

# CHART Scientific Report (Final Report for Phase 2)

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## Advanced Niobium-Tin superconductors for next generation particle colliders

### (WireDev)

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### 1. Introduction / Original goals of this project

Following the latest update of the European Strategy for Particle Physics, released in June 2020, and with the aim of enhancing the potential to discover new particles and phenomena by advancing the energy frontier, plans are progressing to design a future proton-proton collider with a center-of-mass energy in the 100 TeV range, about seven times the design energy of the Large Hadron Collider (LHC). The baseline configuration for this Future Circular Collider (FCC) proposes a tunnel with a circumference of 91 km in the Geneva area. As the collision energy of a circular collider is directly proportional to the magnetic field generated by the bending dipoles, the FCC could achieve collision energies up to 95 TeV by employing Nb<sub>3</sub>Sn-based dipoles operating at 16 T, contingent on lattice optimization.

A preliminary analysis of the main magnet design parameters indicates that a 16 T field in a dipole configuration requires a minimum non-Cu  $J_c$  of 1'500 A/mm<sup>2</sup> at 16 T and 4.2 K (non-Cu  $J_c$  corresponds to the critical current divided by the wire cross-section area minus the Cu stabilizer area). This target, a mandatory performance requirement for a compact accelerator magnet, exceeds by about 50% the performance specified for the industrial production of Nb<sub>3</sub>Sn for the high luminosity upgrade of the LHC (HL-LHC) and the performance gap cannot be bridged by further optimization of existing wires. Therefore, advancing Nb<sub>3</sub>Sn technology to its perceived practical limits necessitates novel processing routes with full control of the material at the nanoscale, while remaining scalable at the industry level.

In this context, UNIGE and CERN signed a research agreement under the auspices of CHART-2, with the goal of investigating methods to achieve the target of 1'500 A/mm<sup>2</sup> at 4.2 K and 16 T in Nb<sub>3</sub>Sn wires, using processes compatible with long-length industrial production. Financial support to this activity was also provided by the Swiss National Science Foundation (Grant No. 200021\_184940).

## 2. Realisation

To achieve the highest performance in Nb<sub>3</sub>Sn wires and meet the non-Cu J<sub>c</sub> requirement for the FCC's 16 T dipoles, research must span various fields, including condensed matter physics, material engineering, and applied science. The current-carrying capacity of type-II superconductors in a magnetic field is determined by their ability to prevent the movement of vortices, known as pinning. In these superconductors, magnetic field can penetrate the material in quantized units, called vortices. These vortices can move under the influence of a current, leading to energy dissipation and loss of superconductivity. Pinning centers are features within the material that "pin" these vortices in place, preventing their movement and thereby maintaining the superconductor's ability to carry high currents without resistance. In Nb<sub>3</sub>Sn, grain boundaries are the primary pinning centers; hence, materials with finer grains have higher current densities. In modern high-performance wires, Nb<sub>3</sub>Sn typically has grain sizes of 100-150 nm. Based on the dependence of pinning force on grain size reported in the literature, reducing the grain size to 50-60 nm is estimated to effectively enhance the non-Cu J<sub>c</sub> beyond the FCC specification.

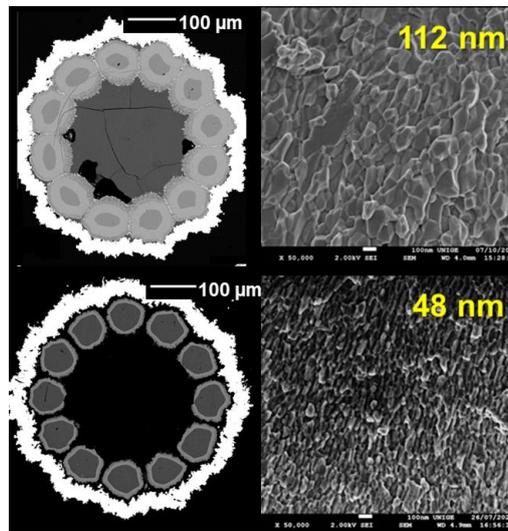
According to scientific literature, the most effective way to inhibit grain growth and increase the critical current performance of Nb<sub>3</sub>Sn is through the use of oxide nanoparticles, particularly via the "internal oxidation" method. This method uses a precursor of Nb-alloys containing a small amount of Zr or Hf and a metal oxide powder that acts as an oxygen source. During heat treatment, the metal oxide powder is reduced, and oxygen diffuses into the Nb-alloy, oxidizing the highly reactive Zr or Hf and forming very fine particles of ZrO<sub>2</sub> or HfO<sub>2</sub> that inhibit the growth of Nb<sub>3</sub>Sn during the reaction with Sn.

In this project, we focused primarily on implementing the internal oxidation method in internal Sn rod-type Nb<sub>3</sub>Sn wires, as they are closest to meeting the performance target set for the FCC. The program was divided into three phases: (i) studying the materials in monofilamentary wires, including testing different Nb-alloy compositions and oxygen sources and their combinations, (ii) developing multifilamentary wires with a reduced number of filaments and an internal Sn source, referred to as "test-bed sub-elements," and (iii) developing methods to implement the internal oxidation in application-ready wires using processes that can be scaled up for industrial production.

### 3. Results / Conclusions / Deliverables

#### 3.1 Grain refinement and enhanced critical current density in internally oxidized Nb<sub>3</sub>Sn

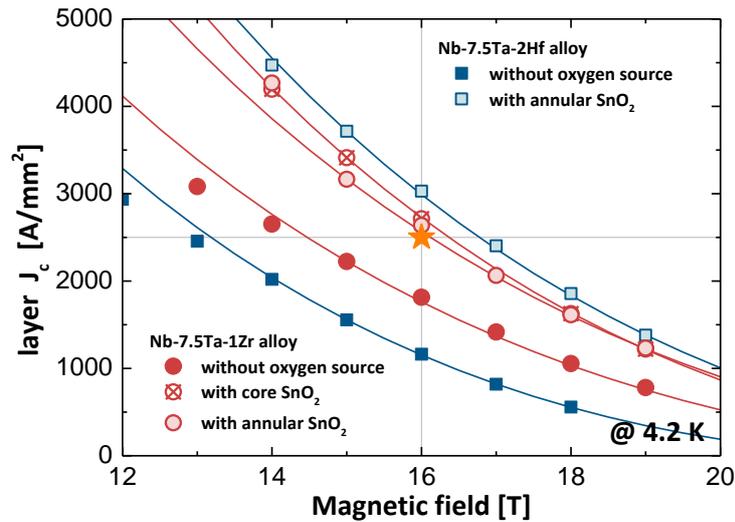
An initial study on monofilamentary wires allowed us to perform a screening of multiple combinations of different Nb-alloys and potential oxygen sources. The next step involved the production of test-bed sub-elements with a reduced number of filaments. Internal Sn rod-type wires are made by restacking a large number of sub-elements, each typically containing more than one hundred Nb-alloy filaments inside a Cu matrix with a Sn core at the center. Our test-bed sub-elements consisted of twelve Nb-alloy filaments in a Cu matrix around a Sn core, with the filaments made from the alloys Nb-1Zr, Nb-7.5Ta-1Zr, and Nb-7.5Ta-2Hf (all weight percentages). This design allowed us to efficiently and quickly test a variety of alloy and oxygen source configurations in a versatile and flexible internal Sn architecture.



**Figure 1** The two pictures on the left depict the cross section of the Nb<sub>3</sub>Sn test-bed sub-element based on Nb-7.5Ta-2Hf filaments without internal oxidation (top) and with internal oxidation (bottom), respectively, reacted at 650°C for 200 h. The two pictures on the right magnify the Nb<sub>3</sub>Sn grain morphology at fractured surfaces, highlighting a pronounced grain refinement due to the internal oxidation (bottom) with respect to the reference wire (top).

Specifically, the oxygen source (SnO<sub>2</sub> nano-sized powders) was positioned either at the core or the periphery of each Nb-alloy filament. Both methods resulted in the diffusion of oxygen from the powder source into the Zr- or Hf-containing Nb-alloys during the heat treatment, leading to the formation of ZrO<sub>2</sub> or HfO<sub>2</sub> nanoparticles and the subsequent refinement of the Nb<sub>3</sub>Sn grains from approximately 100 nm in the reference wires without oxygen to around 50 nm. Samples with refined grains exhibited a significant increase in the layer J<sub>c</sub> (critical current divided by the area of fine-grained Nb<sub>3</sub>Sn). Internally oxidized samples made with Zr alloy achieved a layer J<sub>c</sub> of 2'700 A/mm<sup>2</sup> at 4.2 K and 16 T, while those made with Hf alloy reached up to 3'000 A/mm<sup>2</sup>. Considering that the non-Cu J<sub>c</sub> of a high-performance commercial Nb<sub>3</sub>Sn wire is about 60% of its layer J<sub>c</sub>, these results indicate that the performance of these test-bed sub-elements exceeds the FCC target, which translates into a layer J<sub>c</sub> of 2'500 A/mm<sup>2</sup> at 4.2 K and 16 T. Additionally, our wires exhibited also record-high upper critical fields above 29 T at 4.2 K, more than 1 T higher compared to the values measured in state-of-the-art wires. Magnetization measurements suggest that a point-like defect type contribution to the vortex pinning due to

the presence of  $ZrO_2$  or  $HfO_2$  precipitates combines with the grain boundary mechanism to produce this remarkable enhancement of the layer  $J_c$ .



**Figure 2** Layer  $J_c$  at 4.2 K extracted from transport critical current measurements for test-bed sub-elements based on Nb-7.5Ta-1Zr without oxygen source (solid circles), Nb-7.5Ta-1Zr with  $SnO_2$  in the core of each filament (crossed circles), Nb-7.5Ta-1Zr with  $SnO_2$  at the periphery of each filament (open circles), Nb-7.5Ta-2Hf without oxygen source (solid squares) and Nb-7.5Ta-2Hf with  $SnO_2$  at the periphery of each filament (open squares). All samples were heat treated at  $650^\circ C/200h$ . The enhancement of the layer  $J_c$  at values exceeding the FCC target at 16 T is recorded for all the samples with internal oxidation.

### 3.2 $Nb_3Sn$ layer properties and formation of the oxide precipitates

Internally oxidized samples exhibited a reduced thickness of the reacted  $Nb_3Sn$  layer, indicating a slower diffusion of Sn in the Nb-alloy. The thickness after reaction at  $650^\circ C$  for 200 h decreased from 20-25  $\mu m$  in the test-bed sub-elements without an oxygen source to 4-8  $\mu m$  in those with an internal oxygen source (the filament diameter is approximately 75  $\mu m$ ), regardless of its configuration. Considering a typical internal Sn rod-type wire developed for HL-LHC, whose final Nb-alloy filament size in a sub-element is approximately 1  $\mu m$  and layer thickness is about 10  $\mu m$ , we can argue that this important reduction of the diffusion kinetics in wires with an oxygen source should not be a concern when implementing internal oxidation in application-ready wires.

With the goal of identifying the reaction conditions that maximize the  $Nb_3Sn$  layer thickness while retaining the refined grain microstructure produced by internal oxidation, we performed dedicated heat treatment studies. While with the reaction at  $650^\circ C$  for 200 hours, the fine-grained  $Nb_3Sn$  area occupied only 20-35% of the total filament area, after heat treatments with a reaction step at  $700^\circ C$  for 100 hours these values increased to about 60%, with only a minor increase in grain size, by a maximum of 10%. However, despite the limited grain growth, the layer- $J_c$  at 4.2 K and 16 T decreased from over 3'000  $A/mm^2$  down to 1'900  $A/mm^2$  for the Hf-containing wires, and from 2'700  $A/mm^2$  to 1'200-2'200  $A/mm^2$  for the Zr-containing wires. The decrease in layer  $J_c$  is larger than expected from the modest increase in grain size and can be

related to a change in the relative weight of pinning contributions from grain boundaries and nanoparticles. Magnetic measurements showed that the point-like defect contribution to pinning from oxide precipitates exhibited by the high  $J_c$  wires is missing in wires with depressed  $J_c$  values. The higher heat treatment temperatures may have caused excessive coarsening of the oxide precipitates, making them unsuitable for vortex pinning.

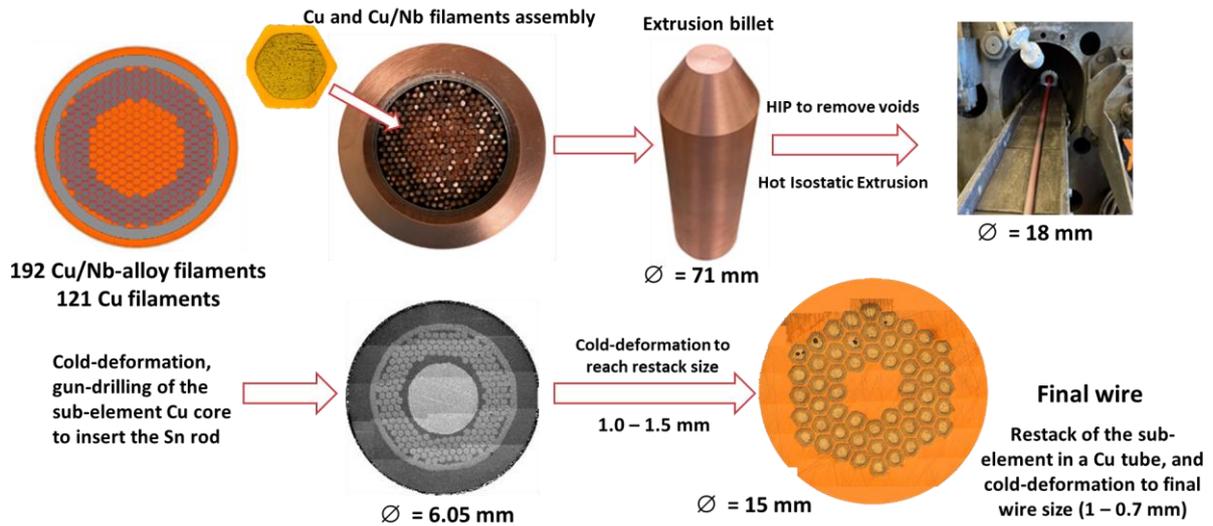
Further investigations through X-Ray Absorption Spectroscopy (XANES) studies were conducted to get a deeper understanding of the internal oxidation process applied to the  $Nb_3Sn$  wires, particularly the mechanism of oxygen transport and oxide precipitation. XANES spectra were gathered on multi-filamentary wires manufactured using a Nb-7.5Ta-1Zr starting alloy and  $SnO_2$  as an oxygen source at the PHOENIX beamline of the Swiss Light Source at the Paul Scherrer Institute. We employed a focused X-ray beam to probe the chemical environment of Zr through various regions of the wire cross-section. We discovered that the vast majority of Zr (>90%) in the  $Nb_3Sn$  layer is indeed oxidized as  $ZrO_2$ , while Zr primarily remains in a non-oxidized state within the residual alloy after heat treatment. The presence of oxidized Zr in the  $Nb_3Sn$  layer of the samples where oxygen was initially located at the core of the Nb-alloy filaments implies that oxygen can diffuse through the Nb-alloy to reach the external regions where  $Nb_3Sn$  forms and form  $ZrO_2$  in this layer, without oxidizing the Zr in the fraction of the alloy that remains unreacted. The insights from this study serve as a valuable addition to understanding the internal oxidation in  $Nb_3Sn$  wires and its influence on superconducting properties. Future investigations are needed to extend this study to Hf in  $Nb_3Sn$  with internally oxidized Hf.

### *3.3 Development of application-ready wires*

Building on the positive results obtained at the test-bed sub-element scale, we launched the development of application-ready wires. This type of wires is produced by stacking and cold-drawing a large number of sub-elements. Our sub-element configuration is based on a layout containing 192 Cu/Nb-alloy hexagonal filament rods placed around 121 sacrificial filament rods made of Cu and surrounded by a Nb-sheet barrier, all contained in a Cu can. Using this basic configuration, we machined and assembled billets with an outer diameter of 71 mm that are hydrostatically extruded to a round rod of 18 mm diameter after compaction by Hot Isostatic Pressing (HIP). The extruded rod is then gun-drilled and a Sn rod is inserted at its center. After drawing to a diameter between 1 and 1.5 mm, the resulting wire is hexagonally shaped and restacked/co-drawn with hexagonal Cu wires in a Cu tube to form the final internal Sn rod-type wire. In our attempt to incorporate an oxygen source into the sub-element, we are following two approaches:

**Sub-Element Level:** Introducing the oxygen source by replacing some of the Cu/Nb-alloy filaments with Cu tubes filled with a metal oxide.

**Filament Level:** Producing by hydrostatic extrusion Cu/Nb-alloy filaments incorporating the oxygen source in longitudinal grooves machined at the surface of the Nb core.



**Figure 3** Illustration of the process for the production of application-ready wires, from the sub-element design, to its assembly, extrusion, cold-deformation and restack

In both cases, we utilize Nb-7.5Ta-1Zr or Nb-7.5Ta-2Hf alloy for the filaments. This is an ongoing development that will require tailored studies to master the deformation of the composites at the filament, sub-element and restack level. However, the success of the project will represent an important step forward in view of the development of Nb<sub>3</sub>Sn-based dipoles capable of attaining the field level required for the FCC.

#### 4. Publications and Outreach

Peer reviewed paper in scientific journals

- F. Buta, M. Bonura, D. Matera, G. Bovone, A. Ballarino, S.C. Hopkins, B. Bordini, X. Chaud, C. Senatore, " Very high upper critical fields and enhanced critical current densities in Nb<sub>3</sub>Sn superconductors based on Nb-Ta-Zr alloys and internal oxidation," J. Phys. Mater., vol. 4, 025003, 2021, DOI: [10.1088/2515-7639/abe662](https://doi.org/10.1088/2515-7639/abe662)
- G. Bovone, F. Buta, F. Lonardo, T. Bagni, M. Bonura, D. LeBoeuf, S. C. Hopkins, T. Boutboul, A. Ballarino, C. Senatore, "Effects of the oxygen source configuration on the superconducting properties of internally-oxidized internal-Sn Nb<sub>3</sub>Sn wires," Supercond. Sci. Technol., vol. 36, 095018, 2023, DOI: [10.1088/1361-6668/aced25](https://doi.org/10.1088/1361-6668/aced25)
- G. Bovone, F. Buta, F. Lonardo, M. Bonura, C. N. Borca, T. Huthwelker, S. C. Hopkins, A. Ballarino, T. Boutboul, C. Senatore, "X-Ray Absorption Spectroscopy to investigate precipitated oxides in Nb<sub>3</sub>Sn wires with an internal oxygen source," IEEE Trans. Appl. Supercond., vol. 34, 6000205, 2024, DOI: [10.1109/TASC.2024.3354232](https://doi.org/10.1109/TASC.2024.3354232)
- F. Lonardo, G. Bovone, F. Buta, M. Bonura, T. Bagni, B. Medina-Clavijo, A. Ballarino, S. C. Hopkins, T. Boutboul, C. Senatore, "Influence of the heat treatment on the layer J<sub>c</sub> of internal-Sn Nb<sub>3</sub>Sn wires with internally oxidized nanoparticles," IEEE Trans. Appl. Supercond., vol. 34, 6000305, 2024, DOI: [10.1109/TASC.2024.3355353](https://doi.org/10.1109/TASC.2024.3355353)

## Presentations at international conferences and workshops

- *Improvement of  $J_c$  and further enhancement of  $B_{c2}$  in Ta-doped  $Nb_3Sn$  with internally oxidized  $ZrO_2$  particles*, Presenting author: Carmine SENATORE, invited oral at SuperFOX 2020, the 5<sup>th</sup> Conference on Superconductivity and Functional Oxides, Santa Margherita Ligure, Italy, February 10 – 12, 2020;
- *Superconducting properties and oxygen diffusion in Ta-doped  $Nb_3Sn$  wires with internally oxidized  $ZrO_2$* , Presenting author: Florin BUTA, contributed oral at ASC2020, the Applied Superconductivity Conference, virtual event, October 24 – November 7, 2020;
- *Frontiers of  $Nb_3Sn$  and REBCO Conductor Technology for Future Applications in High Magnetic Fields*, Presenting author: Carmine SENATORE, invited oral at MRS Spring Meeting 2021, virtual event, April 17 – 23, 2021;
- *Evaluation of approaches to introduce oxygen sources for the internal oxidation of Zr and Hf in rod type  $Nb_3Sn$  wires*, Presenting author: Gianmarco BOVONE, invited oral at EUCAS 2021, the 15<sup>th</sup> European Conference on Applied Superconductivity, virtual event, September 5 – 9, 2021;
- *Recent developments of  $Nb_3Sn$  wires for application*, Presenting author: Carmine SENATORE, invited oral at ISS2021, the 34<sup>th</sup> International Symposium on Superconductivity, virtual event, November 30 – December 2, 2021;
- *The influence of the oxygen-source layout on the high-field behavior of internally-oxidized multifilamentary  $Nb_3Sn$  wires*, Presenting author: Gianmarco BOVONE, contributed oral at ASC2022, the Applied Superconductivity Conference, Honolulu, USA, October 23 – 28, 2022;
- *Frontiers of  $Nb_3Sn$  conductor technology for applications in high field accelerator magnets*, Presenting author: Carmine SENATORE, invited oral at IEEE CSC Italy Chapter Workshop, Rome, Italy, June 13, 2022;
- *X-Ray Absorption Spectroscopy to investigate precipitated oxides in  $Nb_3Sn$  wires*, Presenting author: Gianmarco BOVONE, contributed oral at EUCAS 2023, the 16<sup>th</sup> European Conference on Applied Superconductivity, Bologna, Italy, September 3 – 7, 2023;
- *Influence of the heat treatment on the layer- $J_c$  of internal-Sn  $Nb_3Sn$  wires with internal oxide nanoparticles*, Presenting author: Francesco LONARDO, contributed oral at MT28, the 28<sup>th</sup> International Conference on Magnet Technology, Aix-en-Provence, France, September 10 – 15, 2023;
- *Grain-boundary and oxide-nanoparticle contributions to the layer  $J_c$  of internally oxidized  $Nb_3Sn$  wires*, Presenting author: Gianmarco BOVONE, contributed oral at MEM24, the 11<sup>th</sup> Workshop on Mechanical and Electromagnetic Properties of Composite Superconductors, Spokane, USA, June 10 – 14, 2024;
- *Advancing Superconductor Technology for High Field Applications: Current State and Emerging Trends*, Presenting author: Carmine SENATORE, plenary oral at ICEC 29 – ICMC 2024, 29<sup>th</sup> International Cryogenic Engineering Conference and International Cryogenic Material Conference 2024, Geneva, Switzerland, July 22 – 26, 2024.

## Awards

- Gianmarco BOVONE, 2023 Jan Evetts Award;
- Francesco LONARDO, Best Student Award at the 28<sup>th</sup> International Magnet Technology Conference.

This final report is only a very brief summary of all activities. More detailed scientific reports are published at <https://chart.ch/reports/>