IEEE-CSC & ESAS SUPERCONDUCTIVITY NEWS FORUM (global edition), March 2023.
Presentation given at Applied Superconductivity Conference, Honolulu, HI, USA, October 2022.

Formation and Growth of Oxide Nanoparticles During Nb-Sn Diffusion and Implications for Flux Pinning and Critical Current in APC Nb_3Sn

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Electron microscopy was performed at the Center for Electron Microscopy and Analysis (CEMAS), Ohio State University, USA.

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Motivation

- Internally oxidized Nb_3Sn forms nano-oxide pins (refines grains and pins flux)
  - Shown to increase J_c and shift B_{peak} to higher field – crucial for high-field magnets
- But precise formation mechanism is not fully understood
  - Do the nanoparticles form at the same time as Nb_3Sn, or by precipitation?
  - What is the size distribution of the particles?
  - How can the particles be controlled, e.g. by change of HT temp?
- Evidence can be found in literature, and through careful microscopy

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Hypothesis in Four Parts

1. O & Zr exist in solid solution in the Nb alloy
2. The solubility of O & Zr is much lower in Nb_3Sn than in the Nb alloy
   - Low solubility causes high concentration of O & Zr ahead of Nb_3Sn/Nb interface
3. High O & Zr concentration causes nucleation of ZrO_2 on Nb_3Sn side of interface
4. Precipitates grow via O & Zr transport through Nb_3Sn
   - Either in solution in Nb_3Sn, or via defect structures

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Approach

- Literature Review
  - Some parts of the story are already known, but scattered across the literature
- Microscopy
  - Measure change of particle size with position/HT time
  - Variation of particle size with temperature
- Analytical Model (critical size, growth)
- Numerical Model (Phase field, modelling nucleation)

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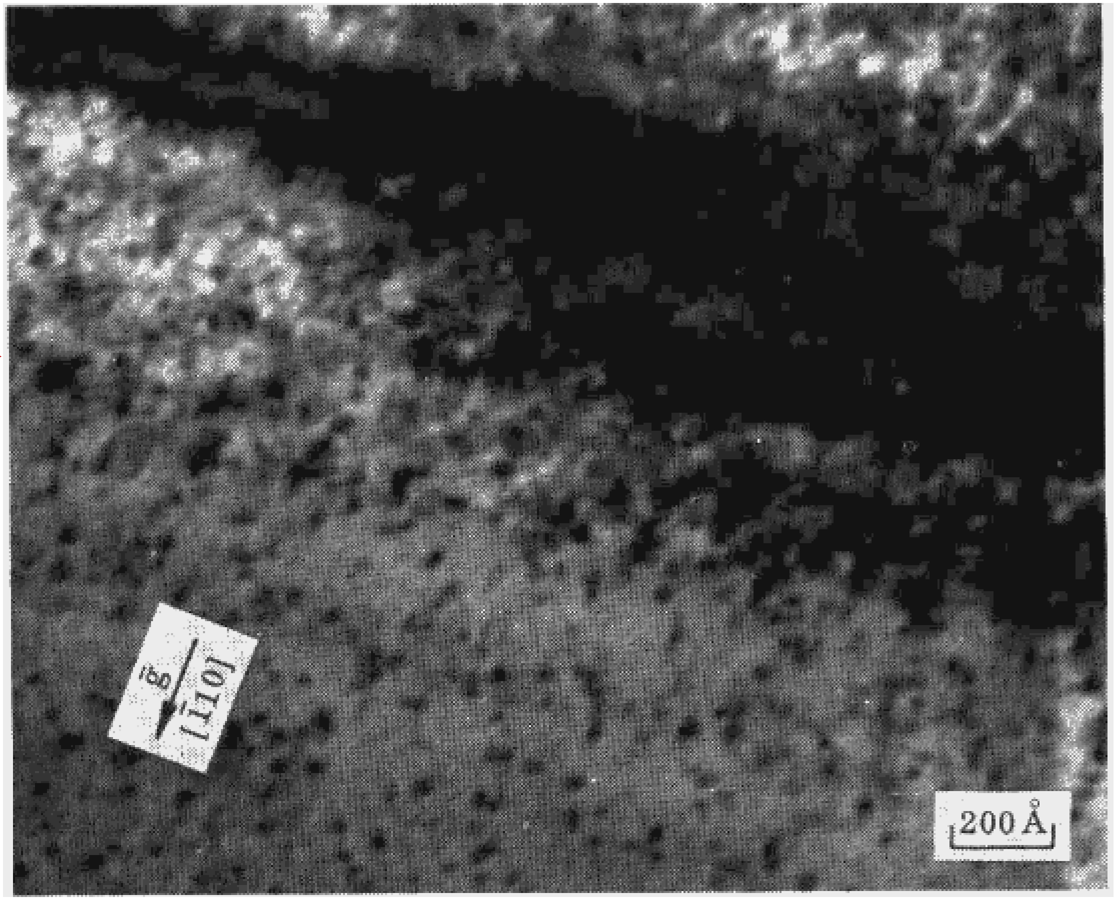
H1. Oxygen & Zr exist in solution in Nb

- Nb alloy can take up to ~ 3% O as BCC-Nb + ZrO_2, according to phase diagram
- Oxidized Nb-1Zr has been seen to have ZrO_2 ~1-3.5 nm size (800°C/240h) [1]
  - At 700°C/0h, ZrO_2 clusters, if present, should be much smaller
- Therefore, whether as solid solution or Zr-O clusters, Zr & O are dispersed



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3. O & Zr concentration at interface causes nucleation of ZrO_2
4. Precipitates grow via O & Zr transport through Nb_3Sn

[1] Bonesteel et al., "Mechanical Properties and Structure of Internally Oxidized Niobium-1% Zirconium Alloy," *Proc. of the Int. Conf. on the Strength of Metals and Alloys*, vol. 9, p. 597-602, 1968.

H2. Lower O & Zr solubility in Nb_3Sn

- Solubility of O in Nb-1Zr ~2.5-3%
  - increases with temperature [from Thermo-Calc]
- In Nb_3Sn, data scarce, but:
  - ~0.3–0.4% O has been found in Nb_3Sn [1]
  - ~0.3% Zr in Nb_3Sn also [2]

[1] D. B. Smathers & D. C. Larbalestier. "An Auger electron spectroscopy study of bronze route niobium-tin diffusion layers." In *Filamentary A15 Superconductors,* pp. 143-154 (1980).
[2] T. Takeuchi, et al., "Effects of the IVa element addition on the composite-processed superconducting Nb_3Sn," *Cryogenics*, vol. 21, no. 10, pp. 585–590, 1981.

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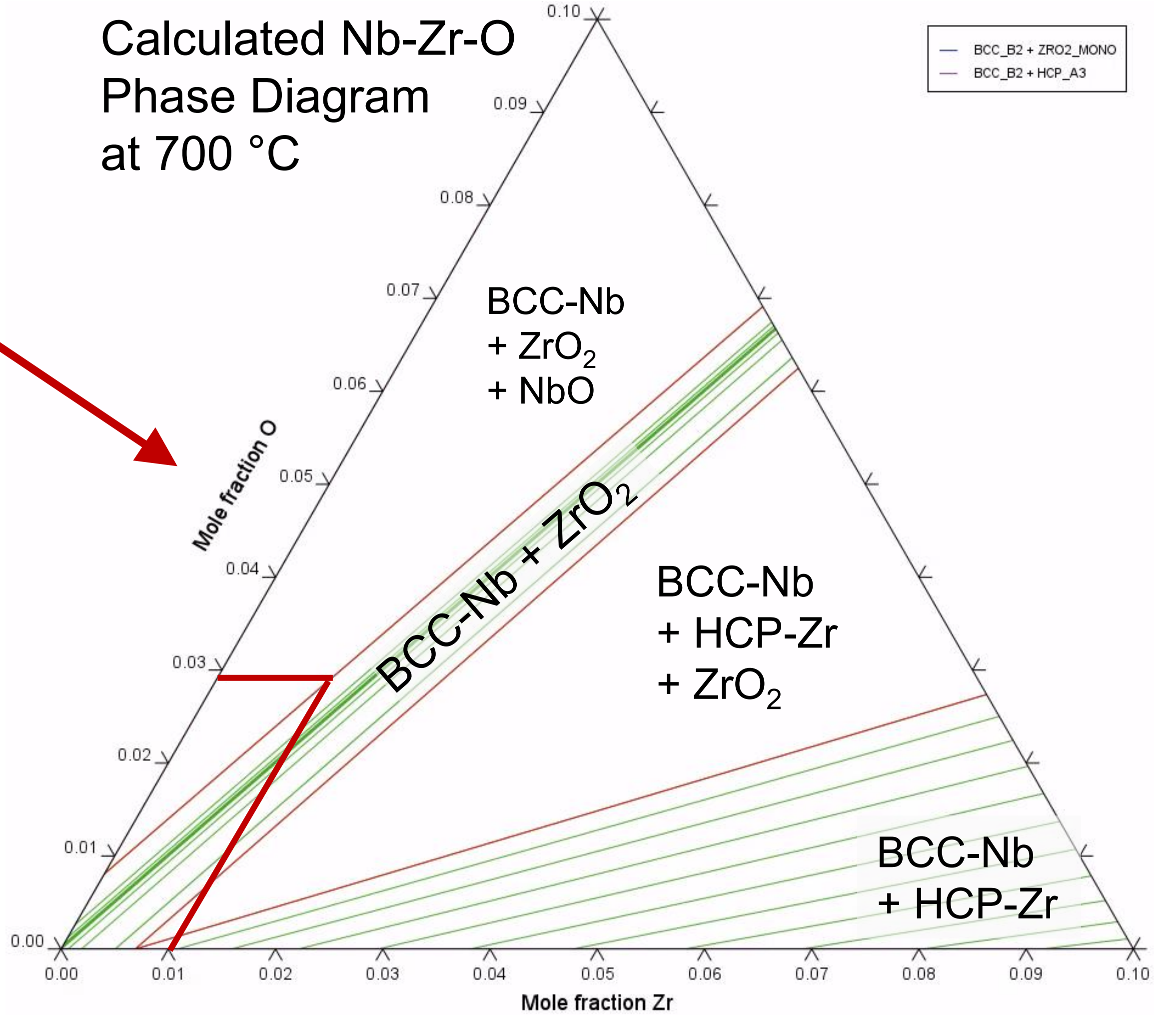
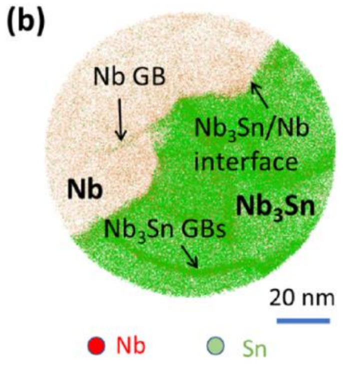
Calculated Nb-Zr-O Phase Diagram at 700 °C



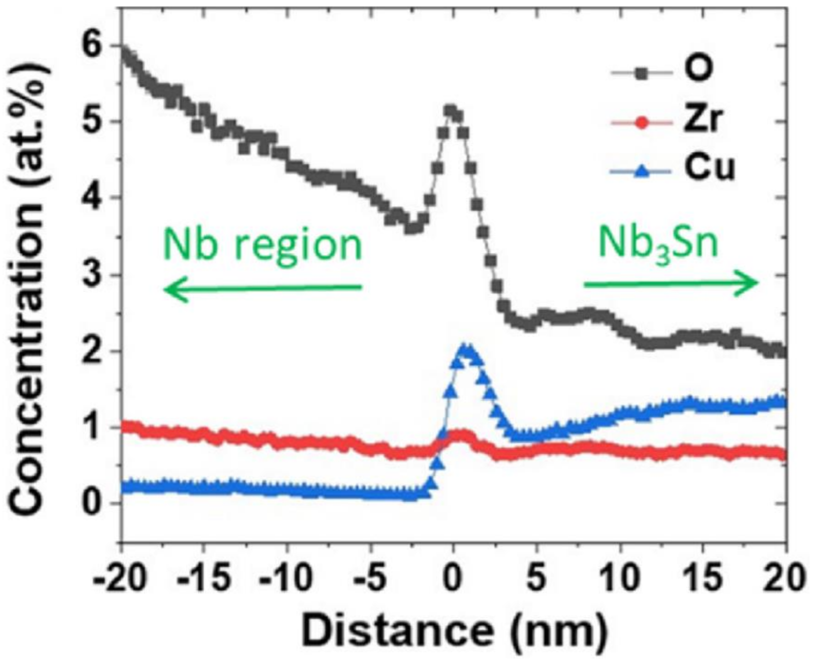
Thanks to Shalini Roy Koneru at OSU for generating the phase diagram

H3. Nucleation at interface

- As Nb_3Sn forms, Zr & especially O pushed ahead of Nb_3Sn/Nb interface [1]
- High Zr & O concentration drives Zr oxide nucleation
- Oxide particles form on A15 side of interface, coherent with surrounding Nb_3Sn



Atom-probe results from Jae-Yel Lee



[1] X. Xu, et al., "Persistent compositions of non-stoichiometric compounds with low bulk diffusivity: A theory and application to Nb_3Sn superconductors," *J. Alloys Compounds*, Art. no. 156182, 2020.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Persistent compositions of non-stoichiometric compounds with low bulk diffusivity: A theory and application to Nb_3Sn superconductors

X. Xu [a, *], M.D. Sumption [b], J. Lee [c], J. Rochester [b], X. Peng [d]

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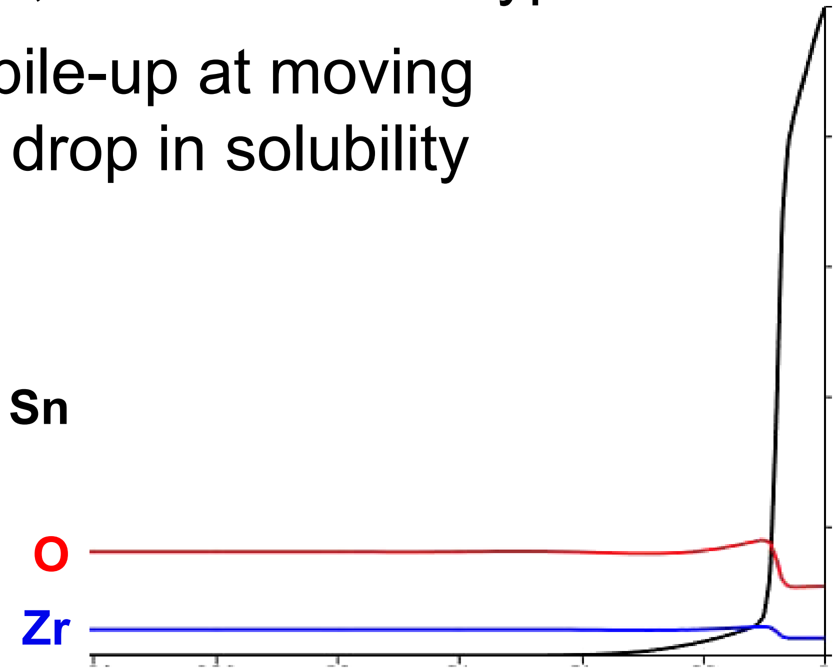
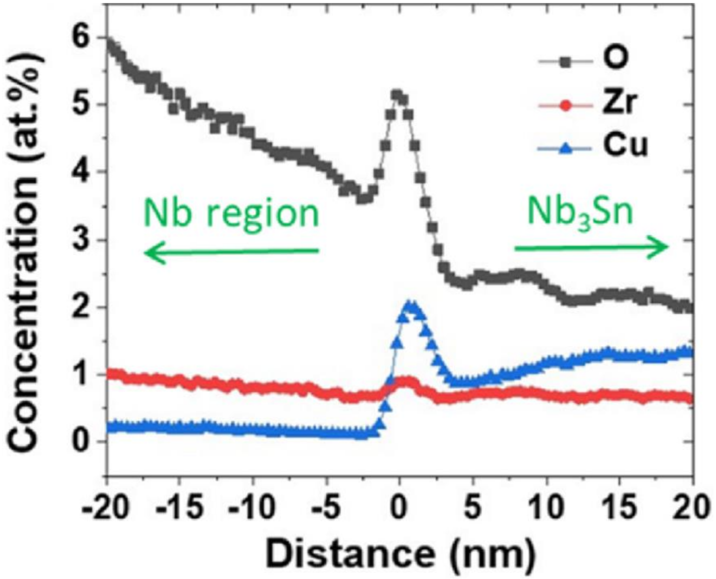
Model of moving interface: diffusion

- Developing phase field model to capture thermodynamics + kinetics
- Not all aspects included yet, but illustrates hypothesis
- Model reproduces Zr & O pile-up at moving Nb_3Sn/Nb interface due to drop in solubility



Phase field model



Atom probe results from J. Lee [1]

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Model of moving interface: precipitate evolution

- Model also illustrates hypothesis of oxide evolution following motion of interface
- Nucleation simulated qualitatively using Langevin noise
- Once fully implemented:
  - should be able to capture nucleation and coarsening
  - corroborate TEM & other observations of nanostructure

Qualitative phase field model showing order parameter of ZrO_2 over time

Classical Nucleation Theory

- Simple model for understanding nucleation at interface
- Energy penalty to nucleate a particle – energy reduction favors nucleation:
  - Simple case, *homogeneous* nucleation of spherical particle:

$$\Delta G = -\frac{4}{3}\pi r^3(\Delta g_v - \Delta g_s) + 4\pi r^2\gamma$$

    Energy change = (–) Volume free energy of ppt + strain energy + interfacial energy

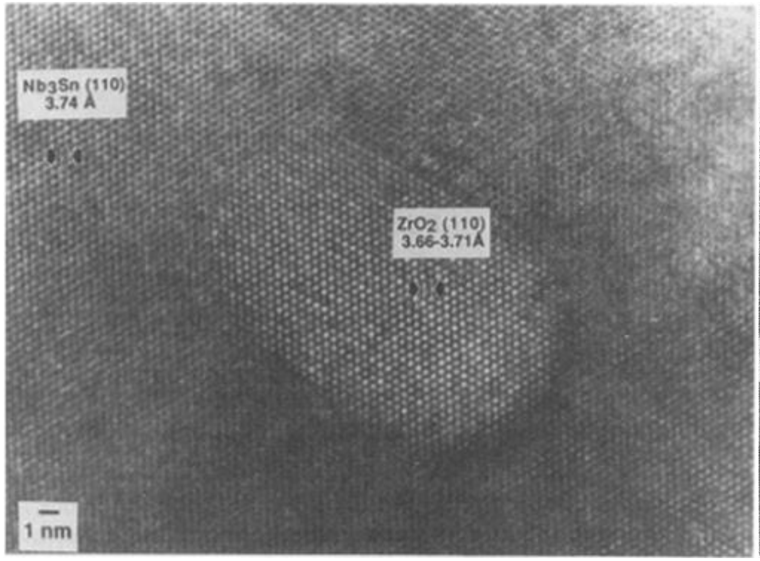
  - Our case, *heterogeneous* nucleation:

    less barrier to formation if an interface is already present

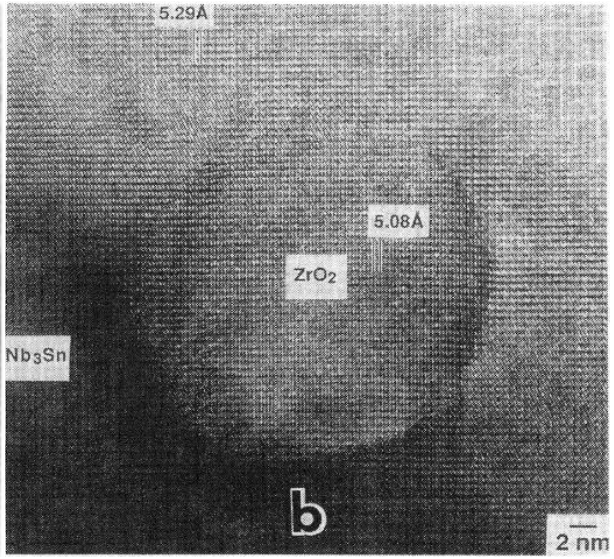
Contributions to nucleation energy

- Volume free energy
  - Changes linearly with temperature
- Strain energy
  - From misfit of crystal structures
- Interfacial energy
  - Less dependent on temperature
  - TEM evidence shows ZrO_2/Nb_3Sn interface is coherent [1–3]
    → low interfacial energy
- Critical radius: size at which reduction in volume energy overcomes interfacial energy

$$r^* = \frac{2\gamma}{(\Delta G_v - \Delta G_s)}$$



Rumaner 1994 [1]



Hall 1990 [2]

[1] L. E. Rumaner, et al., "The role of oxygen and zirconium in the formation and growth of Nb_3Sn grains," *MMTA*, vol. 25, no. 1, pp. 213–219, 1994.
[2] E. L. Hall, et al., "Interface Structure, Grain Morphology, and Kinetics of Growth of the Superconducting Intermetallic Compound Nb_3Sn Doped with ZrO_2 and Copper," *MRS Online Proceedings Library Archive*, vol. 205, ed 1990.
[3] Jae-Yel Lee, unpublished work.

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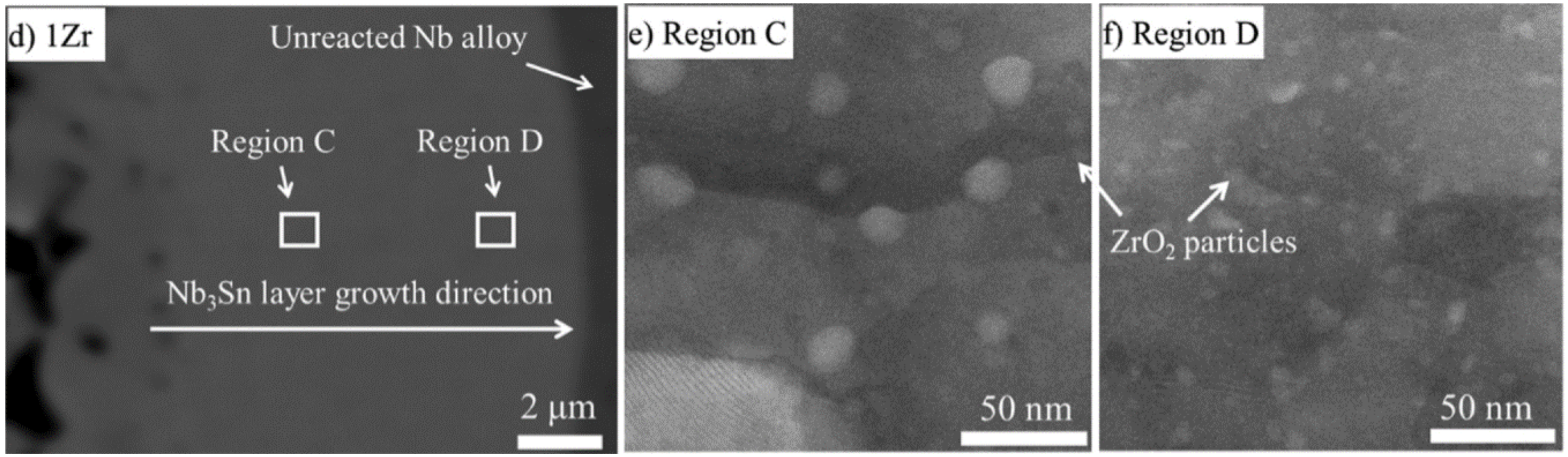
H4. Growth of nanoparticles (time/distance)

- Particle size has been observed to vary through the A15 layer
  - First-formed oxides are larger than those nearest the reaction front
- Very broad particle size distribution, larger particles perhaps at GBs
- Can be explained by transport via lattice and/or defect structures



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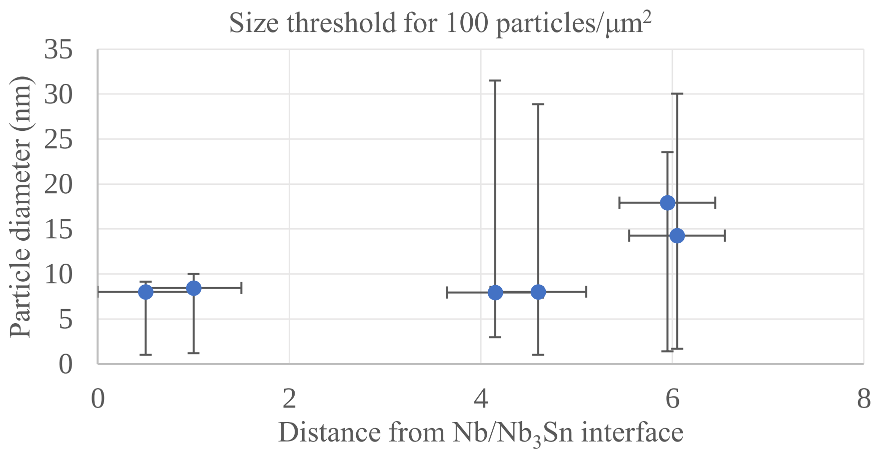
[1] X. Xu *et al.*, "The strong influence of Ti, Zr, Hf solutes and their oxidation on microstructure and performance of Nb_3Sn superconductors," *J. Alloys Compounds*, vol. 857, Art. no. 158270, 2021.

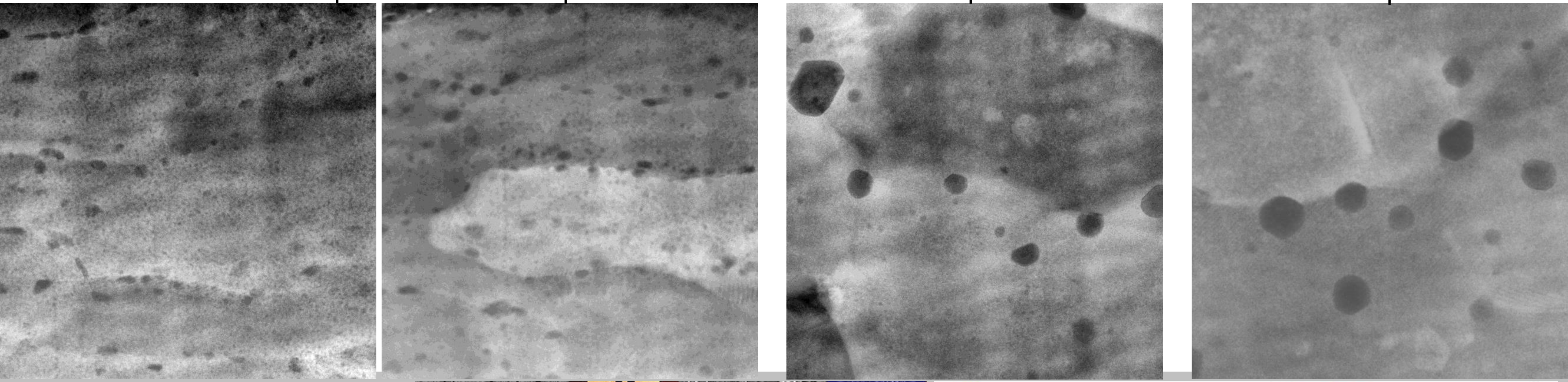
New TEM imaging shows coarsening of particles

- Shows more clearly fine dispersion of particles near interface
  - 1-2 nm with fewer large particles up to ~10 nm
- Coarsen into smaller number of larger particles up to ~30 nm
  - Though some <3 nm particles still observed far from interface
- Very wide particle size distribution overall

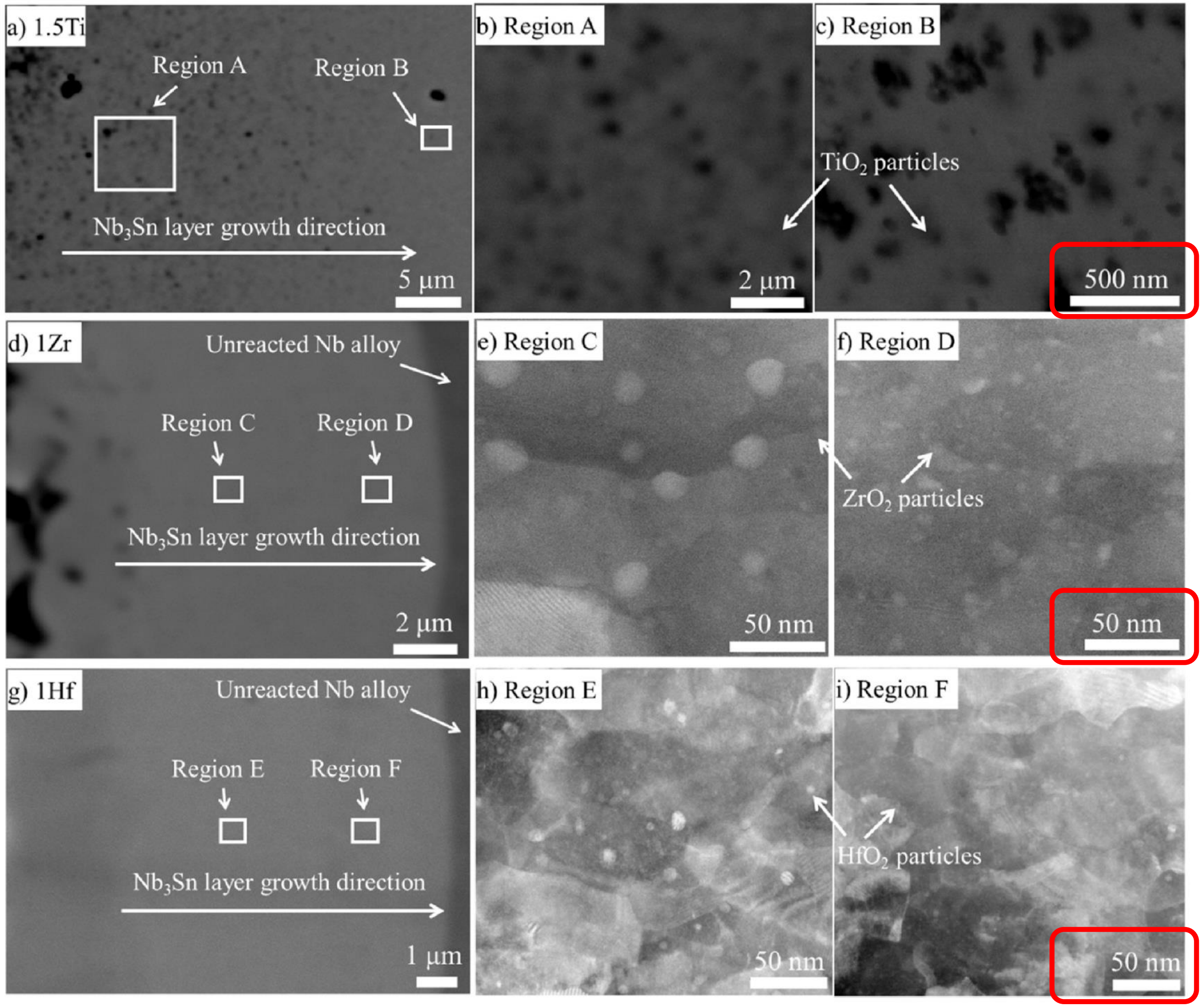


TEM images (200 nm x 200 nm), for Zr+O wire made by Hyper Tech, heat treated at Fermilab 720°C/32h, processed in ImageJ with gaussian blur and "Enhance Local Contrast" function

Distance from interface: 0.5 μm 1 μm 4 μm 6 μm



Starting size of precipitate dictated by thermodynamics



$$\Delta G = \frac{4}{3}\pi r^3(\Delta g_v - \Delta g_s) + 4\pi r^2 \gamma$$

- Applies to not just ZrO_2 but also HfO_2 (and TiO_2)
- Different oxide precipitate materials have different Gibbs energies (and precipitate sizes)
- Larger reduction in Gibbs energy → smaller particles can nucleate
- Can different temperatures also modify size?

[1] X. Xu *et al.*, "The strong influence of Ti, Zr, Hf solutes and their oxidation on microstructure and performance of Nb_3Sn superconductors," *J. Alloys Compounds*, vol. 857, Art. no. 158270, 2021.

Why does this matter? Pin size

- Fluxon size = 2x coherence length ξ [1]
  - $H_{c2}(T) = \frac{\Phi_0}{2\pi[\xi(T)]^2}$ H_{c2} of 26-28 T @ 4.2 K → ξ = 3.4–3.6 nm
- Optimal point pinning *per pin* will occur for particles ~ 7 nm
  - Too small, decreased pinning efficacy
  - Too large, missed opportunity to make more pins
    (though large particle can pin more than one flux line [2])

[1] M. Tinkham, *Introduction to Superconductivity*, 2nd Edition, 1996.
[2] A. E. Koshelev, I. A. Sadovskyy, C. L. Phillips, and A. Glatz, "Optimization of vortex pinning by nanoparticles using simulations of the time-dependent Ginzburg-Landau model," *Phys. Rev. B*, vol. 93, no. 6, p. 060508, 2016.

Why does this matter? Pin spacing

- At 16 T, flux line spacing ~12 nm, optimum pin array would match
  - Calculated spacing on order of ~10 [1] to 40 nm [2], higher if we only count larger particles
  - In an ideal case, for 1% Zr in Nb, if all Zr converted to 7 nm ZrO_2, spacing ~ 33 nm [3]
  - For a given dopant level, smaller pins means more pins, smaller spacing between
- Can tailor wire recipe and heat treatment to target optimum point pinning
  - Choice of oxide material
  - Choice of heat treatment temperature

[1] Jae-Yel Lee, unpublished work.
[2] M. Ortino, "Flux pinning in Nb_3Sn containing artificial pinning centres: a systematic study," Thesis, TU Wien, Vienna, Austria, 2022.
[3] X. Xu *et al.*, "The strong influence of Ti, Zr, Hf solutes and their oxidation on microstructure and performance of Nb_3Sn superconductors," *J. Alloys Compounds*, vol. 857, Art. no. 158270, 2021.

Conclusion

- Multi-part hypothesis confirmed

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- Further work can suggest paths to conductor optimization:
  - Proper material
  - Choice of heat treatment
  - Control size and distribution of precipitates
  - Optimize pinning and J_c

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