Influence of Ti-Hf doping on the Nb₃Sn layer formation for bronze-processed Nb₃Sn wire structure

Taro Morita ¹, ², Tsuyoshi Yagai ¹, Nobuya Banno ², Sigeki Nimori ²

¹Sophia University
²National Institute for Materials Science
Introduction and aim

- Hf-Ta doping to Nb is now of great interest in the field of the Nb$_3$Sn wire development.
- In this work, we investigated the effect of Ti-Hf doping on the microstructure and superconducting characteristics of bronze-processed Nb$_3$Sn wire structure.
Specimens and Experiment

Fabrication

• Intermediate annealing at 550 °C every 50 ∼ 70 % reduction ratio.
• There was no problem with the drawability of the specimens.
• After the drawing, Heat treatment at 700°C × 100 h.

Experiments

• Microstructure: SEM, EDS, EBSD
• $J_c$–$B$: $I_c$ measurement in LHe.

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Table 1: Specification of the specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>N2TH</th>
<th>N1TH</th>
<th>N154T</th>
<th>C02T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (mm)</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Nb core</td>
<td>Nb-2%Ti-1%Hf</td>
<td>Nb-1%Ti-1%Hf</td>
<td>Nb-1.54%Ti</td>
<td>Nb</td>
</tr>
<tr>
<td>Matrix</td>
<td>Cu-8%Sn</td>
<td>Cu-8%Sn</td>
<td>Cu-8%Sn</td>
<td>Cu-8%Sn-0.28%Ti</td>
</tr>
</tbody>
</table>

Figure 1: The precursor structure of the specimens.
Results – Nb$_3$Sn layer formation –

- Ti doping, especially to bronze matrix, promotes significantly Nb$_3$Sn layer formation, as reported in previous studies [1].
Results – Compositional profile of Nb$_3$Sn layer –

TiK composition

SnL composition

Normalized distance (a. u.)

Ti composition (at%)

Sn composition (at%)

0 0.5 1 1.5 2 2.5 3 3.5

0 0.2 0.4 0.6 0.8 1

0 0.2 0.4 0.6 0.8 1

N2TH  N08T  N1TH  CS02T

N2TH  N08T  N1TH  CS02T

WED-PO2-604-06
Composition of Nb$_3$Sn layer

• **Ti composition is largest when Ti is doped to Cu-Sn matrix.** It would be because large amount of Ti moved from Cu-Sn-Ti matrix, and concentrated at the boundary between Cu-Sn-Ti matrix and Nb core. In other Ti-doping methods, Ti almost stayed at the original position in the Nb core.

• **Ti-doping to Cu-Sn matrix also contributes to increase of Sn composition in Nb$_3$Sn layer.**

• Although **Nb-Cu-Sn-Ti quaternary phase** exists in the boundary when Ti is doped to Sn cores and Cu matrix on an internal-tin processed structure [1], there is no compound layer in bronze matrix structure.
Results – Nb₃Sn grain morphology –

Nb₃Sn grain morphology was analyzed by EBSD.

### Nb₃Sn average grain size

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2TH</td>
<td>296.8</td>
</tr>
<tr>
<td>N1TH</td>
<td>292.7</td>
</tr>
<tr>
<td>N154T</td>
<td>301.4</td>
</tr>
<tr>
<td>C02T</td>
<td>306.7</td>
</tr>
</tbody>
</table>

### Equiaxed or Columnar

<table>
<thead>
<tr>
<th>Sample</th>
<th>Equiaxed Area Fraction (%)</th>
<th>Columnar Area Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2TH</td>
<td>40.9</td>
<td>59.1</td>
</tr>
<tr>
<td>N1TH</td>
<td>31.7</td>
<td>68.3</td>
</tr>
<tr>
<td>N154T</td>
<td>39.9</td>
<td>60.1</td>
</tr>
<tr>
<td>C02T</td>
<td>39.5</td>
<td>60.5</td>
</tr>
</tbody>
</table>
Results – Nb$_3$Sn grain morphology –

• There is no significant difference in the grain size among the specimens. Rather, Ti doping to matrix had a tendency to increase the grain size in the wire configuration of this work, although previous studies reported that the smaller grain size can be obtained in Ti doping to Cu-Sn matrix [2, 3, 4]. Presumably, the wire configuration of this work caused an excessive Ti content in the Nb$_3$Sn layer, which results in grain growth in C02T [5].

• Hf doping did not influence so much the grain size.
Results – The microstructure of Nb-2Ti-1Hf core –

IPF map of Nb-2at%Ti-1at%Hf

EBSD maps of Nb-2Ti-1Hf alloy with heat treatment.

EBSD maps of Nb-2Ti-1Hf alloy with heat treatment.
Results – The microstructure of Nb-2Ti-1Hf core –

KAM map of Nb-2at%Ti-1at%Hf
Results – The microstructure of Nb-2Ti-1Hf core –

- Grain size of Nb-2Ti-1Hf core increase with the HT temperature.
- Nb-2Ti-1Hf has similar tendency to Nb-4Ta-1Hf.
- KAM (Karnel Average Misorientation) tends to decrease with increase of HT temperature.

Kernel Average Misorientation (KAM) is correlated with the amount of dislocation and internal strain.
Results – Superconducting characteristics –

- layer $J_c$ in Ti doping to Cu-Sn matrix is the largest, although the specimen has a relatively larger grain size. This could be due to the larger Sn and Ti content in Nb$_3$Sn layer, resulting in a larger $B_{c2}$
- Hf doping to Nb core seems to have additional effect to enhance $B_{c2}$ and $J_{c2}$, because N2TH and even N1TH has a larger $B_{c2}$ than N154T.

Figure 2: (top) layer $J_c$–$B$ characteristics and (bottom) upper critical field estimated by Kramer plot for the specimens.
Discussion – Why Hf-Ti addition did not show significant improvement in superconducting properties? –

- Higher internal strain in a parent Nb core is believed to promote the Sn driving force, and then Nb$_3$Sn nucleation.
- Ti doping is effective way to improve the Sn driving force.
- According to the results, the effect of Ti doping would be much larger than that of Hf doping in bronze-processed structure: improvement in C02T is larger than that in NTH wires.
- As for the correlation between the internal strain in the parent Nb cores and Sn driving force, it needs to be further investigated in detail.
Conclusion

- In this study, we investigated that the effect of Ti-Hf doping on the Nb$_3$Sn microstructure and superconducting characteristics.

- Superconducting characteristics is largest in the case of Ti doping to Cu-Sn matrix on bronze-processed structure. The reason would be the larger Sn and Ti content in Nb$_3$Sn layer. However, in internal-tin processed structure, Ti doping to Cu-Sn matrix is not optimal, because quaternary phase segregates in the boundary of Nb$_3$Sn when Ti doping to Cu matrix which suppresses Sn and Ti diffusion in Nb$_3$Sn layer, as we have recently studied in [1].

- Hf doping would be also effective for enhancing $B_{c2}$ and $J_c$.

- Characterization of Nb-Hf/Cu-Sn-Ti structure is a next subject to further clarify the effect to Hf doping in bronze processed Nb$_3$Sn wires.
T Morita, T Yagai, and N Banno.

Impact of Ti-doping position on Nb₃Sn layer formation in internal Sn-processed Nb₃Sn superconducting wires.
*Cryogenics*, 2021. accepted.

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Composite-processed Nb₃Sn with titanium addition to the matrix.
E N Popova, I L Deryagina, and E G Valova-Zaharevskaya.
The Nb$_3$Sn layers formation at diffusion annealing of ti-doped multifilamentary Nb/Cu–Sn composites.

Insight into the effect of Ti-addition on diffusion-controlled growth and texture of Nb$_3$Sn intermetallic superconductor phase.
Toshihisa Asano, Yasuo Iijima, Kikuo Itoh, and Kyoji Tachikawa. 

Effects of titanium addition to the niobium core on the Composite-Processed \( \text{Nb}_3\text{Sn} \).