Formation and structure of Nb3Sn layers in bronze-processed superconductors under various intermediate heat treatments

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Abstract. Multifilamentary Nb3Sn-based superconducting wires are created and used for various superconducting magnetic systems such as thermonuclear reactors and future large accelerator projects. The crucial role in achieving high superconducting characteristics is played by the structure of Nb3Sn layers, which, in its turn, is determined by a number of factors, such as fabrication route, composition, annealing schedules, etc. In the present study the superconducting layers formation and structure have been studied by SEM and TEM after various regimes of intermediate heat treatments and two-staged diffusion annealing. Optimal heat treatment schedules for the formation of perfect nanocrystalline structure of Nb3Sn layers for an achievement of highest critical current densities have been revealed.

1. Introduction
High magnetic fields are required for practical solution of a number of problems of high energy physics and thermonuclear energetics. They can be obtained in such devices as International Thermonuclear Experimental Reactor (ITER), Large Hadron Collider, Demonstration Power Plant (DEMO), etc. [1-4]. In spite of recent progress in conductors for these devices based on high-temperature superconductors, the present state of development and the fabrication costs are still in favor of multifilamentary Nb3Sn-based wires [5-7]. The Nb3Sn-based wires are multicomponent composites consisting of materials with different mechanical and physical properties, and their fabrication is a laborious high-technological process, numerous factors of which (manufacturing route, wire design, doping, heat treatment schedules, etc.) play a crucial role in the structure of superconducting layers and, consequently, in their current-carrying capacity. Multifilamentary Nb3Sn-based superconductors are produced by various techniques of solid-state diffusion using plastic initial materials and final diffusion annealing [8], and one of the most widely used approaches for their commercial fabrication is the bronze route [9]. The latter includes hot extrusion and multiple cold drawing with intermediate annealing required for avoiding cracking, and the final stage of fabrication is the diffusion annealing at which tin diffuses to Nb filaments and the superconducting Nb3Sn layer is formed. It is known that even before the diffusion annealing some amount of Sn can diffuse to Nb filaments and form thin Nb3Sn layers, referred to as pre-reaction or “parasitic” layers [10-12]. These intermetallic layers are brittle and can cause cracking, and that is why their formation is undesirable. Moreover, the previously formed Nb3Sn grains can grow under the following diffusion annealing which results in the overall grain coarsening. When the Nb3Sn grains get coarser, the amount of grain boundaries, which serve as main pinning centers in these composites, is decreased, and the current-carrying capacity of the wires is lowered [13]. Thus, great attention should be paid to the intermediate annealing schedules, and much work in this direction was done at Bochvar High-Technological Institute of Inorganic Materials [14].
The main goal of the present study is to investigate an effect of different regimes of intermediate annealing of bronze-processed Nb$_3$Sn-based wires on tin diffusion from bronze matrix to Nb filaments and possibility of pre-reacted Nb$_3$Sn layers formation, as well as on the structure of superconducting layers formed at subsequent diffusion annealing.

2. Experimental

The specimens under study were Nb-1.2Ti/Cu-14Sn composites with coupled Nb filaments, worked out, manufactured, heat treated and tested at Bochvar Institute of Inorganic Materials. Two specimens (1 and 2) were rods the diameter of 8.45 mm, containing 13000 coupled Nb filaments doped with 1.2 % Ti in Cu-14%Sn bronze matrix. Four specimens (3-6) were wires of final diameter 0.70 mm, containing 7300 Nb-1.2Ti filaments in the matrix of the same composition, and they had different pre-history (Table 1). These wires were subjected to the two-staged diffusion annealing worked out for ITER [6] and after this treatment they are denoted as 3'-6'. Along with conventional intermediate annealing, brief high-temperature (750°C) treatment (BHTT) was applied at different diameters. The structure was studied by TEM (JEM-200CX) of longitudinal sections and SEM (Quanta-200 with EDAX for microanalysis) of cross sections of these rods and wires. Grain size distributions in Nb$_3$Sn phase were determined from TEM images by the computerized program SIAMS-600.

3. Results and discussion

A fragment of transverse section of sample 1 is shown in figure 1. Coupled Nb filaments look like “dumbbells”, and in centers of filaments there are round inserts of NbTi alloy used for the so-called artificial doping with titanium [15].

To reveal Sn diffusion from bronze matrix into Nb filaments and possible formation of pre-reacted Nb$_3$Sn phase after conventional intermediate annealing and after the additional brief high-temperature treatment, samples 1 and 2 were studied by SEM with microanalysis, which was carried out by three ways: taking X-ray images in radiations of three main elements (Nb, Cu and Sn), along scanning lines in different places of Nb dumbbells (figure 2) and in local points moving from a center of a filament into the bronze matrix.

No definite splashes of Sn concentration at Nb/bronze interfaces which would indicate Sn diffusion and the Nb$_3$Sn phase formation were revealed in sample 1. Actually, distribution of Sn repeats that of Cu, which means that Sn is completely retained in the bronze matrix (figure 2). After the brief high-temperature treatment (750°C, 4 min) of the rod the diameter of 8.45 mm (sample 2) the distribution of elements appeared to be practically the same, and no indication of enhanced Sn diffusion was revealed.
Local microanalysis in several points from centers of Nb filaments to Nb/Cu-Sn interfaces and deeper into the bronze matrix was carried out to get some quantitative, not only qualitative information. The concentration plots based on this analysis also did not reveal noticeable differences between the samples without and with the BHTT, and no evidence of the Nb3Sn formation in both cases was obtained. However, it has been discovered that the Sn/Cu ratio near Nb/bronze interfaces is considerably higher than deep in the matrix, increasing up to 0.38 compared to the nominal value of 0.16 (figure 3). This means that Sn diffuses to Nb filaments even at this early stage of fabrication in both cases, with and without the BHTT.

Although SEM studies did not reveal noticeable differences in the samples without and with the brief high-temperature treatment even directly after it, pronounced differences in the structure of Nb filaments in samples 1 and 2 are observed by TEM studies of longitudinal sections of these rods (figure 4).

In sample 1 (the rod without BHTT) niobium filaments consist of grains elongated in the drawing direction, the width of 200-300 nm (figure 4a). After the BHTT their structure changes, and in some areas almost equiaxed Nb grains are formed as a result of grain boundary migration (figure 4b). The main effect of the high-temperature treatment is the Nb3Sn phase formation, the nuclei and fine (20-30 nm) grains of which are observed in some areas in sample 2 (figure 4c). In the electron diffraction patterns corresponding to such areas the Debye rings belonging to Nb3Sn are present along with the reflections of Nb (figure 4c, insert). Thus, comparing samples 1 and 2 we revealed the effect of brief high-temperature treatment directly after it.
Several composites were subjected to the BHTT on different diameters and then cold drawn to the final diameter of 0.7 mm. Samples 3 and 4 differ in their fabrication route, namely, sample 4 was annealed at 750°C, 6 min on the diameter of 11.5 mm and then deformed to 0.7 mm, whereas for sample 3 only conventional intermediate heat treatments were applied. In this case the effect of the BHTT is smoothened, and the structure of Nb filaments in both samples is practically the same. The filaments consist of highly elongated Nb grains the width of about 100 nm (figure 5a), and in both cases in some filaments there are areas with pre-reacted Nb₃Sn layers (figure 5b). The TEM method is highly localized, and no quantitative estimation of the amount of such areas can be done. However, analysis of a great number of images taken from these samples allows concluding that in the sample with the BHTT the areas with nuclei and fine grains of the pre-reacted superconducting phase are observed more often.

![Figure 4. TEM images of Nb filaments in sample 1 (a) and 2 (b, c): a, b –dark field images in (110)Nb reflections; c – dark-field image in (200)Nb₃Sn and (210)Nb₃Sn reflections](image)

![Figure 5. Dark-field images of Nb filaments in samples 3 (a) and 4 (b): a – in (110)Nb reflection; b –in (110)Nb and (210)Nb₃Sn reflections](image)

The effect of the duration of high-temperature treatment was studied on the next two samples, 5 and 6, annealed on the diameter of 7.75 mm at 750°C for 4 and 8 minutes, respectively. After the annealing for 4 min and subsequent deformation to the final diameter of 0.7 mm (sample 5), Nb grains are uniform, narrow, with straight boundaries, and in some areas the pre-reacted fine-grained Nb₃Sn phase is present. After the longer annealing the structure of Nb filaments is similar, but in some areas there are more equiaxed grains, and the areas with nuclei and grains of the superconducting phase are observed more frequently, indicating that longer high-temperature treatment increases the amount of the pre-reacted layers.

In all the wires studied the two-staged diffusion annealing (575°C, 150 h +650°C, 200 h) results in practically complete transformation of niobium into the superconducting Nb₃Sn phase. In the bronze-processed conductors the superconducting layers consist of three zones of different morphology: a zone of columnar grains adjacent to the residual niobium, a middle zone of fine equiaxed grains and a zone of irregular shaped coarse grains at an interface with bronze matrix [16]. The highest current-carrying capacity of a wire can be reached when the middle fine-grained zone is predominant, because it has...
more uniformly distributed pinning centers (grain boundaries) than the coarse-grained zone, and its composition is closer to stoichiometry, than in the columnar grained zone [17].

The relative amount of the zones of different morphology can be estimated from transverse sections or fractures of the wires [18], which was out of the framework of this study. However, in TEM micrographs of longitudinal sections the areas of three types, fine equiaxed grains (figure 6a), coarse grains (figure 6b) and elongated (columnar) grains, were observed in all the samples. The latter are only seldom revealed in longitudinal sections, but still some amount of them was observed in every sample. More pronounced are the areas with wide grain size scattering and coarse grains, sometimes of not equiaxed but irregular shape.

Figure 6. The Nb₃Sn layers in sample 6' (BHTT 750°C, 8 min): a - fine equiaxed grains; b - irregular shaped coarse grains with wide grain-size scattering

To reveal quantitative differences in the grain structure, TEM images of the Nb₃Sn layers were statistically treated using SIAMS600 program, and the results are given in Table 2.

Table 2. Parameters of grain size distribution in Nb₃Sn layers formed under the two-staged annealing 575°C, 150h + 650°C, 200h. Dₘᵡ, Dₘₐₓ and Dₐᵥ are minimal, maximal and average grain sizes respectively; RMS is root mean square deviation

| BHTT (°C/min) | Dₘᵡ-Dₘₐₓ, nm | Dₐᵥ, nm | RMS, nm |
|--------------|--------------|---------|---------|
| 3'           | 30-230       | 85      | 23.5    |
| 4'           | 30-210       | 80      | 22.8    |
| 5'           | 30-250       | 82      | 25.9    |
| 6'           | 30-320       | 88      | 27.9    |

In all the samples under study the structure of superconducting Nb₃Sn layers is in general quite similar, with no pronounced differences. However, some differences depending on the intermediate annealing regimes have been revealed. Thus, the brief high-temperature treatment for 6 min on the diameter of 11.5 mm affects the structure of the Nb₃Sn layers positively, as both the average grain size and grain size scattering are smaller than in the wire without this treatment (compare samples 3' and 4'). It can be suggested that the BHTT at early stages of deformation results in some additional softening of the bronze matrix and Nb filaments, which results in their more uniform structure, and it promotes more uniform structure of the diffusion layers formed under the last heat treatment.

When the brief high-temperature treatment is carried out at higher deformation, on the diameter of 7.75 mm, it results in the formation of more pre-reacted Nb₃Sn layers and less uniform structure of Nb filaments, especially when this treatment is longer, and as a result the grain structure of superconducting layers is somewhat coarser and less uniform (compare samples 5' and 6' in Table 2). The latter regime (7.75/750°C/8 min) appears not to be beneficial for the formation of perfect Nb₃Sn layers.

Examples of the highest achieved $J_c$ in the Nb₃Sn-based wires of different types are given in [19].

4. Summary
In multifilamentary bronze-processed Nb₃Sn-based superconducting wires Sn diffuses from the bronze matrix to Nb filaments in the process of their fabrication, including multiple cold-drawing with intermediate annealing. Additional brief high-temperature treatment (BHTT) modifies the structure of Nb filaments and affects the grain structure of the Nb₃Sn layers formed under the subsequent diffusion annealing.

The effect of BHTT depends on its duration and wire diameter. After the BHTT at 750°C for 4 min on the diameter of 8.45 mm the structure of Nb filaments is changed, and wide elongated grains in them transform into more equiaxed ones. Besides, it results in the pre-reaction formation of the Nb₃Sn phase.

Under the two-staged diffusion annealing (575°C, 150 h + 650°C, 200 h) practically all the Nb filaments completely transform into the Nb₃Sn phase with grains of three types: fine equiaxed, coarse irregular-shaped and columnar grains. The BHTT on Ø 11.5 mm, 6 min, affects the superconducting layers structure positively, decreasing average grain size and grain size scattering.

Some positive effect of the BHTT (smaller average grain size) is observed when it is applied on the Ø 7.75 mm, 4 min. However, longer BHTT (8 min) on this diameter results in deterioration of the Nb₃Sn structure: average grain size and grain size scattering are increased.

Thus, the brief high-temperature treatments can be applied for the optimization of the superconducting layers structure, but they are recommended at earlier stages of fabrication and should not be too long.

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