Comparison of the grain boundary chemistry of Ta and Ti doped high J_c Nb_3Sn strand by atomic resolution microscopy

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Acknowledgement: This work is supported at NHMFL by the U.S. Department of Energy under Contract NO. DE-FG02-07ER41451 and the State of Florida

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Motivation

- Ta and Ti are widely used as dopants for Nb_3Sn superconducting strands to improve high field J_c and H_{c2}.
- Ti-doped Nb_3Sn high-J_c wires have shown better irreversible strand degradation than Ta-doped high J_c strand.
  - The mechanism is not known and cannot be explained by macrostructural features of the conductor architecture.
- GBs (grain boundaries) are believed vital both for high J_c and mechanical properties.
  - This work studies the GB segregation properties of Ta or Ti doped Nb_3Sn.

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Methodology

- 4 different Nb_3Sn strands.
  - One ITER type Ti-doped Nb_3Sn strand and three high J_c (Ta, Ti, or Ta+ Ti) doped RRP® Nb_3Sn strands
- μ-scale compositional analysis for A15 phase identification
  - EDS (Energy Dispersive X-ray spectroscopy) in FE-SEM
- nano-scale investigation of A15 GB properties
  - Good electron transparent TEM foil for high resolution electron microscopy
  - Atomic resolution TEM/STEM
  - EDS (Energy Dispersive X-ray Spectroscopy)
  - EFTEM (Energy Filtered transmission electron microscopy)
  - EELS (Energy Loss Spectroscopy)

Our capability for analytical microscopy

- JEOL-ARM 200cF (TEM/STEM) with BF, ADF, HAADF
- Spectroscopy: EDS and Dual EELS system
- Dual Beam FE-SEM/FIB system with GIS (Gas Injection System) + Nano-manipulator for TEM sample Prep.
- FE-SEM with EDS (SDD detector)

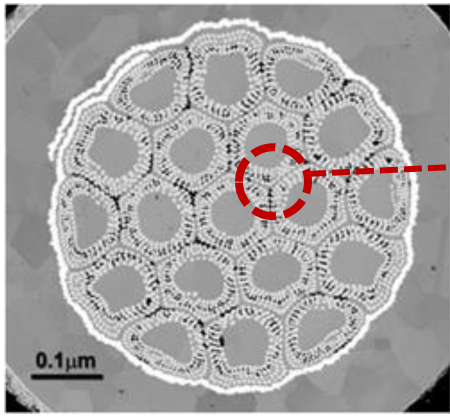
JEM-ARM 200cF

Carl Zeiss 1540 Esb: Dual Beam FE-SEM/FIB + GIS

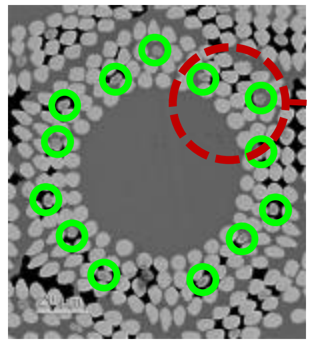
Omniprobe: Auto Probe 200.2

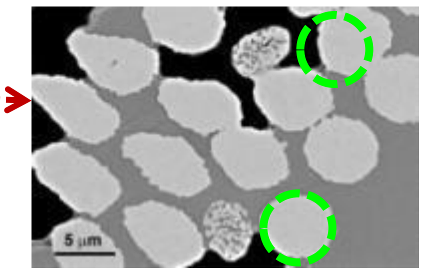
Description of samples

Sample type A: Ti-doped ITER Internal Sn strand, 650°C/200hrs

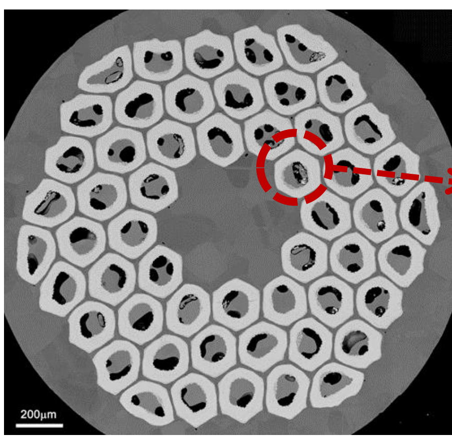


12 distributed Ti sources (Nb-47wt% Ti) in the sub element

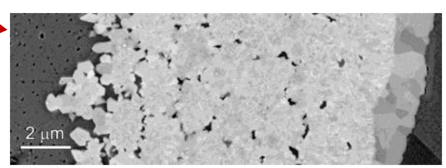




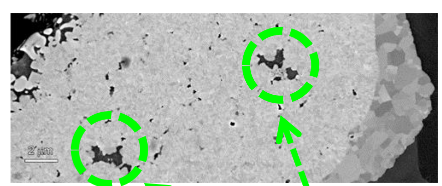
Sample type B: Ti or Ta-doped high J_c Internal Sn RRP® strands, 54/61, 640°C/48hrs



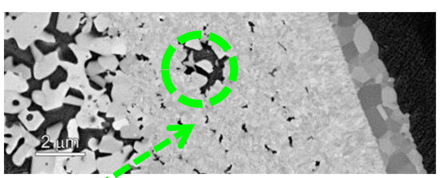
1. 7.5wt% Ta



2. 7.5wt% Ta + 0.3wt% Ti



3. 2at%Ti



Ti source

Irreversible strain results: Ti doping shows higher $\varepsilon_{irr,0}$

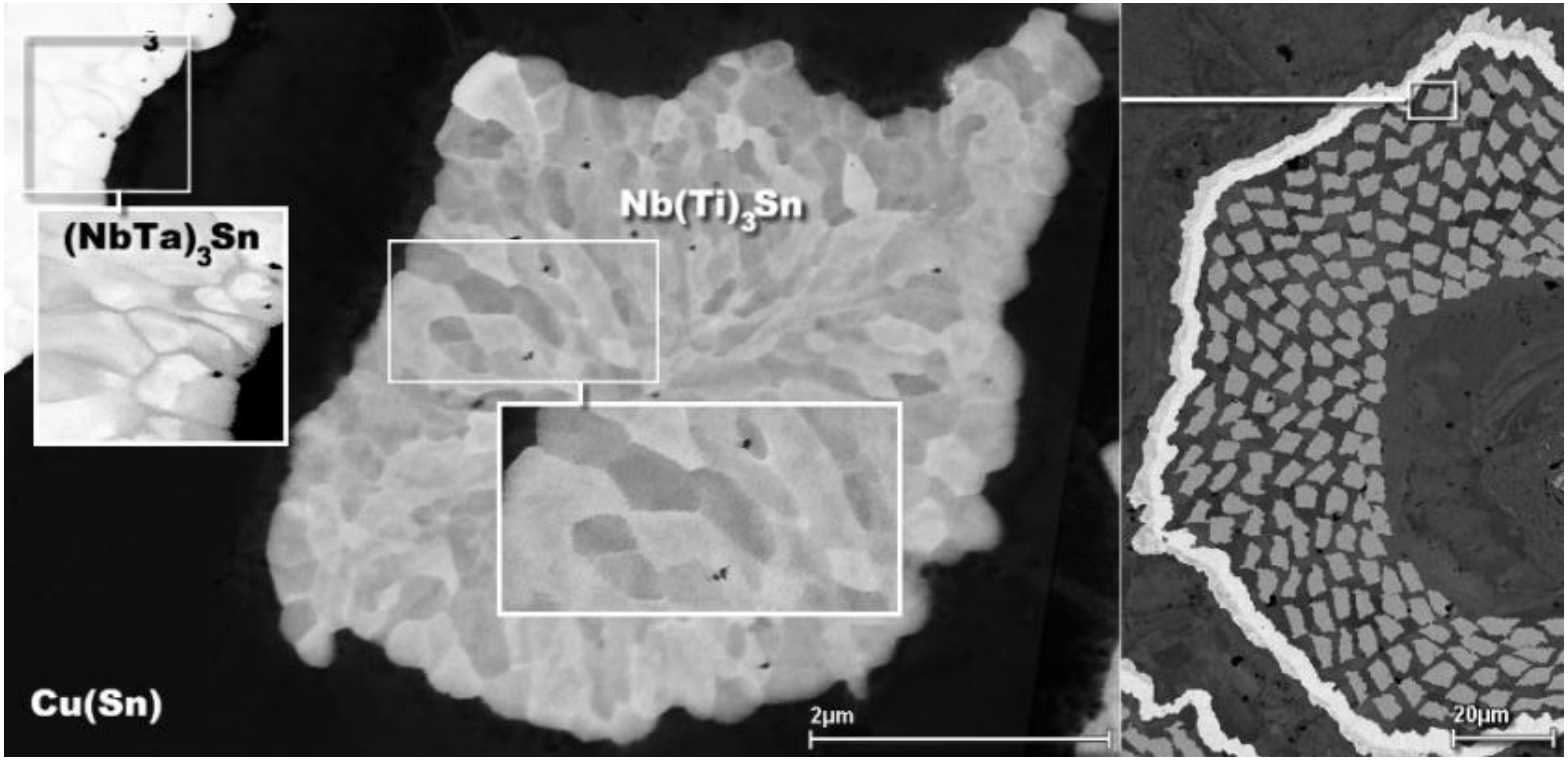
Strand Type	Doping method	Ø (mm)	HT (°C/hrs)	$\varepsilon_{irr,0}$ (%) Avg. 0.1 mV/cm	Non-Cu ac-loss (mJ/cm³)
ITER	Dispersed Nb-Ti rods in pure Nb filaments	0.77	650/200	**0.21**	2136
RRP (54/61)	7.5wt% Ta in each filament	0.7	640/48	0.04	4815
RRP (54/61)	7.5wt% Ta + 0.3wt% Ti in each filament	0.7	640/48	0.06	4812
RRP (54/61)	2at% Ti in each filament	0.7	640/48	**0.24**	4670

Measurement by Dr. N. Cheggour

Nb_3Sn: Grain boundary composition

GBs are known to be Sn-poor, the effect of Ti and Ta-doping on grain boundary composition needs to be determined.

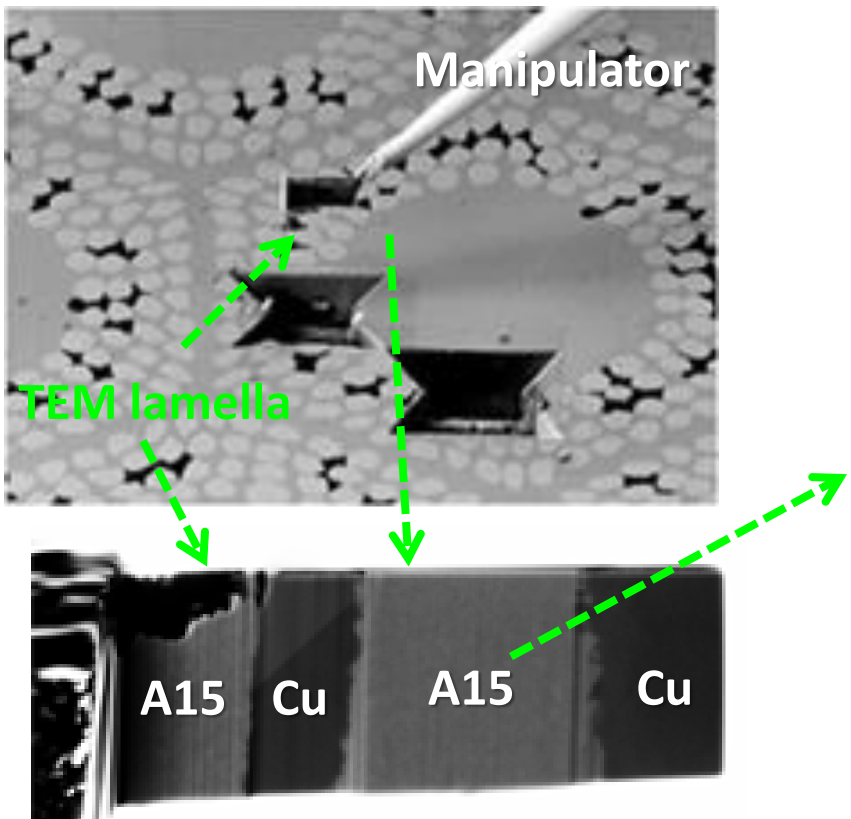
Imaging by Dr. Peter Lee



ITER-CSMC Benchmark III MJR internal $Nb(Ti)_3Sn(Mg)$ strand cross-section: TWC (final HT 256hrs@750°C).

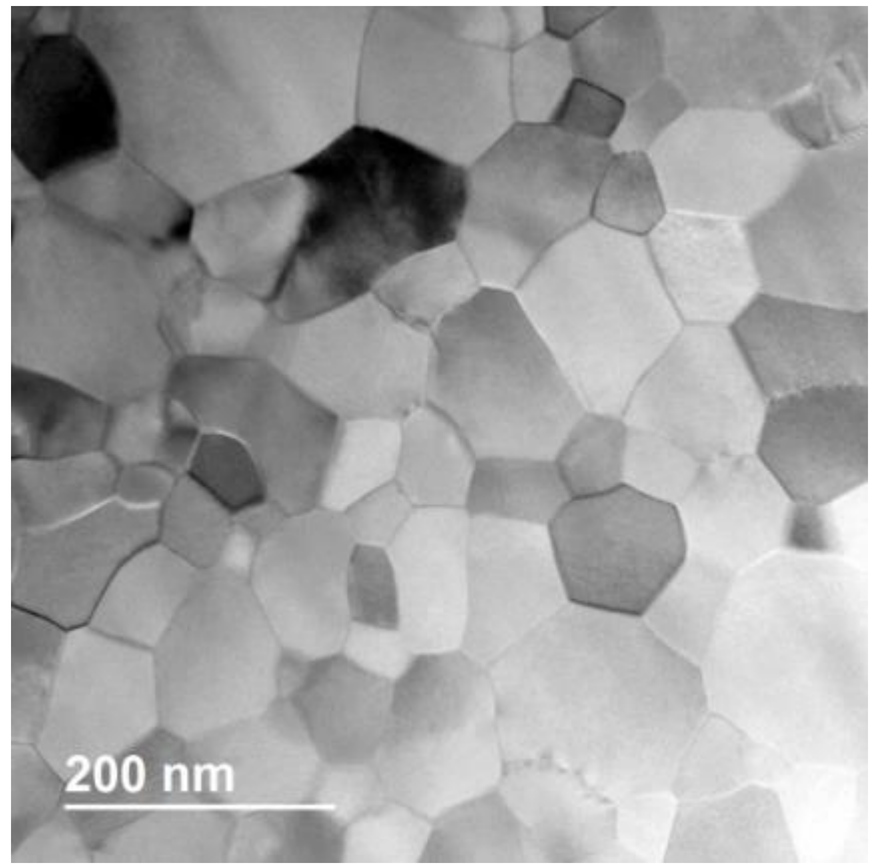
Atomic resolution analytical TEM/STEM can address: Does the dopant segregate at GBs?

TEM sampling by FIB + GIS system



Sample type A: Nb-47wt%Ti rod

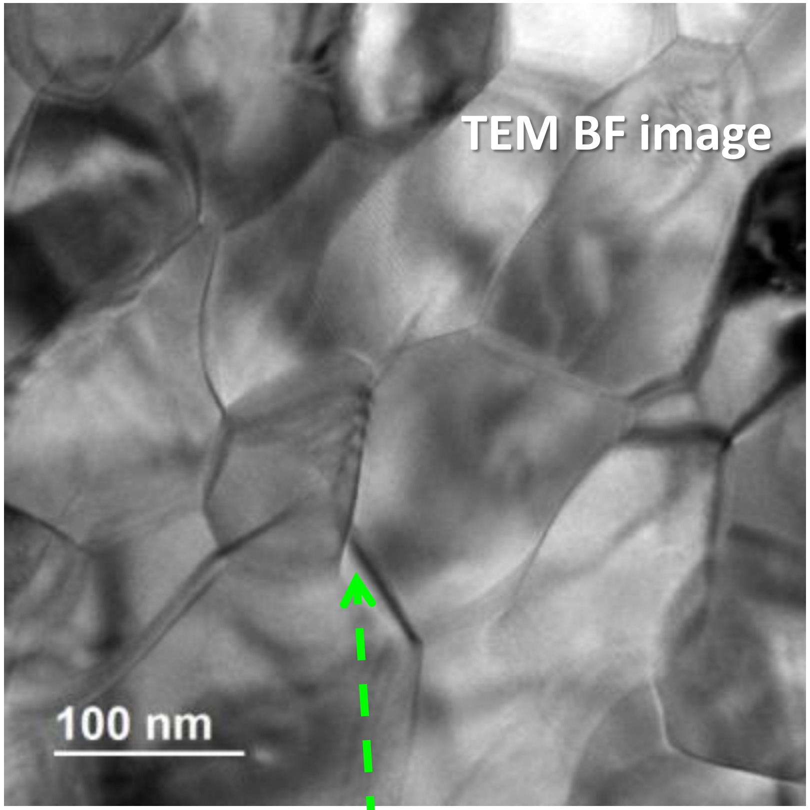
JEOL ARM BF(Bright Field) TEM Image

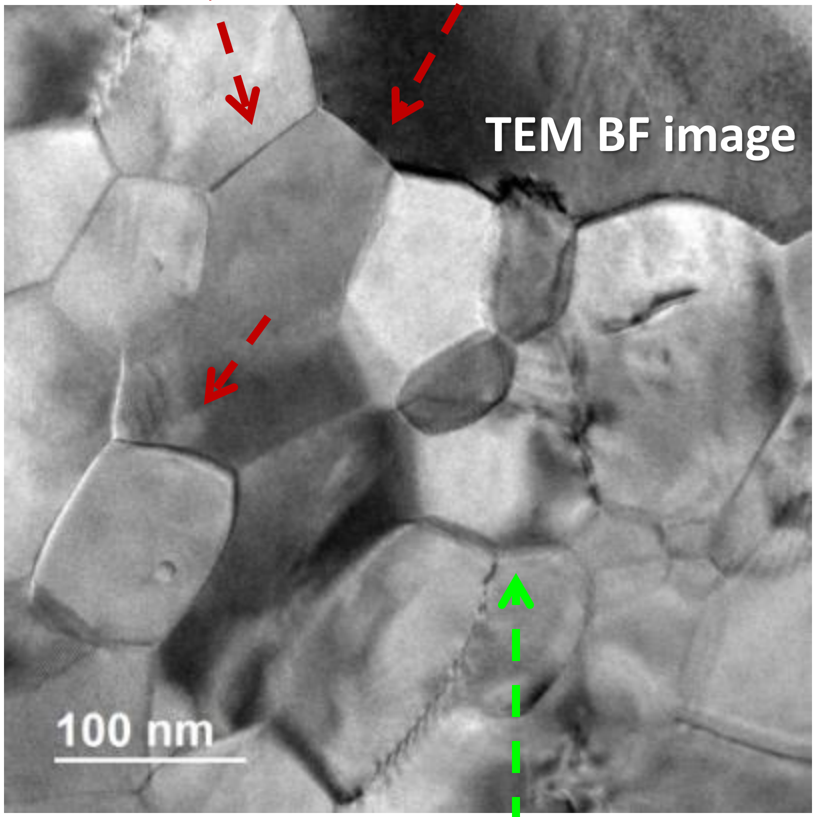


Cleaner and thin TEM foils are required for accurate analytical microscopy

Very clean TEM lamella produced by Low-Voltage FIB milling.

GB plane ǁ to electron beam: higher spectrum signal





Highly tilted GB structure: hard to detect composition signal

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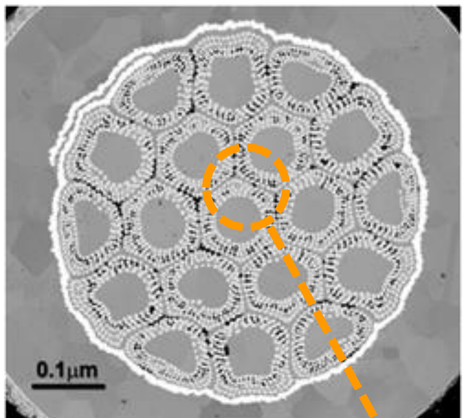
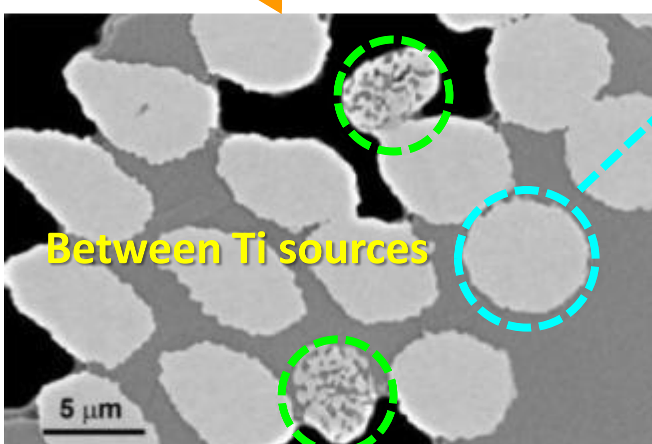
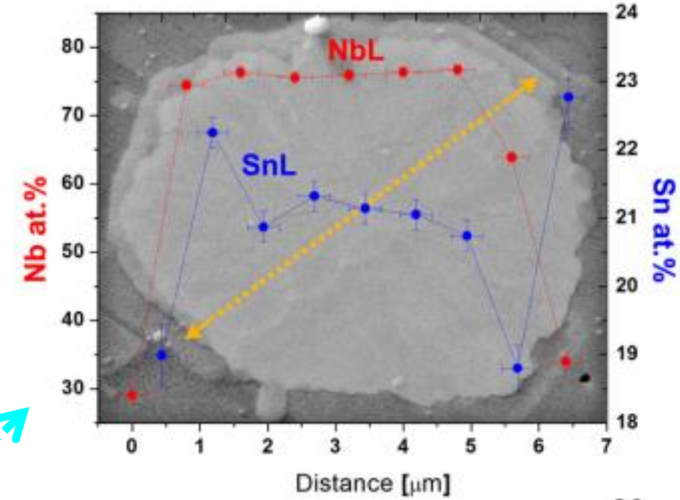
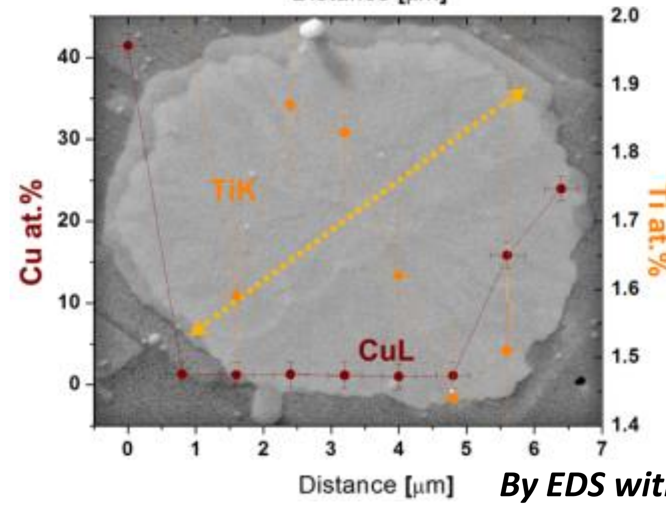
A15 compositions in Ti-doped ITER strand: Sn ≈ 22-23at%, Ti+Sn≈23.5-24.5at%



12 distributed Ti sources (Nb-47wt% Ti) in the sub element







By EDS with FE-SEM

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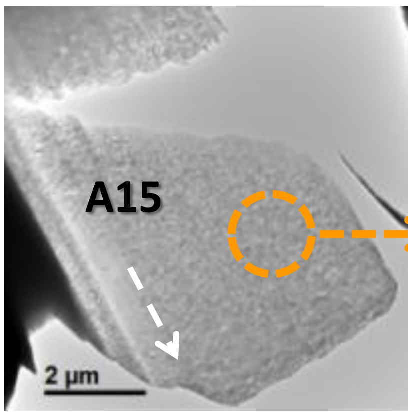
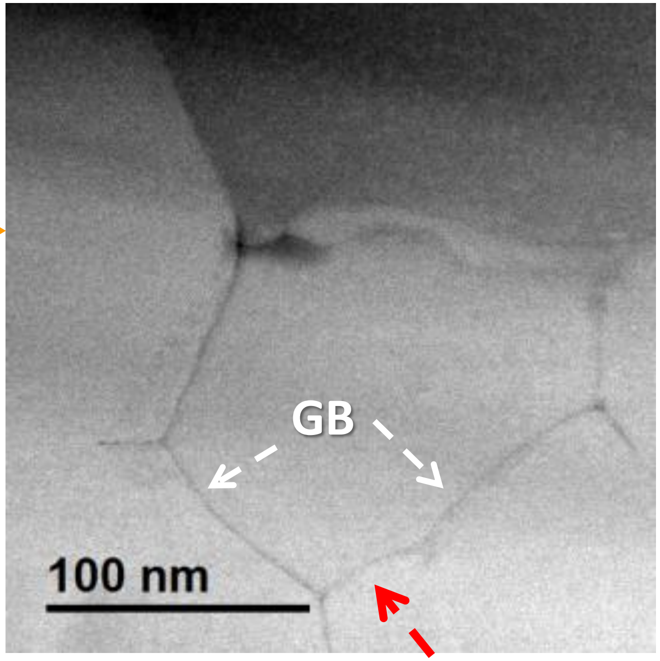
Successfully thinned grain boundary structure

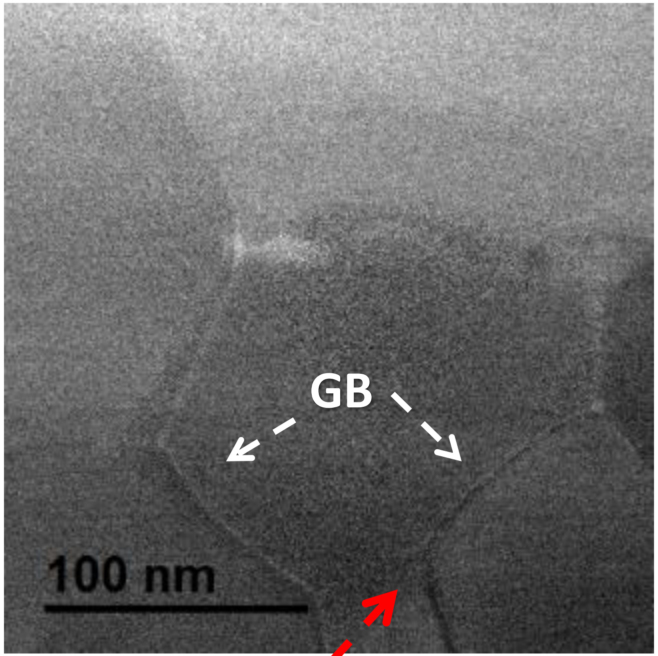
TEM BF Image



STEM ADF image: z-contrast



STEM BF image



Sample type A: Nb-47wt%Ti rod, 650°C/200hrs

GB contrast shows GB segregation

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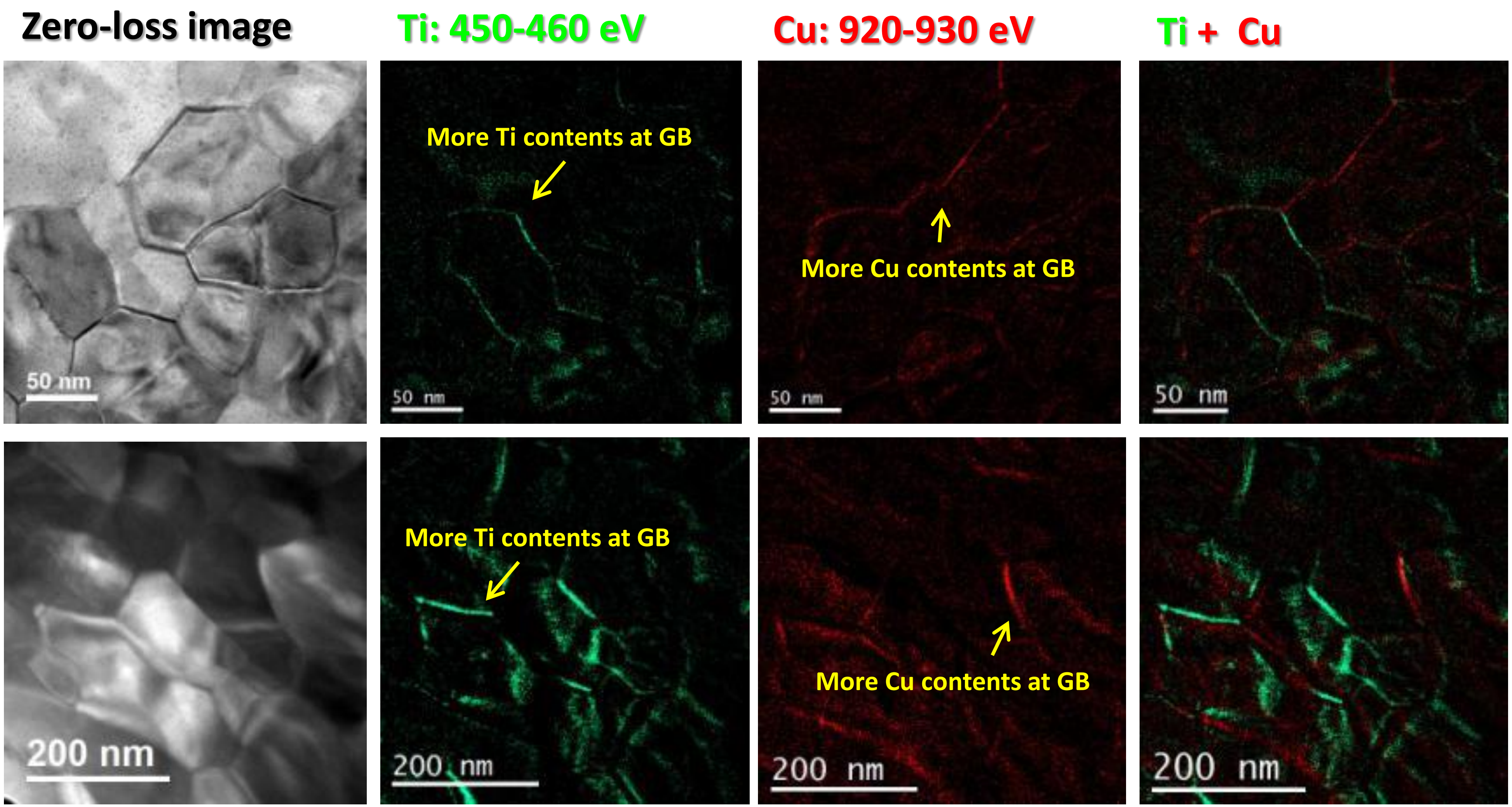
Ti-doped ITER Strand: EFTEM shows extensive Ti, Cu, or Ti & Cu segregation at GBs of Nb_3Sn



Sample type A: Nb-47wt%Ti rod, 650°C/200hrs

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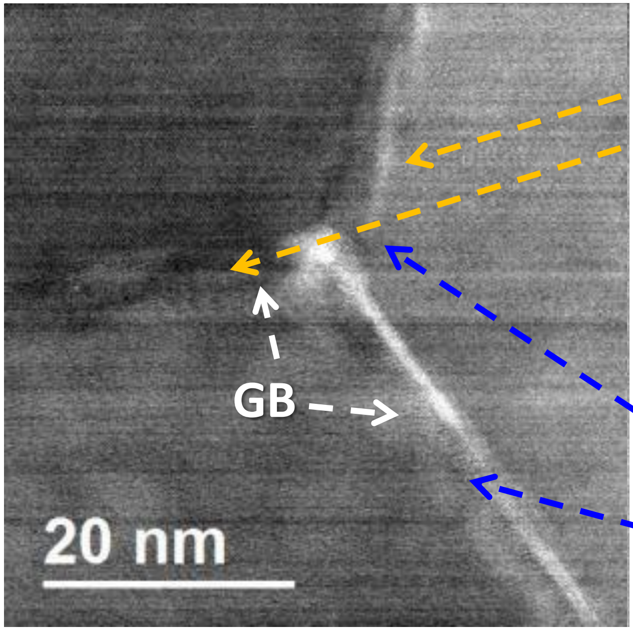
Ti-doped ITER Strand: GB segregation of Ti or Cu can also be observed by STEM-EELS

Sample type A: Nb-47wt%Ti rod, 650°C/200hrs

STEM BF image / STEM ADF image

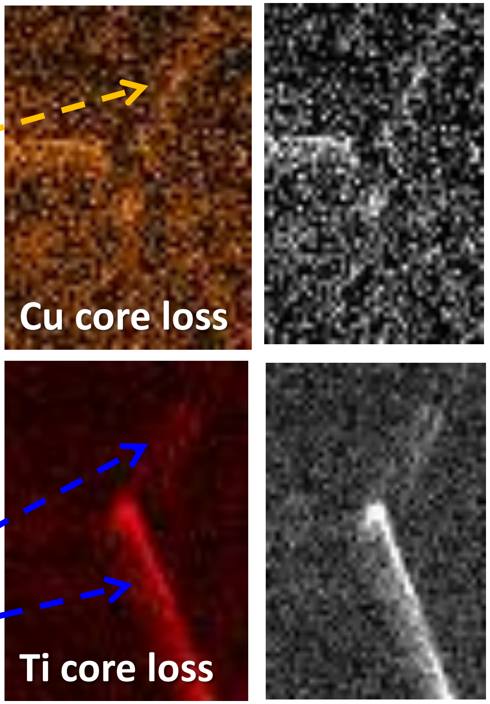


Bright contrast at GB: Cu segregation / Dark contrast at GB: Cu segregation

Bright contrast: Ti segregation / Dark contrast: Ti segregation

EELS spectrum

Color map — Intensity



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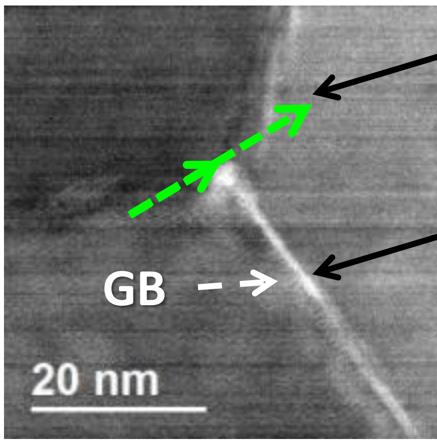
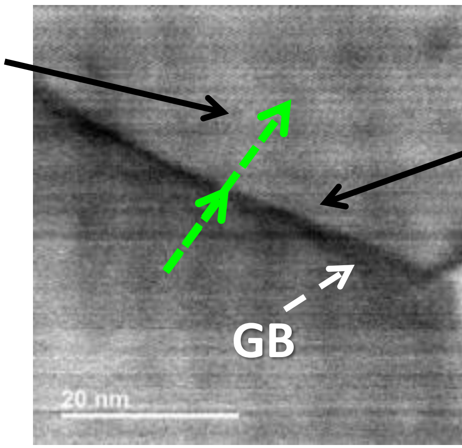
STEM-EDS also confirms Ti or Cu segregation at A15 GBs

STEM BF image: EDS



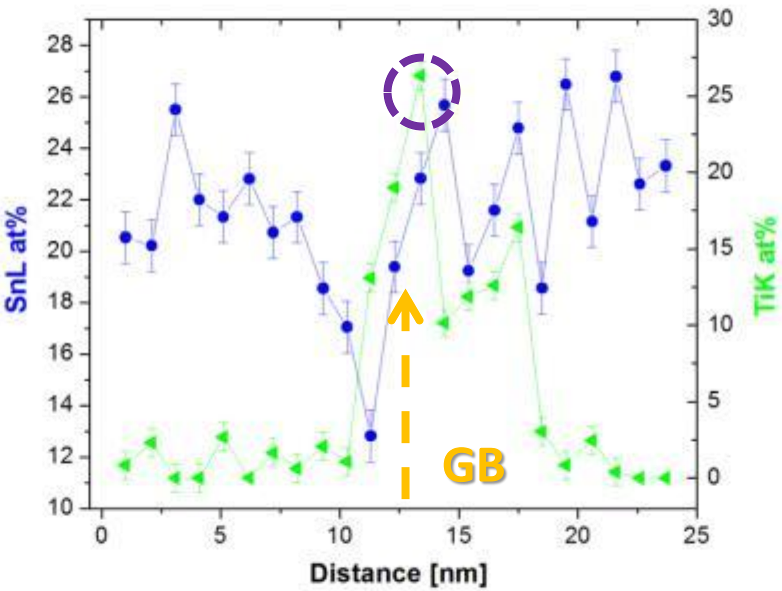
STEM BF image: EDS

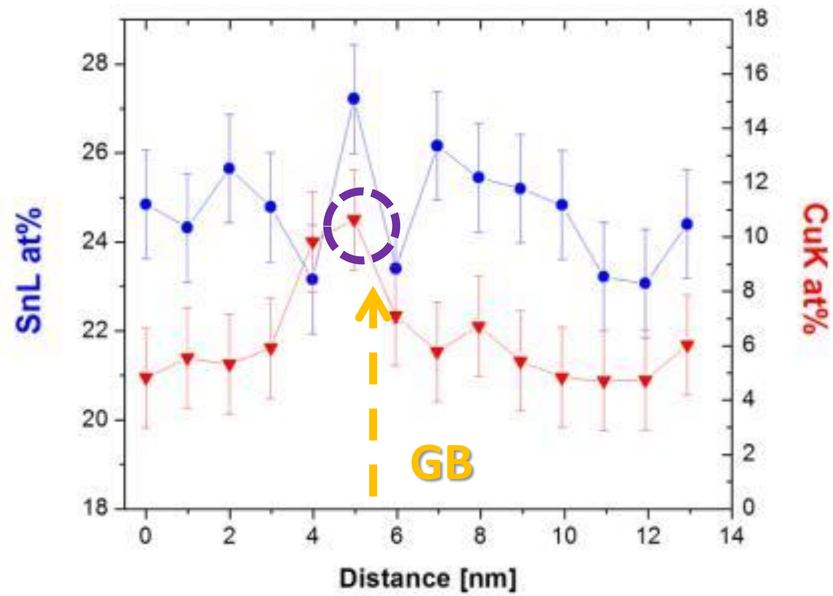


EDS Line scanning

Bright contrast: Ti content at GB

Dark contrast: Cu content at GB





Significant variation is seen in superconducting properties between the 3 RRP® strand types

Doping type	$T_{c,Onset}$ [K]	$T_{c,peak}$ [K]	ΔT_c, K FWHM of $f(T_c)$ peak	ΔT_c, K 10-90% of $1-F(T_{c,Nb})$	$f(T_{c,peak})$	% Nb	RRR *	Volume superfluid at 16T, 2K	H_k * Tesla	$J_c(12T)$ * A/mm^2	$F_{p,max}$ * GN/m^3
7.5wt% Ta	~18.4	17.37	1.50	3.51	0.40	8.7-10	251	38%	22.66	2712	57.6
7.5wt% Ta + 0.3wt% Ti	17.9	16.68	1.87	3.14	0.43	6.8-8.3	432	45%	24.75	2622	49.1
2a% Ti	18.1	17.25	1.42	2.83	0.50	8.1-8.9	369	38%	23.75	2872	56.7

Measurement by Dr. C Tarantini

- **Ti** doping show the highest J_c and pinning force, but **Ta** show the highest T_c.
- **Ta** + **Ti** co-doping shows the lowest T_c, but it has a larger superconducting volume fraction and H_k.

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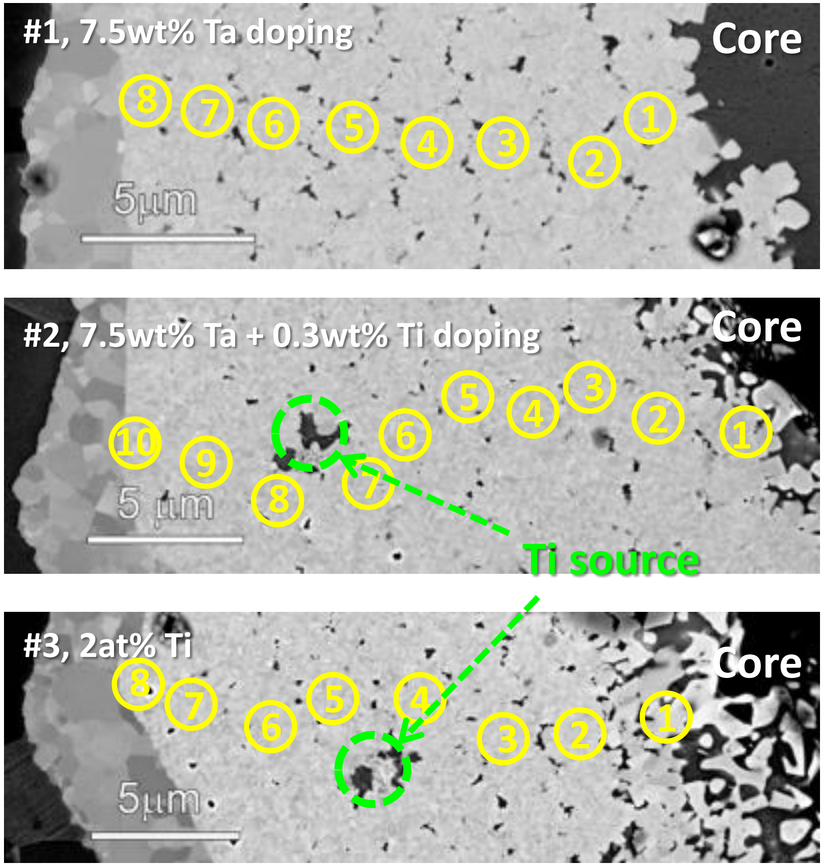
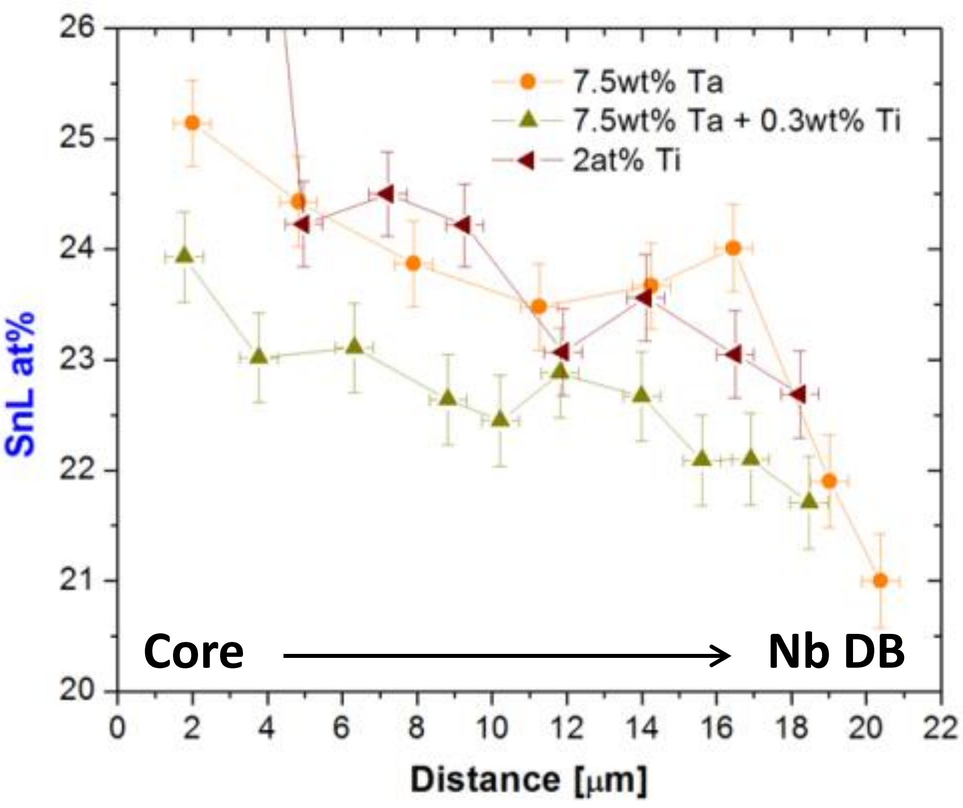
Ta + Ti co-doped strand has lower Sn content and greater gradient while Ta-doped strand is closer to A15 stoichiometry





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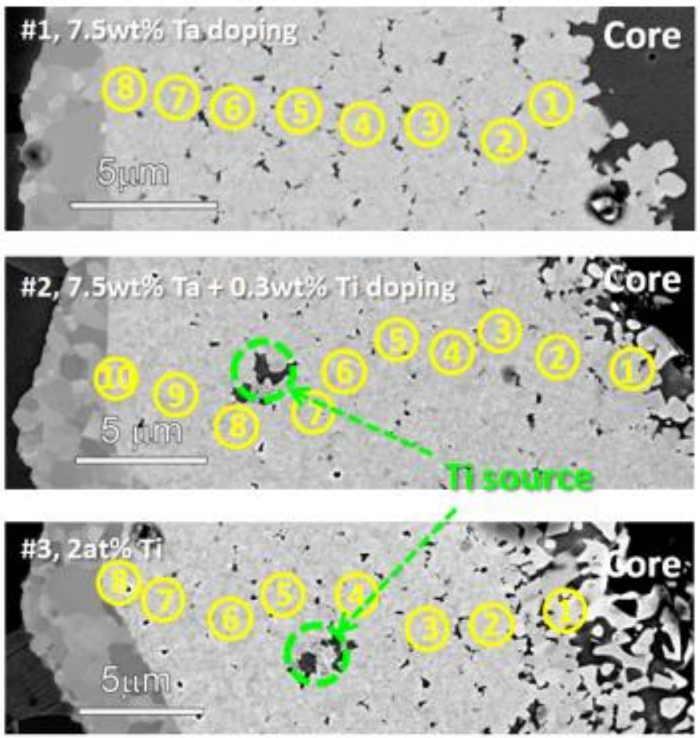
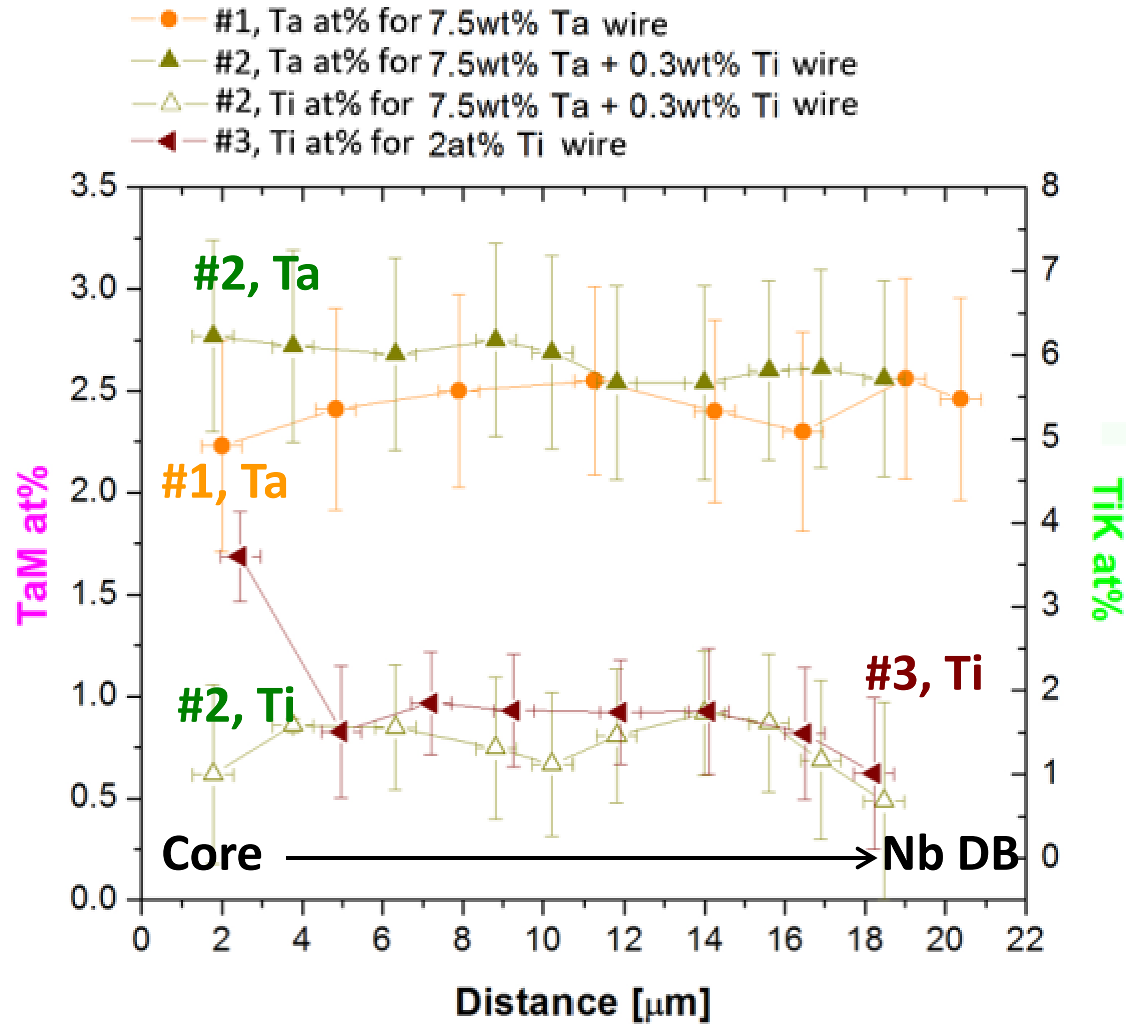
Ta + Ti co-doping method seems to oversaturate Ta in A15 phase compared to single doping method





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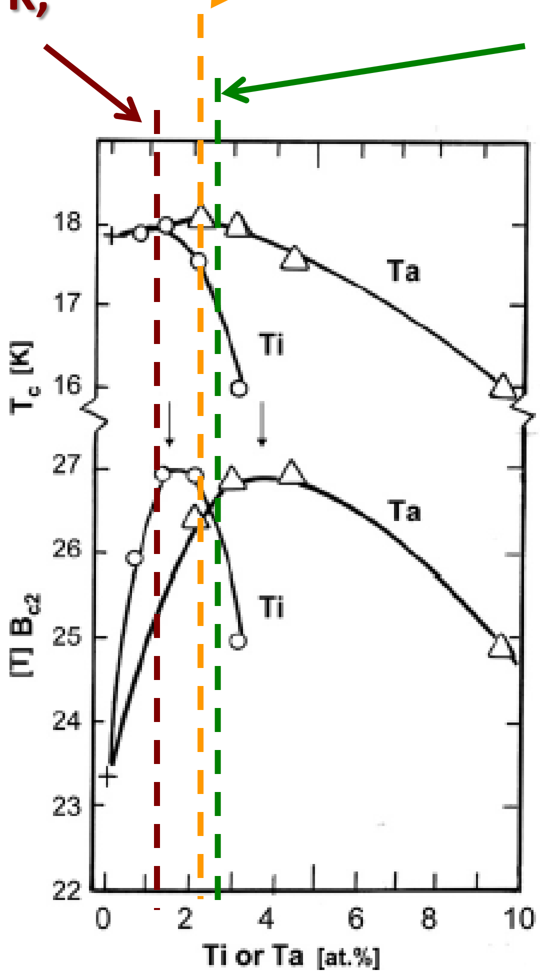
#3, Sn ≈ 23.77 at%, Ti ≈ 1.59 at%, $T_{c,\ onset}$ = 18.1 K, H_k = 23.75 T

#1, Sn ≈ 24.1 at%, Ta ≈ 2.43 at%
$T_{c,\ onset}$ = 18.4 K, H_k = 22.66 T

#2, Sn ≈ 22.77 at%, Ta ≈ 2.65 at%,
Ti ≈ 1.39 at% $T_{c,\ onset}$ = 17.9 K, H_k = 24.75 T

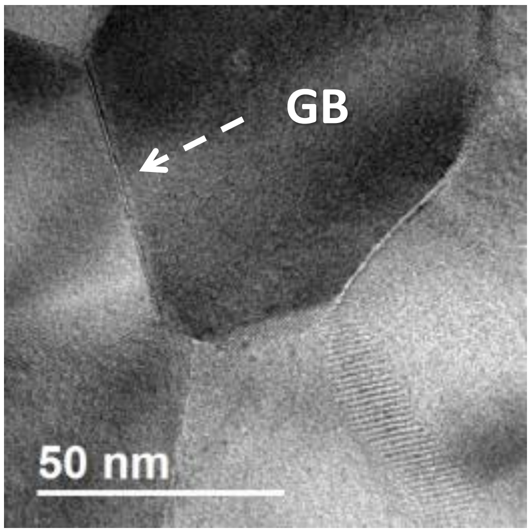


M. Suenaga, et al, JAP 59, 840, (1986)

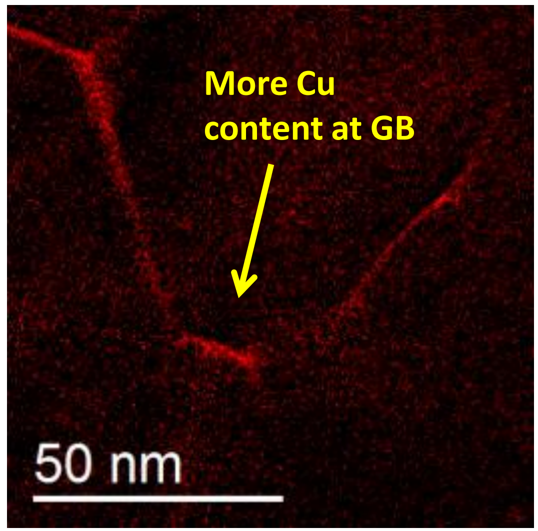
μ-scale composition analysis with FESEM + EDS could explain T_c properties of these three differently doped strands, but variation in J_c, H_{c2}, and $\varepsilon_{irr,0}$ should be addressed by atomic scale analytical microscopy

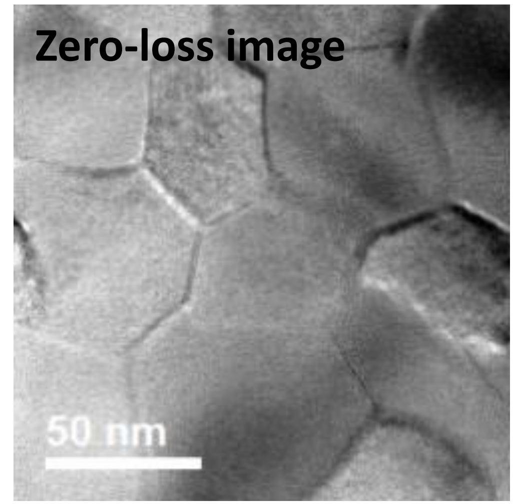
Ta-doped RRP Strand: EFTEM shows only Cu segregations at GBs of Nb_3Sn

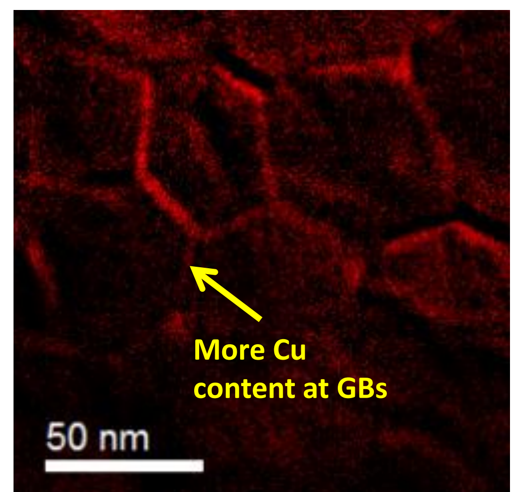
Zero-loss image



Cu: 920-930 eV







Sample type B, #1: 7.5wt% Ta, 640°C/48hrs

No observable Ta GB segregation

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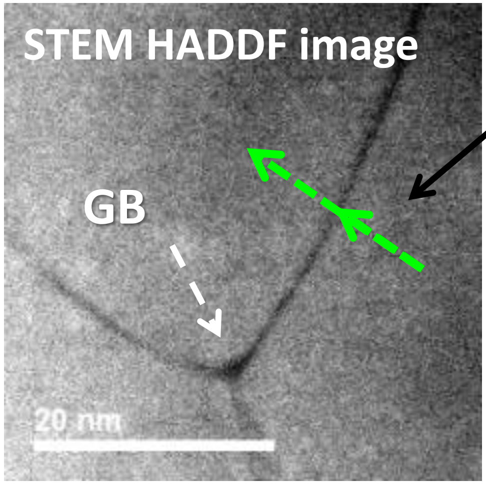
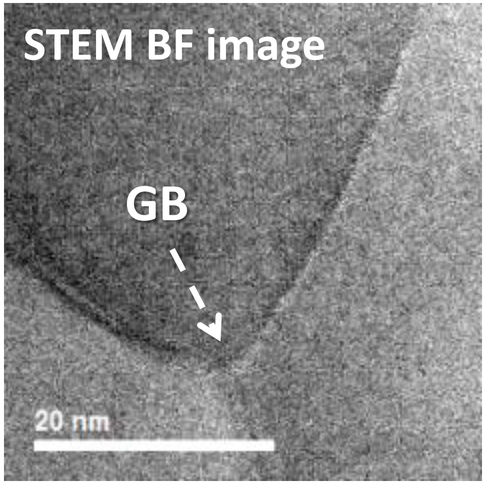
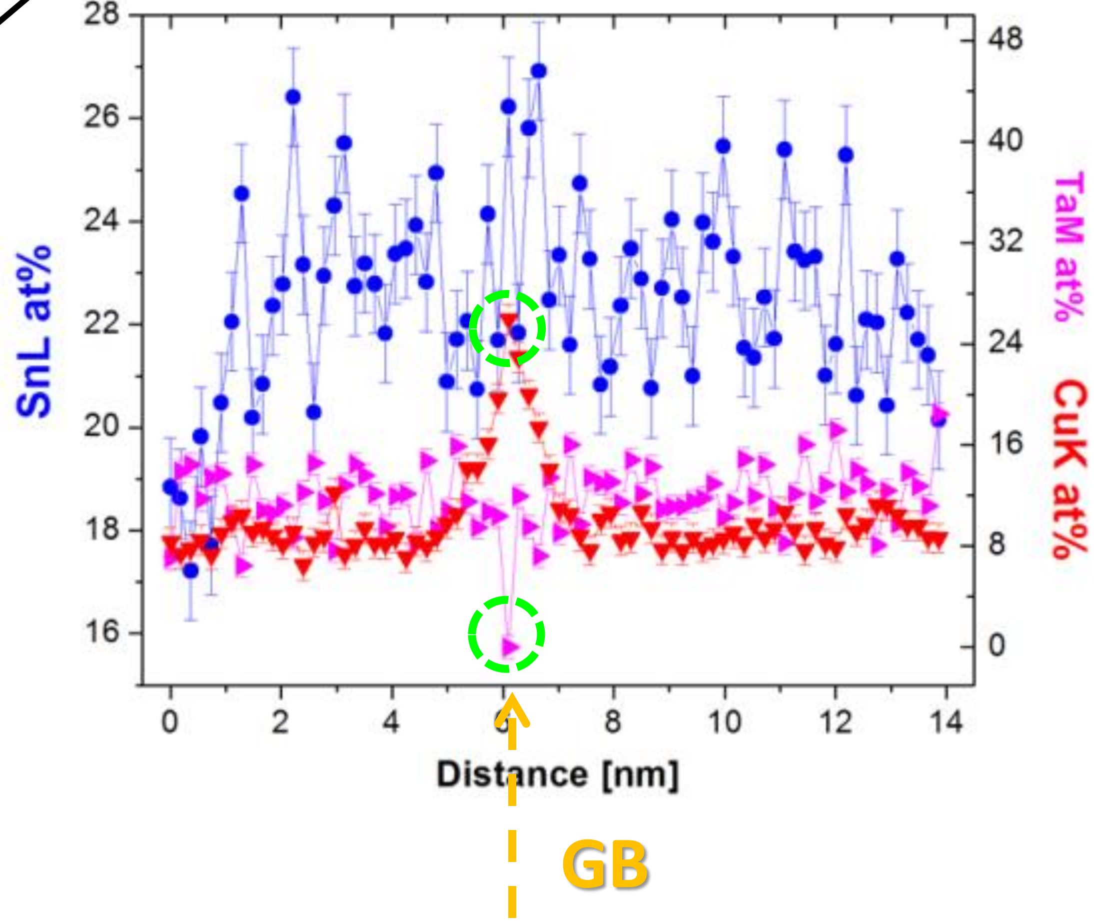
Ta-doped RRP® Strand: STEM-EDS shows GB Cu segregation but no "Ta" segregation





EDS Line scanning



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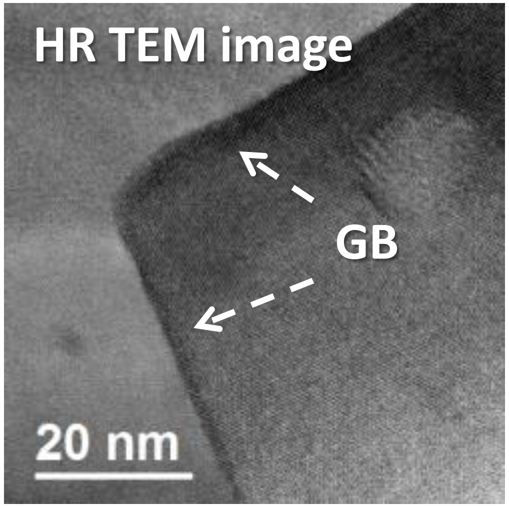
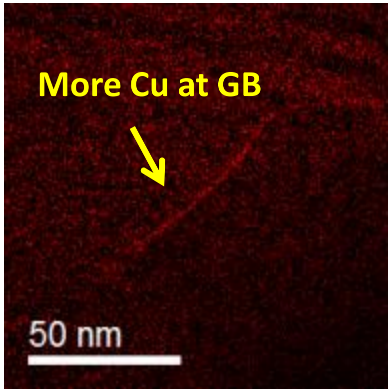
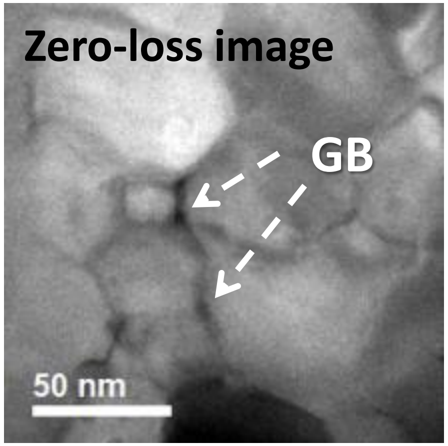
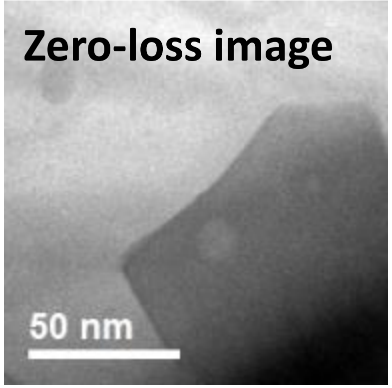
Ti-doped RRP® Strand: EFTEM shows extensive Ti and Cu segregation at A15 GBs



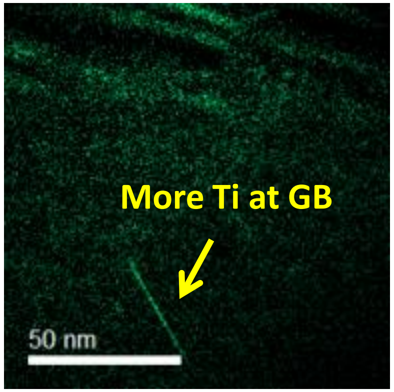
Cu: 920-930 eV



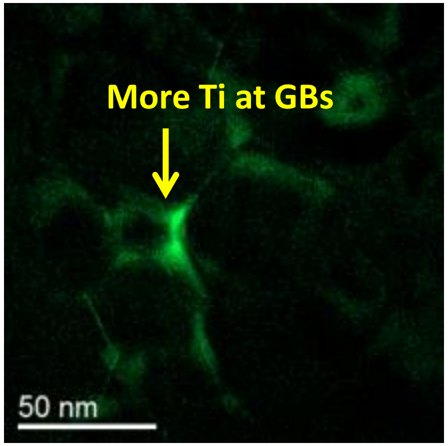




Ti: 450-460 eV



Ti: 450-460 eV



Sample type B, #3: 2at% Ti, 640°C/48hrs

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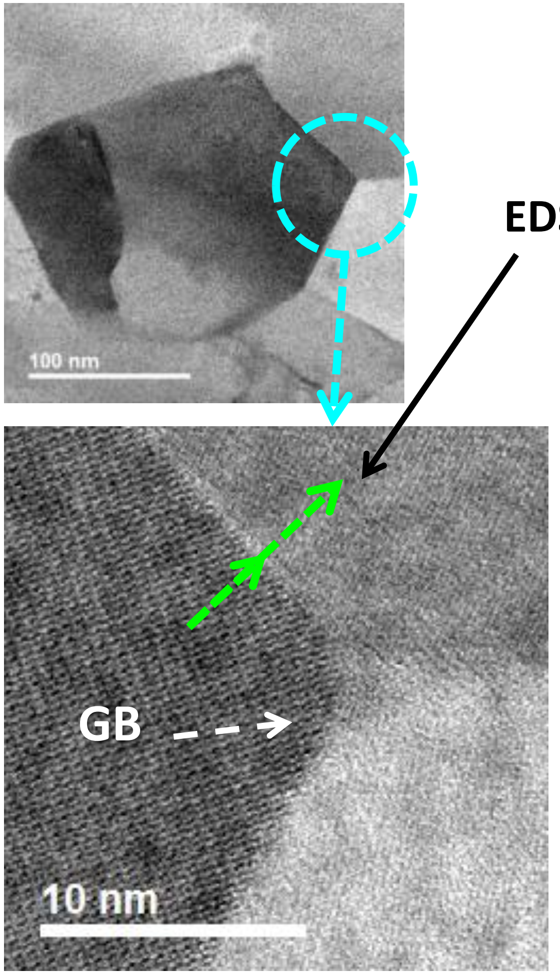
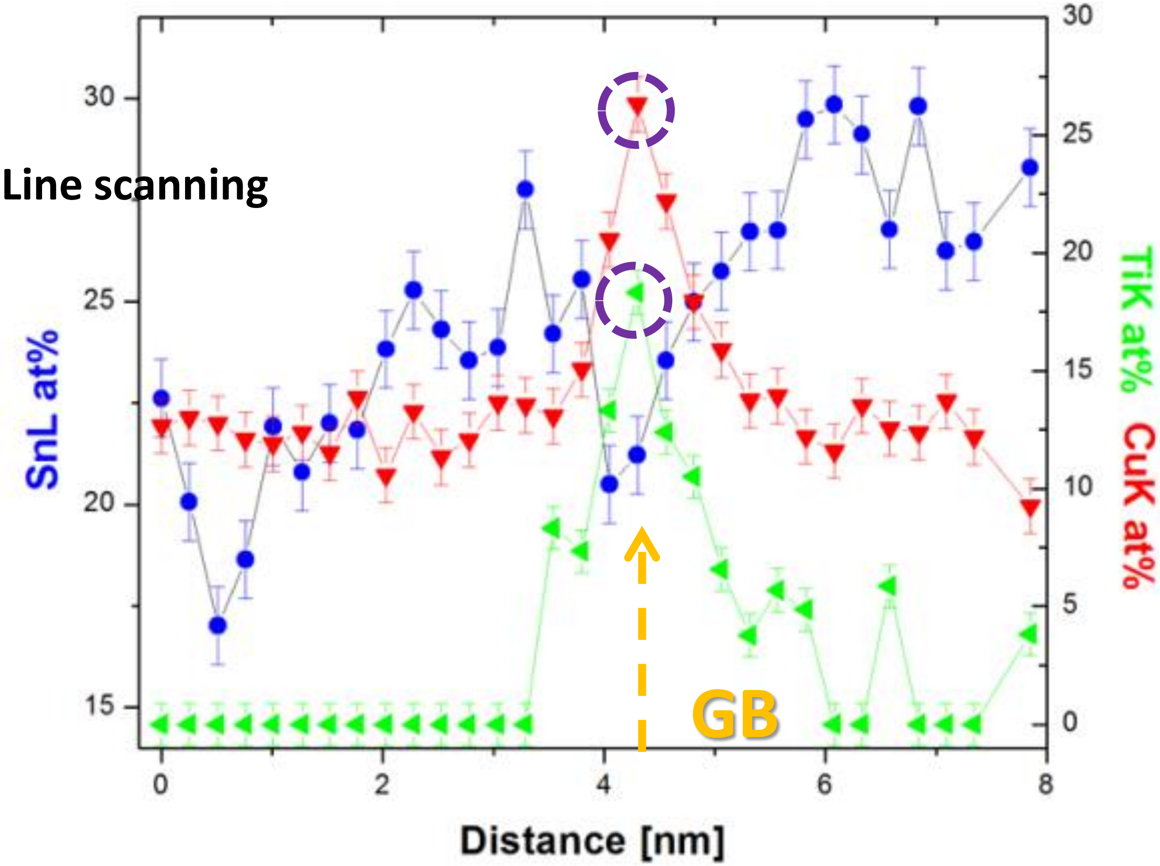
Ti-doped RRP® Strand: STEM-EDS shows Ti and Cu segregation at A15 GBs

STEM BF image



EDS Line scanning



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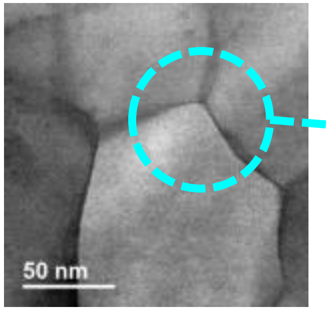
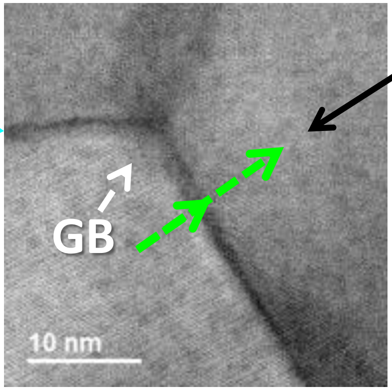
Nb is poor at A15 GB, but Sn does not change across GB

STEM BF image

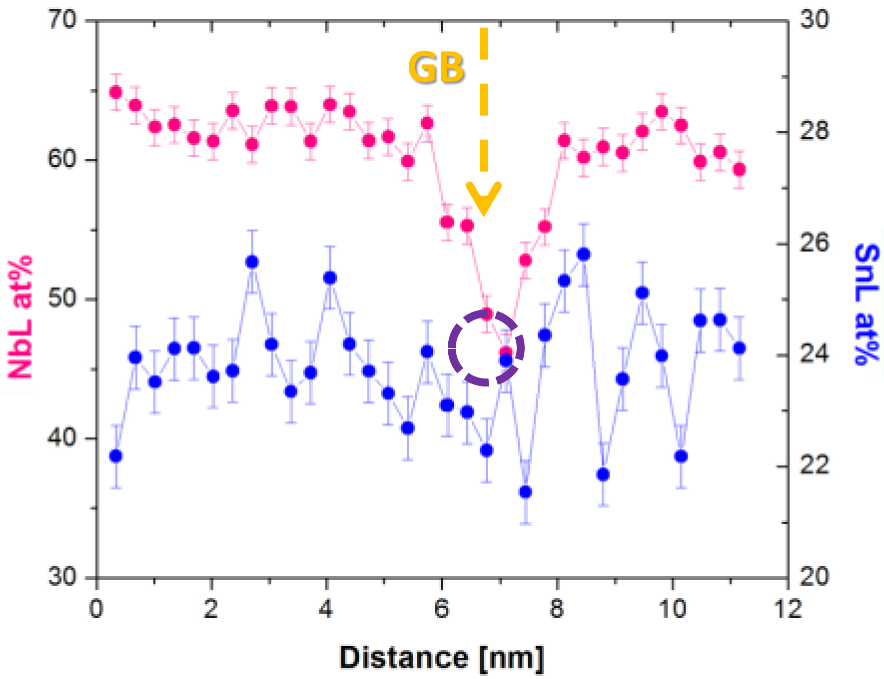


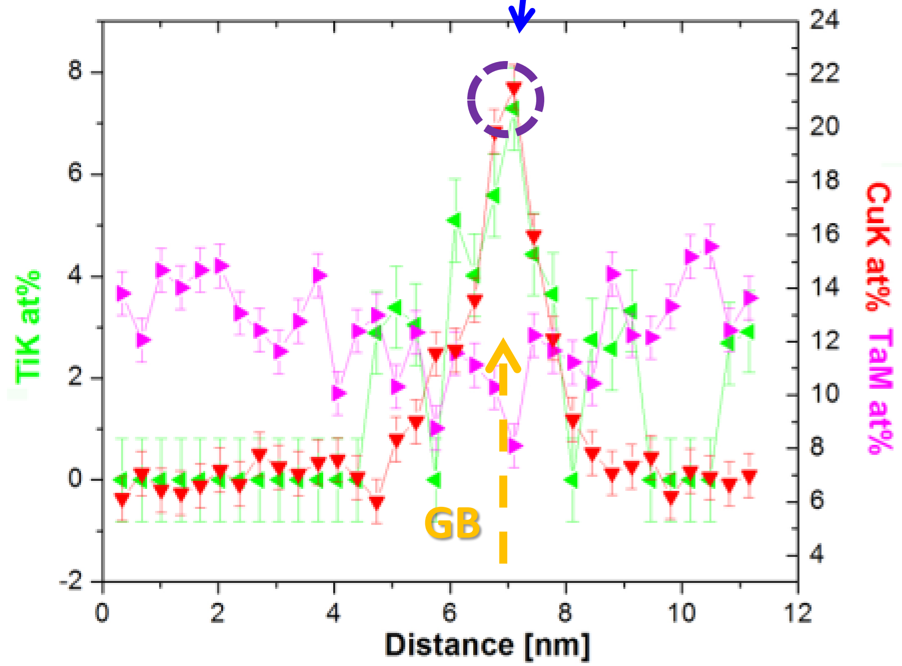


EDS Line scanning

Ta + Ti doped RRP® strand:
7.5w t% Ta + 0.3wt% Ti

Ti and Cu segregation at the GB





Summary

Strand Type	Doping method	$\varepsilon_{irr,0}$ (%) Avg. 0.1 mV/cm	J_c(12T) * A/mm²	Compositions in A15 (at%) (Avg)			GB segregation
				Sn	Ti	Ta	
ITER	Nb-Ti rod	**0.21**	-	22.05	1.70		**Ti**, **Cu**
RRP (54/61)	7.5wt% **Ta**	0.04	2712	**24.1**		2.43	**Only Cu**
RRP (54/61)	7.5wt% **Ta** + 0.3wt% **Ti**	0.06	2622	**22.77**	1.39	2.65	**Ti**, **Cu**
RRP (54/61)	2at% **Ti**	**0.24**	**2872**	23.77	1.59		**Ti**, **Cu**

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Conclusion 1

- Solid A15 phase identification with FE-SEM+EDS can properly determine the effect of doping on SC properties of Nb_3Sn strand.
  - Optimized Ta doping can enhance T_c compared with Ti.
  - Ti doping may reduce Sn content in A15 phase; it may be due to Ti replacement on Sn site.
- However, GBs effect of alloyed-Nb_3Sn strand on wire properties should be accomplished with atomic resolution analytical microscopy.

Conclusion 2

- Grain boundaries are both the primary flux-pinning centers and locations of mechanical weakness in Nb_3Sn strands
  - We have known for many years (e.g. Suenaga Auger studies) that the global GB composition changes with doping.
  - But we do not know it there are the variations with position, heat treatment, and architecture.
- Recent Atom probe measurements (MJR Sandim SuST *2013*) and in this study a new generation of high-resolution analytical TEM/STEM combined with new sample Prep techniques now make it possible to determine grain boundary compositions in a wide variety of materials.
  - We can now start to answer these crucial questions. In this study we find these new results:
    - Ti and Cu sometimes alternatively segregate at GBs in RRP® and ITER strand.
    - Ti GB segregation levels vary significantly from grain to grain in RRP® and ITER strand (Ti doped by distributed Nb-47T rods).
    - However, Ta does not deposit at the GBs of A15.