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Microstructural study of brass matrix internal tin multifilamentary Nb_3Sn superconductors

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ABSTRACT

Zn addition to the Cu matrix in internal-tin-processed Nb_3Sn superconductors is attractive in terms of the growth kinetics of the Nb_3Sn layers. Sn activity is enhanced in the Cu–Zn (brass) matrix, which accelerates Nb_3Sn layer formation. Here, we prepared multifilamentary wires using a brass matrix with a Nb core diameter of less than 10 µm and investigated the potential for further J_c improvement through microstructural and microchemical studies. Ti was added into the Sn cores in the precursor wire. Microchemical analysis showed that Ti accumulates between subelements consisting of Nb cores, which blocks Sn diffusion through this region when the spacing between the subelements in the precursor wire is a few microns. The average grain size was found to be about 230 nm through image analysis. To date, matrix J_c values of 1470 and 640 A/mm^{-2} have been obtained at 12 and 16 T, respectively. The area fraction of Nb cores in the filamentary region of the precursor wire was about 36.3%. There was still some unreacted Nb core area after heat treatment. Insufficient Ti diffusion into the Nb_3Sn layers was identified in the outer subelements. These findings suggest that there is still room for improvement in J_c.

1. Introduction

Nb_3Sn superconducting wire is currently an essential component of high-field magnets such as high-resolution NMR, fusion, and accelerator magnets. Although after careful optimization, Nb_3Sn wires finally seem to be approaching full J_c performance, e.g., in terms of the area ratio of elements (Nb, Sn and Cu) and cross-sectional design, maximizing the volume fraction of the Nb_3Sn filaments in the wire assembly [1-3], there is still a strong demand for higher J_c performance in applications like the Future Circular Collider (FCC) and DEMO reactor projects.

The key to further improving J_c characteristics lies in enhancing grain boundary pinning and improving the stoichiometry of the Nb_3Sn layer. As an interesting approach to refining the grain morphology, a research group at Ohio State University is employing a method based on internal Zr oxidation in the Nb layer for powder-processed Nb_3Sn. Zirconium oxide particles formed in the Nb_3Sn layers seems to act as pins that suppress Nb_3Sn grain growth [4-6]. A very fine grain morphology was identified with an average grain size of less than 100 nm in the Nb_3Sn layer and a peak shift in the maximum flux pinning force to a higher magnetic field, which could bring about J_c improvement at high magnetic fields.

Regarding the composition of the Nb_3Sn layer, it has been found that even high-performance strands still have a significant Sn compositional gradient across this layer [7,8]. Detailed microstructural and microchemical studies are now underway to broaden our fundamental understanding of Nb_3Sn phase formation [9-12].

Recently, we have proposed a new approach to enhancing J_c performance by improving the growth kinetics of the Nb_3Sn layer. We have been exploring new effects arising from the addition of alloying elements into the Cu matrix in internal tin (IT)-processed Nb_3Sn conductors, since the IT process can use different alloy matrices. Zn is one attractive additive in terms of the growth kinetics of the Nb_3Sn layer. Zn does not penetrate the Nb_3Sn layers, but rather, remains homogeneously in the matrix. Our recent studies revealed that a thicker Nb_3Sn layer forms and the residual Sn content decreases appreciably in the Cu–Zn (brass)-matrix wire, as compared to a pure Cu-matrix wire [13-15]. The initial results showed that the Nb_3Sn layer in the brass matrix sample was about 1.5 times thicker than that in the Cu matrix sample [13]. Thicker Nb_3Sn layers result in better J_c characteristics in brass-matrix wires. The study of Zn addition into the Cu–Sn (bronze) matrix of Nb_3Sn superconductors dates back to 1978 [16], and followed even earlier studies on the addition of a third element, such as Zr or Al, into Nb_3Sn and V_3Ga [17-19]. These studies revealed that although the solubility of Zn in bronze is quite limited, the Nb_3Sn growth rate is enhanced appreciably upon Zn addition. An-

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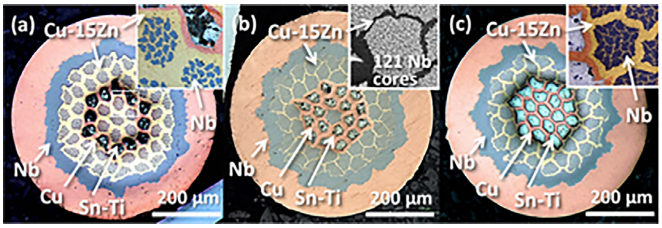

Fig. 1. Cross-sectional images of multifilamentary Nb_3Sn precursor wires: (a) MF817, (b) MF4477, and (c) MF684.

other previous study demonstrated that during the interdiffusion between brass and Sn, higher Zn compositions increase the Sn diffusion rate in brass [20]. This indicates that, as a solute, Zn could enhance Sn activity in the matrix, thereby accelerating Nb_3Sn layer formation. The enhancement of Sn activity could lead not only to a thicker Nb_3Sn layer, but also to improvement in the compositional gradient of Sn in the Nb_3Sn layer [21].

Against this background, we developed multifilamentary IT-processed Nb_3Sn wires using a brass matrix. Three types of cross-sectional wire design were considered. The diffusion behavior of Sn, Zn, and Ti during the reaction was investigated through elemental mapping using electron probe microanalysis (EPMA) and energy dispersive X-ray spectroscopy (EDX). The elemental composition was also measured. The average grain size was determined by image analysis of fractographs obtained using field-emission scanning electron microscopy (FESEM). The microstructure and J_c characteristics were correlated and the potential for further J_c improvement was investigated.

A Zn-solidified matrix might also help to reinforce strands by solid solution strengthening. The present brass IT process would no conflict with other new approaches such as internal Zr oxidation or state-of-the-art wire processing such as RRP (Restack Rod Process) [1]. We expect that the proposed technique will contribute to a breakthrough in J_c characteristics, complementing other approaches.

2. Experimental

2.1. Wire fabrication

Alpha brass with a typical Zn content of less than 35 wt% has excellent cold workability but is subject to work hardening [13]. Thus, in the fabrication of brass-matrix wires, we prepared Nb/brass composites and Sn/Cu composites separately, and finally stacked them together. This approach allowed us to conduct an intermediate annealing step on the Nb and brass.

In the present study, a Cu-15 wt%Zn alloy was used as the matrix since work hardening of Cu-35 wt%Zn was relatively large for cold drawing. Cu-15 wt%Zn was used as an imitation of gold, and is hence referred to as gold brass (GB). 1.6 wt% Ti was added to the Sn. Three kinds of wires with different cross-sectional designs (labeled MF817, MF4477 and MF684) were prepared (see Fig. 1). The current process is based on the standard double-stacking rod-in-tube process. First, a single Nb core is inserted into a brass tube and cold drawn into a Nb/brass single-core wire. Several pieces of the Nb/brass single-core wire are then stacked again in a brass tube and cold drawn into a multifilamentary Nb/brass subelement wire. Sn/Cu single-core wires are prepared as well. Finally, the multifilamentary Nb/brass subelement wires and the Sn/Cu single-core wires are stacked in a Cu tube with a Nb sheath as a barrier, and the bundle is cold drawn into a fine multifilamentary precursor wire.

For example, in the case of MF684, a Cu-15 wt%Zn tube with outer/inner diameters of 15.0/13.5 mm was prepared. Then, a Ø13.4 mm Nb rod was inserted into the resulting tube. The single-core composite was cold drawn into a Ø2.15 mm wire and shaped hexagonally (1.85 mm in height). Nineteen pieces cut from this wire were restacked in a Cu-15 wt%Zn tube with outer/inner diameters of 11.5/10.0 mm. The multifilamentary Nb/brass subelement rod was cold drawn into a Ø1.2 mm wire and shaped hexagonally (1.0 mm in height). A hexagonal Sn-1.6 wt%Ti/Cu single-core wire was prepared in addition to the Nb/brass single-core wire, using a Cu tube with outer/inner diameters of 13.0/10.0 mm and a Ø9.5 mm Sn-16 wt%Ti rod. The size of the hexagonal Sn single-core wire was the same as that of the multifilamentary Nb/brass subelement wire. Finally, thirty-six pieces of the multifilamentary Nb/brass subelement wire and nineteen pieces of the Sn/Cu single-core wire were stacked in a Cu tube with a Nb barrier, and cold drawn into wires (Fig. 1(c)).

All wires were prepared in-house by swaging and die drawing. Intermediate annealing of the Nb/brass composites was typically carried out only twice at 650 °C for 2 h each time, before stacking into the subelement composite and the final multifilamentary billet. This intermediate anneal was effective in relieving work hardening in not only brass but also Nb. The Vickers hardness of Cu-15 wt%Zn and Nb were reduced from 200 to 85 kgf/mm^2 and from 150 to 100 kgf/mm^2, respectively [15]. No intermediate annealing is necessary for the Sn/Cu composites. The specifications of the wires are listed in Table 1. SS-Cu and SS-GB (GB: gold brass) are reference samples for compositional analysis. They were fabricated through a single stacking process by using pure Cu and Cu-15 wt%Zn matrices, respectively [15].

2.2. Measurement and analysis

The primary heat treatment consisted of four steps: 100 h/210 °C, 100 h/550 °C (50 h for MF684), 100 h/650 °C, and 200 h/700 °C. The samples were sealed in a glass tube under 1 atm argon and heat treated in an open furnace. EPMA and EDX maps for the samples were obtained after heat treatment at 550 °C, 650 °C, and 700 °C. EPMA and EDX samples were prepared by a standard micrographic technique. Each sample was embedded in a conductive phenolic resin and finally polished by a 0.05 μm sol-gel alumina suspension.

The average Nb_3Sn grain size was determined through image analysis. A fractograph of the wire was captured by FESEM. An area between the center and the outermost boundary of the Nb_3Sn filament was selected and measured. The number of grains in this area was counted. Assuming circular grains, the average grain size was calculated from the area and the number of grains.

The critical current I_c was measured by the standard four-probe resistive method for short specimens with a voltage tap distance of 1 cm. I_c was determined at an electrical field of 1 μV/cm. Here, J_c was the matrix J_c value, calculated by dividing I_c by the cross-sectional area excluding the sheath area (including the Cu stabilizer and Nb diffusion barrier), because in our simple drawing process without extrusion machines, the outermost barrier thickness cannot be reduced to a practical level. The matrix J_c could almost be regarded as a non-Cu J_c, since the volume fraction of the barrier would only be a few percent of the filamentary region in practical wires.

3. Results

3.1. Microstructural and microchemical analysis

MF817 was the first design of the double-stacked multifilamentary wires [15]. The area fraction of Nb cores is 23.5%. The matrix area fraction is 63.5%, which is much larger than those for practical IT-processed Nb_3Sn conductors. The spacing between adjacent