!**

Strand with internal oxidation source --mono

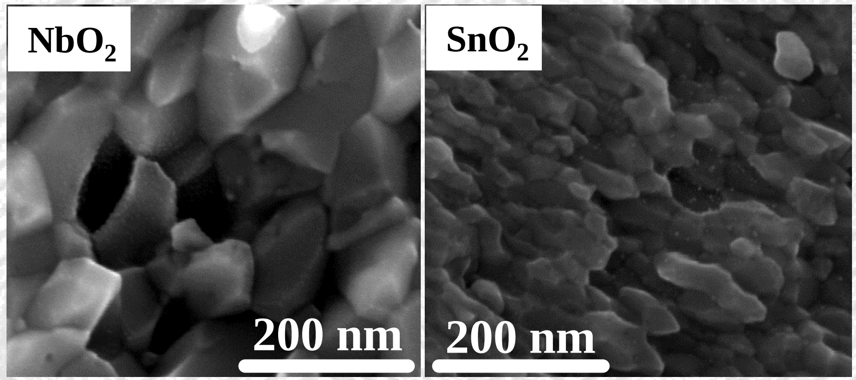
A green-state subelement:



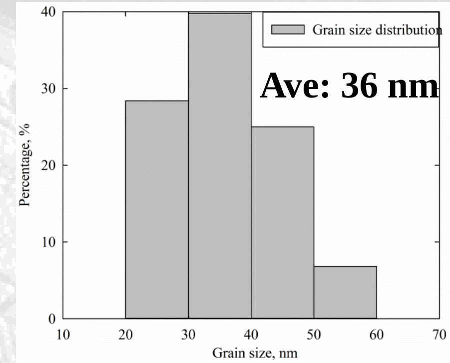
A control: NbO_2, which does not supply O.

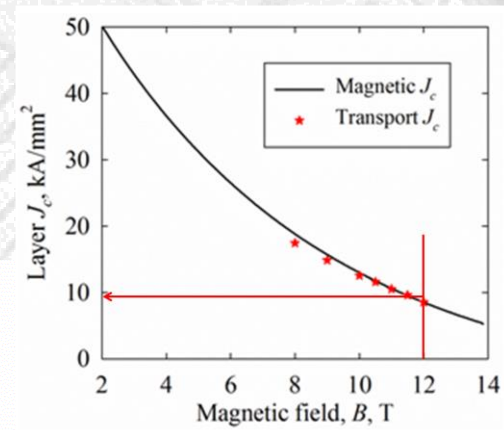
Wires with NbO_2 and SnO_2: 650 C for 150 h:

NbO_2: < 0.3at.% O, SnO_2: supplied >3 at.% O.

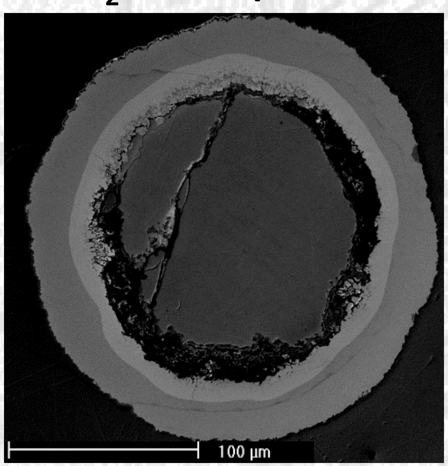


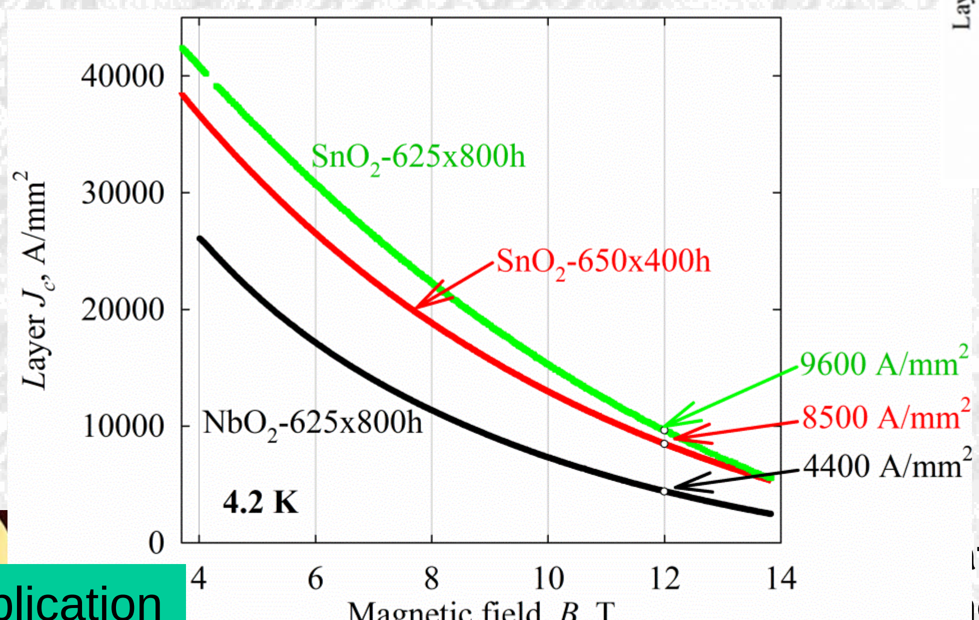
Average grain sizes: 104 nm and 43 nm.





SnO_2-650 °C / 400h:





The 12 T layer J_c of the state-of-the-art Nb_3Sn strands is 5 kA/mm², so the SnO_2-625x800h doubles this record.

OSU-HTR Patent application

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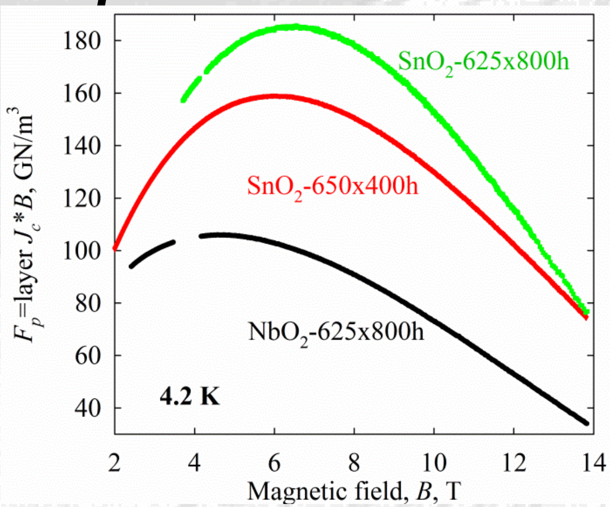
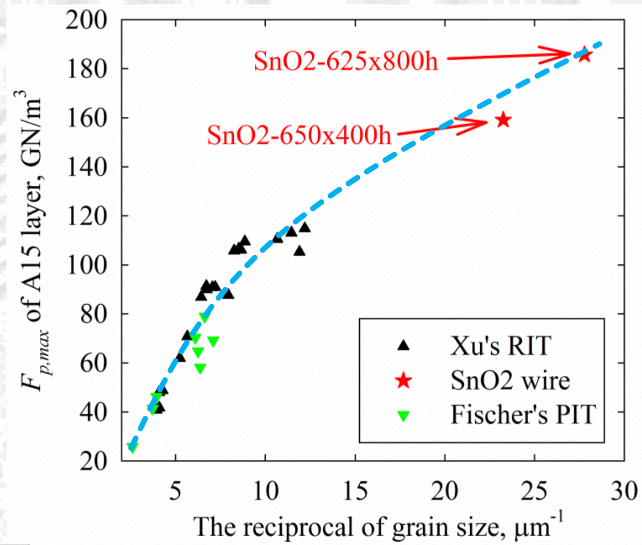
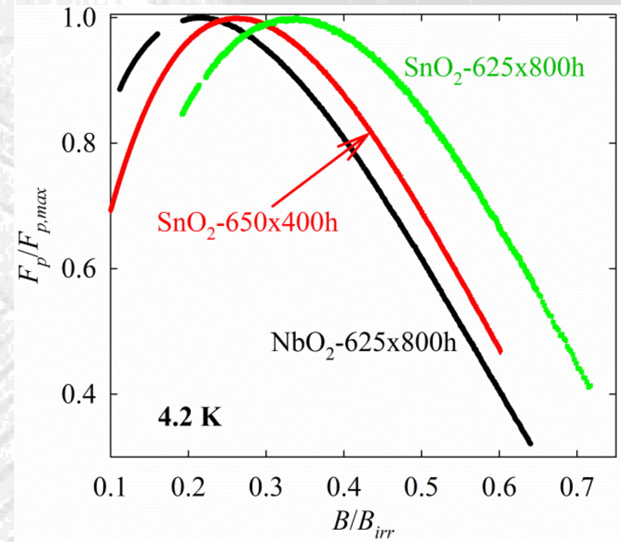
F_p-B curves of Internal oxidation strands



$F_{p,max}$ vs reciprocal of grain size:

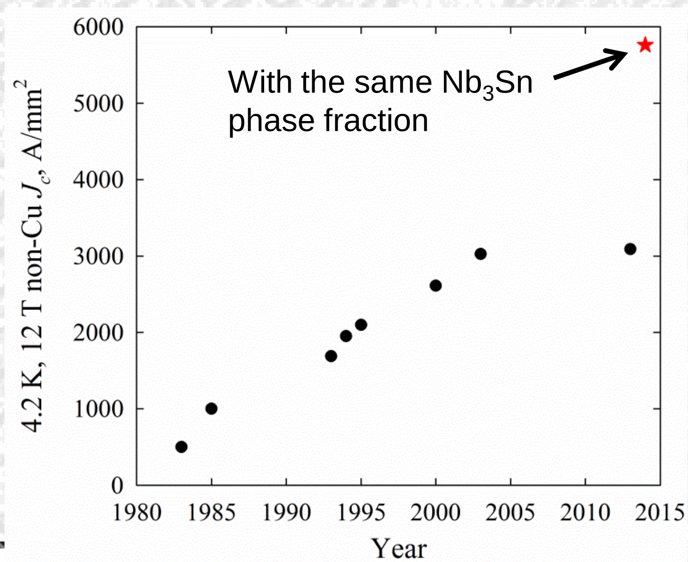


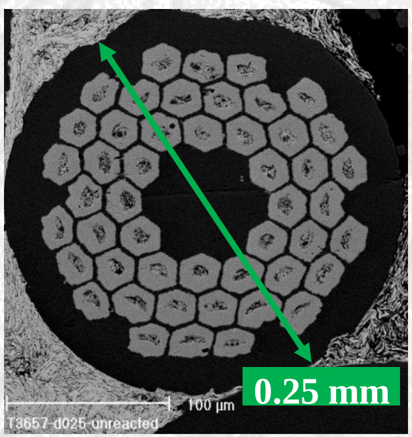
Normalized F_p-B curves:



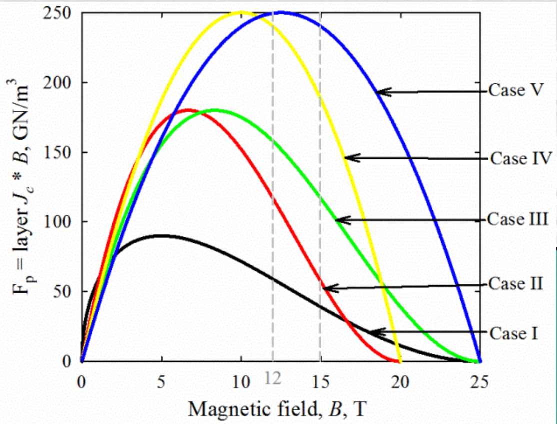
B_{c2} was obtained by fitting the F_p-B curve using F_p=Kb^p(1-b)^q.

	NbO_2 - 625 C	SnO_2 - 650 C	SnO_2 - 625 C
B_{c2}, T	20.9	23	20
Grain size	104 nm	45 nm	36 nm
F_p-B curve peak	0.22B_{c2}	0.26B_{c2}	1/3B_{c2}
12 T layer J_c, A/mm²	4400	8500	9600





As grain size d is < 50 nm, reducing d shifts the curve both to the up and to the right.



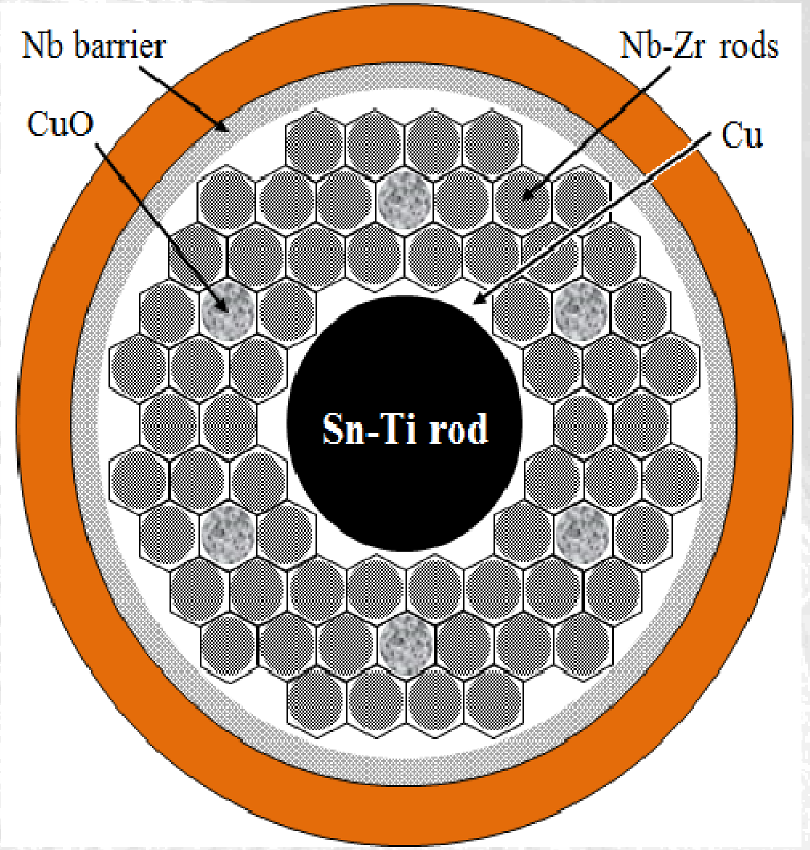
A naive look at the limits of J_c in Nb_3Sn (Rosy scenario)

Engineering J_c and I_c for the five different cases:

		I. Present state-of-the-art RRP strands	II. The wire with SnO_2 - 625 C / 800h	III. Only improve B_{irr} to 25 T by Ti doping, etc.	IV. Only refine the grain size to 25 nm	V. Both improve the B_{irr} to 25 T and refine the grain size down to 25 nm
Grain size, nm		100 - 120	36	36	25	25
F_p-B peak		$0.2B_{irr}$	$0.34B_{irr}$	$0.34B_{irr}$	$0.5B_{irr}$	$0.5B_{irr}$
$F_{p,max}$, GN/m^3		~90	180	180	~250	~250
B_{irr}, T		25	20	25	20	25
12 T	Layer J_c, A/mm^2	5,000	9,600	16,400	20,000	20,800
	Non-Cu J_c, A/mm^2	3,000	5,760	9,840	12,000	12,480
	Engineering J_c, A/mm^2	1,600	3,050	5,200	6,360	6,600
	I_c, A	800	1,530	2,620	3,200	3,320
15 T	Layer J_c, A/mm^2	2,700	3,800	7,800	12,500	16,000
	Non-Cu J_c, A/mm^2	1,600	2,280	4,680	7,500	9,600
	Engineering J_c, A/mm^2	850	1,210	2,480	4,000	5,100
	I_c, A	430	610	1,250	2,000	2,560

Note: Assuming all the five cases have the same Nb_3Sn area fraction with the state-of-the-art RRP strands: the Nb_3Sn area fraction in a subelement is 60%, the non-Cu area fraction in a strand is 0.53, the wire diameter is 0.8 mm.

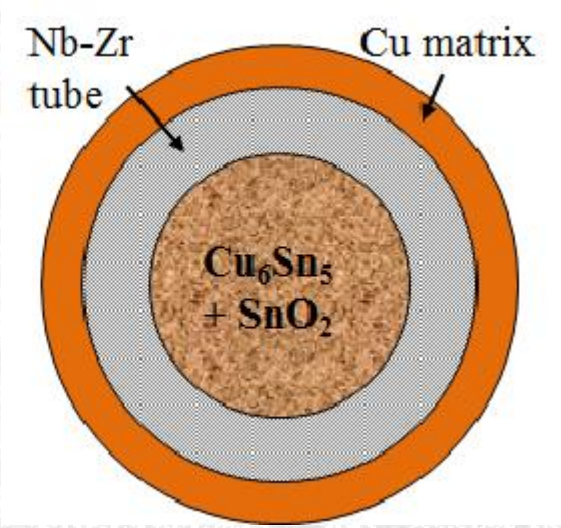
APC RRP?

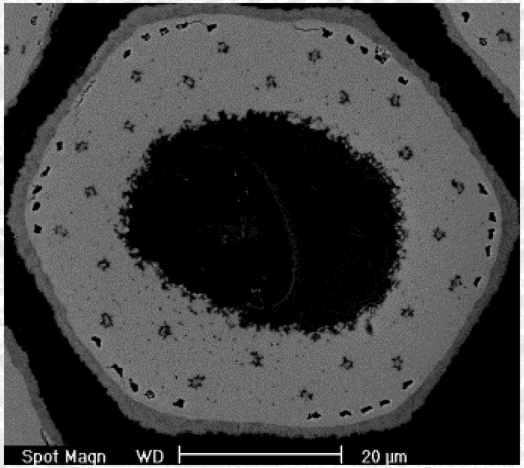


Not Only Tube Conductor, but PIT, Bronze, or Internal Sn distributed barrier (e.g., RRP) –

As long as a structure allows for the addition of oxide powder in a proper position, so that oxygen can be transferred, this structure is OK.

PIT:





Patent: Xu, Peng, Sumption, PCT/US2015/016431.

What to expect from a Practical Conductor J_c and J_e (15 T)

- Layer J_c of RRP, Tube and PIT is 5000 A/mm^2, with 60% A15 in subelement for RRP, and 50% for PIT and Tube
- At 15 T J_c is 2700 A/mm^2, $J_{c,nonCu}$ (RRP) = 1600 A/mm^2, and Tube/PIT 1350 A/mm^2

At 12 T for APC

- Layer Jc of 10 kA/mm^2 seen at 12 T in mono
- Assuming 50% fill factor, $J_{c,nonCu}$ (12 T) should reach 4750 A/mm^2
- For a RRP-like design, then $J_{c,nonCu}$ (12 T) should reach 5760 A/mm^2 in Binary

At 15 T for APC

- Layer J_c of 3800 A/mm^2 extrapolated from 14-15 T in mono
- Assuming 50% fill factor and mixed powders, tube $J_{c,non}$ (15 T) should reach 1805 A/mm^2 (Binary)
- For RRP-like design, then $J_{c,nonCu}$ should reach 2165 A/mm^2 15 T (Binary)
- With ternary push of B_{c2} to 25 T, a significant further increase would be seen at 15-18 T

So…. How to add the ternary?

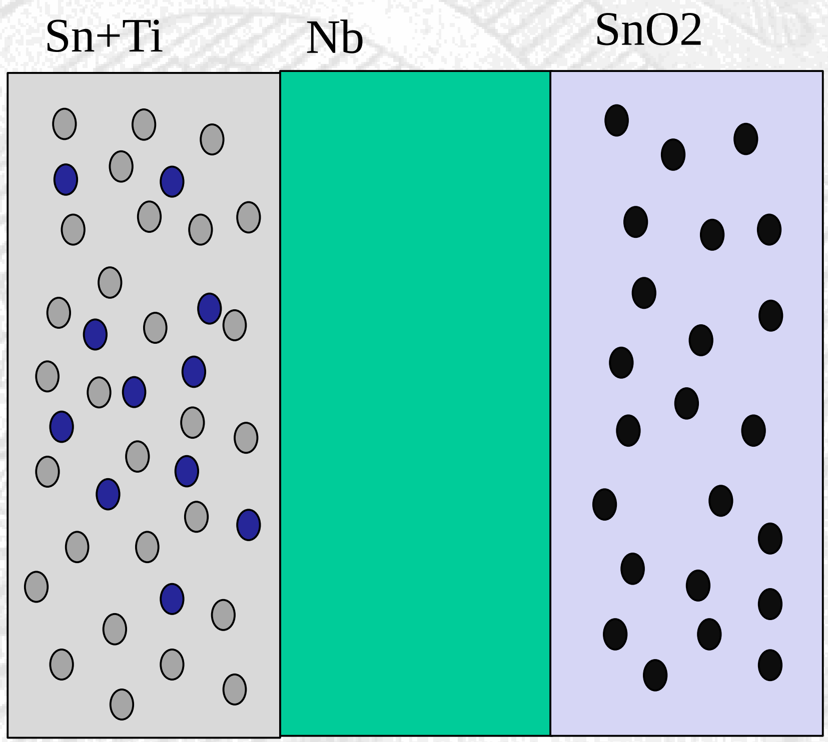
Some possible methods: (1) Ti, (2) Ta

- We choose Ti, as it leads to a better strain tolerance conductor – and, it can be added to the allow after drawing
- But – you can't add it in the same area as the SnO_2 – because Ti is a powerful oxygen getter

Before HT

Pre-HT

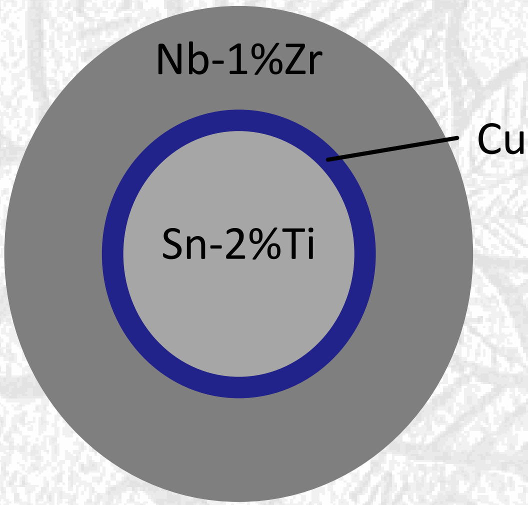
Reaction



So, its possible to add it into the Nb-Zr to start – but we plan to add it afterward

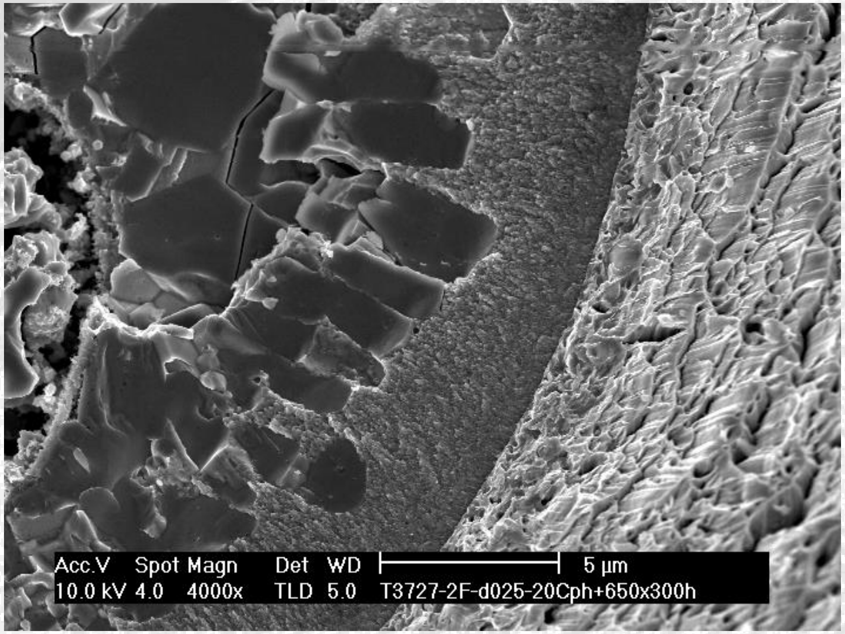
First try – back to Externally oxygen source: T3727-2

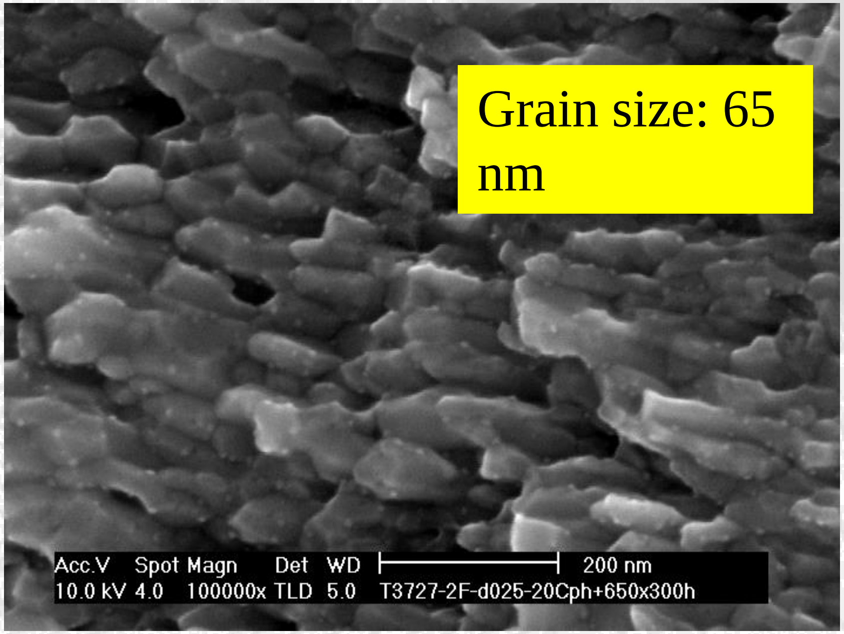
- Externally oxidized prototype
- Single filament
- Baked at 650°C for 300h
- 14 samples in presence of varying amounts of oxygen

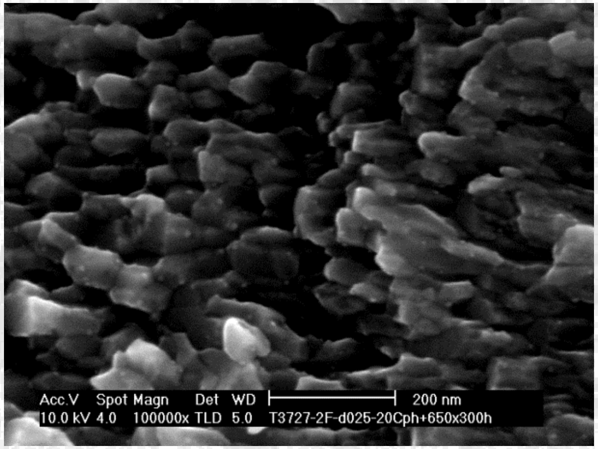


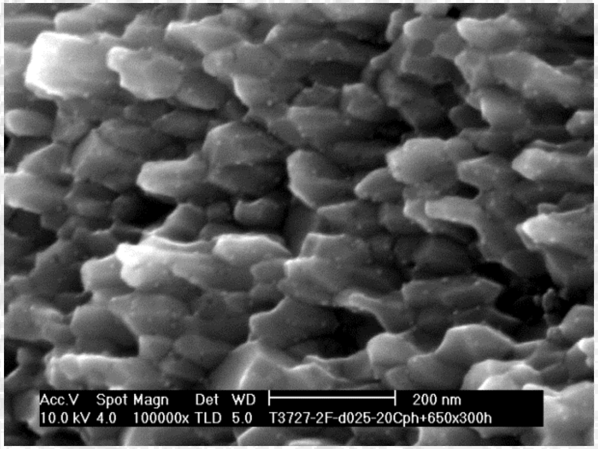
Sample Number	CuO content (mg, ±0.1)	Heat treatment
1	1.6	20 C/h + 700Cx100h
2	1.6	20 C/h + 650Cx300h
3	2.6	20 C/h + 700Cx100h
4	2.3	20 C/h + 650Cx300h
5	5.1	20 C/h + 700Cx100h
6	4.2	20 C/h + 650Cx300h
7	9.0	20 C/h + 700Cx100h
8	9.1	20 C/h + 650Cx300h
9	12.1	20 C/h + 700Cx100h
10	11.9	20 C/h + 650Cx300h
11	17.4	20 C/h + 700Cx100h
12	17.5	20 C/h + 650Cx300h
13	31.0	20 C/h + 700Cx100h
14	30.4	20 C/h + 650Cx300h

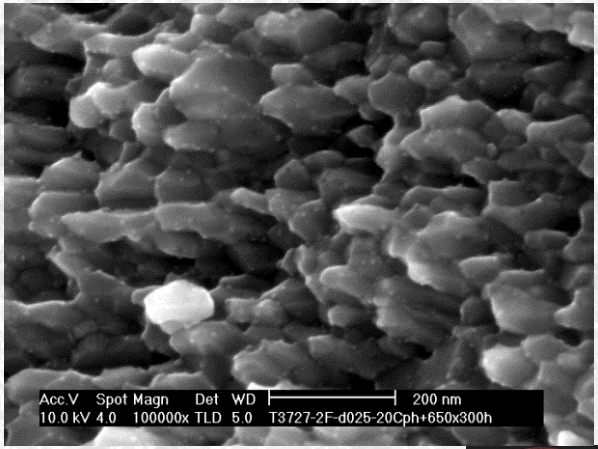
Externally oxidized fracture: T3757-2



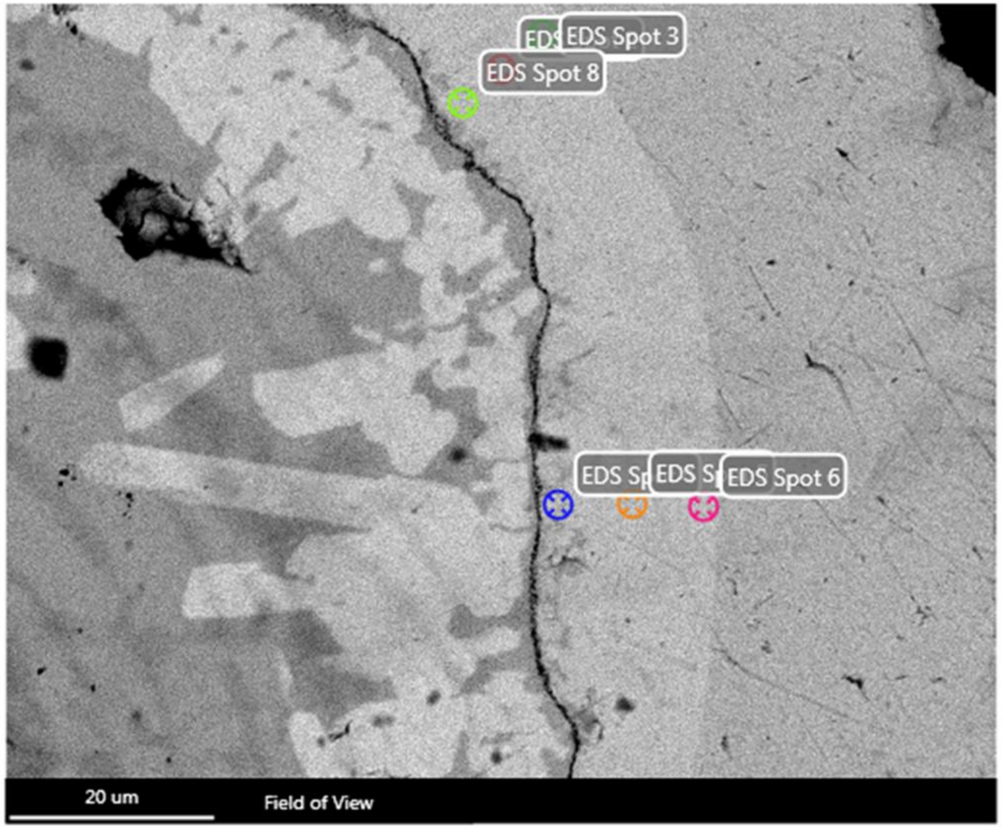




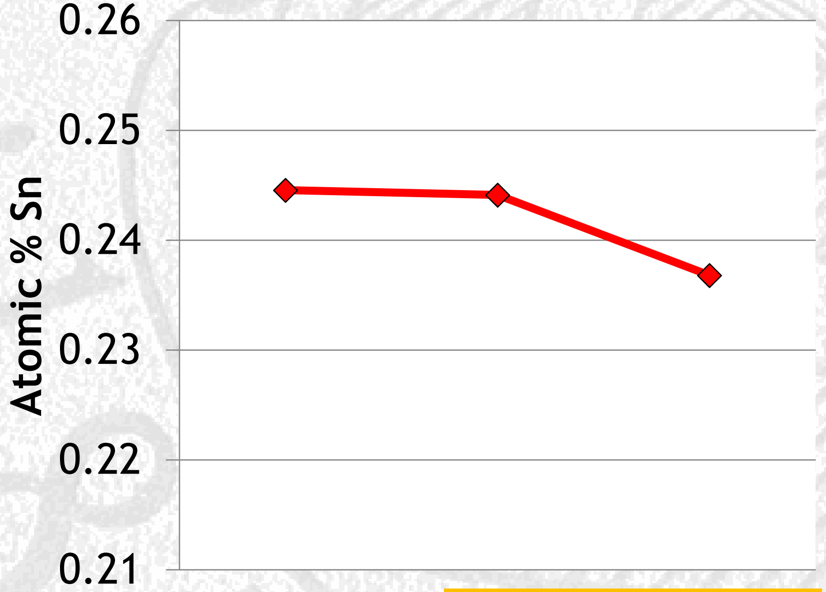




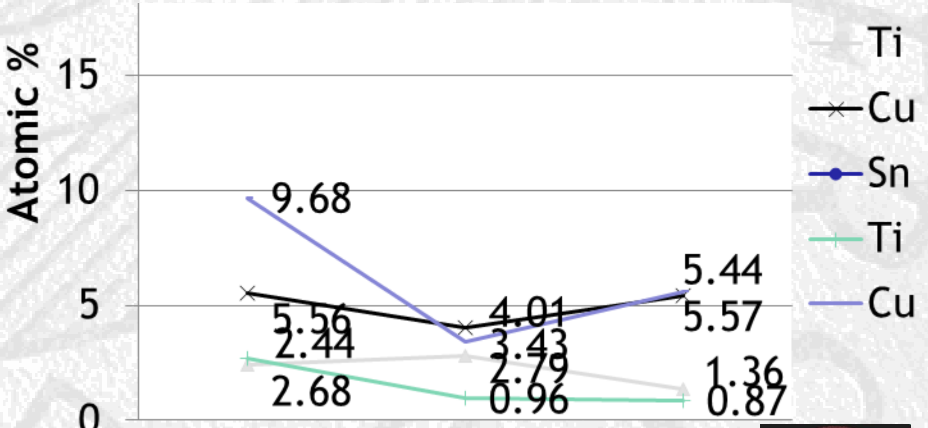
External Oxidized 2 – Sn and Ti content



Sn Content in Nb-Sn and (Nb,Ti)-Sn



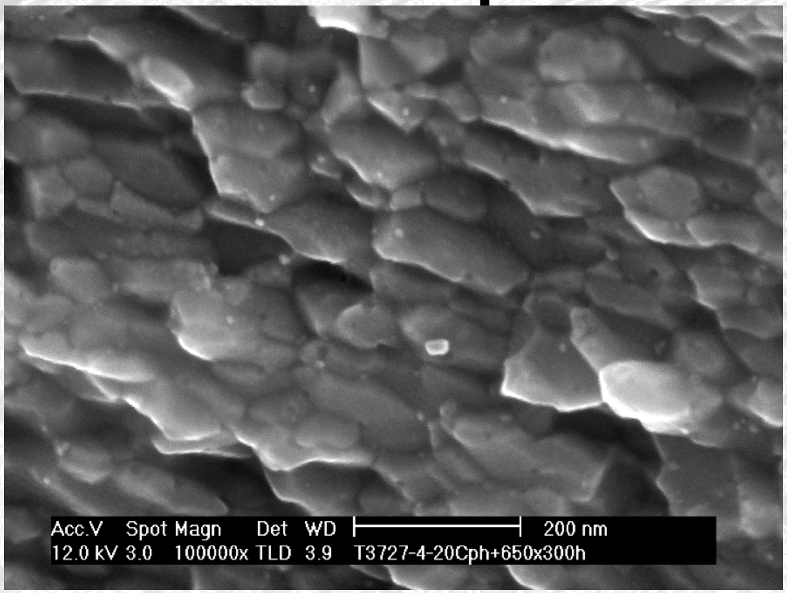
Ave Ti = 1.9% at



Higher oxygenated samples 4,6,8

- More samples with increasing amounts of oxide
  - SEM images (polished and fracture)
  - EDS compositional analysis
  - J_c and B_{c2} using PPMS

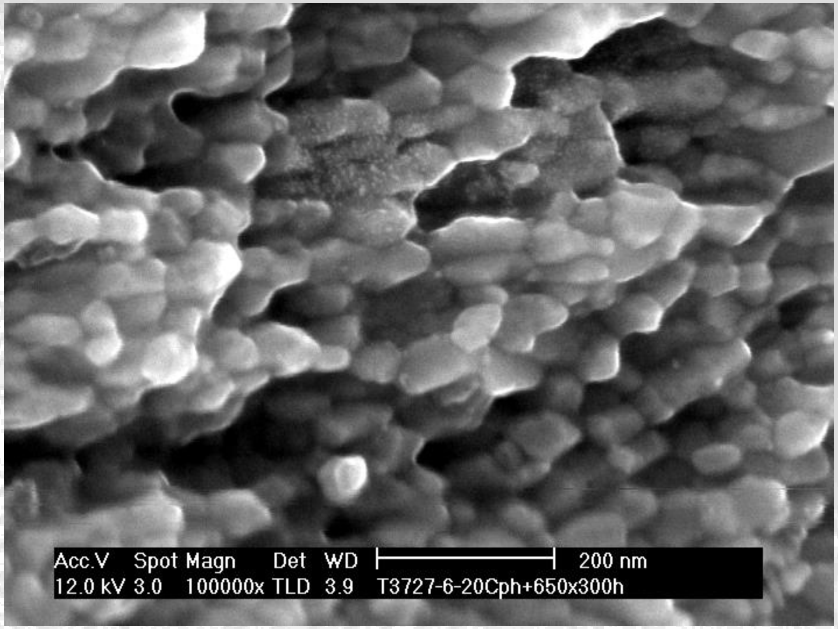
Fracture SEM for higher content oxygen external oxidized samples



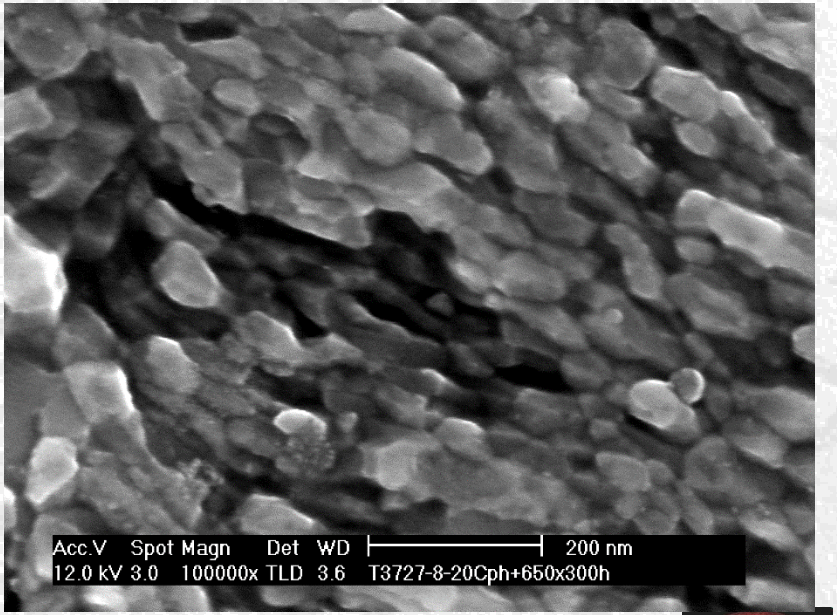
Sample	Grain size nm
2	65
4	55
6	53
8	48

6

4

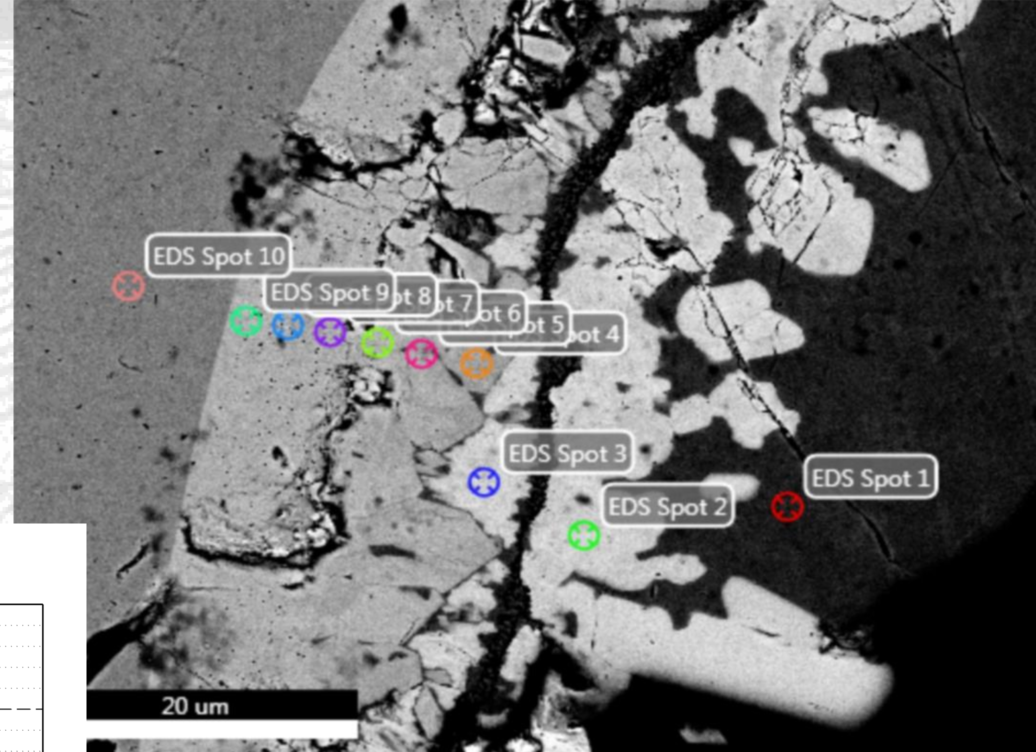


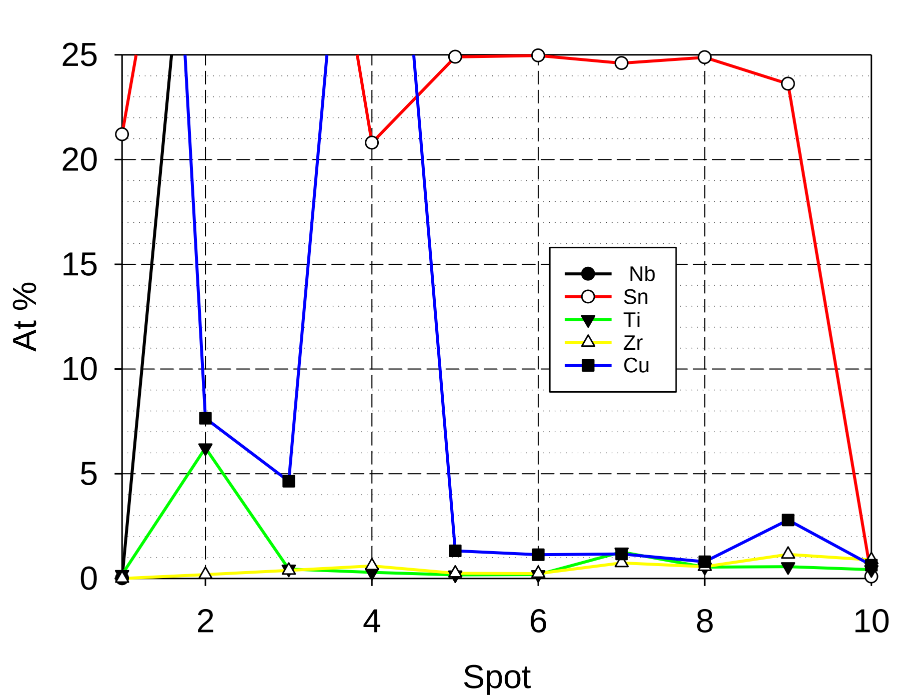
8

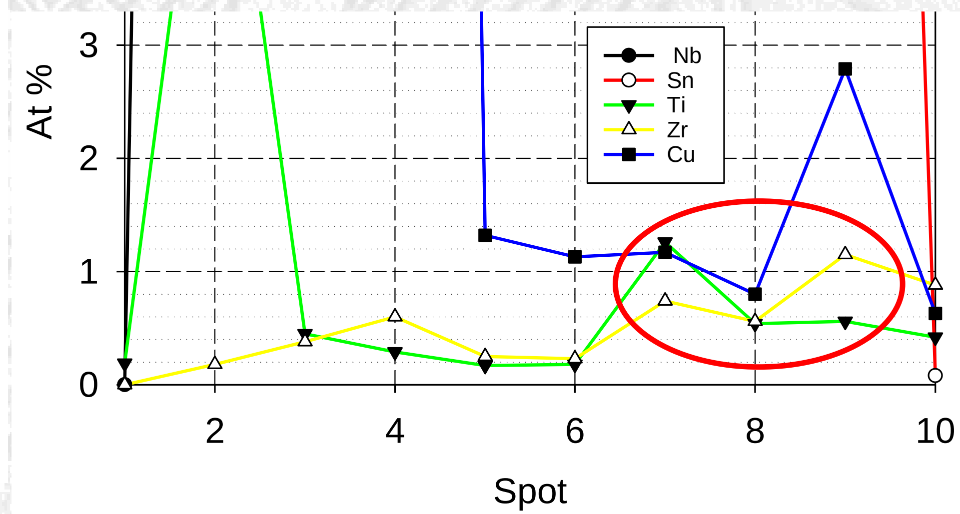


EDS 4

Ave Ti = 1.6 at%

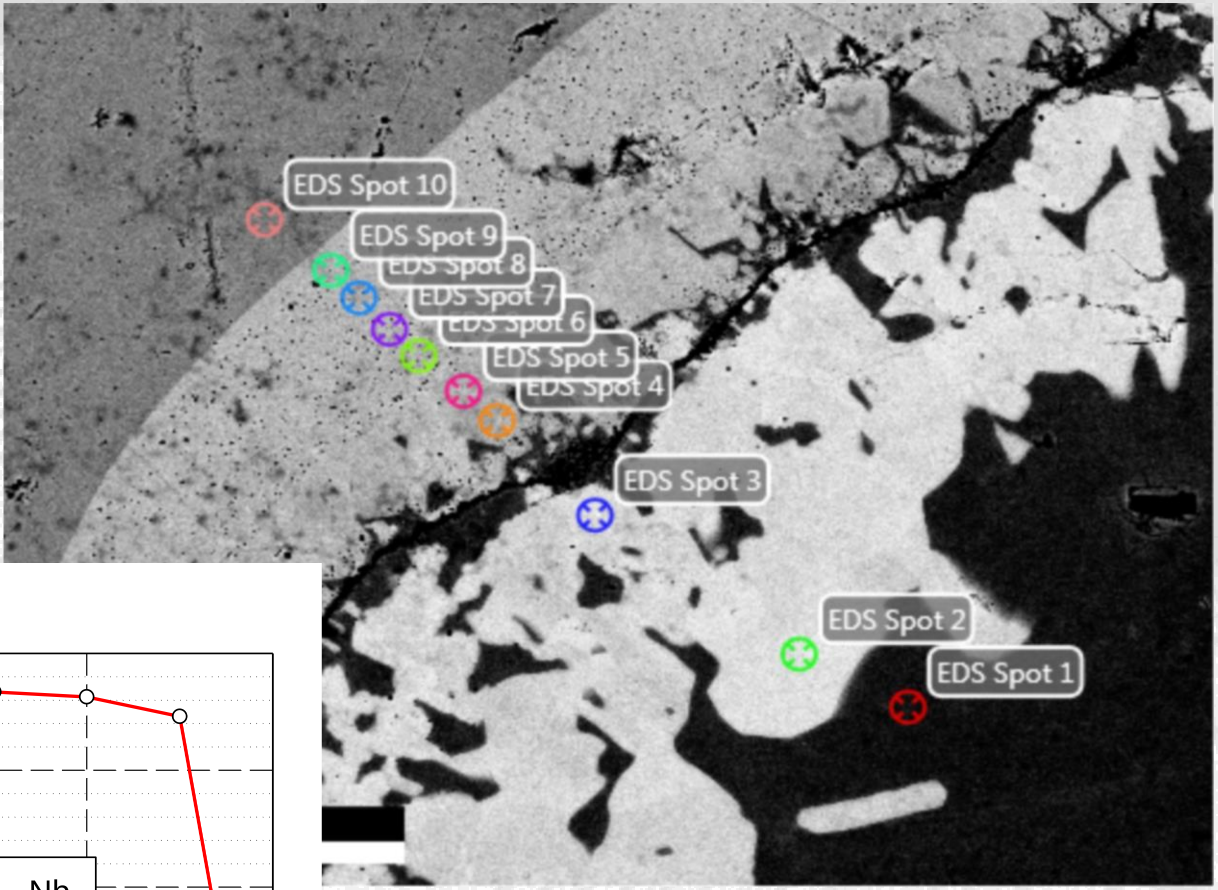


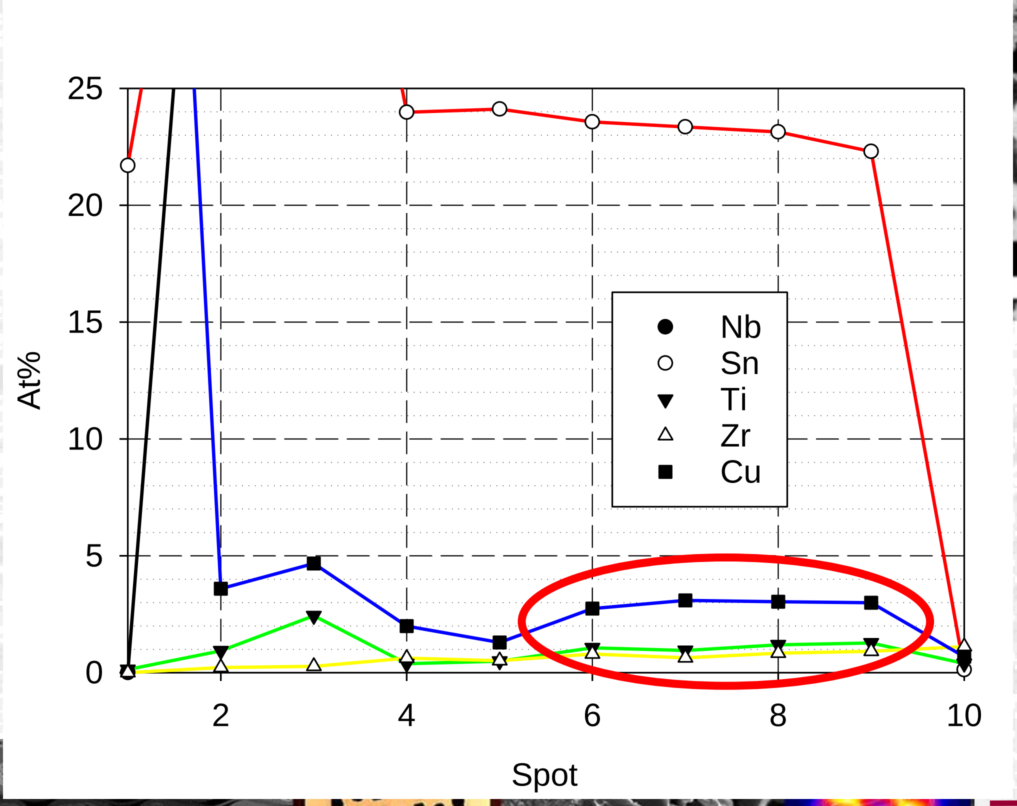


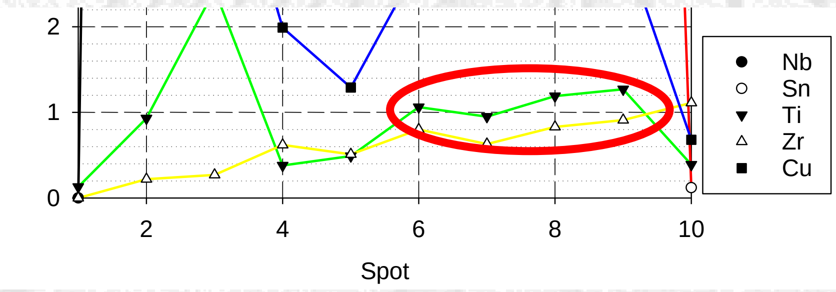


EDS 6

Ave Ti = 1.1% at



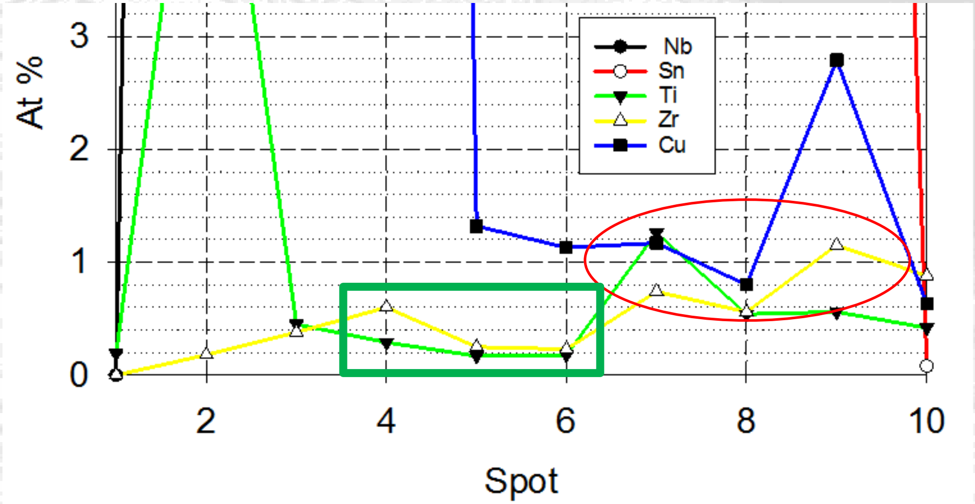




Trends in grain size, Ti, and B_{c2}

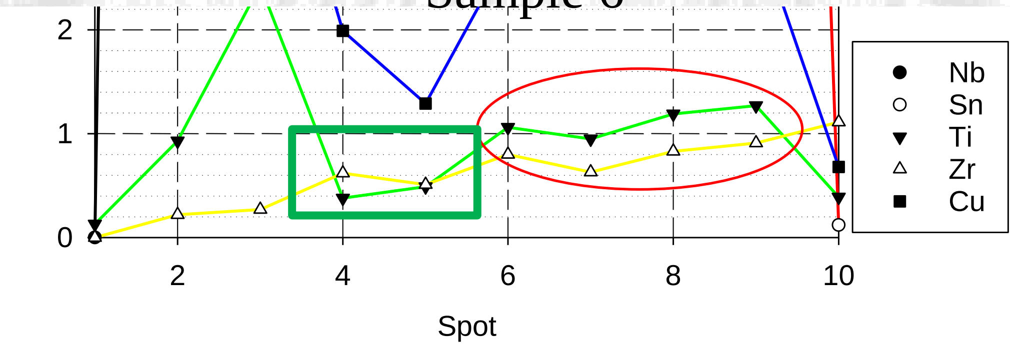
Sample	Grain size (nm)	Ave Ti %	Bc2 (T)
2	65	1.9	22.6
4	55	1.6	20.3
6	53	1.1	21.3
8	48	0.25	21.7

Sample 4

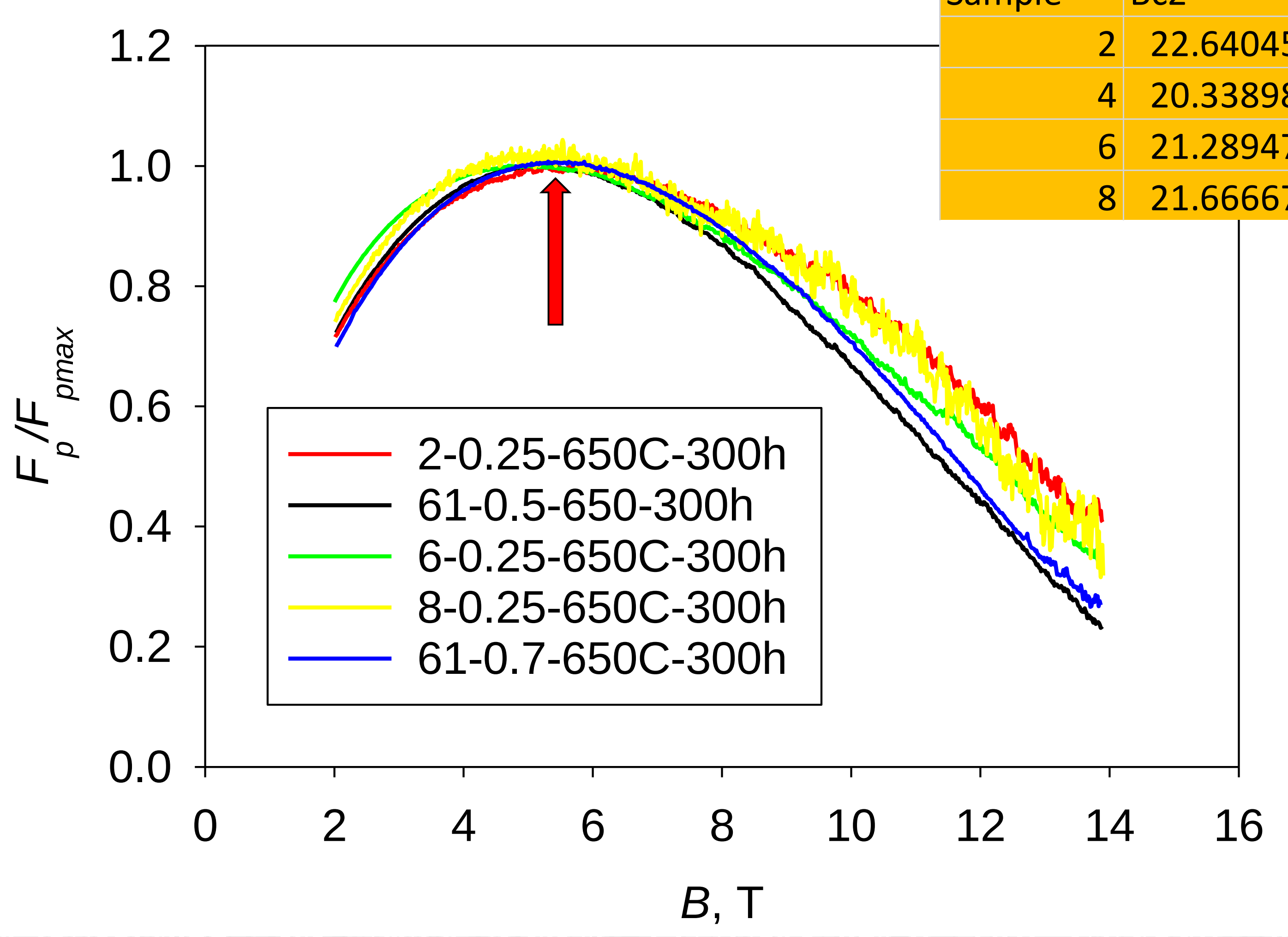


- **Decreasing Ti with excess oxidation**
- **Coarse grain A15 (converted from 6:5) has less Than FG A15 (direct formation)**

Sample 6

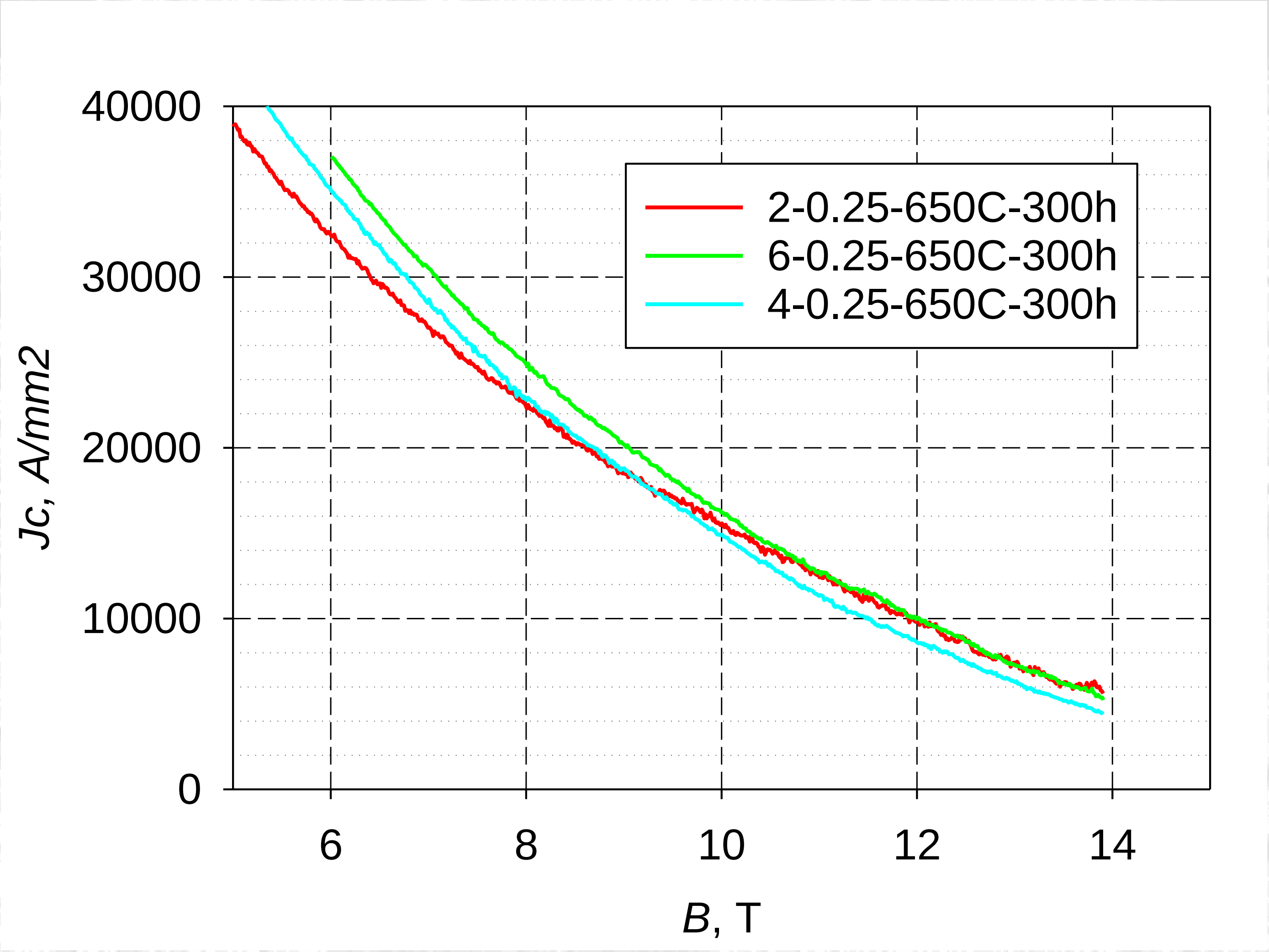


Normalized F_p



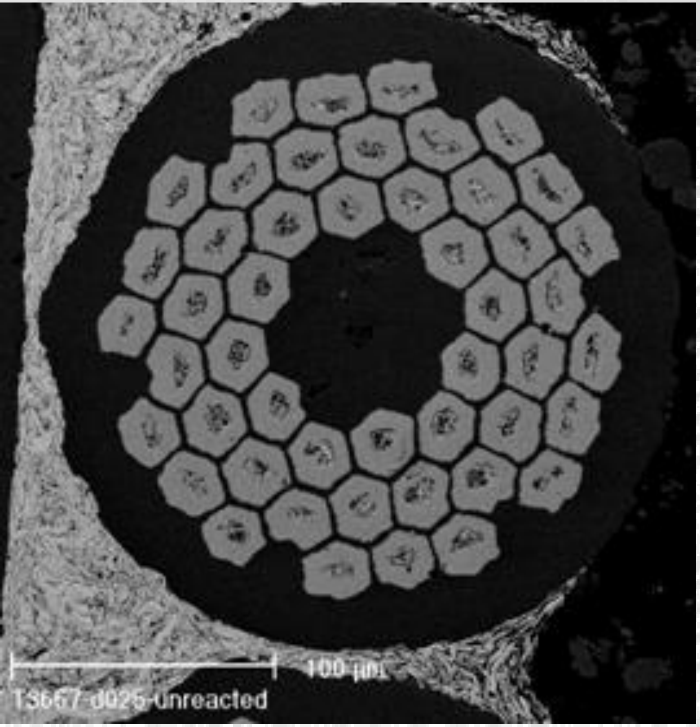
Sample	Bc2	bmax	bmax/bc2
2	22.64045	5.6	0.247345
4	20.33898	5.5	0.247345
6	21.28947	5	0.234858
8	21.66667	5.25	0.242308

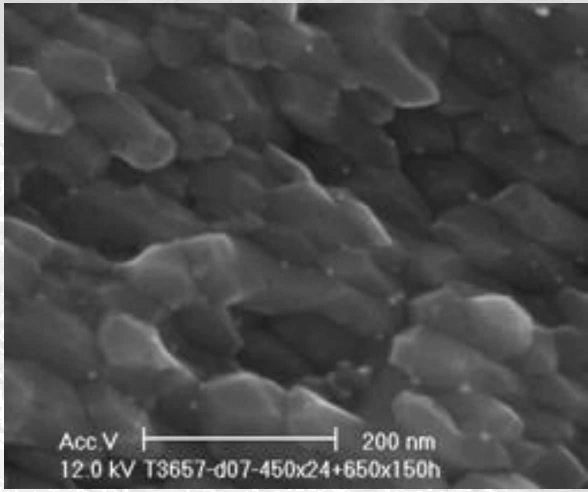
Magnetic J_c for External oxidized strands

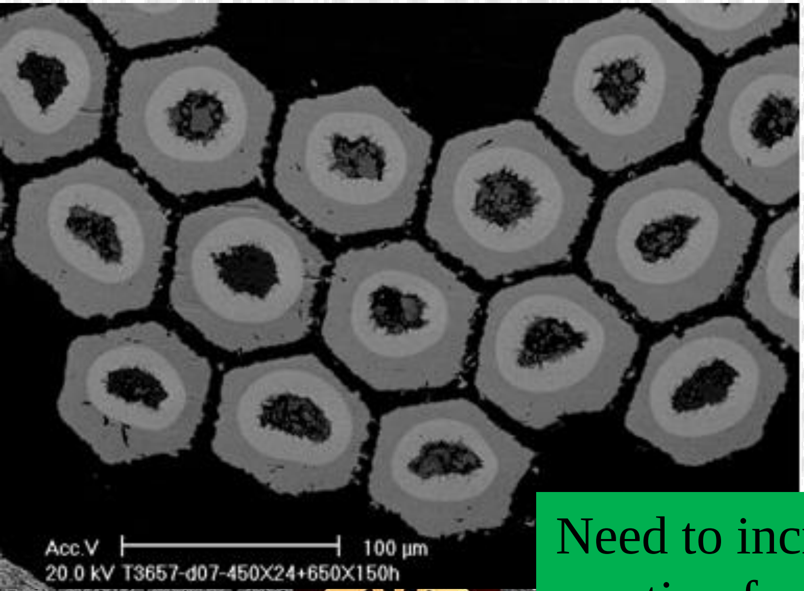


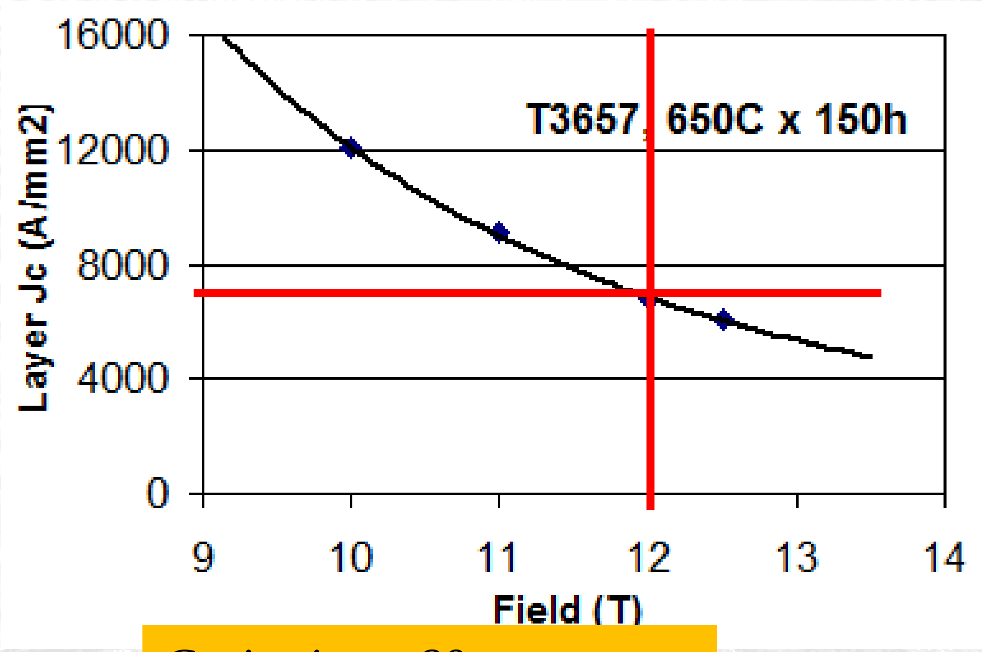
Area related Uncertainty for sample 2

Initial Multi development --Thick Nb barrier 61 restack





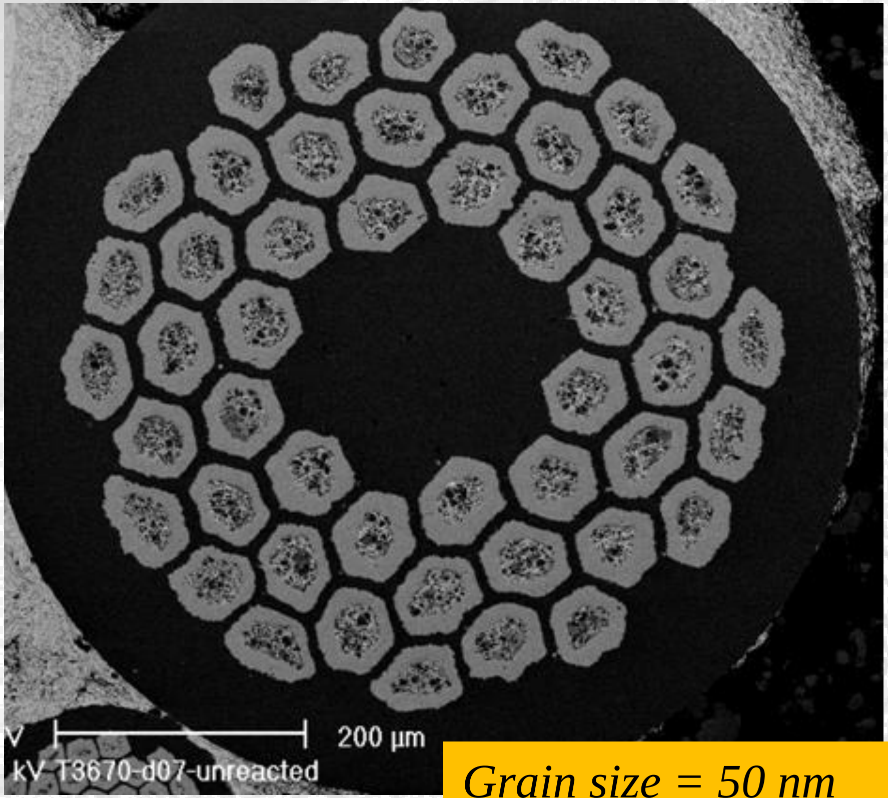




Need to increase reaction fraction!

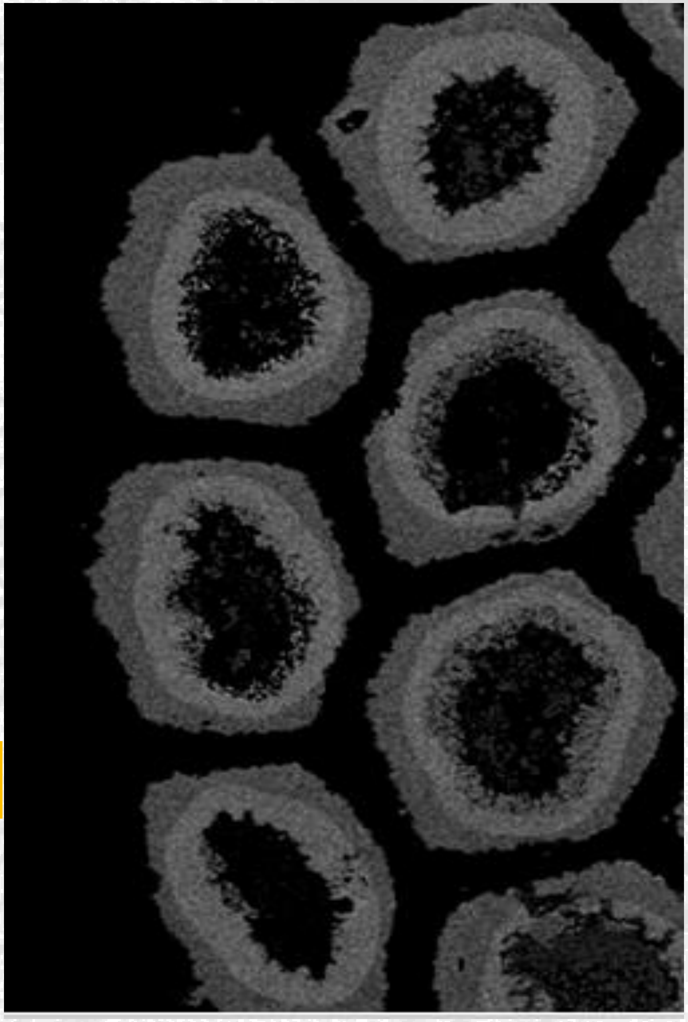
Grain size = 80 nm
J_c 12 T = 6800 A/mm^2

Thin Nb barrier 61 restack- HTR



Grain size = 50 nm

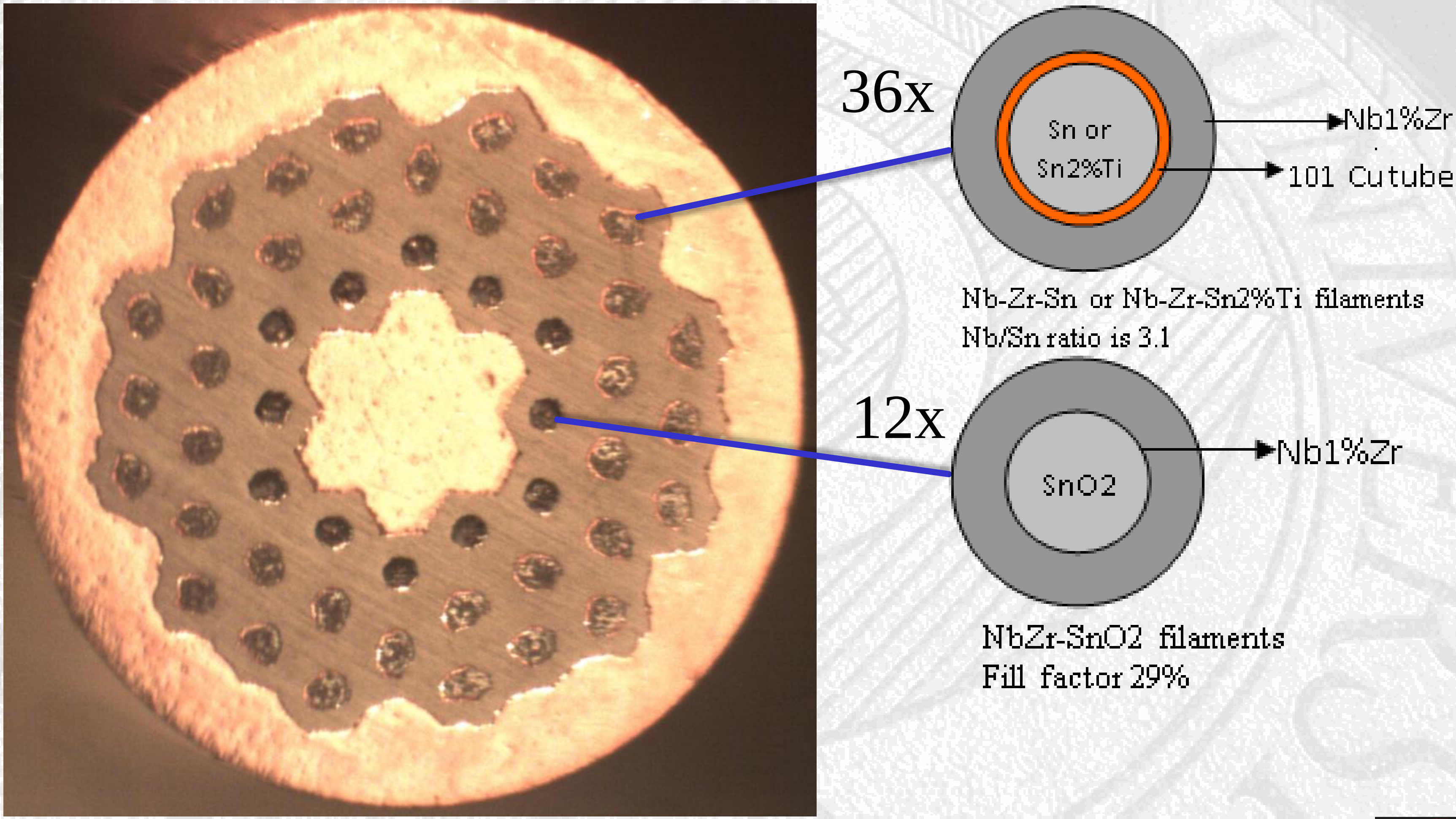
Unreacted strand



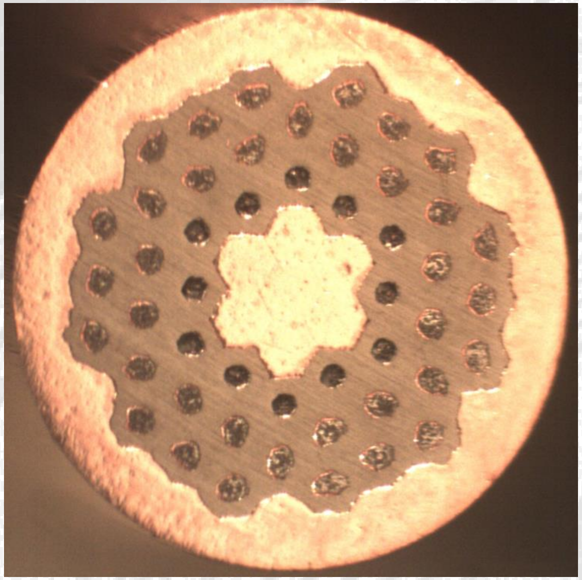
Reacted strand

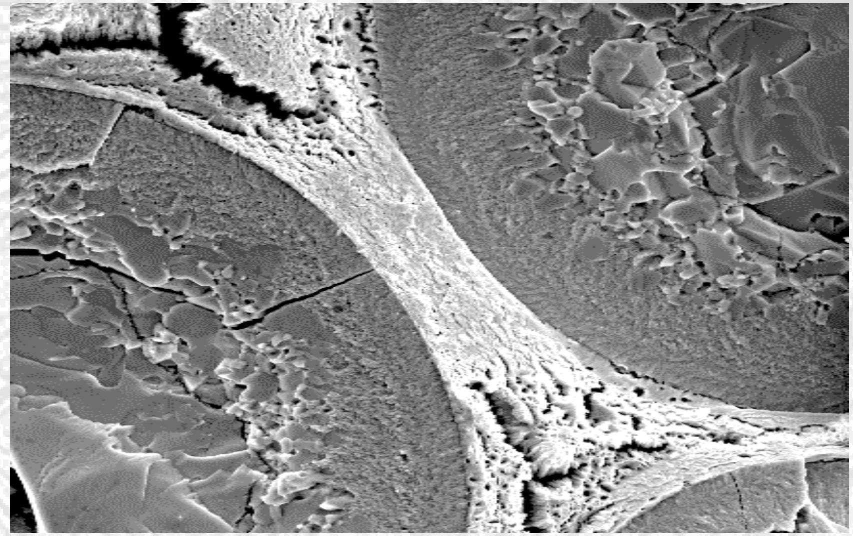
Modified design and HT leads to
Grain size reduction
Reaction fraction reaching 20% (need more)!

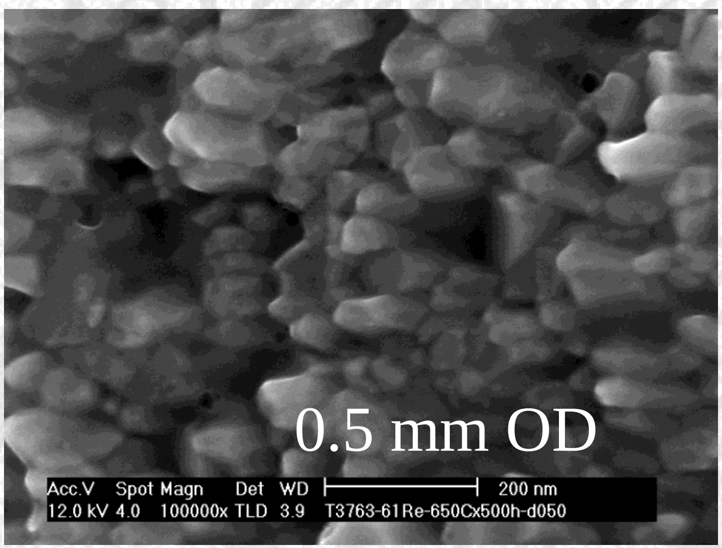
More recent Multi I



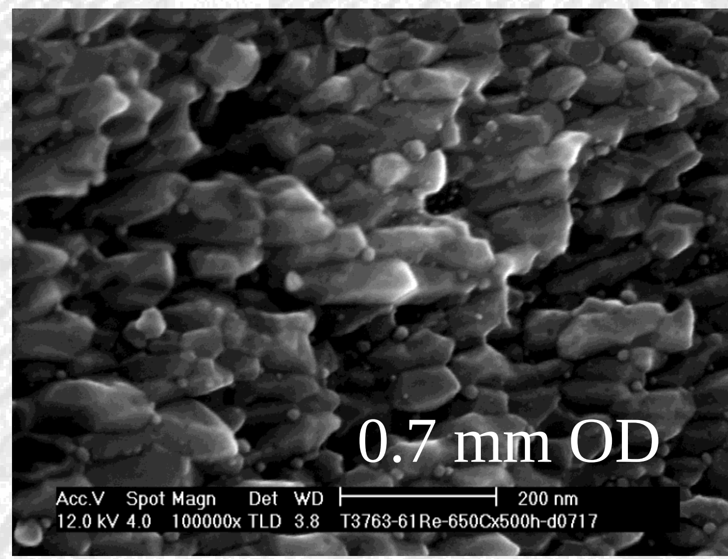
61-0.7 mm OD multi-650C/500h







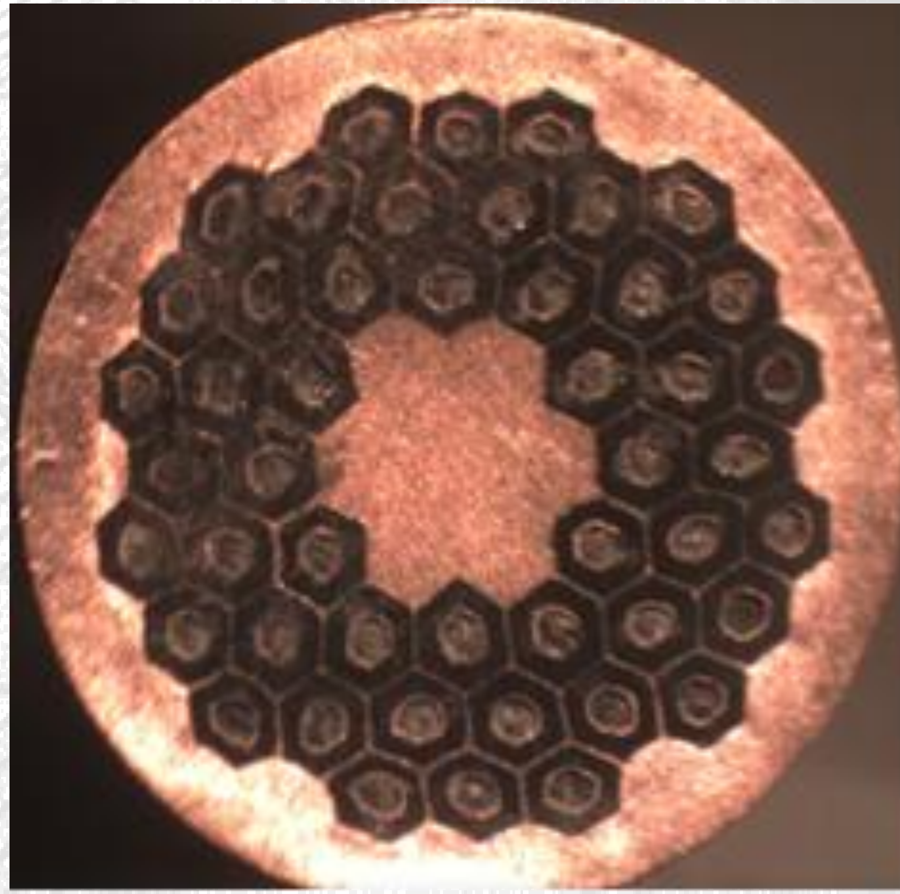
50 nm grain size



Strand Design Progression, New Strand Design

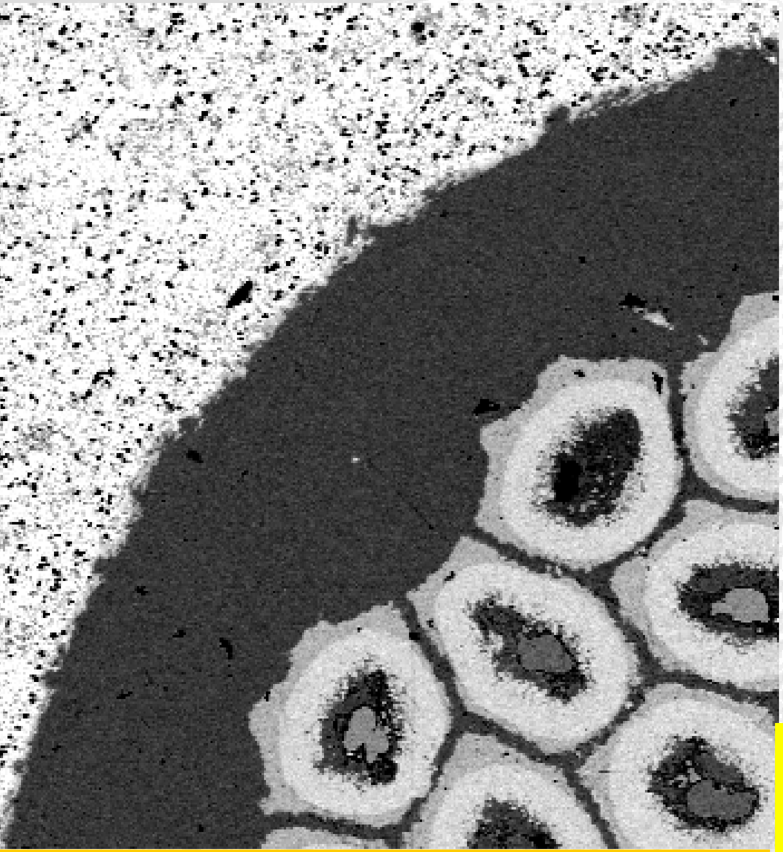
Note: 57.5% non-Cu

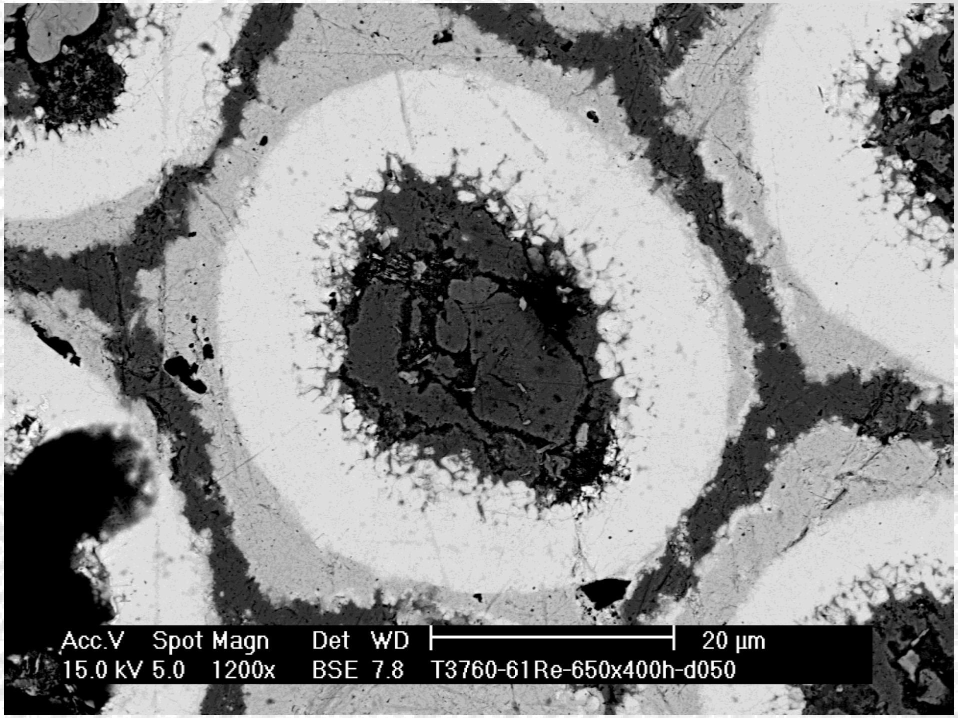
Push for retaining reduced grain size while increasing non-Cu fraction and % reaction under the barrier



0.5 mm OD strand

New Strand Results





Typical for RRP, Tube and PIT
Non-Cu = 50%
A15/nonCu = 60% (RRP)
A15/Non-Cu=40% (Tube and PIT)

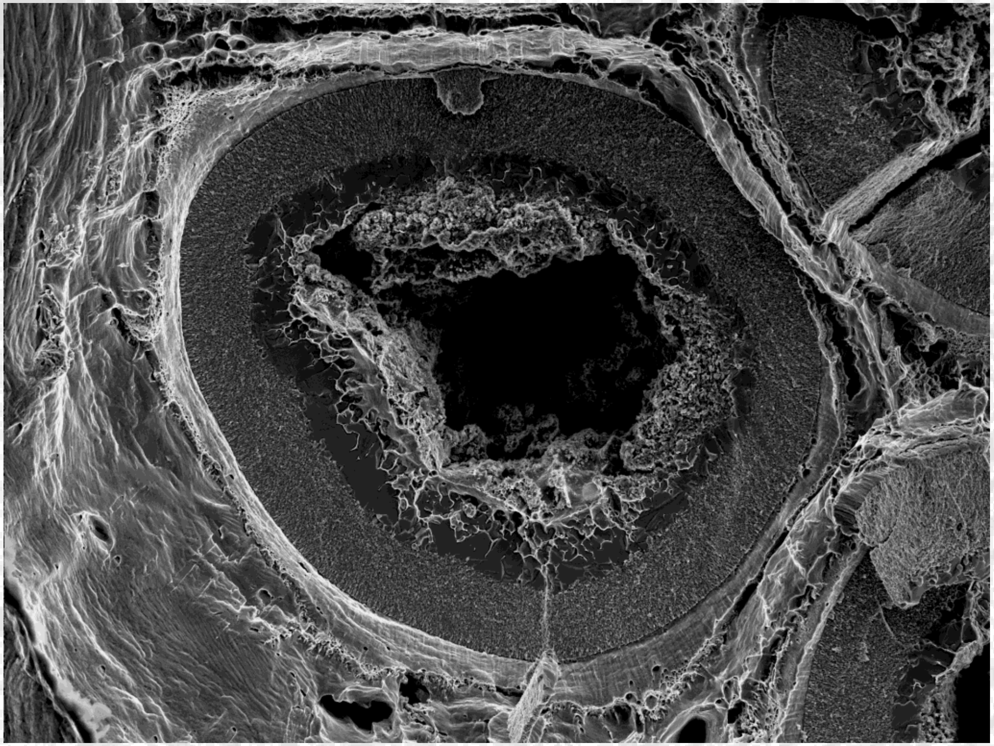
Non-Cu fraction = 57.5%
A15 in non-Cu fraction = 33%

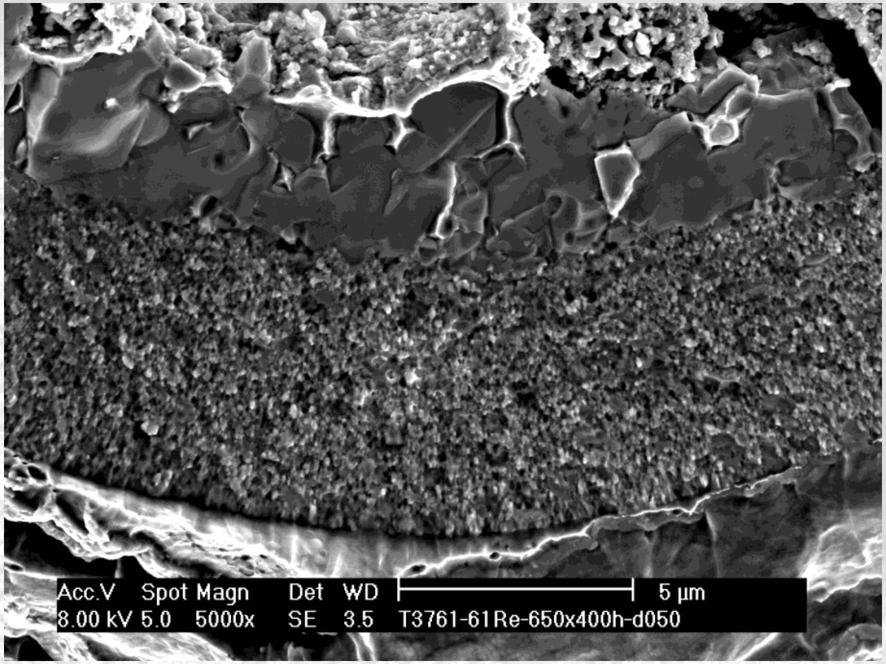
3000 A/mm2 at 12 T
2400 A/mm2 at 12 T

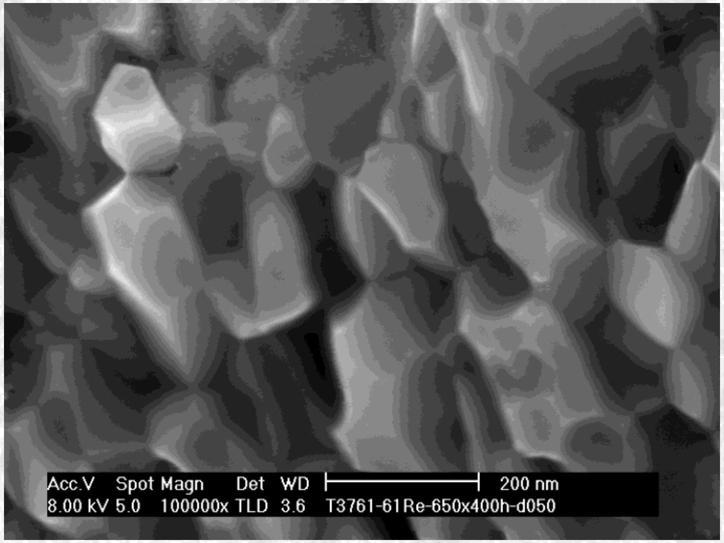
10000 * 0.33 = 3300 A/mm2, leads to expectation (prepare now to measure) of 3300 A/mm2 12 T.

Target of 50% Conversion seems realistic
-- 10000 * 0.5 => 5000 A/mm2

Fracture

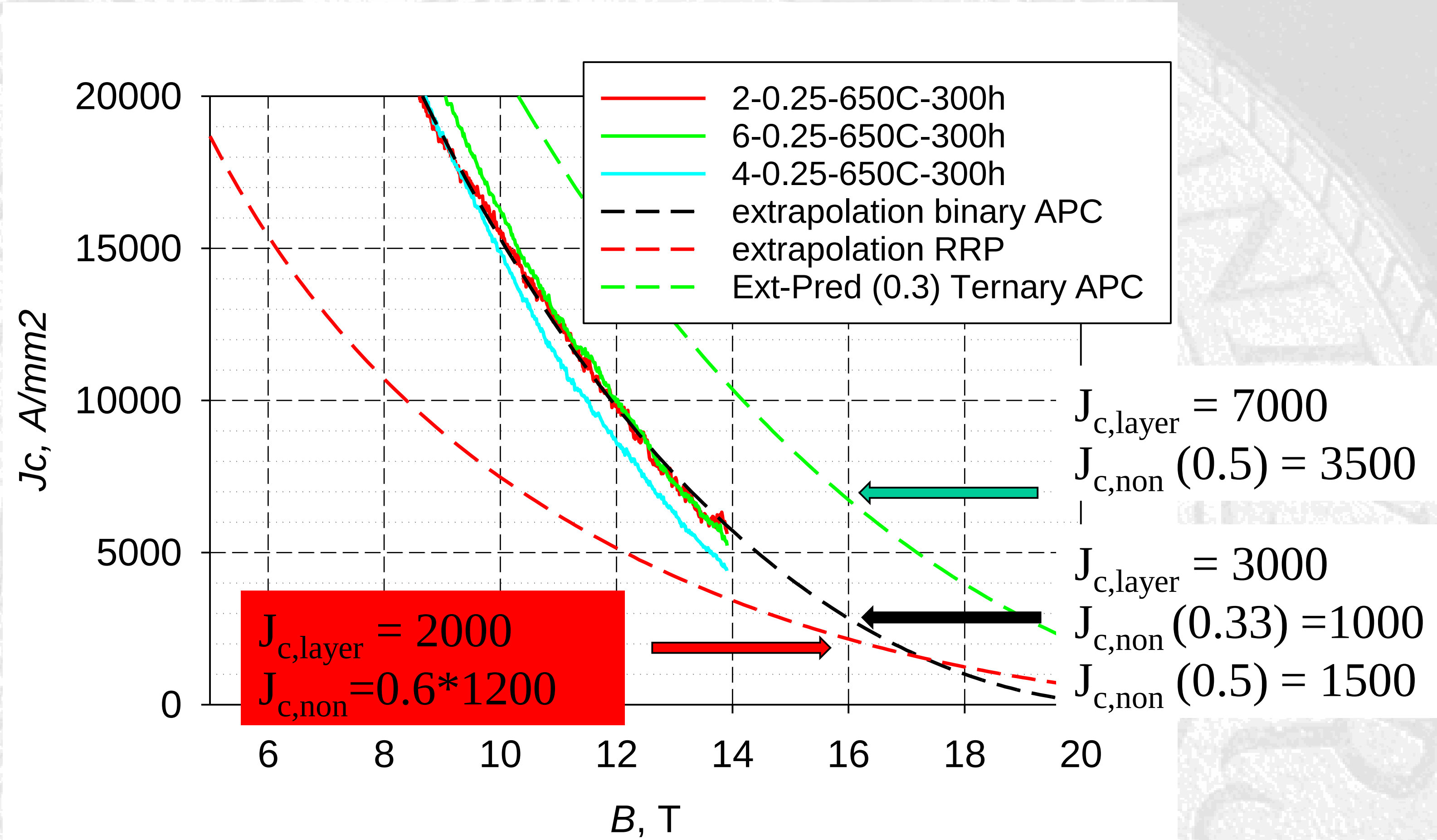






HT optimization needed

High Field Comparison



Summary and Conclusions

- We have demonstrated grain refinement by a factor of 3 and a doubling of 12 T J_c in monofilaments
- Internal oxidation can be used in many Nb_3Sn strand types, including Tube (demonstrated) PIT (proposed), RRP/RIT (proposed) etc.
- Ternary strands under development: Possible to inject Ti into internally oxidized Nb3Sn layers
- Sn contents remain high with Ti additions, but Bc2 increase not yet seen – may need to add more Ti
- Multifilamentary strands have been demonstrated with refined grains and enhanced Jc values.
- New designs which have push non-Cu fraction to above 50% and reaction fraction to above 30% are demonstrated (measurements underway) These need (1) To be optimized, and (2) To be demonstrated for a ternary alloy with the ternary alloy B_{c2}
- This route is very promising for future Nb_3Sn development