

# ADVANCES IN Nb<sub>3</sub>Sn PERFORMANCE

A. Godeke\*, Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

## Abstract

Nb<sub>3</sub>Sn wires with non-Cu critical current densities ( $J_c$ ) that surpass 3 kAmm<sup>-2</sup> at 12 T and 4.2 K are commercially available in piece lengths longer than 10 km. Accelerator-type magnets that utilize these conductors have achieved record magnetic fields. This article summarizes key developments in the last decade that have led to these significant improvements in the performance of Nb<sub>3</sub>Sn wires.

## INTRODUCTION

The non-Cu  $J_c$  of Internal-Tin wires has approximately doubled from 1993 to 2003 [1]. Dipole magnets, constructed using Internal-Tin wires, have achieved consistently increasing magnetic fields, up to a present record of 16 T [2]. The article starts with a summary of the main properties of Nb<sub>3</sub>Sn, discusses how optimizations of these properties have led to the high  $J_c$  values, and provides an overview of existing and promising new wire manufacturing techniques.

## MAIN PROPERTIES OF Nb<sub>3</sub>Sn

### Composition and superconducting properties

Nb<sub>3</sub>Sn was discovered in 1954 by Matthias *et al.* [3]. Nb<sub>3</sub>Sn is not a line compound, but is stable from about 18 to 25 at.% Sn [4]. In this composition range, it occurs in the A15 structure and this phase is generally referred to as A15. Two Sn rich line compounds, Nb<sub>6</sub>Sn<sub>5</sub> and NbSn<sub>2</sub> are also stable below 930°C. The A15 phase undergoes a slight cubic to tetragonal distortion at temperatures below 43 K for compositions above about 24.5 at.% Sn, which has detrimental effects on the upper critical magnetic field ( $H_{c2}$ ). The tetragonal phase therefore has to be prevented. The net effect of Sn deficiency is a suppression of the achievable field-temperature phase boundary [5]. The  $H_{c2}$  and critical temperature ( $T_c$ ) are maximized at an optimal composition of about 24.5 at.% Sn. Alloying with Ti and Ta has limited effect on  $T_c$ . It does, however, prevent the tetragonal distortion from occurring and increases the resistivity, both of which result in an increase of  $H_{c2}$  [6]. An optimal  $H_{c2}$  is obtained with 1.5 at.% Ti addition and with 4 at.% Ta addition. The difference in effectiveness of Ti and Ta can be explained by assuming that Ta appears at the Nb sites, leading to (Nb<sub>1-x</sub>Ta<sub>x</sub>)<sub>3</sub>Sn, and that Ti appears at the Sn sites, leading to Nb<sub>3</sub>(Sn<sub>1-x</sub>Ti<sub>x</sub>) [7].

### Pinning capacity

A summary on literature results indicates a consistent, logarithmic dependence of the maximum pinning force on reciprocal grain size [4]. This dependence indicates that the grain boundaries are the main pinning centers in Nb<sub>3</sub>Sn. The grain size in Nb<sub>3</sub>Sn wires is only slightly dependent on the reaction time, but depends very strongly on the reaction temperature [8]. Optimal pinning of flux-lines occurs when the average grain boundary density approaches the flux-line spacing. The flux-line spacing for optimal alignment of the flux-line lattice with grain boundaries,  $a_0$ , can be calculated through  $a_0 = (3/4)^{1/4}(\phi_0/\mu_0 H)^{1/2}$  [9], in which  $\phi_0$  is the magnetic field quantum and  $H$  is the magnetic field. This leads to  $a_0 = 12$  nm, for a typical medium operating magnetic field of 12 T. The average grain size in wires ranges from 100 to 200 nm and is therefore one order too large for optimal pinning. The larger flux-line density compared to the grain boundary density leads to collective pinning and causes the field dependence of the pinning force to peak at only 20% of  $H_{c2}$ , i.e. typically around 5 T, resulting in a strongly reduced pinning force at operational magnetic fields in the 10 to 15 T range [8]. A reaction at an as low as possible temperature is therefore desirable, but this conflicts with the goal to obtain Sn-rich A15 volumes in wires. The heat treatment is therefore always a compromise in present wires.

### Strain dependence

Strain has a detrimental effect on the superconducting properties. Present understanding suggests that strain modifies the phonon frequency spectrum and density of states [10, 11], and thus changes the electron-phonon interaction strength. The net effect of this on the superconducting properties is a reduction of the available field-temperature phase boundary ( $H_{c2}(T)$ ) [12, 13, 14, 15]. The dominant strain component that causes this reduction of  $H_{c2}(T)$  is the distortional second, or deviatoric, strain invariant [16, 17].  $H_{c2}$  and  $T_c$  have, in first approximation for practical deviatoric strain values, a linear dependence on deviatoric strain [16, 18], which translates to a parabolic-like dependence of the critical current in wires under axial strain [14]. Several models have been developed over the years to describe the strain dependence of Nb<sub>3</sub>Sn. These range from empirical one dimensional axial strain models [19, 20], and empirical three dimensional strain models [15, 18], to more fundamental oriented approaches [10, 11] that provide insight on the relative effects of the various strain invariants [21]. An excellent review of these developments was recently provided by Markiewicz [22]. There are ongoing efforts to generate

\*Electronic mail: agodeke@lbl.gov

a deeper level of understanding of the exact physics that determines the non-hydrostatic strain dependence in practical superconductors. An notable example of this is the work of Salvetti and collaborators at the Massachusetts Institute of Technology, who attempt to calculate the strain sensitivity of Nb<sub>3</sub>Sn using ab-initio calculations [23]. In conclusion it can be stated that a deeper understanding of strain sensitivity is under development, but at present it is unclear whether it will be possible to address and improve the strain sensitivity of practical conductors.

## STATUS OF COMMERCIAL Nb<sub>3</sub>Sn WIRES

### *Bronze processed wires*

The Bronze process can be considered to be the ‘classic’ Nb<sub>3</sub>Sn wire manufacturing process. It is a proven technology and Bronze wires are being produced by a large number of manufacturers in long lengths with very fine (about 5 μm) filaments. The achievable non-Cu  $J_c$ <sup>1</sup> is, however, limited to substantially below 1 kAmm<sup>-2</sup> as a result of the limited solubility of 16% Sn in Cu. This results in a rapidly depleting Sn source, which causes a Sn gradient of around -4 at.% Sn μm<sup>-1</sup> in the A15 [24], and therefore a low A15 fraction that is rich in Sn.

### *Powder-in-Tube wires*

**European Advanced Superconductors** Powder-in-Tube (PIT) wires were first made by the Dutch Energy Research Foundation (ECN) in the Netherlands and have been commercialized by Shape Metal Innovation, Enschede, the Netherlands (SMI), which is now part of European Advanced Superconductors, Hanau, Germany (EAS). The history and development of PIT wires is extensively reviewed elsewhere [8]. The PIT process combines an abundant Sn source with a relatively large current density (over 2500 Amm<sup>-2</sup>) and fine filaments (around 35 μm). The abundant Sn source results in relatively high Sn content in the A15, with a typical Sn gradient of around -0.3 at.% Sn μm<sup>-1</sup>. This means that PIT wires contain a relatively large A15 fraction that is rich in Sn. Wires can presently be manufactured at SMI/EAS in about 45 kg net production units. The maximum non-Cu  $J_c$  has recently surpassed 2600 Amm<sup>-2</sup> in 1.25 mm wires, comprising 288 filaments at 35 μm. These wires were developed for the Next European Dipole (NED) program.

**Supercon Inc.** PIT wires are also produced at Supercon, Shrewsbury MA, USA, as is extensively described elsewhere [8]. Supercon abandoned the use of NbSn<sub>2</sub> powder, in favor of alternative powders, renaming the process to Internal-Tin-Tube process. Their most recent process involves pure Sn in Nb tubes that contain Nb-47wt.%Ti tubes that forms Nb-1.5at.%Ti alloy (and thus optimized ternary

Nb<sub>3</sub>Sn) during the reaction. The Nb(-alloy) tubes are surrounded by a thin Ta layer that allows for a full reaction of the tubes without the risk of poisoning the stabilizing Cu with Sn. Non-Cu  $J_c$  values of 1800 Amm<sup>-2</sup> have been achieved in this layout.

**SupraMagnetics** SupraMagnetics, Plantsville, CT, is producing PIT wires with jet milled Cu<sub>5</sub>Sn<sub>4</sub> powder as described elsewhere [2]. This powder is more cost effective and provides more Sn for the reaction compared to the NbSn<sub>2</sub> powder that is originally used in PIT wires. A key modification in SupraMagnetic’s wire design is the use of octagonal, as opposed to hexagonal, filaments, which enables the implementation of Monel and Glid Cop Al-15 as internal strengthening inside the wires. 52 filament wires with 17.2% Monel between the filaments have been drawn down to 0.25 mm diameter, resulting in 20 μm filaments. Recent versions incorporating Glid Cop and 52 filaments have been drawn down to 0.5 mm diameter. Non-Cu  $J_c$  values of 2000 Amm<sup>-2</sup> have been achieved in earlier Monel reinforced wires.

**Supergenics I LLC** Supergenics, Jefferson, MA, in collaboration with HyperTech Research, Columbus, OH, are developing promising PIT-like wires employing pure Sn and Sn-alloy cores as a Sn source. Proof-of-principle single sub-element wires of this type at 0.25 mm diameter, have achieved non-Cu  $J_c$  values of 2572 and 2733 Amm<sup>-2</sup> in versions without, and with a Ta diffusion barrier, respectively. Wires with 246+25 filaments at 18 μm carry a non-Cu  $J_c$  of 2050 Amm<sup>-2</sup>, whereas versions with 35 μm filaments have achieved 2250 Amm<sup>-2</sup>. A billet of 37 mm diameter and 1 m long was successfully used to manufacture 2 km of wire at 0.7 mm diameter. The companies are presently scaling up to a 37 mm diameter billet with 5 m length.

### *Internal-Tin wires*

The development of Internal-Tin (IT) wires, mostly focussing on IT wires from Oxford Instruments Superconducting Technology (OST), was recently reviewed by Dietterich [2]. OST has switched from Modified Jelly Roll and Hot Extruded Rod processes, to the Rod Restack Process (RRP<sup>®</sup>) as the standard manufacturing process. OST produces low loss, medium current wires, that utilize Nb 47wt.%Ti rods in the subelements to provide the alloying Ti. A single Ta diffusion barrier surrounds the entire subelement stack.  $J_c$  values between 800 and 1200 Amm<sup>-2</sup> are typically obtained in these wires, and the filaments inside the subelements are designed to remain separated after reaction. OST also produces high current versions of the RRP<sup>®</sup> wires, in which the filaments inside the subelements are designed to grow together, through removal of the inter-filamentary Cu, to form a single A15 volume. Each subelement is surrounded by a Nb-Ta diffusion barrier, which is designed to partially react and con-

<sup>1</sup>All values are at 12 T, 4.2 K without self-field corrections, unless stated otherwise.

tribute to the  $J_c$ . 54/61 filament versions of the high current RRP<sup>®</sup> design are manufactured in lengths over 10 km, with filaments around 80  $\mu\text{m}$  and  $J_c$  values that surpass 3000  $\text{Amm}^{-2}$ . Compositional analysis on the high current wires indicates the the Sn content is relatively flat at about  $24 \pm 1$  at.% Sn in the A15 volume [25]. High current RRP<sup>®</sup> wires therefore have a large A15 fraction that is close to optimal composition. This high Sn-rich A15 fraction, and an optimization of the A15 fraction in the non-Cu, are the main reasons these wires carry record current densities. The production of the high current wires is presently measured in tons per year with consistent  $J_c$  values of  $2960 \pm 110$   $\text{Amm}^{-2}$  and residual resistive ratio's (RRR) around 200. A relatively large effective filament diameter, in combination with a very high  $J_c$ , and RRR values that can be reduced as a result of barrier deformations during the cabling process, however, results in low and medium field instability issues in the high current wires. OST initially attempted to counteract these by applying Ta rods inside the subelements to sub-divide the A15 ring, but this proved difficult to scale up to large production units. OST is therefore presently addressing the relatively large subelement size by restacking to reduce the sub-element size. The most successful present version is a 114/127 restack that yields sub-elements around 40  $\mu\text{m}$  in diameter and further restacks are under development.

## SUMMARY

The recognition of a high Sn content in the A15 being a prime parameter to produce very high current density  $\text{Nb}_3\text{Sn}$  wires has resulted in the development of 3000  $\text{Amm}^{-2}$  class Internal-Tin wires that are now commercially manufactured in long lengths. Wires manufactured with the Powder-in-Tube process are achieving  $J_c$  values that are now approaching similar current densities. The manufacture of very high current density wires with effective filaments below 50  $\mu\text{m}$  is a common target for both processes. Bronze processed wires are, as a result of the limited solubility of Sn in Cu, presently not achieving record current densities, but their very small filament diameter of around 5  $\mu\text{m}$  renders Bronze processed wires still desirable for applications that require very low losses. Alternative wire manufacturing processes are under development. These alternative approaches show very promising potential, but none is yet being produced commercially.

## ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, High Energy Physics, US Department of Energy under contract No. DE-AC02-05CH11231. The author would like to acknowledge valuable input from colleagues at:

- Lawrence Berkeley National Laboratory, Berkeley, CA, USA
- University of Twente, Enschede, the Netherlands

- Applied Superconductivity Center and the National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL, USA
- Plasma Science and Fusion Center, Massachusetts Institute of Technology, Cambridge, MA, USA
- University of Geneva, Geneva, Switzerland

and from the following companies for their valuable input and approval to include their latest results:

- Shape Metal Innovation, Enschede, the Netherlands
- European Advanced Superconductors, Hanau, Germany
- Supercon, Shrewsbury MA, USA
- SupraMagetics, Plantsville, CT, USA
- Supergenics I LLC, Jefferson, MA, USA
- Oxford Instruments Superconducting Technology, Carteret, NJ, USA

## REFERENCES

- [1] J. A. Parrell, M. B. Field, Y. Zhang, and S. Hong, *Adv. Cryo. Eng. (Materials)* **50B**, 369 (2004).
- [2] D. R. Dietderich and A. Godeke, *Cryogenics* **48**, 331 (2008).
- [3] B. T. Matthias, T. H. Geballe, S. Geller, and E. Corenzwit, *Phys. Rev.* **95**, 1435 (1954).
- [4] A. Godeke, *Supercond. Sci. and Techn.* **19**, R68 (2006).
- [5] M. C. Jewell, A. Godeke, P. J. Lee, and D. C. Larbalestier, *Adv. Cryo. Eng. (Materials)* **50B**, 474 (2004).
- [6] M. Suenaga, D. O. Welch, R. L. Sabatini, O. F. Kammerer, and S. Okuda, *J. Appl. Phys.* **59**, 840 (1986).
- [7] R. Flükiger et al., *Supercond. Sci. and Techn.* **21**, 054015 (2008).
- [8] A. Godeke, A. den Ouden, A. Nijhuis, and H. H. J. ten Kate, *Cryogenics* **48**, 308 (2008).
- [9] A. Godeke and D. R. Dietderich, Improved pinning in  $\text{Nb}_3\text{Sn}$  through grain refinement and alloying, To be published, 2008.
- [10] W. D. Markiewicz, *Cryogenics* **44**, 767 (2004).
- [11] W. D. Markiewicz, *Cryogenics* **44**, 895 (2004).
- [12] A. Godeke, B. ten Haken, and H. H. J. ten Kate, *IEEE Trans. Appl. Supercond.* **12**, 1029 (2002).
- [13] A. Godeke, *Performance Boundaries in  $\text{Nb}_3\text{Sn}$  Superconductors*, PhD thesis, Univ. of Twente, Enschede, The Netherlands, 2005.
- [14] A. Godeke, B. ten Haken, H. H. J. ten Kate, and D. C. Larbalestier, *Supercond. Sci. and Techn.* **19**, R100 (2006).
- [15] B. ten Haken, A. Godeke, and H. H. J. ten Kate, *J. Appl. Phys.* **85**, 3247 (1999).

- [16] B. ten Haken, *Strain effects on the critical properties of high-field superconductors*, PhD thesis, Univ. of Twente, Enschede, The Netherlands, 1994.
- [17] B. Ten Haken, A. Godeke, and H. H. J. Ten Kate, *IEEE Trans. Appl. Supercond.* **5**, 1909 (1995).
- [18] A. Godeke, B. Ten Haken, and H. H. J. Ten Kate, *Physica C* **372–376**, 1295 (2002).
- [19] J. W. Ekin, *Cryogenics* **20**, 611 (1980).
- [20] D. M. J. Taylor and D. P. Hampshire, *Supercond. Sci. and Techn.* **18**, S241 (2005).
- [21] W. D. Markiewicz, *IEEE Trans. Appl. Supercond.* **15**, 3368 (2005).
- [22] W. D. Markiewicz, *Supercond. Sci. and Techn.* **21**, 054004 (2008).
- [23] M. Salvetti,  $T_c$  strain sensitivity of Al, Nb, Nb<sub>3</sub>Sn and Nb<sub>3</sub>Al using ab-initio computations, Private communication, 2008.
- [24] V. Abächerli et al., *IEEE Trans. Appl. Supercond.* **15**, 3482 (2005).
- [25] P. J. Lee and D. C. Larbalestier, *IEEE Trans. Appl. Supercond.* **15**, 3474 (2005).