Formation and Growth of Oxide Nanoparticles During Nb-Sn Diffusion and Implications for Flux Pinning and Critical Current in APC Nb₃Sn

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

• Internally oxidized Nb$_3$Sn forms nano-oxide pins (refines grains and pins flux)
  – Shown to increase $J_c$ and shift $B_{\text{peak}}$ 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$_3$Sn, 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
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$_3$Sn than in the Nb alloy
   - Low solubility causes high concentration of O & Zr ahead of Nb$_3$Sn/Nb interface

3. High O & Zr concentration causes nucleation of ZrO$_2$ on Nb$_3$Sn side of interface

4. Precipitates grow via O & Zr transport through Nb$_3$Sn
   - Either in solution in Nb$_3$Sn, or via defect structures
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)
H1. Oxygen & Zr exist in solution in Nb

- Nb alloy can take up to ~ 3% O as BCC-Nb + ZrO₂, according to phase diagram
- Oxidized Nb-1Zr has been seen to have ZrO₂ ~1-3.5 nm size (800°C/240h) [1]
  - At 700°C/0h, ZrO₂ clusters, if present, should be much smaller
- Therefore, whether as solid solution or Zr-O clusters, Zr & O are dispersed

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H2. Lower O & Zr solubility in Nb₃Sn

- Solubility of O in Nb-1Zr ~2.5-3%
  - increases with temperature
  [from Thermo-Calc]
- In Nb₃Sn, data scarce, but:
  - ~0.3–0.4% O has been found in Nb₃Sn [1]
  - ~0.3% Zr in Nb₃Sn also [2]

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Thanks to Shalini Roy Koneru at OSU for generating the phase diagram.
H3. Nucleation at interface

- As Nb$_3$Sn forms, Zr & especially O pushed ahead of Nb$_3$Sn/Nb interface [1]
- High Zr & O concentration drives Zr oxide nucleation
- Oxide particles form on A15 side of interface, coherent with surrounding Nb$_3$Sn


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Atom-probe results from Jae-Yel Lee
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$_3$Sn/Nb interface due to drop in solubility

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
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$_3$Sn interface is coherent [1–3] → low interfacial energy
- Critical radius: size at which reduction in volume energy overcomes interfacial energy

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

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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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 $\rightarrow$ smaller particles can nucleate
- Can different temperatures also modify size?

Why does this matter? Pin size

- Fluxon size = 2x coherence length $\xi$ \[1\]
  - $H_{c2}(T) = \frac{\Phi_0}{2\pi[\xi(T)]^2} \quad H_{c2}$ of 26-28 T @ 4.2 K $\rightarrow \xi = 3.4–3.6$ nm

- Optimal point pinning per pin will occur for particles $\sim 7$ 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])

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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

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 $J_c$