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# State of the art powder-in-tube niobium–tin superconductors

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ABSTRACT

Powder-in-tube (PIT) processed niobium–tin wires are commercially manufactured for nearly three decades and have demonstrated a combination of very high current density (presently up to 2500 A mm$^{-2}$ non-Cu at 12 T and 4.2 K) with fine (35 μm), well separated filaments. We review the developments that have led to the present state of the art PIT niobium–tin wires, discuss the wire manufacturing and A15 formation processes, and describe typical superconducting performance in relation to magnetic field and strain. We further highlight successful applications of PIT wires and conclude with an outlook on possibilities for further improvements in the performance of PIT niobium–tin wires.

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## 1. Introduction

The construction of superconducting magnets that are able to generate magnetic fields in the 10–22 T range requires the use of wires that are based on the A15 phase of intermetallic niobium–tin, generally referred to as $Nb_3Sn$ wires. $Nb_3Sn$ superconducting magnets are used in high energy physics (HEP), Fusion Energy applications such as the international thermonuclear experimental reactor (ITER), in chemical analysis in nuclear magnetic resonance (NMR) systems, and in standard high field laboratory magnets.

A common requirement is obviously a high critical current density ($J_c$) but in HEP this is combined with a large adiabatic and dynamic stability. Such stability can be achieved by fine, well separated, twisted filaments with a close proximity of stabilizing high purity Cu. The high ramp-rates in experimental fusion reactors generate significant, undesired, AC losses that can be counteracted by extensive twisting of fine filaments in wires, and by using transposed wires in a cable. Both HEP and fusion typically require an optimized $J_c$ at about 50% of the upper critical magnetic field ($H_{c2}$), but this optimization is often hindered by the required fine filaments. In NMR, AC losses are less of an issue but a very high $H_{c2}$ is needed to retain sufficient current carrying capacity at very high magnetic fields.

$Nb_3Sn$ wires can be manufactured through various processes. The main commercial processes to date are the Bronze process [1], the internal-tin (IT) process [2], and the PIT process. The Bronze process utilizes Nb or Nb–alloy rods that are embedded in a high Sn bronze matrix, which is surrounded by a diffusion barrier and a pure Cu stabilizer. Wire drawing requires intermediate annealing steps after about 50% area reduction, due to the work hardening of the bronze. The Bronze process results in very fine ($\leqslant 5$ μm) filamentary wires which can carry relatively low critical current densities as a result of a limited solubility of Sn in the bronze.

In the IT process, a Sn or Sn-alloy core is surrounded by Nb or Nb-alloy rods in a Cu matrix (Rod Restack process or RRP), or by expanded Nb or Nb-alloy mesh which is layered with Cu (Modified Jelly Roll or MJR process). The resulting filament regions (sub-elements) are surrounded by a diffusion barrier and a pure Cu stabilizer. The filaments within a sub-element often grow together during the A15 formation reaction, resulting in an effective filament of the size of a sub-element. IT processed $Nb_3Sn$ wires can carry up to a present record non-Cu current density of about 3000 A mm$^{-2}$ at 12 T and 4.2 K. (All the $J_c$ values in the remainder of this article are quoted at 12 T and 4.2 K, unless mentioned otherwise.) The high current IT wires have been hindered by a relatively large effective filament size (typically $\geqslant 60$ μm), but recent restacking attempts have reduced the attainable sub-element sizes in IT wires down to below 50 μm, i.e., approaching PIT level [3,4].

Bronze and IT processed wires thus for long had either a high $J_c$ *or* fine filaments. The PIT process has been, until very recently, the only process available to combine fine filaments *and* a close to record $J_c$.

## 2. History of powder-in-tube wires

### 2.1. The ECN process

Manufacture of superconducting wires utilizing a powder in a tube was first proposed by the Netherlands Energy Research Foundation (ECN), Petten, The Netherlands in 1975, and initially referred to as the ECN process. The first PIT processes [5,6] involved filling V tubes with $V_2Ga_5$ or $VSi_2$ powders plus 5–10%

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Cu. These tubes were stacked inside a pure Cu matrix, drawn down to final dimension, and reacted to create multifilamentary $V_3Ga$ and $V_3Si$ wires.

The first prototype Nb–Sn PIT wires were manufactured in 1977 [7] from $NbSn_2$ plus 5–15% Cu powder in a Nb tube. Multiple tubes were stacked in a pure Cu matrix to yield a 36 filament $Nb_3Sn$ wire. ECN further developed a 180 filament prototype, demonstrated an A15 layer $J_c$ of 2400 A mm$^{-2}$, and predicted 600 A mm$^{-2}$ overall [8], which was indeed achieved about 5 years later.

In 1981, Elen et al. [9] reported on a first production wire, of which about 20 kg was manufactured. This was a 19 filament wire with a diameter of 0.56 mm, which carried 3270 A mm$^{-2}$ in the A15 layer and 248 A mm$^{-2}$ overall. The latter translates, using the reported fractions, to about 475 A mm$^{-2}$ non-Cu. Extrusion was attempted but hindered by Nb tube perforation and the powder specification proved critical for extrusion possibilities.

Production runs of 18 filament wire [10] pointed out the relevance of the powder specifications in relation to the achievable core diameter. Also a 36 filament wire was manufactured by drawing only and a 54 filament, >90% Cu version was successfully extruded and drawn. Veringa et al. [11] then reported an extensive A15 growth kinetics study, and determined a minimum required Cu content in the powder for A15 formation below 700 °C, which was later reported to be 3 wt.% [12].

In 1984 the reported $J_c$ had increased to 500 A mm$^{-2}$ overall and 1140 A mm$^{-2}$ non-Cu [12]. Here, also a first attempt to create ternary A15 was reported through the addition of Ti, Ta, Mg and Ga to the powder core. Ti, Ta, Mg have no apparent effect on the critical properties, presumably since they do not diffuse sufficiently into the A15. With the addition of Ga, the large grain intermediate phase at the core is prevented, but Ga also slows the reaction. A striking agreement is presented between measurements and calculations [13,14] of adiabatic stability as a function of magnetic field and A15 diameter, indicating intrinsic stability in PIT wires for all magnetic fields at A15 diameters below 55 μm.

In 1988, 200 kg of a 36 filament wire was manufactured and a 192 filament wire was at the production stage [15]. Developments towards smaller filament size using restacks resulted in up to 1332 filament prototype wires. Smaller filaments clearly required a shorter reaction time, presumably as a result of smaller diffusion distances. Reported non-Cu current densities for the 36 and 1332 filament wires are 1730 A mm$^{-2}$ and 1650 A mm$^{-2}$, respectively at 11 T, leading (assuming 20% $J_c$ loss per tesla) to a $J_c$(12T) of 1384 A mm$^{-2}$ and 1320 A mm$^{-2}$, respectively.

By 1990 [16], the 192 filament wire with 55% Cu appears as a standard product with an average non-Cu $J_c$(11T,4.2 K) of 2120 A mm$^{-2}$ yielding (at −20%/T) $J_c$(12 T) ≅ 1700 A mm$^{-2}$. This wire was used to manufacture Rutherford-type cables which were measured at the University of Twente, Enschede, The Netherlands, to carry 19.3 kA at 11 T and 4.2 K, indicating about 10% cabling degradation.

*2.2. Powder-in-tube wires from ShapeMetal Innovation*

During the first half of the 1990's, ECN discontinued the manufacture of PIT wires. However, the development and manufacture of PIT wires was continued by ShapeMetal Innovation (SMI), Enschede, The Netherlands. SMI focussed on the manufacture of 36 filament wire for very high magnetic field applications and a 192 filament version for HEP magnets. Also development of wires with an increased number of filaments and smaller filament diameter continued at SMI. These developments resulted in the production of a 0.9 mm diameter, 492 filament wire with a filament diameter of about 20 μm and a Cu fraction of 54% [17]. The reported non-Cu current density is 1890 A mm$^{-2}$ at 10 T and 4.2 K, which translates (at −20%/T) to just over 1200 A mm$^{-2}$ at 12 T.

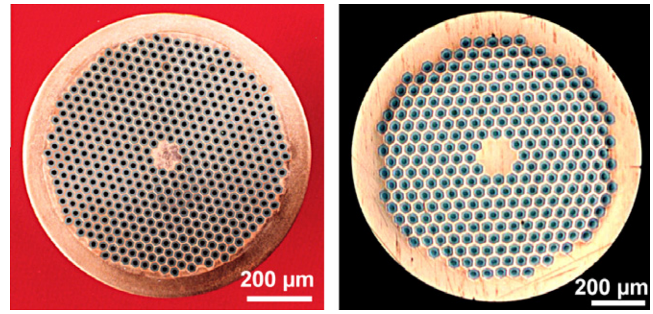


**Fig. 1.** Modern 504 filament (left) and 288 filament (right) PIT wires, manufactured by SMI.

Further optimization of the layout, powder specifications and manufacturing procedures led to a 0.9 mm diameter, 504 filament wire with about 25 μm filaments and a Cu fraction of 52% [18]. This wire carried a non-Cu $J_c$ of 2680 A mm$^{-2}$ at 10 T and 4.2 K, translating to over 1700 A mm$^{-2}$ at 12 T. Also, cold hydrostatic extrusion was successfully employed. For the first time a successful ternary wire was manufactured through the use of a Nb–7.5 wt.% Ta tube in a 37 filament wire with a Cu fraction of 43%. This ternary wire carried about 1750 A mm$^{-2}$, and 217 A mm$^{-2}$ at 20 T and 4.2 K. This was combined with an increased effective critical field of 25.5 T, compared to an extrapolated 21 T for the binary wires. In the end of the 1990's also new optimized binary and ternary 192 filament wires were manufactured by SMI with reported non-Cu current densities of 1955 A mm$^{-2}$ and 2250 A mm$^{-2}$, respectively [19]. The latter value translates, using 2380 μm$^2$ and 935 μm$^2$ for the non-Cu area and the fine grain A15 area, respectively [20], to over 5700 A mm$^{-2}$ in the fine grain A15.

Modern SMI-PIT wires include low AC loss binary and ternary versions of a 504 filament, 0.81 mm wire (Fig. 1, left), with approximately 25 μm filaments, 55% Cu and $J_c$ ≅ 1350 A mm$^{-2}$ and 1950 A mm$^{-2}$ for the binary and ternary versions, respectively. Modern high current density conductors include a ternary 288 filament, 1.255 mm wire (Fig. 1, right), with approximately 35 μm filaments, 55% Cu and a $J_c$ = 2500 A mm$^{-2}$ (Section 4).

*2.3. Powder-in-tube wires from Supercon*

The success of the PIT process to combine a very high non-Cu current density with a small filament diameter, the possibility to draw wires without intermediate heat treatments, the short reaction heat treatment, and the clear potential for further optimizations, stimulated Supercon, Shrewsbury MA, USA, to also start PIT manufacture with some novel modifications [21]. Their early process does not use commercial Nb or Nb–7.5 wt.% Ta tubes, but tubes that are fabricated in-house from fine grain Nb, Nb–Ta and Nb–Ti alloy sheet. This creates the possibility to use commercially available alloys (e.g., Nb–7.5 wt.% Ta and Nb–48 wt.% Ti) and adjust the ternary percentages to what is optimal for the superconducting properties, i.e., 1.5 at.% Ti or 3.5 at.% Ta [22]. This is both cost effective and benefits from the homogeneity and fine granularity that come with the commercial large scale manufacture of alloys. In addition, Supercon investigated various methods for cost effective $NbSn_2$ powder manufacture, which are detailed in their publication. A key modification in their process is that the filaments are surrounded by a thin Ta diffusion barrier. This enables a complete transformation of the Nb or Nb-alloy tube to A15, without the risk of poisoning the Cu matrix.

Supercon's initial attempts to fabricate wires were hindered by a too large particle size in the powder. Development of powder manufacturing processes [23] resulted in a successful 18 filament