

**PHASE TRANSFORMATIONS DURING THE REACTION HEAT TREATMENT  
OF Nb<sub>3</sub>Sn SUPERCONDUCTORS**

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**Abstract**

The evolution of Nb containing phases during the diffusion heat treatment of three different high critical current Nb<sub>3</sub>Sn strand types is compared, based on synchrotron X-ray diffraction results that have been obtained at the ID15 beam line of the European Synchrotron Radiation Facility (ESRF). In all strands studied, Nb<sub>3</sub>Sn formation is preceded by the formation of a Cu-Nb-Sn ternary phase, NbSn<sub>2</sub> and Nb<sub>6</sub>Sn<sub>5</sub>. As compared to the PIT and Tube Type strand, the amount of these phases formed in the RRP strand is relatively small. In the RRP strand subelements with a fine filament structure Nb<sub>3</sub>Sn grows more quickly, thereby preventing to a large extent the formation of the other higher tin phases.

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Presented at the 9th European Conference on Applied Superconductivity (EUCAS'09)  
13-17 September 2009, Dresden, Germany

Geneva, Switzerland

13 November 2009

# Phase transformations during the reaction heat treatment of Nb<sub>3</sub>Sn superconductors

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**Abstract.** The evolution of Nb containing phases during the diffusion heat treatment of three different high critical current Nb<sub>3</sub>Sn strand types is compared, based on synchrotron X-ray diffraction results that have been obtained at the ID15 beam line of the European Synchrotron Radiation Facility (ESRF). In all strands studied, Nb<sub>3</sub>Sn formation is preceded by the formation of a Cu-Nb-Sn ternary phase, NbSn<sub>2</sub> and Nb<sub>6</sub>Sn<sub>5</sub>. As compared to the PIT and Tube Type strand, the amount of these phases formed in the RRP strand is relatively small. In the RRP strand subelements with a fine filament structure Nb<sub>3</sub>Sn grows more quickly, thereby preventing to a large extent the formation of the other higher tin phases.

## 1. Introduction

During the diffusion heat treatment (HT) of Nb<sub>3</sub>Sn superconductors the precursor elements form various intermetallic phases and finally the superconducting Nb<sub>3</sub>Sn [1]. The formation of Nb containing phases prior to Nb<sub>3</sub>Sn nucleation and growth can degrade the microstructural and microchemical homogeneity in the fully reacted strand, and it is therefore of interest to investigate how the strand design and the overall elemental composition of its sub-elements influence these transformations.

High energy synchrotron X-ray diffraction is an excellent tool for monitoring phase transformations in Nb<sub>3</sub>Sn strands during *in-situ* reaction HT's. Previously we have reported the phase transformations that occur in a low loss Nb<sub>3</sub>Sn strand [2], a PIT strand [3] and a RRP strand [4]. Here we compare the phase transformations that occur in the RRP and PIT strand with those in a Tube Type Nb<sub>3</sub>Sn strand. In order to allow for a semi-quantitative comparison of the phase evolutions, synchrotron diffraction measurements were performed for the three high critical current ( $J_c$ ) strand types with identical experimental settings.



## 2. Experimental

Cross sections of the Restacked Rod Process (RRP<sup>®</sup>) strand [5] produced by Oxford Superconducting Technology, the Powder-in-Tube (PIT) strand [6] produced by Shape Metal Innovation (now part of Bruker EAS) and the Tube Type strand [7] from Hyper Tech Research are presented in figure 1. The nominal diameter of the PIT B215 strand is 1.25 mm. In order to allow for a semi-quantitative comparison of the diffraction results and to investigate the influence of the subelement size, diffraction measurements have also been performed with a PIT B215 strand that has been drawn down to  $\varnothing=0.80$  mm. The nominal non-Cu volume fractions in the RRP, Tube Type and PIT strands are 51.9 %, 45.1 % and 46.5 %, respectively. For the Tube Type strand the atomic fractions within the subelements are 4.35 at.% Cu, 21.9 at.% Sn and 73.3 at.% Nb [8]. For the other samples the exact composition of the subelements is not known.

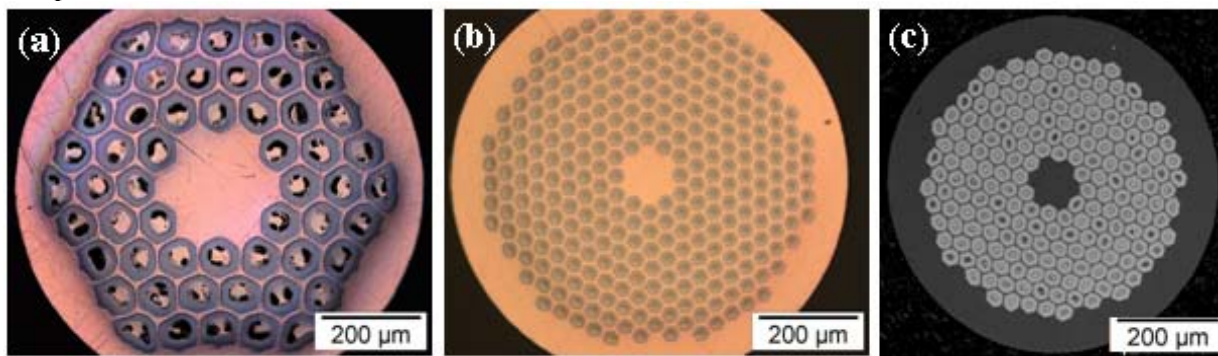


Figure 1: Cross sections of the three strand samples investigated, (RRP billet #7419 with 54 subelements,  $\varnothing=0.80$  mm, non-Cu=51.9 vol.% (a), PIT B215, with 288 subelements,  $\varnothing=0.80$  mm, non-Cu=45.1 vol.% (b), and Tube Type T1505 with 192 subelements,  $\varnothing=0.70$  mm, non-Cu=46.5 vol.% (c)).

The phase transformations in the different strand samples were monitored by high energy ( $\sim 90$  keV) synchrotron X-ray diffraction measurements. During the *in-situ* HT with a temperature ramp rate of 100 °C/h and a 4 h-700 °C isothermal holding step, diffractograms were acquired every 5 minutes. HTs were performed in a dedicated X-ray transparent furnace built at ID15 that enables an accurate sample temperature control during the diffraction experiments. For more information about the diffraction experiment refer to [3]. The present experiment has been optimised for high angular resolution, on the expense of the recorded lattice spacing (*d*-spacing) range. The radially integrated diffractograms acquired for the Tube Type, PIT and RRP strands during *in-situ* HT at 480 °C are shown in figure 2.

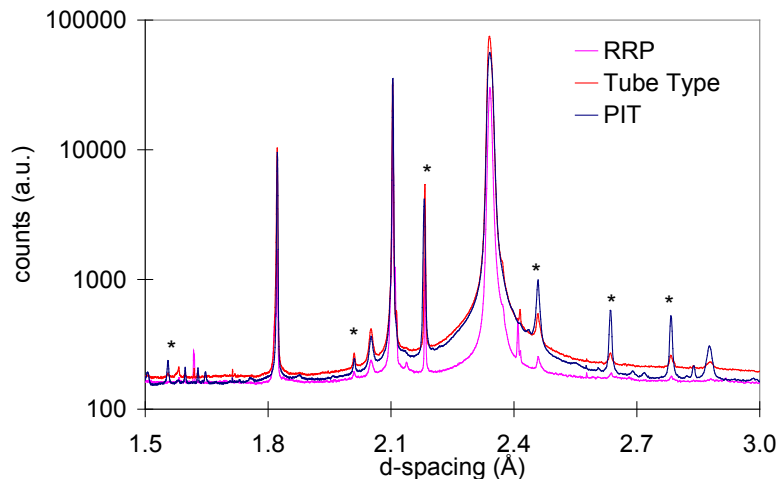


Figure 2: Diffractograms of the RRP, Tube Type and PIT strand acquired during *in-situ* HT at 480 °C. The diffraction peaks that have been assigned to a Cu-Nb-Sn phase are labeled with an asterisk.

The colour intensity plot shown in figure 3 summarizes the 130 diffractograms that were acquired during the reaction HT of the Tube Type strand. A semi-quantitative description of the evolution of all Nb containing phases as a function of temperature has been obtained by monitoring the area of characteristic diffraction peaks. In figure 3 the reflections that have been selected for peak area measurements are labelled in red. Prior to peak area measurements diffractograms were normalized to the X-ray flux reaching the sample, in order to correct for fluctuations of the Synchrotron beam current during the experiment. Diffraction peak areas obtained for the 1.25 mm diameter PIT strand are significantly smaller than those for the 0.8 mm PIT strand, due to the stronger X-ray self absorption in the larger diameter strand sample. In order to facilitate a comparison between the diffraction data of the 1.25 mm diameter strand with that of the other samples, all PIT-1.25 mm data has been multiplied by an arbitrarily chosen factor of 3.

Since the non-Cu volume in the RRP strand exceeds the non-Cu volume in the tubular strands, the peak area comparisons may somewhat overestimate the phase content in the RRP strand with respect to that in the tubular strands.

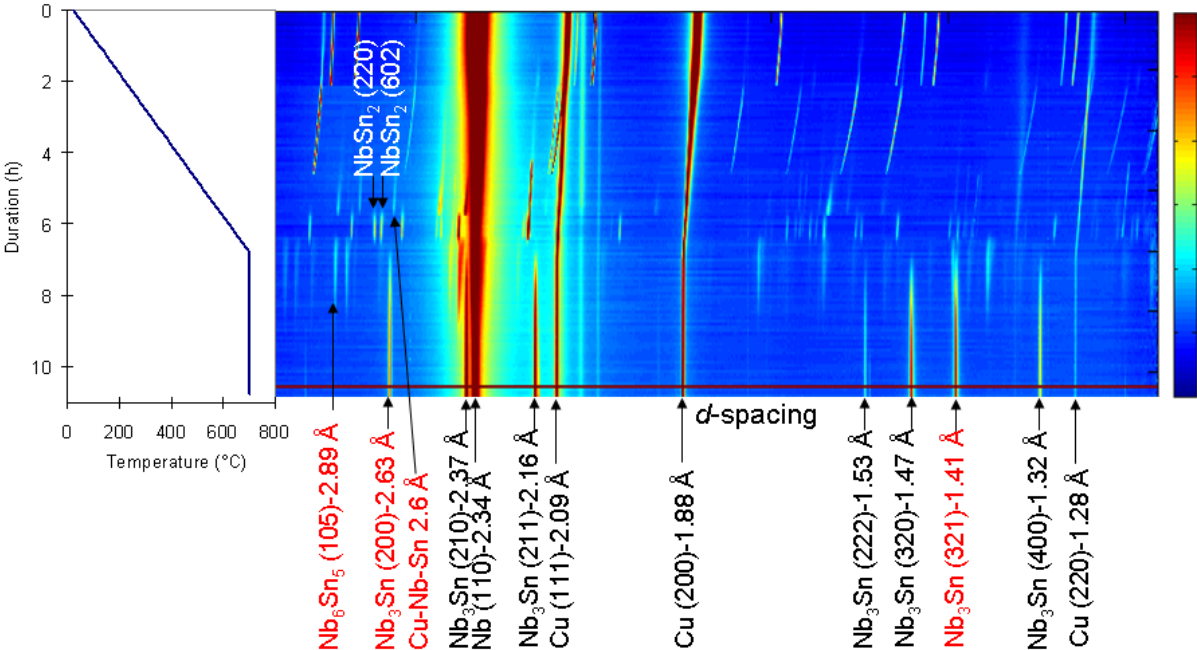


Figure 3: Colour intensity plot summarising 130 diffractograms that have been acquired during *in-situ* HT of the Tube Type  $Nb_3Sn$  strand with a ramp rate of 100 °C/h and an additional 4 h-700 °C isothermal step. The reflections that were used for peak area measurements are labeled in red and white. The *d*-spacing axis is inverted with respect to figure 2.

### 3. Results

#### 3.1. Cu-Nb-Sn ternary phase formation

Formation of at least one Cu-Nb-Sn ternary phase has been observed previously in RRP [9] and later in a PIT strand [3]. As shown in figure 2 characteristic Cu-Nb-Sn diffraction peaks are also detected during the diffusion HT of the Tube Type strand at 480 °C. The Cu-Nb-Sn phase evolution in the three strand types is compared in the left plot of figure 4. Most Cu-Nb-Sn is formed in the PIT strand, probably mostly in the initial powder core. By analytical Transmission Electron Microscopy it can be shown that in the PIT strand some Cu-Nb-Sn is also formed at the inside of the pre-cursor tube [10].

For the RRP strand the Cu-Nb-Sn evolution during the HT without holding steps (this experiment) is compared with the Cu-Nb-Sn growth during a HT with additional 2 h-390 °C and 2 h-482 °C isothermal holding steps, which has been reported in [4]. Because of different experimental settings the peak areas obtained with both experiments can not be compared. However, it can be seen that isothermal holding steps, in particular above the  $\text{Cu}_6\text{Sn}_5$  decomposition temperature of 415 °C, can promote the formation of Cu-Nb-Sn.

#### 3.2. $\text{NbSn}_2$ formation

The  $\text{NbSn}_2$  evolution in the different strand types is compared in the right plot of figure 4. Similar amounts of  $\text{NbSn}_2$  are formed in the PIT and Tube Type strands. In the RRP strand less  $\text{NbSn}_2$  is formed and the temperature interval during which the amount of  $\text{NbSn}_2$  exceeds the detection limit is relatively small. The Cu-Nb-Sn and  $\text{NbSn}_2$  peak area evolutions in the PIT strand with 1.25 mm and 0.80 mm diameter are similar.

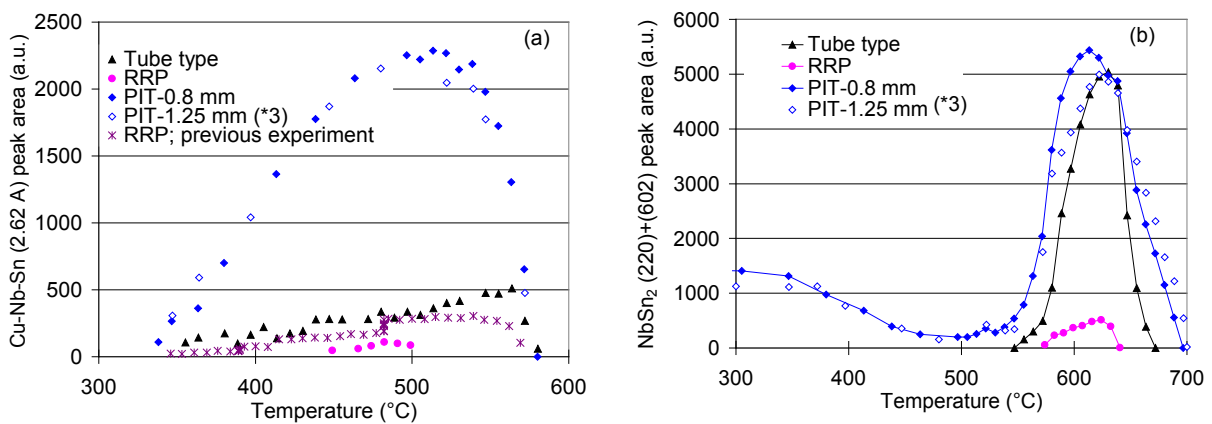


Figure 4: Cu-Nb-Sn ( $d$ -spacing=2.62 Å) (a) and  $\text{NbSn}_2$  (220)+(602) peak area (b) evolution in the different strand samples during a 100 °C/h HT. The peak areas of the PIT-1.25 mm strand have been multiplied by a factor of 3.

#### 3.3. $\text{Nb}_6\text{Sn}_5$ formation

The  $\text{Nb}_6\text{Sn}_5$  phase evolution as a function of temperature and HT duration is presented in figure 5. Similar amounts of  $\text{Nb}_6\text{Sn}_5$  are detected in the PIT and Tube Type strand, whereas a relatively smaller amount of  $\text{Nb}_6\text{Sn}_5$  is formed in the RRP strand. The temperature and duration after which  $\text{Nb}_6\text{Sn}_5$  starts to decompose in the different strand types differ significantly.

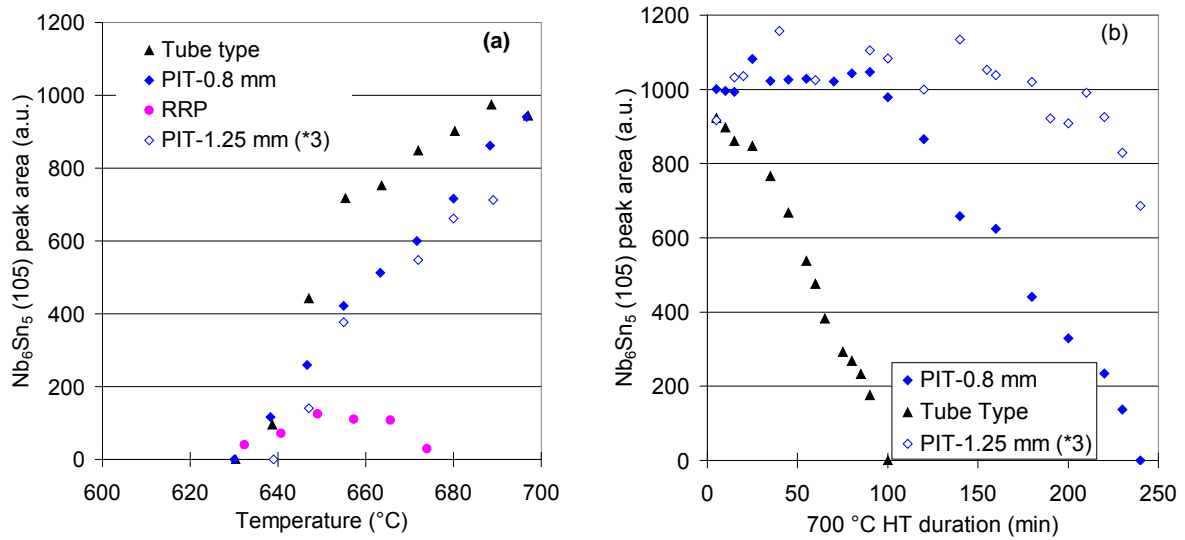


Figure 5:  $Nb_6Sn_5$  (105) peak area as a function of temperature (a) and as a function of 700 °C HT duration (b). The peak areas of the PIT-1.25 mm strand have been multiplied by a factor of 3.

### 3.4. $Nb_3Sn$ formation

In the RRP strand  $Nb_3Sn$  growth is detected at comparatively low temperature (at 510 °C and 530 °C for (200) and (321) oriented  $Nb_3Sn$  reflections, respectively). In the PIT and Tube Type strands  $Nb_3Sn$  is detected at significantly higher temperatures and, contrary to the RRP strand, for PIT and Tube Type strands  $Nb_3Sn$  (321) reflections are observed at a lower temperature than the  $Nb_3Sn$  (200) reflections.

In figure 6 the  $Nb_3Sn$  growth during a 4 h-700 °C HT is compared for the 3 strand types (left) and for the 0.80 mm and 1.25 mm PIT strand (right). In the RRP strand the  $Nb_3Sn$  grains detected have predominantly a (200) orientation, while in the PIT and Tube Type strand they exhibit mostly a (321) orientation parallel to the strand drawing axis. The difference in  $Nb_3Sn$  (321) to  $Nb_3Sn$  (200) intensity ratio between the RRP strand and the tubular strands is also observed after complete reaction of the different strand types.

In the RRP strand the 700 °C HT duration needed for a complete reaction is roughly 10 h, while in the tubular strand types significantly longer HT durations are needed to achieve a complete reaction at 700 °C.

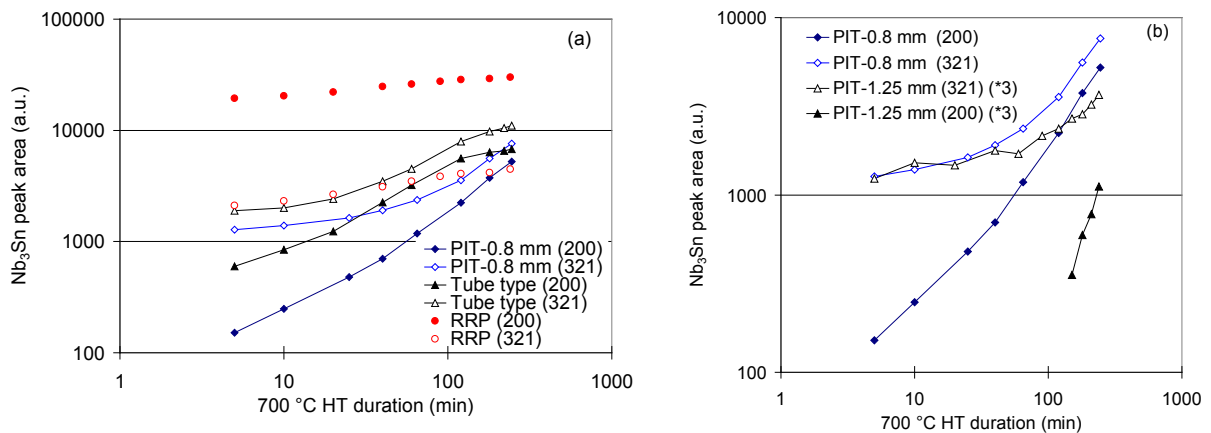


Figure 6: Comparison of  $Nb_3Sn$  (200) and (321) peak area evolution vs. 700 °C HT duration for the 3 different strand types (a) and for PIT-1.25 and PIT-0.80 (b). The peak areas of the PIT-1.25 mm strand have been multiplied by a factor of 3.