EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH
Laboratory for Particle Physics

Departmental Report

**CERN/AT 2008-41**

# HEAT TREATMENT OPTIMIZATION STUDIES ON PIT $Nb_3Sn$ STRAND FOR THE NED PROJECT

T. Boutboul[1], L. Oberli[1], A. den Ouden[2], D. Pedrini[3], B. Seeber[4] and G. Volpini[3]

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1 CERN, Geneva, Switzerland.
2 University of Twente, Faculty of Science and Technology, Enschede, The Netherlands
3 INFN-Milan/LASA, Milano, Italy
4 University of Geneva, Geneva, Switzerland

Presented at the Applied Superconductivity Conference (ASC 2008)
17-22 August 2008, Chicago, USA

CERN
Accelerator Technology Department
CH - 1211 Geneva 23
Switzerland

01 March 2009

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***Abstract*— For the Next European Dipole (NED) program, a Powder-In-Tube (PIT) strand was successfully developed by SMI. This high-performance $Nb_3Sn$ strand presents a non-copper critical current density of ~ 2500 A/mm$^2$ at 12 T applied field and 4.2 K and a filament diameter around 50 µm. Extensive heat treatment optimization studies were performed in order to maximize both critical current and RRR, with a plateau temperature down to 625 $^o$C and duration up to 400 hours. It appears that a critical current enhancement of ~ 10 % can be achieved for a reaction schedule of 320 hours at 625 $^o$C with non-copper critical current density respectively exceeding 2700 and 1500 A/mm$^2$ at 12 and 15 T (4.2 K). Thanks to this modified heat treatment, this strand completely fulfils the NED stringent specification.**

***Index Terms*—Niobium compounds, superconducting wires, low-temperature superconductors, superconducting materials measurements.**

## I. INTRODUCTION

THE Next European Dipole (NED) project is a Joint Research Activity of the Coordinated Accelerator Research in Europe (CARE) program [1]. The main goal of NED was initially to design, to develop and to fabricate a large aperture and high-field (~ 15 T) superconducting $Nb_3Sn$ dipole magnet. However, due to financial limitations, NED was mainly refocused on the development and the production of a high-performance $Nb_3Sn$ conductor. The $Nb_3Sn$ strand NED specifications, summarized in [2], are very demanding. Indeed, in addition to very high critical currents targeted respectively corresponding to 3000 and 1500 A/mm$^2$ in the non-copper part at 12 T and 15 T (4.2 K), a filament diameter of ~ 50 µm is requested for a strand diameter of 1.25 mm. This requirement imposes to stack between 250 and 300 sub-elements within the final billet, which is not an obvious task [2]. In 2004, two contracts were placed at Alstom-MSA (Internal Tin Diffusion method) and SMI (Powder-In-Tube route [3]).

During its R&D phase, SMI successfully developed [2-4] a $(Nb\text{-}Ta)_3Sn$ strand, called B215, including 288 filaments (~ 50 µm in diameter). A cross-section view of this strand is presented in Fig. 1. For this strand, the maximal critical current ever measured for the heat treatment (HT) schedule recommended by the company (84 hours at 675 $^o$C) is 1397 A, corresponding to ~ 2500 A/mm$^2$ in the non-copper region at 4.2 K and 12 T applied field. This strand presents as well fair RRR values (in the 70-80 range) and only few flux jumps as shown by magnetization measurements [2-4].

In this work, HT optimization studies for both critical current and RRR were carried out on B215 strand and the most relevant results of those studies are presented in this article.

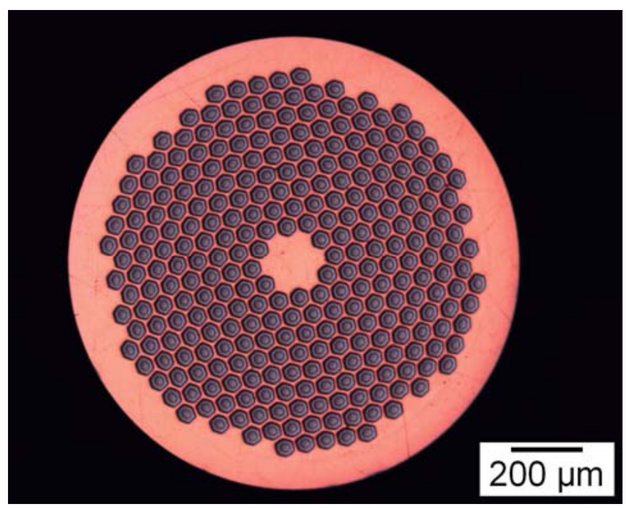


Fig.1. A cross-section view of the strand B215 at 1.25 mm diameter.

## II. HT OPTIMIZATION: MOTIVATION AND METHOD

For $Nb_3Sn$ formation, the choice of the reaction temperature and duration has to be a compromise between the amount of A15 phase formed, favored by higher temperature and longer duration, and its phase quality [5], mainly characterized by a moderate grain size and a high tin content. Higher temperatures provide generally higher upper critical field and a more homogeneous A15 phase but as well larger grains, which could be detrimental to material pinning center density and thus to critical current density [6]. The $Nb_3Sn$ phase of a PIT wire is composed of a fine grain (~ 200 nm in size) zone and a coarse grain (~ 1-2 µm in size) region representing ~ 30

Manuscript received August 18, 2008. This work was supported in part by the European Community-Research Infrastructure Activity under the FP6 “Structuring the European Research Area” program (CARE, contract number RII3-CT-2003-506395)

T. Boutboul and L. Oberli are with CERN, AT department, CH-1211 Geneva 23, Switzerland (corresponding author: phone: +41-22-7679588; fax: +41-22-7676300; e-mail: thierry.boutboul@cern.ch).

A. den Ouden is with University of Twente, Faculty of Science and Technology, P.O. Box 217, 7500 AE Enschede, the Netherlands (e-mail: A.denOuden@tnw.utwente.nl).

D. Pedrini and G. Volpini are with INFN-Milan/LASA, via Fratelli Cervi 201, 20090 Segrate (Milan), Italy (e-mails: danilo.pedrini@mi.infn.it, giovanni.volpini@mi.infn.it).

B. Seeber is with University of Geneva, 20 rue de l’Ecole de Médecine, CH-1211 Geneva, Switzerland (e-mail: Bernd.Seeber@physics.unige.ch).

% of the A15 total area, as shown in Fig. 2. These coarse grains are thought to have a negligible contribution to the critical current, due to pinning center deficiency.

Fisher [7] investigated the effect of reaction conditions on the superconducting characteristics of PIT binary and ternary Ta-alloyed $Nb_3Sn$, for reaction temperature between 675 $^oC$ and 1000 $^oC$. He showed that, for ternary PIT strands, a treatment of 64 hours at 675 $^oC$ constitutes an adequate HT schedule in terms of formed A15 phase amount and quality. This reaction schedule was adopted by SMI as the standard reaction treatment for their strands. In recent years, following HT trials that provided a critical current enhancement of ~ 5 %, 84 hours at 675 $^oC$ became the HT schedule recommended by SMI [8].

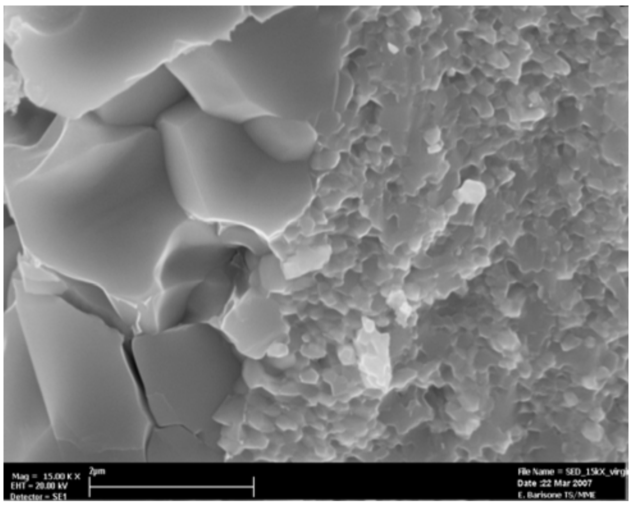


Fig.2. A SEM view (x 15000) of a B215 strand fractured sample reacted at 675 $^oC$ during 84 hours showing both coarse (left) and fine (right) grains.

To our best knowledge, very few investigations were done with a reaction temperature lower than 675 $^oC$. Such studies were performed at Twente University but they did not provide conclusive results. In this work, the main idea was to optimize the critical current of the B215 strand by lowering the reaction temperature in order to, tentatively, further reduce fine grain size and coarse grain area dimensions in $Nb_3Sn$ phase.

Due to small amount of available B215 strand and to limited reaction furnace resources, a systematic optimization study with a broad scanning of both reaction temperature and duration was not feasible. Instead, a specific HT schedule was selected as a tentative. Then the critical current and the RRR of the reacted samples were measured and their cross-sections examined by means of a microscope to evaluate the extent of the reacted area. Eventually, according to those results, the next HT schedule was chosen. The main results of this study are presented in the next section.

## III. Prominent results

### A. Overview

In the frame of the optimization studies, various reaction conditions were tried with a temperature ramp of 50 $^oC$/hour, similar for all treatments, and a reaction plateau variable in both temperature and duration. The treatment temperatures, investigated in this work, are: 660 $^oC$ (duration of 84 hours), 650 $^oC$ (84 and 120 hours) and 625 $^oC$ (200, 260, 320 and 400 hours). In this article, the most successful results, i.e. for HT schedules of 120 hours at 650 $^oC$ and particularly 320 hours at 625 $^oC$, are reported.

### B. HT schedule of 120 hours at 650 $^oC$

For this reaction schedule, consistent critical current ($I_c$) data were measured at CERN and Twente University with a maximal value of 1410 A at 12 T and 4.2 K, corresponding to a non-copper critical current density of ~ 2520 A/mm$^2$. Although this slight $I_c$ enhancement (~ 1%) is not significant, one should mention that the measurements are more reproducible with an $I_c$ data scatter of less than 3 % as compared to HT recommended by SMI (~ 6 %). $I_c$ measurements performed by Geneva University at high applied fields confirmed the ~ 1 % enhancement at 15 T and 4.2 K (762 A) as compared to the sample treated during 84 hours at 675 $^oC$. The Kramer extrapolated upper critical field, $\mu_o H_{c2}^K$, was found to be 25.6 T, i.e. similar to that observed for the standard schedule of 84 hours at 675 $^oC$ [3].

As already reported in a previous publication [2], the B215 strand was used to fabricate a 40-strand Rutherford cable at Lawrence Berkeley National Laboratory (see the cable cross section in Fig. 3). Preliminary measurements at CERN indicated a moderate critical current degradation of 4-8 % due to cabling [2]. Since then, this degradation level was confirmed by measurements done at Twente University. However, measurements, performed at INFN-Milan on both virgin and extracted strand samples treated during 84 hours at 675 $^oC$, showed a more significant degradation (10-13 %).

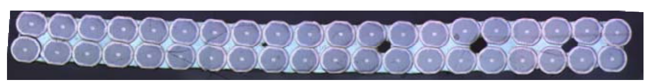

Fig.3. A cross-section view of the Rutherford-type cable produced at LBNL with B215 strand.

From the RRR point of view, the HT schedule of 120 hours at 650 $^oC$ appears to be, as well, more favorable than 84 hours at 675 $^oC$ for achieving high values. Indeed, for virgin samples, RRR values were generally found to be larger than 100 (with a maximal value of 143) for 120 hours at 650 $^oC$, as compared to values not exceeding 80, for the standard reaction schedule. For extracted strands, the same trend was observed since samples treated during 120 hours at 650 $^oC$ did not show a significant degradation (RRR ~ 100) contrary to RRR between 30 and 60 for standard reaction extracted samples.

### C. Reaction at 625 $^oC$

After the trials at 650 $^oC$, we decided to further decrease the reaction temperature. During the low reaction temperature investigations performed at Twente and already mentioned above, an onset temperature of 625 $^oC$ for the $Nb_3Sn$ formation was observed. As a preliminary test, a B215 strand sample was treated at ~ 620 $^oC$ during 61 hours to check reaction feasibility at such a low temperature. When looking at the SEM micrograph of the treated sample shown in Fig. 4, we observe the presence of a thin $Nb_3Sn$ ring already reacted (dark grey in Fig. 4), thus confirming A15 formation feasibility at this low treatment temperature. However, we also observe the existence of a large area of $Nb_6Sn_5$ (white layer close to tube core in Fig. 4). This $Nb_6Sn_5$ region, representing at least ~ 25 % of potential $Nb_3Sn$ phase, is composed of micrometric coarse grains that are converted into $Nb_3Sn$ coarse grains [7] during the HT. Therefore, the hope to significantly reduce the coarse grain area, by lowering the reaction temperature to 625 $^oC$, is not likely to be fulfilled.

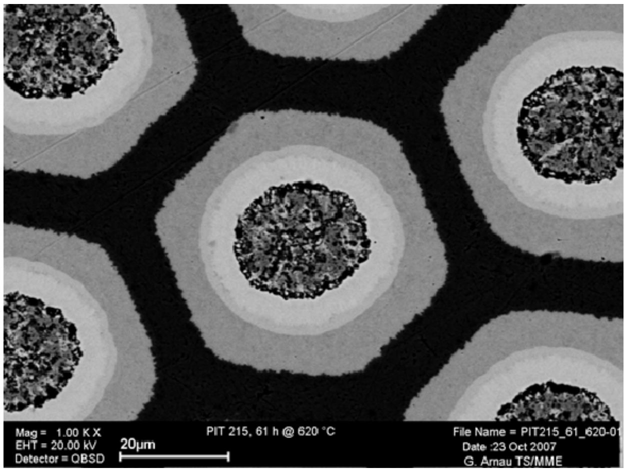


Fig. 4. A SEM view (x 1000) of a B215 sample reacted during 61 hours at ~620 $^oC$ showing a thin $Nb_3Sn$ ring (dark grey) and an adjacent $Nb_6Sn_5$ layer (white, close to tube core).

After two trials at 625 $^oC$ (durations of 200 and 260 hours), two B215 strand samples were reacted at 625 $^oC$ during 320 hours and tested at CERN. Two additional virgin samples were sent to Twente for a similar HT schedule; after reaction they were measured at the High Field Magnet Laboratory at Nijmegen. At 12 T applied field and 4.2 K, all the samples, measured either at CERN or at Nijmegen, showed an impressive critical current around 1500 A, the values consistently spanning between 1494 A and 1539 A (~ 3 % spread). The corresponding critical current density in the non-copper part is between 2660 and 2740 A/mm$^2$. These critical currents and critical current densities are unprecedented and they constitute a new record for this kind of strand. One should mention that the highest $I_c$ value at 12 T and 4.2 K, i.e. 1539 A, represents an enhancement of ~ 10 % as compared to the standard HT schedule (84 hours at 675 $^oC$). The critical current measurements at Nijmegen were performed up to 22 T applied field. The critical currents at 15 T and 4.2 K, as extracted from these measurements, are for both strands 859 and 823 A. These two values are greater than the minimal critical current requested by NED specification at 15 T (818 A). This fact is undoubtedly an outstanding achievement for the NED program. These critical currents respectively represent an $I_c$ enhancement of 14 % and 9 % as compared to standard HT schedule. They correspond to a non-copper critical current density of 1470 and 1530 A/mm$^2$ at 15 T and 4.2 K. Nijmegen measurements for the highest current sample are shown in Fig. 5, together with $I_c$ data measured at Geneva University for a treatment of 84 hours at 675 $^oC$ and with the NED specified value at 15 T and 4.2 K. From Nijmegen measurements for 320 hours at 625 $^oC$, the $\mu_o H_{c2}^K$ value is found to be 26.3 T and is therefore higher than that for the standard reaction schedule, 25.6 T, despite the lower treatment temperature. From Nijmegen preliminary measurements on extracted strands treated at 625 $^oC$/320 hours, a reasonable critical current cabling degradation of ~ 5-6 % was observed.

The RRR data are impressive, as well, for the reaction at 625 $^oC$ during 320 hours with values around 220 (180) as measured at CERN on virgin samples treated at CERN (Twente University). For extracted samples, the values are ~ 130. Therefore both virgin and extracted strands have RRR values within NED specifications, thanks to the new HT schedule. In Table I, the main characteristics achieved for 320 hours at 625 $^oC$ and standard reaction are summarized, together with the NED specified values.

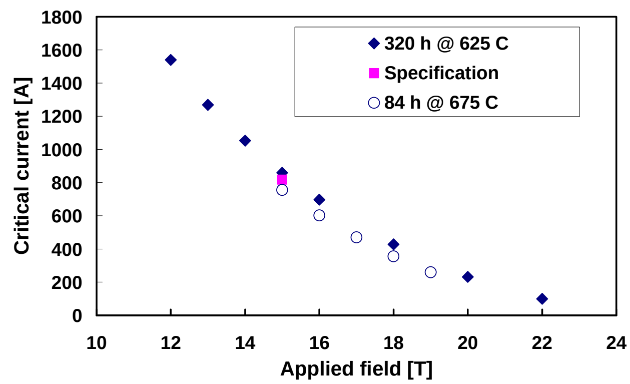


Fig. 5. The critical current of B215 strand as measured at Nijmegen for a treatment of 320 hours at 625 $^oC$ and by Geneva University for a standard reaction of 84 hours at 675 $^oC$, together with the NED specified value at 15 T.

A last HT trial was performed at 625 $^oC$ during 400 hours. Although the critical current at 12 T is similar to that of the 320 hours reaction, the RRR values are smaller: ~ 120 for virgin strands and less than 90 for extracted strands, showing a slight tin poisoning of the copper stabilizer.

TABLE I
MAIN CHARACTERISTICS FOR B215 STRAND (ACHIEVED VS SPECIFICATION)

| HT | D [mm] | $D_{eff}$ [μm] | Cu/non-Cu | Ic, 15 T [A] | RRR, virgin | RRR, extr. |
|---|---|---|---|---|---|---|
| 675 $^oC$/84 h | 1.258 | 49.8 | 1.22 | 756 | 70-80 | 30-60 |
| 625 $^oC$/320 h | 1.258 | 49.8 | 1.22 | 823-859 | ~ 220 | ~ 130 |
| Specification | 1.250 ± 0.004 | < 50 | 1.25± 0.10 | > 818 | > 200 | > 120 |

D is the strand diameter before HT. $D_{eff}$ is the effective filament diameter, as determined from filament dimensions before HT [2]. RRR for virgin and extracted strands are the data after full reaction.

## IV. SEM EXAMINATIONS

SEM examinations were performed at CERN on B215 samples reacted either at 625 $^oC$ during 320 hours or following the standard reaction schedule. The first goal was to assess the filament reaction rate. This was done on micrographs of polished samples by means of analySIS$^{TM}$ software. In Fig. 6, the micrograph of a sample reacted 320 hours at 625 $^oC$ is presented as an example. It appears that for the modified HT schedule 25 % of the tube is still un-reacted niobium barrier as compared to 23 % for the standard reaction. This enlarged diffusion barrier can obviously be correlated to the enhanced RRR values measured for the samples reacted at 625 $^{o}$C during 320 hours. Therefore, despite the ~ 10 % enhancement in critical current, the sample reacted at 625 $^{o}$C/320 hours presents less reacted $Nb_3Sn$ than the sample treated at 675 $^{o}$C/84 hours.

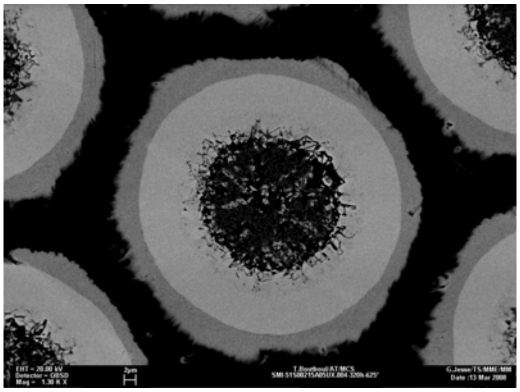

Fig. 6. A SEM view (x 1300) of a B215 sample reacted at 625 $^{o}$C/ 320 hours.

The second issue was to evaluate the $Nb_3Sn$ quality by measuring its tin content, for the two reaction schedule cases. This was done by means of SEM/EDS analyses performed on polished samples. It appears that, for 320 hours at 625 $^{o}$C sample, the fine grain region contains in average a nearly stochiometric content of 24.7 at. % Sn, as compared to 24.2 at. % Sn for the standard reaction.

Afterwards, the ratio of coarse grains in the $Nb_3Sn$ phase was estimated on the basis of micrographs of fractured samples. It was found that ~ 30 % of the A15 area is composed of coarse grains for both schedules: 320 hours at 625 $^{o}$C (29 %) and 84 hours at 675 $^{o}$C (31 %). This insignificant difference thus confirms that lowering the reaction temperature to 625 $^{o}$C can not reduce the coarse grain ratio.

Last but not least, SEM fractographs were used to determine the fine grain size of the $Nb_3Sn$ phase. Although SEM is definitely not a convenient tool for such a task and TEM would be more suitable, large statistics (several dozens in every case) were used in order to improve the reliability of the evaluated mean values. The mean fine grain size was found to be smaller for the sample treated at 625 $^{o}$C during 320 hours (~ 160 nm) than for the sample reacted in a standard way (~ 180 nm). This reduced grain size indicates a more efficient pinning, which explains, at least partly, the $I_c$ enhancement observed for the 320 hours at 625 $^{o}$C reaction.

## V. Conclusions

During its R&D phase for NED, SMI developed a Powder-In-Tube $Nb_3Sn$ strand with ~ 50 µm filament size and a non-copper critical current density of ~ 2500 A/mm$^2$ at 12 T and 4.2 K, when reacted with the heat treatment recommended by the firm (84 hours at 675 $^{o}$C). A reaction schedule optimization study was launched at CERN in order to improve strand performance, with treatment temperature down to 625 $^{o}$C and duration in the 84-400 hours range.

For samples reacted at 625 $^{o}$C during 320 hours, a critical current increase of ~ 10 % as compared to the recommended heat treatment was observed with a record value of ~ 1500 A and an impressive non-copper critical current density of ~ 2700 A/mm$^2$ at 12 T and 4.2 K. This corresponds to a critical current density of ~ 4800 A/mm$^2$ in the whole $Nb_3Sn$ layer, including both fine and coarse grains. Assuming a critical current density in coarse grains of 30 % of its value in fine grains, the critical current in the fine grain region would be around 6000 A/mm$^2$, which would constitute a record value.

At 15 T and 4.2 K, the critical current exceeds the NED specified value (818 A), corresponding to a critical current density in non-copper part of more than 1500 A/mm$^2$. This is obviously a considerable achievement for the NED project since very high amperage was obtained together with a small filament size (~ 50 µm) for a 1.25 mm strand diameter. Preliminary measurements on extracted strands showed a reasonable critical current cabling degradation of ~ 5-6 %.

For the optimized heat treatment, the RRR values are as well impressive: ~ 220 (~ 130) for virgin (extracted) strands. Such high RRR data should contribute to an enhanced dynamic stability in cables and magnets based on such strands.

SEM examinations showed that samples reacted at 625 $^{o}$C during 320 hours have slightly less reacted $Nb_3Sn$ than standard HT samples, despite their enhanced critical current. However, the improved current abilities of the former samples can be explained by a higher quality A15 phase with a higher tin content (24.7 versus 24.2 at. % Sn in average) and fine grain size reduced (160 nm versus 180 nm in average).

Last year, EAS purchased the Powder-In-Tube technology from SMI and the technology transfer is nearly achieved. EAS is currently manufacturing the final strand for NED with a design similar to that of B215 strand.

## Acknowledgment

The authors would like to warmly thank for their useful help: G. Arnau, E. Barisone, A. Bonasia, Z. Charifoulline, S. Geminian, P. Jacquot, G. Jesse, D. Leroy, S. Mathot, D. Richter, J.-L. Servais (CERN), S. Wessel (Twente University), S.A.J. Wiegers and J.A.A.J. Perenboom (the Nijmegen High Field Magnet Laboratory).

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