Potential for Improvement in PIT and RRP® Strand

Peter J. Lee, Chiara Tarantini, Charlie Sanabria, Chris Segal, David C. Larbalestier
Nb₃Sn still the superconductor of choice

• Relatively low cost compared to HTS
• Available in good enough quality for the building of test magnets
• But . . .
  – Current performance is insufficient to meet FCC goals of critical current densities (≥ 1500 A/mm² at 16 T) and filament diameters ≤ 20 μm
Progress in Round Wire $J_c$ (4.2 K, non-stabilizer)

- It has been over 10 years since there has been a significant increase in Nb$_3$Sn $J_c$

Notes:

- Nb$_3$Sn data from Parrell et al. 2004
  
  http://dx.doi.org/10.1063/1.1774590

- Bi-2212 strand manufactured by OST

For Nb$_3$Sn the improvements have been in $D_{eff}$, RRR and yield = Better magnet conductor
But much recent progress . . .

1. **PIT** - the **bundled barrier** has enabled **higher Sn** that allows **more A15**. New HT encourages small grains. **For the first time** $J_c > 2600 \text{ A/mm}^2$ at 12 T. However, tubes have broken and effects seem to be long range, suggesting that real $J_c$ would be much higher - need mechanical analyses.

2. **RRP** (internal Sn) - **Nausite control HT**: significant improvement for small sub-elements, enables high $J_c$ and reduction in $D_{eff}$. Is the FCC $D_{eff}$ target in sight with Ta dividers? $J_c$ (FCC) is not far off – perhaps it will be achieved with uniform $H_{c2}$ distribution across the layer.

3. **APC** - detailed study of the Motowidlo conductor is underpinning our APC design effort - we clearly see both refined grains AND a point pinning contribution. The challenge now is to get $H_{c2}$ up too.
PIT is held back in three major ways:

1. About 1/4 of the A15 formed is LG A15 (13% of 53% area)
   - This observation is nearly independent of reaction temperature (630°C-670°C) for full-length reactions.
   - **BUT:** We found that, *early in the reaction*, LG A15 formation IS temperature dependent!
   - We try to optimize the early hours of the HT to maximize SG A15 growth before LG A15 starts forming. (Multistage HT)

2. Much tube remains unreacted (21-24%)
   - RRP is more effective with only ~10% un-reacted Nb
   - BEAS and CERN developed a new wire (bundle barrier) to drive up $J_c$ without loss of RRR – previous talk
   - **Bundle barrier allows more tin, more reaction**
   - We apply multistage HT to bundle barrier wires

3. There are filament breaks and locations of tin breach
   - Filament breaches are often observed
   - These are **quite long, up to centimeters in length**, occurring more in outer filaments
     - Do inner filaments as a group have higher $J_c$?
     - Etch wire to measure $I_c$

   - Only **small grain A15** carries current
   - Large and core grains of A15 do not carry any current
LG A15 formation is temperature dependent early in reaction

Full reaction in 620°C-670°C range

620/100 + 640/120h

SG 40.2%
LG 13.3%
\( J_c = 2380 \text{ A/mm}^2 \) (12T, 4.2 K)

670/75

SG 42.3%
LG 13.7%
\( J_c = 2404 \text{ A/mm}^2 \) (12T, 4.2 K)

Increasing Temperature

630°C
10h
650°C
4.75h
670°C
4.5h
690°C
1.66h

Only SG A15 has formed

LG A15 formation with time and temperature

630°C
12h
650°C
8.33h
670°C
5h
690°C
2h

LG A15 formation with time and temperature

Only SG A15 has formed

620°C-670°C range

Only SG A15 has formed

LG A15 has nucleated with Cu
Multistage heat treatments further delay LG A15 formation while growing SG A15.

Multistage heat treatments improve all phases and morphologies, but 12 T Jc decreases.

<table>
<thead>
<tr>
<th>Heat treatment description</th>
<th>Heat treatment (temp/dwell time)</th>
<th>Jc (A)</th>
<th>Jc SG-layer (A/mm²)</th>
<th>Nb Total</th>
<th>core A15</th>
<th>LG A15</th>
<th>SG A15</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEAS recommended</td>
<td>620/100+640/120</td>
<td>501</td>
<td>2237</td>
<td>5564</td>
<td>23.4%</td>
<td>56.0%</td>
<td>13.3%</td>
</tr>
<tr>
<td>Multistage C</td>
<td>Stage C +630/210</td>
<td>491</td>
<td>2192</td>
<td>4926</td>
<td>24.0%</td>
<td>57.3%</td>
<td>1.2%</td>
</tr>
<tr>
<td>% change from recommended HT</td>
<td></td>
<td>-2%</td>
<td>-2%</td>
<td>-11.5%</td>
<td>+4.3%</td>
<td>-52%</td>
<td>-12.8%</td>
</tr>
</tbody>
</table>

Transport properties went down

Microstructure improved
SG/LG ratio improved from 3.0 -> 3.8
PIT summary

• HT optimization can reduce LG volume
• External barrier successfully implemented
  – Can this be fully exploited with Sn leakage?
• HT should be optimized for 16 T
Potential for RRP Nb$_3$Sn

- Indications that HT needs to be reoptimized for 16 T
- Nausite-control HT provides breakthrough in $J_c$ for small $D_{\text{eff}}$
- Quaternary doping may help achieve FCC targets
Conductor HT should target >680°C for 15-16 T optimization $B_{c2}^*$ of 27.5 T

$B_{c2}^*(4.22 \, \text{K}), T$

Temperature of HT, °C

0.85 mm 108/127

54/61

108/127, 0.78 mm

132/169, Std. Sn

132/169, –5% Sn

0.85 mm 108/127

Trends suggest opportunity to achieve FCC $J_c$ target by reacting at 675-700°C

Adapted from L. Cooley – LTSW’17

MQXF HT:
210°C/48 h + 400°C/48 h + 665°C/75 h

$B_{c2}^*(4.22 \, \text{K}), T$

Critical current density at 15 T, 4.2 K (A/mm²)

Kramer extrapolation field (T)

27.5 T
High-field properties improve at > 680 °C

680 °C is where \( H_K \) and % of high-field A15 rise quickly

Extrapolated irreversibility field \( H_{Irr} \) at 4.2 K and the maximum of \( f(T_c,16T) \) as a function of HT.

\[ $\varnothing = 0.7 \text{ mm, 54/61 stack}$ \]

But at >680°C, $F_p$ & RRR may be compromised

1% of filaments react through at 680°C → RRR = ~100 or less

$\varnothing = 0.7$ mm, 54/61 stack

Reconsider Ta+Ti doping for 16 T optimization

- 54/61 high $J_c$ strands heat treated at 640°C/40h with three different dopants:
  - Only Ta
  - Ta+Ti
  - Only Ti

**Ta+Ti Doping: Lower $J_c$(12 T) but Higher Kramer Field**

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Dopant</th>
<th>Billet ID</th>
<th>Subs/Stack</th>
<th>Final HT</th>
<th>Nb at %</th>
<th>Sn at %</th>
<th>Ta at %</th>
<th>$T_{c,Onset}$ K</th>
<th>$\mu_0H_k$ T</th>
<th>Non-Cu $J_c$(12T,4.2K) A/mm²</th>
<th>A15 layer $J_c$(12T,4.2K) A/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>4 at. %Ta</td>
<td>8781</td>
<td>54/61</td>
<td>640°C/40h</td>
<td>72.46</td>
<td>25.17</td>
<td>2.37</td>
<td>18.4</td>
<td>22.66</td>
<td>2712</td>
<td>4860</td>
</tr>
<tr>
<td>Ta+Ti</td>
<td>4 at. %Ta +1 at%Ti</td>
<td>9362-5</td>
<td>54/61</td>
<td>640°C/40h</td>
<td>71.41</td>
<td>24.64</td>
<td>2.60</td>
<td>1.37</td>
<td>17.9</td>
<td>24.75</td>
<td>2622</td>
</tr>
<tr>
<td>Ti</td>
<td>2 at%Ti</td>
<td>9415-BE</td>
<td>54/61</td>
<td>640°C/40h</td>
<td>74.87</td>
<td>23.40</td>
<td>1.73</td>
<td>18.1</td>
<td>23.75</td>
<td>2872</td>
<td>5065</td>
</tr>
</tbody>
</table>
Reconsidering Ta+Ti doping for 16 T optimization

- At 0 T the larger homogeneity of the Ti sample is obvious
  - more intense peak, narrower distribution (just slightly lower $T_c$ onset).
- Ta+Ti is the worst one:
  - the distribution peaks below 17 K and the peak is wider.

Analysis by Chiara Tarantini

- At 15 T the Ti-doped sample is still better than the Ta but Ta+Ti is better than both (the volume fraction still in SC state at 15 T goes from 42-43% in the Ta or Ti samples to 50% in the Ta+Ti).
- This suggests better performance of Ta+Ti at larger fields despite the inferior performance at 12 T.
Micro-chemistry: Ti doped more homogeneous

**Ti-doping Standard Sn**

- NbL
- CuL
- SnL
- TiK

Sn very uniform

**Ta-doping Standard Sn**

- NbL
- CuL
- SnL
- TaM

Sn variation most noticeable toward barrier

Clear honeycomb structure in the Ta map

Z-H. Sung’s analysis
Doping: If Ti is close to max – Try Ti+Ta

• 7.5 Ta + 2 Ti is regarded as overdoped for RRP but is this the best for 16 T?
• Do we need custom Ta + Ti alloy?
• Can Nausite control gain us even more?
• Do we need doped APC Nb₃Sn . . .
Nausite Control: Use single 350°C HT to optimize Nausite ring and increase the Cu diffusion

Nausite Membrane 0.65 µm thickness

Nausite Membrane 0.29 µm thickness

Images and values are from a wire with $D_s = 35$ µm
Conventional 3-step HT lacks Nausite control

Remaining $\eta$ produces liquid and more Nausite

Temperature vs. Time Graph:
- 215°C
- 400°C
- 665°C

Temperature vs. Time Graph:
- 350°C
- 665°C
2-stage Nausite control HT reduces wasted Nb$_3$Sn

Excess Nausite ends up as disconnected Nb$_3$Sn.

New Nausite control HT can eliminate wasted Nb$_3$Sn.
Nausite control HT: Minimizes liquefaction and increasing the critical current appreciably

**Standard HT**
(215°C/48h + 400°C/48h + 665°C/50h)

**New HT**
(350°C/400h + 665°C/50h)

<table>
<thead>
<tr>
<th>Wire Size</th>
<th>(J_c) (12 T)</th>
<th>(J_c) (16 T)</th>
<th>(H_k) (self field)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85</td>
<td>2719</td>
<td>1126</td>
<td>24.56</td>
</tr>
<tr>
<td>0.70</td>
<td>2598</td>
<td>1006</td>
<td>23.77</td>
</tr>
<tr>
<td>0.60</td>
<td>2415</td>
<td>859</td>
<td>22.89</td>
</tr>
</tbody>
</table>

Wire sizes:
- 0.85 mm, \(D_s = 50\) µm
- 0.70 mm, \(D_s = 41\) µm
- 0.60 mm, \(D_s = 35\) µm

New data last week thanks to HanPing Miao and colleagues at Bruker-OST
### Table from Bernardo Bordini this morning

**B. Bordini and A. Ballarino Presentations at FCC Week 2017**

<table>
<thead>
<tr>
<th>Layout</th>
<th>Sub-Element size</th>
<th>( J_c ) (12 T), RMS [A/mm^2]</th>
<th>( J_c ) (15 T), RMS [A/mm^2]</th>
<th>( B_{c2} ) (4.3 K), RMS [T]</th>
<th>( J_c ) (16 T), RMS [A/mm^2]</th>
<th>( J_c ) (18 T), RMS [A/mm^2]</th>
<th>Degradation ( J_c ) (15% rolling) [%]</th>
<th>Minimum RRR (15% rolling) -</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7 mm RRP</td>
<td>46 μm</td>
<td>2676, 68</td>
<td>1410, 58</td>
<td>24.5, 0.39</td>
<td>1098, 55</td>
<td>610, 47</td>
<td>0</td>
<td>&gt;100</td>
</tr>
<tr>
<td>0.85 mm RRP</td>
<td>55 μm</td>
<td>2835, 44</td>
<td>1601, 33</td>
<td>25.9, 0.19</td>
<td>1289, 30</td>
<td>785, 25</td>
<td>0</td>
<td>&gt;100</td>
</tr>
<tr>
<td>0.85 mm Bundle Barrier PIT</td>
<td>39 μm</td>
<td>2323, 83</td>
<td>1342, 49</td>
<td>26.7, 0.1</td>
<td>1093, 40</td>
<td>688, 26</td>
<td>5.5 %</td>
<td>&gt;150</td>
</tr>
</tbody>
</table>

**Wire Size**

<table>
<thead>
<tr>
<th>Wire Size</th>
<th>Billet</th>
<th>Stack</th>
<th>Sub-Element size</th>
<th>( J_c ) (12 T)</th>
<th>( J_c ) (16 T)</th>
<th>( H_k ) (self field)</th>
<th>RRR</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85</td>
<td>16630-2C</td>
<td>132</td>
<td>50</td>
<td>2946</td>
<td>1307</td>
<td>25.58</td>
<td>304</td>
</tr>
<tr>
<td>0.70</td>
<td>16630-2B</td>
<td>132</td>
<td>41</td>
<td>2979</td>
<td>1296</td>
<td>25.34</td>
<td>244</td>
</tr>
<tr>
<td>0.60</td>
<td>16630-2A</td>
<td>132</td>
<td>35</td>
<td>2910</td>
<td>1207</td>
<td>24.68</td>
<td>140</td>
</tr>
</tbody>
</table>

**New Nausite Control HT**
A significant advance for small $D_{\text{eff}}$

- Nausite control HT significantly increases $J_c$
- But more is needed!
\( D_{\text{eff}} \)

- With Nausite control can we get to RRP \( J_c \) Plateau with 40 \( \mu m \) subelements
- Is 20 \( \mu m \) now possible with a simple sub-division?
- Will dividers interfere with the Nausite ring/membrane?
RRP Example using Ta Filaments to subdivide each sub-element

- Previous attempts assumed far more subdivision would be necessary:
  - 6 dividers = \(~10\%\) loss in Nb$_3$Sn area

Sn core size was deliberately reduced in this composite.
MO imaging demonstrates successful subdivision

Zero Field Cooled, $T=6\,\text{K}$

Increasing Field

All sub-elements divided and cores penetrated

$1200\,\text{Oe}$

MO imaging by Anatolii Polyanskii
Pinning Nb-Ti vs Nb₃Sn

- Grain boundary pinning in Nb₃Sn is not as efficient as α-Ti pinning in Nb-47Ti

![Image of Nb₃Sn microstructure](image1)
![Image of Nb-47Ti microstructure](image2)
OSU (see next talk) has shown that the internal oxidation of Zr in Nb-1Zr developed at GE for tape can be applied to wire . . . .

**IF** there is no Cu to block Oxygen diffusion.

SnO$_2$ + Cu$_5$Sn$_4$ Powder

SupraMagnetics PIT APC

Cu

Nb-1Zr
SupraMagnetics (Cu₅Sn₄+SnO₂) PIT Process

SnO₂ powder mixed with phase pure < 3 μm Cu₅Sn₄
Precipitates prefer GB intersections

Precipitates at intergranular fracture surface

Transgranular fracture: no precipitates

Precipitates along GB intersection

But not all precipitates may be within FESEM resolution, and fractographs reveal only intergranular surfaces.

Visible Precipitate Distribution: ~100 nm spacing

200 nm
A15 Grain Size Sensitive to Composition

Cu$_5$Sn$_4$+SnO$_2$, composition A

Cu$_5$Sn$_4$+SnO$_2$, composition B

HT 625 °C

0.020" Ø

0.039" Ø

300h/625 °C

Core

Core

Nb

Nb
Microstructural Gradients: Suggest grain growth

300h/625 °C

- Smallest grains ~ 30 nm diam. furthest from core (i.e. newest grains)
- Middle of layer ~ 40 nm

Steep gradient in Grain Boundary Density

Cu₅Sn₄+SnO₂, composition A
Magnetization: A shift in the peak pinning force curve for Compo A compared to Compo B.

Shape close to the point defect curve

Curves follow a grain boundary behavior

300h/625 °C
Kramer plot: Smallest grains = Less GB-like, less $H_{\text{irr}}$

$\mu_0 H_{\text{irr}} = 7.87 \, \text{T}$

$\mu_0 H_{\text{irr}} = 17.54 \, \text{T}$

$\mu_0 H_{\text{irr}} = 19.06 \, \text{T}$

$\mu_0 H_{\text{irr}} = 8.69 \, \text{T}$

~ 40 nm

Suppressed $H_{\text{irr}}$

More grain-boundary-like
PIT APC Summary

• Preliminary results show an average grain size as small as 30 nm.
• A shift in the peak pinning force curve toward higher magnetic field is demonstrated.
• The volume percent SnO$_2$ is an important parameter in the control of grain size and homogeneity of the A15 layer.
• Additional control is available through HT.
• These results provide strong evidence for a new and economical route to a very high current density Nb$_3$Sn strand.
• But there is evidence that the $H_{irr}$ is suppressed for small grain sizes.
• A different approach may be required to meet FCC targets.
Recent progress . . .

1. **PIT** - the bundled barrier has enabled higher Sn that allows more A15 and new HT enable a more favorable SG/LG ratio - for the first time $J_c > 2600 \text{ A/mm}^2$ at 12 T.
   - However, tubes have broken and effects seem to be long range, suggesting that real $J_c$ would be much higher - need for mechanical design.

2. **RRP** (internal Sn) - Nausite control HT: significant improvement – effective reduction in $D_{eff}$. With Ta subdivision the FCC defective target is in sight. $J_c$ (FCC) is not far off - and future work not presented here is addressing a more uniform $H_{c2}$ distribution across the layer.

3. **APC** - clearly see both a refined grain AND a point pinning contribution. The challenge now is to get $H_{c2}$ up too.
   - The next talk will focus on new developments in APC conductors.
Acknowledgments

• We would like to thank
  – our collaborators:
    CERN, Bruker-EAS and Bruker-OST, US-MDP
    Lance Cooley (FermiLab/MDP) for suggestions
  – Funding support from:
    • CERN and by the U.S. Department of Energy, Office of Science, Office of High Energy Physics under Award Number DE-SC0012083. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490 and the State of Florida.