Advances in Nanoscale Analysis of Hf doped Nb₃Sn wires using Atom Probe Tomography

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Requirement: High Performance Nb$_3$Sn for FCC

• Operational $J_c$ in Nb$_3$Sn superconductor: 1500 Amm$^{-2}$ and RRR > 150 at 16 T (4.2 K)
• Needs radical improvements in performance of Nb$_3$Sn filaments

Schematic of the FCC
www.home.cern/science/accelerators/future-circular-collider
Optimising the Superconducting Properties

• For high $J_C$ at 16 T the pinning force function will require both grain boundary and secondary point pinning

$$F_P = A_{GB} \left( \frac{H}{H_{IRR}} \right)^{0.5} \left( 1 - \frac{H}{H_{IRR}} \right)^2 + A_{PD} \left( \frac{H}{H_{IRR}} \right) \left( 1 - \frac{H}{H_{IRR}} \right)^2$$

• Grain boundaries and optimised point defects are on the scale of the coherence length (3-4 nm in Nb$_3$Sn)

• Nanostructural analysis is required to visualise grain boundaries, secondary phases and local chemistry changes on this scale
What is Atom Probe Tomography?

- 3-Dimensional characterisation technique
- High spatial and chemical resolution
- Sensitivity down to ppm

Animation adapted from Dr A. J. London

\[ \frac{m}{n} \approx 2eV \left( \frac{t_{\text{flight}}}{L} \right)^2 \]
Additions for Point Defects

- Addition of Group IVB elements Zr and Hf to produce oxide nanoparticles [1,2]
- Ta known addition to increase the upper critical field
- Obvious shift to point pinning function seen in Hf doped sample

![Graph of Nb-Ta4 sample](image)

![Graph of Nb-Ta4-Hf1 sample](image)

Sample studied in this work

Are nanoparticles present in the Nb$_3$Sn region?
Atom Probe Tips from Nb₃Sn layer

HfO₂ molecular (cluster) ions

Tip 1

Tip 2

Tip 3

Tip 3 Isoconcentration surface HfO²⁺

HfO²⁺ 1.5 ionic%

<table>
<thead>
<tr>
<th>Tip</th>
<th>Average HfO₂ Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.7</td>
</tr>
<tr>
<td>2</td>
<td>3.1</td>
</tr>
<tr>
<td>3</td>
<td>2.9</td>
</tr>
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</table>
• Cu is located at grain boundaries
• Additional isolated Cu regions are present within grains
Oxide Source

• **No oxygen** added to the alloy

• Are HfO$_2$ nanoparticles present within the Nb-Ta-Hf alloy before reaction?

![Pre-heat treatment](image1)

![Post-heat treatment](image2)

Nb-4Ta-1Hf
Pre-Heat Treatment Nb-Ta-Hf alloy: Hf distribution

There is no sign of HfO$_2$ clusters

Hf ions

Tip 4  20 nm  Tip 5  20 nm  Tip 6  20 nm

Nb-Ta$_4$-Hf$_1$
Post Heat Treatment Nb-Ta-Hf alloy

Now the unreacted regions of metallic alloy do contain HfO$_2$ nanoparticles.

Tip 7  20 nm  Tip 8  20 nm  Tip 9  20 nm
Oxygen content in pre-heat and post-treatment Nb-Ta-Hf alloy is very similar, with far lower oxygen in the Nb$_3$Sn layer which is confined to purely oxide clusters.

<table>
<thead>
<tr>
<th>Pre-heat treatment Nb alloy (Oxygen at%)</th>
<th>Post-heat treatment Nb alloy (Oxygen at%)</th>
<th>Nb$_3$Sn (Oxygen at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.59</td>
<td>3.66</td>
<td>0.49</td>
</tr>
<tr>
<td>1.95</td>
<td>3.61</td>
<td>0.87</td>
</tr>
<tr>
<td>3.83</td>
<td>1.36</td>
<td>0.16</td>
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</table>
We can also study the reaction process

Sn diffuses in → NbSn₂ → Nb₆Sn₅ → Nb₃Sn

550°C/100h and 670°C/100h
Residual $\text{Nb}_6\text{Sn}_5$

- $\text{Nb}_3\text{Sn}$ shown with the dark green surface
- The rest of the tip is $\text{Nb}_6\text{Sn}_5$
- HfO$_2$ clusters seen in $\text{Nb}_6\text{Sn}_5$ as well as the $\text{Nb}_6\text{Sn}_5$

TEM image of $\text{Nb}_3\text{Sn} - \text{Nb}_6\text{Sn}_5$

S. Balachandran et al. 2019
Supercond. Sci. Technol. 32 044006
Cu preferentially partitioned into the Nb\textsubscript{6}Sn\textsubscript{5}

<table>
<thead>
<tr>
<th>Location</th>
<th>(\text{Nb}_3\text{Sn} ) Copper at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.47</td>
</tr>
<tr>
<td>2</td>
<td>0.39</td>
</tr>
<tr>
<td>3</td>
<td>0.07</td>
</tr>
<tr>
<td>4</td>
<td>0.56</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Location</th>
<th>(\text{Nb}_6\text{Sn}_5 ) Copper at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.38</td>
</tr>
<tr>
<td>6</td>
<td>2.41</td>
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</table>


Presentation given at Applied Superconductivity Conference, Honolulu, HI, USA, October 2022.
Next Steps: Comparison of Oxygen content to a Commercial Alloy

<table>
<thead>
<tr>
<th>Pre-heat treated Monofilament Nb-4Ta-1Hf alloy (at%)</th>
<th>Commercial Nb-4Ta-1Hf alloy (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.59</td>
<td>2.17</td>
</tr>
<tr>
<td>1.95</td>
<td>1.09</td>
</tr>
<tr>
<td>3.83</td>
<td>1.04</td>
</tr>
</tbody>
</table>

• Evidence of larger HfO$_2$ precipitates in the commercial alloy
• Next step is to compare oxygen content across alloys using EPMA

BSD image of a commercial alloy

EDX courtesy of Junliang Liu
Conclusion

• HfO$_2$ nanoparticles are found in the post-heat treatment Nb-Ta-Hf alloy, the Nb$_6$Sn$_5$ and the Nb$_3$Sn layer

• The oxygen was originally dissolved in the Nb-Ta-Hf alloy, leading to the formation of these oxides during heat treatment

• Nanoscale Cu islands are also present in the Nb$_3$Sn (and may contribute to pinning)

• Nb$_6$Sn$_5$ contains a larger concentration of Cu than the Nb$_3$Sn that forms from it (approx. 2at%)

• Different Nb-Ta-Hf alloy compositions can be compared to determine the best starting material for producing optimal superconducting properties