Suppressed Formation of Large Grain Nb$_3$Sn in Powder in Tube Conductors for the Next Generation if Accelerator Magnets

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Abstract— **The next generation of superconducting accelerator magnets for the Large Hadron Collider at CERN will require large amounts of Nb$_3$Sn superconducting wires and the Powder-In-Tube (PIT) process, which utilizes a NbSn$_2$-rich powder core within tubes of Nb(7.5wt%Ta) contained in a stabilizing Cu matrix, could provide sufficient performance. However, the critical current density, J_c, is limited by the formation of a large grain (LG) A15 layer which does not contribute to transport current, but occupies 25-30% of the total A15 area, thus it is important to understand how this layer forms so it can be minimized. During heat treatment, the powder core undergoes a complex reaction with the Nb-Ta tube (which is inscribed with a Cu sleeve) to form a ternary Sn-Nb-Cu phase (Nausite) as early as ~200 °C. Upon further heating, the Nausite decomposes into NbSn$_2$ + Cu at ~610 °C, which then rapidly forms Nb$_6$Sn$_5$ at 630 °C before finally transforming to Nb$_3$Sn. We have made two critical new observations: 1.) The Nb$_6$Sn$_5$ is Cu-containing while NbSn$_2$ is not (nor is A15 but this is well known) and 2.) The initiation of the LG formation can be controlled at a wide range of temperatures relative to the formation of the small grain (SG) A15. The initial LG A15 can be uniquely identified as a decomposition product of the Nb$_6$Sn$_5$/Cu by the layer of rejected Cu around it. Thus the LG is not only of low pin density, but is disconnected by the layers of rejected Cu. We have found for single step reactions limited to 630 °C-690 °C that the maximum SG A15 layer thickness is about 1.9 µm before LG A15 and Cu precipitates form. We have also found that multistep heat treatments in the same temperature range can increase the SG A15 layer thickness without creating the undesired LG morphology. Our goal is to use such heat treatments to greatly suppress the LG A15 and drive J_c (12 T, 4.2 K) to exceed 3,000A/mm^2.**

I. Introduction

THE POWDER-IN-TUBE (PIT) manufacturing process has been used to produce multifilament Nb$_3$Sn wires for over 30 years [1]. Starting with the earliest variants at ECN, followed by Shape Metal Innovations (SMI), and today Bruker EAS, two morphologies of Nb$_3$Sn A15 grains are always formed during the reaction; a small grain (SG) and a large grain (LG). The small grain (~150 nm) region forms an outer layer in contact with the remaining unreacted Nb tube. The large grains, easily exceeding 1 µm in diameter also tend to be surrounded by a penetrating Cu phase at the edge of the core (Fig. 1). Historically, The LG A15 was observed to have formed from the Nb$_6$Sn$_5$ layer which precedes the A15 reaction, Sn diffuses through this layer to grow the small grain A15 layer by reaction with the Nb tube [2],[3]. It should be noted that LG A15 does not form in any appreciable amount in

the internal Sn method [4]. Given this state of the art conductor, the recommendations to improve the PIT method are to consume more diffusion barrier without loss of RRR [5] and to suppress the formation of LG A15 as it does not contribute to transport current but occupies 25-30% of the total A15 area [6], [7].
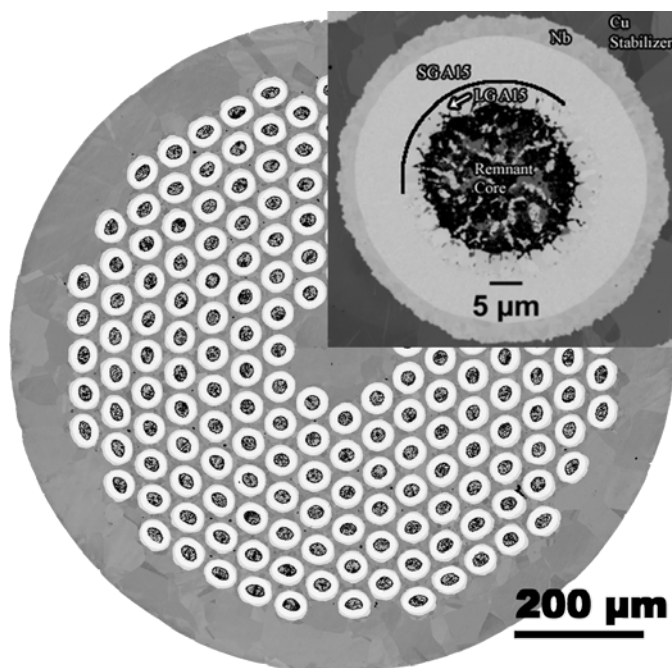

Fig. 1. FESEM-BSE images of polished, transverse cross-sections of a reacted Bruker PIT wire 1mm in diameter with 192 superconducting filaments within a matrix of stabilizing Cu. Inset image is of a typical filament.

II. Procedure

In order to suppress the LG A15, we first needed to develop a better understanding of its formation by microstructural analysis. A series of experiments were performed in which short samples were sealed in quartz tubes and heated at 100 °C/hour to a final temperature of 630, 650, 670, or 690° C. During the heat treatment, samples were pulled from the furnace and quenched in an ice bath, locking in the high temperature microstructure to observe the conditions under which LG A15 forms. After reaction, the samples were mounted in a conducting puck, polished, and imaged by FESEM, primarily using back scattered electrons which are sensitive to the atomic number of each phase. After imaging,

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we use the widely used open-source software package Fiji [8] (based on ImageJ [9]) to quantify the average layer thickness of each phase present during different stages of the reaction.

III. RESULTS AND DISCUSSION

A. LG formation at different temperatures

Over 60 samples were imaged to accurately determine under what conditions the LG A15 begins to form. Following this series of experiments we made some crucial new discoveries regarding this process. Firstly, the SG A15 layer forms well before the LG A15 layer and this SG layer can be grown to a significant thickness before LG forms. The maximum thickness of the SG A15 layer absent of large grains is dependent on temperature (Fig. 2). At 630° C the layer thickness is about 0.5 μm after 10 hours, but in the following two hours we see large grains begin to form while the SG layer continues to thicken, now at 0.85 μm. The thickest SG layer we have so far managed to achieve without LG formation is 1.9 μm at 670°C. However it appears that higher temperatures will not produce a thicker SG A15 layer as after 2 hours at 690°C it is only 1.6 μm thick and LG A15 has begun to form.
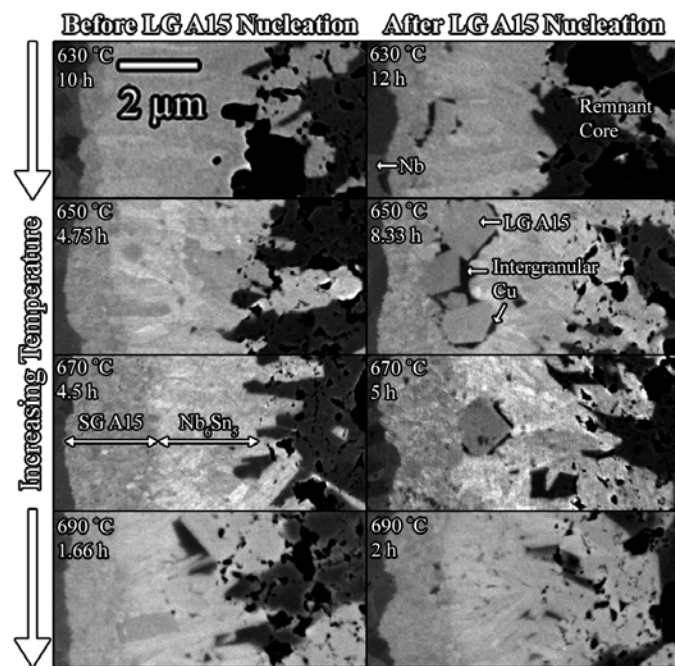

Fig. 2. FESEM-BSE images of polished, transverse cross-sections of 8 different samples showing the dependance of LG formation as a function of temperature. In the left column, only a SG A15 layer has formed of varying thickness, while in the right column more time has elapsed and we see the appearance of LG A15 and Cu precipitates. Each row is one temperature (630, 650, 670, or 690°C), which increases moving down the panel. Relevent phases are labeled on various panels.

Based on these results, it was possible to design a multi-step heat treatment aimed at avoiding LG A15 formation. While this first attempt at a multi-step heat treatment still formed some LG A15, the SG A15 layer was about 2.2 μm, higher than any single step heat treatment (Fig. 3).

IV. CONCLUSION

Understanding the conditions surrounding formation of LG A15 will be important to prevent or minimize it so that the J_c can be increased. Here we demonstrate through microstructural observations that it is possible to control the LG/SG A15 ratio early on in the reaction. The next step is high resolution chemical composition analysis using EDS in either the SEM (or TEM if higher resolution is required) to determine if local variations in Sn or Cu lead to the formation of large grains. We are now also exploring multistep heat treatments to further determine how the reaction temperature affects the rate of formation for both A15 layers.
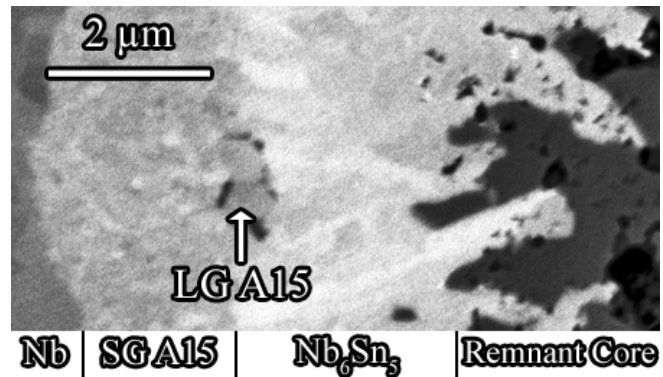

Fig. 3. FESEM-BSE image of a polished, transverse cross-section demonstrating that the layer thickness of SG A15 can be increased significantly before nucleation of LG A15 utilizing a heat treatment of multiple steps. Approximate phase boundaries are denoted below image.

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