Phase Transformations During the Reaction Heat Treatment of Internal Tin Nb₃Sn Strands With High Sn Content

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Abstract—The phase transformations that occur during the reaction heat treatment (HT) of Nb₃Sn superconductors depend on the overall elemental composition of the strand subelements. In the case of modern high J_c strands with a relatively low Cu content, liquid phases are present during large temperature intervals and phases that can be detrimental for the microstructural and microchemical homogeneity of the fully reacted strand are formed. We report synchrotron X-ray diffraction measurements during *in-situ* reaction HT of a state-of-the-art high J_c Nb₃Sn internal tin strand. In this strand, Cu₃Sn is formed upon Cu₆Sn₅ decomposition at 415 °C, a Sn-rich ternary Cu-Nb-Sn phase is detected in the approximate temperature interval 345 °C-575 °C, and NbSn₂ is present in the temperature interval 545 °C–630 °C. The formation of voids in the strand subelements has been monitored by synchrotron microtomography during in-situ reaction HT.

Index Terms—Accelerator magnets, diffraction, superconducting filaments and wires, tomography.

I. INTRODUCTION

M ODERN Nb₃Sn strands of the internal tin (IT) design can achieve very high critical current densities and are therefore considered for building high field accelerator magnets for application in high energy physics. Presently the Nb₃Sn strands with the highest critical current densities are fabricated by the Restacked Rod Process (RRP¹) by Oxford Instruments, Superconducting Technology (OI-ST), USA [1].

The brittle superconducting A15 phase in Nb₃Sn superconducting strands is produced from the ductile precursor elements Nb and Sn during a reaction heat treatment (HT). During this HT, the precursor elements interdiffuse with the Cu in the subelement bundle, forming various intermetallic phases and finally the superconducting Nb₃Sn. Since the phase transformations that occur prior to Nb₃Sn nucleation and growth can degrade the microstructural and microchemical homogeneity of the fully reacted strand, it is necessary to understand how

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the strand design and the overall elemental composition of its subelements influence these transformations.

For IT Nb₃Sn strands with a Cu to Sn at.% ratio of approximately 10 and 2.4, the phase transformations prior to the Nb₃Sn nucleation and growth have been reported in [2] and [3], respectively. In these studies phase analysis has been performed by energy dispersive X-ray spectroscopy (EDS) in the scanning electron microscope (SEM) on metallographic cross sections of *ex-situ* heat treated strand samples. X-ray diffraction (XRD) is an alternative tool for phase analysis. Previously we have reported XRD results acquired during *in-situ* strand reaction HTs of a Nb₃Sn IT strand with a relatively high Cu to Sn at.% ratio of about 8 [4] and of a state-of-the-art powder-in-tube (PIT) strand with much lower Cu content [5].

In the case of IT strands with a high Cu to Sn at.% ratio within the subelements the pure Sn initially present in the strand is successively transformed into Cu–Sn intermetallics with increasingly high Cu content (Cu₆Sn₅, Cu₃Sn, Cu₄₁Sn₁₁, Cu_{5.6}Sn). After the Nb₃Sn formation the Sn concentration in the matrix is reduced below its solubility limit in Cu. In more recent high J_c Nb₃Sn strands the Cu concentration within the strand subelements has been strongly reduced. At least one Cu–Nb–Sn ternary phase is formed during the lower temperature HT when the Nb filaments are partly dissolved in the strand matrix [3].

In the present article, we describe the phase transformations occurring during the reaction HT of a state-of-the-art Nb₃Sn strand of the RRP design, based on XRD results that have been obtained at the European Synchrotron Radiation Facility (ESRF) High-Energy Scattering Beamline ID15B during *in-situ* reaction HT. The XRD results are complemented by EDS measurements on metallographic cross sections of *ex-situ* heat treated strand samples. The influence of the different phase transformations on the void growth has been studied by synchrotron tomography during an *in-situ* HT. The total strand volume change after full reaction has before and after the reaction HT.

II. EXPERIMENT

A. The Sample

The sample studied is a Nb₃Sn RRP strand fabricated by OI-ST (billet #7419). The strand with a nominal diameter of 0.8 mm contains 54 Nb–Ta alloy filament bundles, each surrounded by distributed diffusion barriers. The strand has an effective filament diameter of about 80 μ m and it can reach 12 T, 4.2 K non-Cu critical current density values close to

 $3000 \text{ A} \cdot \text{mm}^{-2}$, at the same time maintaining a high purity Cu stabiliser with a RRR of well above 200 [6]. More details about the OI-ST RRP strands can be found in [1].

B. In-Situ Synchrotron XRD and Microtomography

Diffraction measurements were carried out at the ID15B high energy beamline of the ESRF in transmission geometry, using an 89.1-keV monochromatic X-ray beam. Debye–Scherrer diffraction pattern were acquired with a MAR345 image-plate detector.

During the *in-situ* HT with a temperature ramp rate of 100 °C h^{-1} and three short isothermal holding steps, diffractograms were acquired every 5 min. *In-situ* heating was performed in a dedicated X-ray transparent furnace built at ID15 that enables an accurate sample temperature control during the diffraction experiments. For the temperature measurement, a thermocouple was directly attached to the strand sample. The estimated accuracy of the temperature measurement is better than ± 5 °C.

Absorption microtomography was performed at ID15A using a high energy filtered white X-ray beam. The tomography setup is described in detail in [7]. The ramp rate during the tomography measurements was again 100 °C h⁻¹, but without any isothermal holding steps.

A typical reaction HT for the RRP strand recommended by OI-ST is increasing the HT temperature with 25 °C h⁻¹ to 210 °C, holding 100 h at 210 °C, ramping with 50 °C h⁻¹ to 400 °C, holding 50 h at 400 °C and then ramp with 50 °C h⁻¹ to the final reaction temperature. Since the synchrotron beam time cost for such a standard HT lasting about one week would be prohibitive, the HT schedule used in the present study has been changed such that it can be performed within about 14 h. Therefore, the temperature intervals during which the different phases are detected during the *in-situ* diffraction measurements may differ somewhat from the temperatures at which the phases are formed during the reaction HT of a magnet coil.

C. SEM and EDS

Cross sections of *ex-situ* heat treated strand samples where observed with an SEM Leo 430 using a 20-keV electron beam and a solid state diode detector for recording backscattered-electron (BSE) images. The compositional contrast, with regions of increasing atomic number appearing increasingly brighter, given by the BSE images allowed the identification of the constituents of the strand microstructure to a resolution better than 0.1 μ m.

An EDS system Oxford Isis 300 with a Si(Li) detector coupled to the SEM was used in the standardless mode for the quantitative elemental analysis. For the constituents of small size in the order of the micrometer, particularly large cases were targeted to overcome the relatively poor lateral resolution of the EDS point analyses, at least one order of magnitude worse than BSE imaging.

III. RESULTS

A. In-Situ Synchrotron Diffraction

During the *in-situ* HT with a ramp rate of 100 °C h⁻¹ and isothermal heating for 2 h at 390 °C, 2 h at 482 °C, and 2.75 h at 659 °C, a total of 170 diffractograms were acquired. For phase analysis the 2-D diffraction patterns have been integrated into 1-D patterns and a color intensity diagram of all is shown in Fig. 1. Before the onset of Nb₃Sn formation, four phases (apart from Cu and Nb) could be identified, notably (β -) Sn, Cu₆Sn₅, Cu₃ Sn, and NbSn₂. A fifth phase was detected but could not be identified by comparison with published reference patterns. Since the diffraction pattern of this unidentified phase is detected in the same temperature interval during which a Cu–Nb–Sn ternary phase is detected by EDS in *ex-situ* heat treated samples, we assume that these diffraction peaks are characteristic for the previously reported Cu–Nb–Sn phase ([3], [1], and [5]).

Some faint diffraction peaks that appear upon NbSn₂ dissolution at about 620 °C may indicate the formation of a small amount of Nb₆Sn₅ at this temperature, but because these peaks are relatively weak and partly overlap with prominent peaks of other phases, Nb₆Sn₅ could not be unambiguously identified. However, it can be concluded that if Nb₆Sn₅ is formed during the reaction HT of the RRP strand, its amount is much smaller than the amount of Nb₆Sn₅ that is formed in a Nb₃Sn PIT strand, which has been studied previously by synchrotron diffraction under similar experimental conditions [5]. In the PIT strand Nb₆Sn₅ could be identified easily and it was even possible to obtain the semiquantitative evolution of Nb₆Sn₅ during the HT.

The phase growth results are summarized in Fig. 2. At first pure Sn is transformed into Cu_6Sn_5 . When heating with a ramp rate of 100 °C h⁻¹, this transformation occurs mainly above 232 °C in the presence of liquid Sn. Cu_6Sn_5 decomposes entirely at 415 °C. At the same temperature Cu_3Sn appears and the presumed Cu–Nb–Sn ternary phase grows markedly. The growth of the presumed Cu–Nb–Sn ternary phase coincides with a slight decrease of the Nb (211) peak area, which indicates that part of Nb is incorporated into a Cu–Nb–Sn ternary phase. The vanishing of the Cu–Nb–Sn phase at about 560 °C coincides with the growth of NbSn₂ and at about 620 °C the Nb₃Sn (200) peak starts to grow.

B. Metallographic Examination of Ex-Situ Heat Treated Samples

In order to study the effect of longer HTs and to examine the spatial distribution of the phases detected by XRD within the RRP strand, metallographic cross sections of *ex-situ* heat treated strand samples have been analysed in the SEM by EDS and by optical microscopy. The individual *ex-situ* HTs of 10-h 340 °C, 10-h 410 °C, 10-h 540 °C, and 10-h 590 °C have been achieved under vacuum, each with a ramp rate of 60 °C h⁻¹. A 10 h duration of the isothermal HT has been chosen in order to limit a possible influence of the ramp rate on the results. BSE images of the respective cross sections are shown in Fig. 3. The phases that have been identified by EDS are labelled in the images.

After the 340 °C HT the Sn inside the diffusion barriers has been partly transformed into Cu_6Sn_5 . The presence of pure Sn (bright areas in the BSE-SEM image) indicates that after 10 h heating at 340 °C the Sn transformation into Cu–Sn intermetallics is not complete and that there remains some liquid Sn in the strand at the end of this HT step. During the 10-h 410 °C HT part of the Cu_6Sn_5 in the Sn cores is transformed into Cu_3Sn (lower z and, therefore, darker regions in the BE images) and into a Cu–Nb–Sn ternary phase that contains roughly 69 at.% Sn. After the *ex-situ* 10-h 540 °C HT the Cu inside the diffusion barrier is mainly present in the form of Cu_3Sn and partly in the Cu–Nb–Sn ternary phase. The Nb



Fig. 1. Variation of the diffraction patterns of the OI-ST Nb₃Sn RRP strand during *in-situ* HT cycle with ramp rate $100 \degree C h^{-1}$ and additional isothermal plateaus 2-h 390 °C, 2-h 482 °C, and 2.75-h 659 °C. Diffractograms have been acquired every 5 min, i.e., the temperature resolution of the experiment is 8 °C. The diffraction peaks labelled with a star are tentatively assigned to a Cu–Nb–Sn ternary phase.



Fig. 2. Relative variation of the diffraction peak areas of all Sn containing phases detected in the OI-ST RRP strand as a function of the reaction HT temperature and duration. The Sn(101), Cu₆Sn₅ (202), NbSn₂ (220), Nb₃Sn (200), and Cu₃Sn peak with *d*-spacing d = 3.23 Å have been chosen for peak area measurements. An unidentified phase, for which the evolution of the diffraction peak area (peak with *d*-spacing ~ 2.78 Å) is also plotted, is presumably a ternary Cu–Nb–Sn phase. Peak areas have been scaled in order to fit into the plot and to facilitate comparison.

filaments closest to the Sn reservoirs have been transformed into NbSn₂. After the *ex-situ* 10-h 590 °C HT, Sn is mainly present in the form of Cu₃Sn, and some Nb₆Sn₅ in the filament region closest to the Sn source.

In Fig. 4, a secondary electron image of an RRP fracture sample after 17-h 695 °C HT is shown. The initially separated filaments within the nonreacted subelement have coalesced to a single filament that exhibits a homogenous fine grain Nb₃Sn microstructure, as it is typical for high critical current density

 Nb_3Sn conductors [8]. Only a small ring closest to the Sn core is composed of coarse grains, presumably the strand region that has been converted into Nb_6Sn_5 prior to Nb_3Sn formation.

The influence of a 220 °C isothermal holding step on the Cu₃Sn growth during subsequent 400 °C HT has been examined by comparing optical micrographs obtained after 400 °C HT, either with or without prior 314-h 220 °C holding step. As can be seen in Fig. 5, after both HTs most Sn is still present as Cu₆Sn₅.



Fig. 3. OI-ST RRP strand cross sections after 10-h 340 °C, 10-h 410 °C, 10-h 540 °C, and 10-h 590 °C HT (ramp rate 60 °C h⁻¹). After the 340 °C HT, the Sn core has been transformed into Cu₆Sn₅ and some pure Sn remains close to the filaments (bright region in the BE images). During the 410 °C HT, part of the Cu₆Sn₅ is transformed into Cu₃Sn and a Cu–Nb–Sn ternary phase that contains roughly 69-at.% Sn. After the 540 °C HT Sn is in the form of Cu₃Sn, Cu–Nb–Sn and NbSn₂ and during the 590 °C HT Sn is present in the form of Cu₃Sn and some Nb₆Sn₅, which is detected around the filaments closest to the Sn source. NbSn₂ was not detected after the 590 °C HT.



Fig. 4. Secondary electron image of OI-ST-RRP fracture sample after 17-h 695 $^{\circ}$ C HT. A thin coarse grain region is present at the filament region closest to the Sn source.

C. Void Formation and Strand Volume Change During the Reaction HT

The formation of voids during the reaction HT of the OI-ST RRP strand has been monitored by high energy synchrotron microtomography. The strand cross sections of a nonreacted RRP strand and the same strand after *ex-situ* 17-h 695 °C HT are presented in Fig. 6.

In Table I, the strand diameter, length, and pore volume before and after full reaction HT of the RRP strand are summarized. As has been shown previously for other Nb₃Sn strands [9], [10], the length of the free standing straight RRP strand contracts slightly during a full reaction HT. This contraction is caused by the Nb filament relaxation during the Cu annealing HT, prior to the Nb₃Sn formation. The main strand volume increase is caused by an increase of the strand cross-sectional area by 4.9% during the reaction HT. The void volume that is formed during the reaction HT corresponds with about 5% of the total strand cross section.

The void volume change has also been measured during an *in-situ* reaction HT of the RRP strand with a ramp rate of 100 °C h⁻¹ (without any isothermal holding steps). The void volume as a function of the HT temperature is shown in Fig. 7. A first marked increase of void volume occurs between 220 °C and 245 °C. The main void volume increase occurs at temperatures above 600 °C. For comparison, the void volume evolution during the reaction HT of the IT strand with a Cu to Sn at.% ratio of 8 [4] is presented as well.

RRP strand cross sections and 3-D views of the pores in the strand acquired by synchrotron microtomography at different temperatures during the *in-situ* reaction HT are shown in Fig. 8. In the reconstructed 3-D images the superconductor material has been transparently depicted.

IV. DISCUSSION

A. Phase Transformations

The overall elemental composition of the Nb₃Sn strand subelements has a strong influence on the phase transformations that occur during the strand reaction HT. While in low J_c strands with high Cu content only pure Sn liquefies during the reaction HT [4], in high J_c strands, with much smaller Cu to Sn ratio, liquid phases are invariably present in the strand during larger temperature intervals. In particular a peritectical decomposition of Cu₆Sn₅ into Cu₃Sn and liquid occurs at 415 °C. In strands that contain a relatively large amount of Cu with respect to Sn, the Cu₆Sn₅ to Cu₃Sn transformation readily takes place at relatively low temperatures and it can be completed entirely below the Cu₆Sn₅ decomposition temperature of 415 °C [2], [4].

The dissolution of the Nb filaments in a ternary phase and the transformation of the inner Nb filaments into NbSn₂, and possibly into Nb₆Sn₅, may degrade the microstructural and microchemical homogeneity of the fully reacted strand. In the OI-ST RRP strand the Cu–Nb–Sn ternary phase has been detected in the temperature interval of approximately 345 °C–575 °C, similar to the temperature interval during which the ternary phase exists in a Nb₃Sn PIT strand produced by SMI [5]. In both Nb₃Sn strand types, the ternary phase disappears upon formation of NbSn₂, which is present in the RRP strand in the temperature interval 545 °C–630 °C, again similar to the temperature interval in which NbSn₂ is formed in the Nb tubes of the PIT strand.

A relatively small amount of Nb₆Sn₅ in the filament region closest to the Sn source is observed in the metallographic OI-ST RRP strand cross sections after 10-h *ex-situ* 590 °C HT. The amount of Nb₆Sn₅ that is formed during the *in-situ* HT with a ramp rate of 100 °C h⁻¹ is so small that it can not be unambiguously detected by the diffraction experiment. This is an important advantage of the OI-ST RRP strand design over the present SMI PIT [5] and Tube Type strands [11], in which more than 20 vol.% of the Nb tubes can be transformed into Nb₆Sn₅ prior to the formation of Nb₃Sn. It is assumed that Nb₆Sn₅ formation in the Nb precursor tubes prior to Nb₃Sn formation significantly reduces the current carrying fine grain Nb₃Sn cross-sectional area.

As outlined above, the *in-situ* HT during the diffraction measurements reported here differs from the HT schedule recommended by the strand manufacturer. Therefore, the temperature intervals during which the different phases have been detected by the *in-situ* XRD measurements might differ somewhat from the temperatures at which these phases are present during the reaction HT of a magnet coil. The influence of the different HT



Fig. 5. OI-ST-RRP strand cross section after 40-h 400 $^{\circ}$ C HT (left) and 314-h 220 $^{\circ}$ C +50-h 400 $^{\circ}$ C (right). After both HTs, Sn is mainly present in the form of Cu₆Sn₅ (bright grey) with some Cu₃Sn (dark grey). The Cu–Nb–Sn ternary phase that is also formed cannot be seen in the low resolution optical micrographs. The black regions in the true color images are voids.

TABLE I

STRAND DIAMETER, STRAND CROSS-SECTIONAL AREA, CROSS-SECTIONAL AREA OF ALL PORES IN THE OI-ST-RRP STRAND, AND STRAND LENGTH BEFORE AND AFTER 17-h 675 °C REACTION HT. THE PORE CROSS SECTION OF 0.0267 mm² CORRESPONDS WITH 5% OF THE TOTAL STRAND CROSS SECTION

	Diameter (µm)	Strand cross section (mm ²)	Pore cross section (mm ²)	Length (mm)
Before HT	803±1.7	0.507	0	304.2
After HT	823±1.2	0.532	0.0267	304.0
	(+2.5%)	(+4.9%)		(-0.07%)



Fig. 6. OI-ST RRP strand cross section before HT (left) and after 17-h 695 $^{\circ}$ C HT (right), obtained by synchrotron microtomography. The total void cross section is 0.027 mm², which corresponds with 5.0% of the total strand cross section.

schedules depends on whether the phase transformations are mainly determined by the thermodynamics or by the kinetics of formation. Only when the kinetics have a strong influence, the temperature intervals during which the different phases are detected will shift to lower temperatures with decreasing ramp rate.

In order to predict the phases that can grow during the reaction HT of Nb₃Sn strands with different elemental composition and to optimize HT cycles, Cu–Nb–Sn ternary phase diagrams, as they exist for instance for a temperature of 675 °C [12], are needed also at lower temperatures. The influence of ternary and quaternary additions, in particular of Ti, on the phase transformations needs to be considered as well [13].

B. Void Formation

The void volume in the fully reacted RRP strand, which corresponds with about 5% of the total strand volume, is similar to the strand volume expansion during the reaction HT. One reason for the void formation might be density changes during the strand reaction HT.



Fig. 7. Void cross section in the OI-ST RRP strand in percent of the total strand cross section as a function of the HT temperature (ramp rate 100 °C h⁻¹). For comparison, the void volume evolution during the reaction HT of an IT strand with high Cu/Sn ratio is shown as well [4].

It is well known that the Nb₃Sn volume is approximately 37% larger than the Nb precursor volume. However, the void and strand volume results presented here indicate that the Nb₃Sn volume does not increase with respect to the sum of the Nb and Sn volumes from which it is formed. When void formation during the reaction HT of the RRP strand is suppressed by a high-pressure thermal treatment [14], the strand cross-sectional area even shrinks by about 2% with respect to that of the nonheat-treated RRP strand. This indicates that the Nb₃Sn density is higher than the density of the Nb and Sn precursor in the stoichiometric quantities, which can explain part of the void volume that is formed in the RRP strand. The calculated Nb₃Sn density is indeed significantly higher than the weighted average of the Cu and Sn densities (8.90 versus 8.15 g \cdot cm⁻³, respectively [15]). Therefore, a strand volume expansion during the reaction HT invariably causes the formation of a corresponding void volume in the reacted strand.



Fig. 8. 2-D cross sections of the RRP strand (top) and the corresponding 3-D images of the pores within the strand acquired by synchrotron microtomography at different temperatures during *in-situ* HT with a ramp rate of $100 \degree C h^{-1}$. In the 3-D reconstructed images the strand materials have been transparently depictured in order to visualise the pores. The middle line shows a top view and the bottom line a lateral view on the pores.

As can be seen in Fig. 7, the void volume evolution as a function of HT temperature observed in the RRP strand differs markedly from that in an IT strand with relatively high Cu/Sn ratio studied previously [4]. In the high Cu/Sn ratio IT strand three different void growth mechanisms could be distinguished, notably an agglomeration of pre-existing voids that are initially so small that they cannot be detected by synchrotron microtomography, density changes during the formation of Cu–Sn intermetallics and the formation of voids due to differences in the diffusivity of Cu in Sn and Sn in Cu (Kirkendall voids [16]). The *in-situ* experiment of the high Cu/Sn ratio strand was stopped at 540 °C, i.e., before the onset of Nb₃Sn formation. Tomograms of the high Cu/Sn ratio strand acquired after full *ex-situ* reaction HT have shown that the main void volume increase in this strand occurs also above 540 °C, as it is observed in the RRP strand.

The first marked increase of void volume in the RRP strand between 220 $^{\circ}$ C and 245 $^{\circ}$ C coincides with the melting of pure Sn at 232 $^{\circ}$ C. Sn melting itself can only cause a slight decrease of porosity, due to the Sn volume expansion upon melting. It can be assumed that pre-existing pores agglomerate more easily in the presence of liquid Sn, which may explain the volume increase of the detected pores in this temperature interval.

Unlike in the high Cu/Sn ratio strand, the formation of the relatively small Kirkendall voids is not observed in the RRP strand. One reason for this might be that the formation of Kirkendall porosity in the RRP strand is suppressed because of stresses in the strand that prevent void growth, or that Kirkendall voids in the RRP strand are so small that they cannot be resolved by synchrotron microtomography (the filament size and interfilament spacing within the RRP strand are much smaller than in the low Sn IT strand studied previously). If Kirkendall porosity is suppressed in the RRP strand, this can be advantageous in view of the homogeneity of Sn supply to the Nb precursor filaments.

In the high Cu/Sn ratio strand, the void volume decreases strongly upon transformation of Cu–Sn intermetallics into lower density bronze. Due to the relatively small Cu to Sn ratio in the RRP strand, a transformation of Cu–Sn intermetallics into bronze can only take place after a significant progress in the formation of Nb₃Sn formation, such that the Sn content in the Sn source is reduced below the Sn solubility limit in bronze. Therefore, only a slight decrease of void volume is observed in the RRP strand before the Sn starts to diffuse into the Nb filaments.

V. CONCLUSION

The phase transformations during the reaction HT of a state-of-the-art high J_c Nb₃Sn strand of the RRP design have been described. The phase transformations that occur in the RRP strand with relatively low Cu content are similar to those that have been observed in a Nb₃Sn PIT strand. However, an important advantage of the OI-ST RRP strand design over the PIT design is that much less Nb₆Sn₅ is formed during the reaction HT of the RRP strand. Isothermal holding steps below the Sn melting temperature of 232 °C and the Cu₆Sn₅ decomposition temperature of 415 °C do not have a strong influence on the phases that are present in the RRP strand at the onset temperature of Nb₃Sn formation.

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Marco Di Michiel biography not available at the time of publication.

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