Longitudinal and Transverse Cross-Sectional Microstructure and Critical Current Density in Nb₃Sn Superconductors

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Abstract—The longitudinal and transverse cross-sectional microstructures of several internal tin Nb₃Sn strands have been systematically investigated. The critical current densities of these strands were then correlated with their design parameters. It is observed that the occurrence of certain coarse grain structures is related to the location of the filaments with respect to the subelements as well as to the strand. Experimental evidence suggests that the existence of these coarse grains is related to Sn distribution during the early stages of the heat treatment. It is also noticed that some coarse grains have high aspect ratio features, confirming the need to study the longitudinal fracture surface. We report in this paper the observation of some unusual grain sizes and morphologies. It appears that, of the high-Sn content Nb₃Sn conductors investigated in this paper, a strand's global composition has a weaker influence on the critical current density (J_c) than local and structural factors, such as the local Cu:Nb area ratio (LAR) and filament layout.

Index Terms—Critical current, Cu-Nb-Sn, fractography, internal tin, microstructure, Nb₃Sn, superconductor.

I. INTRODUCTION

It is well accepted nowadays that in Nb₃Sn superconductors, grain boundaries are the dominant flux pinning centers. A fine microstructure (high grain boundary density) of stoichiometric Nb₃Sn therefore improves the critical current density, a parameter crucial to applications. Homogeneity, both radial and longitudinal, is essential to the conductor's performance. In this paper, we shall complement conventional transverse cross-sectional metallography with longitudinal observations, and report the distribution and morphology of coarse grains. We will also compare the J_c of internal tin strands of different designs, and correlate the superconducting properties with the microstructure and subelement architecture.

II. EXPERIMENTAL SETUP

In this work, we studied 9 different billets of internal tin (including OST's RRP) strands manufactured by 3 different manufacturers: Alstom (63468, 14508, 21234, 24234), Luvata (samples P2, P3, W—Luvata prefers no specific wire identification), and OST (7419, 10400). These strands are all of different design and architecture: some with a copper core at re-stacking (higher Cu to non-Cu ratio), some without; some with a Nb diffusion

TABLE I
DESIGN PARAMETERS OF WIRES STUDIED

	Billet number	Wire diameter	Number of subelement	Subelement diameter	LAR	J_c 4.2 K, 12T (kA mm ⁻²)
OST	7419	0.8 mm	54	78 μ m	0.25	> 3
	10400	1.0 mm	108	66 μ m	0.25	> 3
Alstom	63468	1.25 mm	246	54 μ m	0.30	1.1-1.4
	14508	1.25 mm	78	90 μ m	0.30	1.8-2.1
	21234	1.25 mm	234	54 μ m	0.30	1.9-2.1
	24234	1.25 mm	234	54 μ m	0.30	~1.5

barrier only (of different thickness), some with an extra Ta barrier; a total number of subelements between 19 and 246; some binary (only Nb and Sn in a Cu matrix), and some with additions of Ta or Ti, or both. The subelement composition varies slightly, but would all qualify as high-Sn content (within a few percents) internal tin strands. Some design parameters are shown in Table I.

Short strand samples were heat treated in a tube furnace under vacuum to prevent oxidation. Heat treatments (HT's) were based on the manufacturers' recommendations. The ends of the samples were crimped to prevent Sn leakage. Samples for microstructural investigation were quenched in air or in water at different stages of the HT. Samples for critical current testing were mounted on Ti-6Al-4V holders and heat treated and cooled in box furnaces under vacuum.

Transport critical current density (J_c) measurements were performed at CERN using facilities described in [1], and at the University of Geneva. Electron microscopy was performed in a Carl-Zeiss Sigma FEGSEM. For EDS and the imaging of polished cross-sections, the acceleration voltage applied was typically 7 or 10 kV to optimize the EDS spatial resolution. Fractography was performed in the aforementioned FEGSEM, typically with a 3 kV acceleration voltage, on samples freshly fractured by bending using an in-lens detector. The longitudinal fracture surface was studied on pulled out filaments and along large voids using dynamic focus.

III. RESULTS AND DISCUSSION—MICROSTRUCTURE

The theoretical optimal grain size (assuming triangular grains with sides a) for flux pinning in a hexagonal close packed flux line lattice depends on the applied magnetic field according to the equation:

$$a = \sqrt{(2\phi_0)/(\sqrt{3}B)} \quad (1)$$

where ϕ_0 is the magnetic flux quantum and B the flux density.

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Fig. 1. The three classes of coarse grains reported in this paper: (a) local peri-filamentary, (b) regional, and (c) global. These representative micrographs were obtained from Luvata samples P3 (a), (b), and W (c) after full HT, but comparable features could be identified in all the wires examined.

For applications at 12 T, the optimal grain size is therefore ~ 14 nm. In fractured samples of internal tin strands, typically the fine equiaxed grains can be sub-100 nm, but there are often coarse grains at least several times bigger.

We report on the occurrence, nature and distribution of coarse grains in three regions (Fig. 1). The first is the region around each Nb filament (peri-filamentary), regardless of its location in the subelement. Two types of coarse grain, formed by different mechanisms, have been identified in the peri-filamentary region, and they are discussed below in Section III-A. Secondly, the subelement core and the innermost Nb filaments are considered in Section III-B. Relatively coarse and geometrically complex microstructures containing ternary phases are identified in the Sn-rich core itself; and the adjacent region of peri-filamentary coarse grains (as described in Section III-A) is considerably thicker than for filaments further from the core. Thirdly, it is shown that the distribution of peri-filamentary grains within a subelement depends on the radial position of those filaments in the strand. As discussed in Section III-C, a larger population of coarse grains typically appears in the side of the subelement nearer to the strand center.

A. Peri-Filamentary Coarse Grains

For the coarse grains surrounding a filament, we have observed two distinct types: one allowing Sn diffusion, and one apparently impermeable to Sn.

For the first type, [Fig. 1(a)] when examined in transverse fracture surfaces the grain size usually seems only a couple of times bigger than the fine Nb_3Sn grains and with apparently similar aspect ratio. However, longitudinal fracture surfaces suggest that these features may be associated with several very different types of longitudinal structures, including some with large aspect ratio, which will be further described below in Section III-D. There is evidence that at least some types of these peri-filamentary coarse grains develop from a ternary Cu-Nb-Sn phase with composition in the vicinity of 15–18 at% Cu, 23–28 at% Nb, 56–60 at% Sn which exists at temperatures below 500°C [2] and which is similar to that reported by Naus [3]. It is thought that NbSn_2 and Nb_6Sn_5 may be responsible for some of the other types of these peri-filamentary coarse grains [4].

The second type is an unusual “diffusion barrier” type of coarse grain, which appears to be able to prevent the formation of fine Nb_3Sn grains by blocking the diffusion of Sn. It is typically thin but very long in the transverse cross section, often appearing to extend around half the circumference of the filament, inside of which there is usually a large unreacted Nb core. Although its fracture surface in the longitudinal direction has no characteristic features, in the transverse cross section it has a

Fig. 2. “Diffusion barrier” type of coarse grain as observed in OST 7419.

very smooth fracture surface, suggesting that it is a brittle compound (Fig. 2). The formation of this type of coarse grain does not have an obvious relation to the Sn gradient in the subelement, judging from the fact that it can be found close to both the core and the barrier of the subelement. EDS mapping analysis suggests that it contains only Nb and Sn, but it was not possible to determine the composition due to its small size.

B. Coarse Grains in and Near the Subelement Core

There are several types of feature observed in the Sn core region and near the first layer of filaments. In the latter region, the structure is very similar to the peri-filamentary coarse grains (type 1) reported above, but the grains are often larger still or there are more layers of grains [Fig. 1(b)]. In the fully reacted wires, very often the fine-grained region for filaments near the core is much smaller than in those filaments closer to the diffusion barrier. In wires quenched before reaching the final annealing temperature, the unreacted Nb core is seen to be reducing in size, with the coarse grains growing inwards, suggesting that they are Nb-containing.

In the Sn core region, several types of coarse grained structure (Remark: what we see may be perhaps not grain but phase boundaries, but for expedience we will keep the reference ‘coarse grain’ here) of some Cu-Nb-Sn and, in Ti-containing samples, some previously unreported $(\text{Ti}, \text{Nb})_2\text{Sn}_3$ ternary compounds have been observed far into the core, suggesting extensive Nb dissolution with relatively rapid Nb diffusion. For the heat treatments applied, these ternary compounds are mostly detected at temperatures above the decomposition of Cu_6Sn_5 (η phase) and before Nb_3Sn formation. Indeed, for the wires investigated, it appears that the formation of the ternary phase is facilitated if η phase was in contact with the Nb filaments: in cases where η phase has mostly been transformed into Cu_3Sn (ε phase), there is much less of the ternary phase. Since liquid Sn could persist above η phase decomposition point until there is enough Cu (or Nb and Ti) to convert it to the higher-melting ε or other phases, it is likely that the observed

Fig. 3. (a) BEI of the polygon and rod ternary phase with fine 'multi-phase' microstructure as seen in Luvata sample P3, quenched at 490°. (b) Fractograph of a polygon showing an uneven surface, as seen in Alstom 63468, quenched at 590°C. Comparable features are seen in other wires.

Fig. 4. Polished cross section BEI (a), (d) and FEGSEM fractographs (the rest) revealing a 3D intertwined structure. At high magnification some are like Archimedean solid (h) and some have a terrace feature (g). These representative micrographs were obtained from the final stage of the respective HT's of OST 10400 (a), (c), Alstom 14508 (b), Luvata samples P3 (d), (i) and P2 (e), and OST 7419 (f), (g), (h).

transportation of Nb far into the subelement core in the form of Cu-Nb-Sn compound was liquid-assisted.

These ternary compounds have very characteristic features. First we observed both the polygon and rod types, similar respectively to those in wires and pellet samples reported by Naus [3]. Our fractography shows that what appears to be a multi-phase structure in polished surface metallography is likely a single phase with an uneven surface in close contact with Cu-rich bronze (Fig. 3).

We also observed three other forms of ternary compound: i) a curled and intertwined structure, which looks like loose threads [Fig. 4(a)] or dissolved compounds [Fig. 4(d)] in conventional metallography, but is actually an interconnected open structure [Fig. 4(b), 4(c), 4(e), and 4(f)] when seen in fractography; ii) a sub-micron Archimedean solid type of polyhedron structure [Fig. 4(h)]; and iii) a twisted structure with terrace feature [Fig. 4(i)]. These do not reach far into the subelement core but remain close to the filaments, and appear to grow from the peri-filamentary coarse grains [Fig. 4(e)].

Fig. 5. (a) A fully heat treated Luvata sample P3 showing a triangular area with coarse peri-filamentary grains and (b) a Luvata sample P3 quenched before Nb₃Sn formation showing a triangular area of Sn distribution whose vertices point to the strand center.

The composition of these structures is typically close to 13 at% Cu-23 at% Nb-64 at% Sn before Nb₃Sn formation. As with the peri-filamentary ternary phase reported above, some of these structures remain after final annealing, but with a composition very close to stoichiometric Nb₃Sn, with a few at% of Cu coming from either solid solution, fine precipitation or the surrounding phases.

C. Global Distribution of Coarse Grains

It is noticed that after drawing, the restacked subelements—especially those near the perimeter and those in wires whose architecture includes a Cu core—are often deformed and skewed (not round or symmetrically hexagonal).

We identified a global pattern of where coarse grains are more likely to be found, which matches the Sn distribution at the early stages of the heat treatment. Fig. 5(a) shows a transverse fracture surface of the Nb₃Sn microstructure in an annealed sample, with peri-filamentary coarse grains in a triangular arrangement pointing to the strand center. Fig. 5(b) shows a BEI of a subelement quenched after 10 h at 440°C, clearly showing a non-uniform Sn distribution, with a very similar triangular region of Sn-rich phases reaching the diffusion barrier on the side closer to the strand center. This specific region is also where typically the inter-filamentary spacing is larger (more open filament layout), suggesting the formation of coarse grains is related to the local composition (LAR) and to the phase formation during the low temperature HT stages. This phenomenon has been observed in many subelements in different samples, especially those with a high LAR.

It has also been observed that in some cases there is little diffusion of Sn-rich phases beyond the first layers of Nb filaments at low temperatures, and the subelement core retains a very high Sn content. This appears to occur mainly in billets with a low LAR and more layers of closely-packed Nb filaments. The Nb₃Sn microstructure of these samples, as observed in transverse fractography, typically contains a markedly thicker layer of coarse grains in the subelement core on the side closer to the strand center, with little or no triangular area of peri-filamentary coarse grains [Fig. 1(c)]. Again this has been observed regularly. A classic example is our Luvata sample W, which has a 19/19 restack subelement structure. All 18 subelements surrounding the central one show this feature.

Of the 9 billets investigated, OST's RRP strands and sample W of Luvata have an LAR of 0.25, whereas the Luvata samples P2 and P3, and all Alstom strands, have nominal LARs of 0.34 and 0.3 respectively. It has been noticed that in the Luvata and Alstom strands some of the heavily deformed subelements have strong local variations in LAR. The nominal LAR has a

Fig. 6. Fractographs at the same magnification of the Luvata sample P2, showing three different types of coarse grains which would not have been revealed in the transverse cross section. The coarse grains have markedly different aspect ratios, with (b) and (c) also showing different orientations with respect to the filament axis.

Fig. 7. The periodic structure with (a) angular and (b) round grains, as seen in Luvata sample P2 after full HT.

clear influence on both the global Nb_3Sn microstructure as described above and on J_c (see Section IV below), but it would be the actual LAR that has the strongest influence on the local microstructure and phase development, and thereby the overall homogeneity.

D. Longitudinal Features

During our investigation of the fractographical features, we observed that there is a much wider range of longitudinal features in internal tin strands than in bronze route wires [5], which cannot be revealed in the transverse cross section. We present some of them here.

The coarse grains are usually observed close to the subelement core, but in samples with high LAR also in the inter-filamentary region. Fig. 6(a) is the most common type, quite similar to the fine grains, and only a few times larger. However, there are also some very large grains many times bigger still: Fig. 6(b) shows several grains of what appears (from BEI contrast) to be a Cu-Nb-Sn ternary phase, and Fig. 6(c) has a fracture surface suggestive of liquid state reaction. Such coarse grains are expected to be very detrimental to J_c , because the number of pinning centers in a volume depends on the number of grains, and a grain with a dimension some ten times bigger means a volume about a thousand times larger.

We have also observed some periodic structures in the longitudinal direction. Fig. 7(a) shows a structure with directional growth that is more commonly found near the diffusion barrier than the subelement core, which suggests the possibility of some crystallographic orientation effect due to drawing, as Sn does not retain any preferred directions [6]. These grains are not much bigger than the fine grains in the transverse cross section, but some can be several times as long in the axial direction. Fig. 7(b) shows a round structure similar to Fig. 6(a). Sometimes when found in the first layer of filaments closest to the subelement core, it grows out into the core as shown in Fig. 4(f).

Fig. 8. Non-Cu J_c versus nominal local Cu:Nb area ratio (LAR).

IV. CRITICAL CURRENT DENSITY

Having identified that LAR has a clear effect on the microstructure, and knowing that high J_c depends on a fine grain size, we plotted the measured J_c of those samples with similar Nb barrier and subelement sizes and included a range of samples heat treated differently, against their nominal LAR (Fig. 8). A clear correlation can be seen.

Despite not treating the HT schedule as a separate factor here, we would like to emphasize nevertheless of its optimization according to wire design, especially in high LAR samples, because the J_c could differ by 20% or more, as found in the samples investigated in this paper.

V. CONCLUSION

In the high-Sn content internal tin strands investigated, some coarse Nb_3Sn grains are found to relate to Sn distribution at the low temperature stages, and J_c is found to decrease with increasing LAR. We therefore conclude that a low LAR is conducive to a fine microstructure and high J_c .

Seeing that some grains have large aspect ratios and that little work on this has been reported in the literature, we believe that there is a need to study the longitudinal fracture surface to enhance our ability to fully characterize strands.

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