Effect of diffusion annealing regimes on the structure of Nb$_3$Sn layers in ITER-type bronze-processed wires

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Abstract. The goal of the present study is to characterize the growth kinetics and structural parameters of the Nb$_3$Sn layers formed under various regimes of the diffusion annealing of bronze-processed Nb/Cu-Sn composites. The structure of the superconducting layers is characterized by their thickness, average size of equiaxed grains and by the ratio of fractions of columnar and equiaxed grains. It was found that at higher diffusion annealing temperatures (above 650°C) thicker superconducting layers are obtained, but the average sizes of equiaxed Nb$_3$Sn grains even under short exposures (10 h) are much larger than after the long low-temperature annealing. At the low-temperature (575 °C) annealing the relative fraction of columnar grains increases with increasing annealing time. Based on the data obtained, optimal regimes of the diffusion annealing can be chosen, which would on the one hand ensure complete transformation of Nb into Nb$_3$Sn of close to the stoichiometric composition, and on the other hand prevent the formation of coarse and columnar grains.

1. Introduction

The Nb$_3$Sn-based superconducting composites under study were developed and manufactured by bronze technology at the Bochvar Institute of Inorganic Materials (VNIINM, Moscow, Russia) [1]. Superconductors of such design have high critical characteristics in magnetic fields up to 12 T, which allowed them to participate in the ITER project [2]. At present, they are the main candidates for use in the superconducting magnetic systems of future large accelerator projects at CERN and thermonuclear reactors. Particularly, Nb$_3$Sn superconductors are planned to be used in the Future Circular Collider (FCC) project that considers the creation of magnetic fields up to 16 T [3]. To further increase the critical characteristics in high magnetic fields for similar applications attention should be paid to studying the growth of the superconducting layers in industrial conductors manufactured by up-to-date technologies.

The goal of the present study is to characterize the growth kinetics and structural parameters of the Nb$_3$Sn layers formed under various regimes of the diffusion annealing.

The current-carrying capacity of superconductors in high magnetic fields depends on several basic parameters, such as the value of the upper critical field of the superconducting compound, and the amount and structure of the superconducting phase [4]. Other parameters of importance include...
structural assembly features of a conductor, the average size of the initial niobium filaments before diffusion annealing, etc.

It is well known that in niobium-tin superconductors the highest values of the critical temperature $T_c$ and upper critical field $H_c$ are achieved when the phase composition approaches a slight deviation from the stoichiometric composition of Nb$_3$Sn in the region of 24.5 at.% [5]. The content of tin in the layer increases (this leads to an approach of its composition to the stoichiometric one) with an increase in the annealing temperature.

It is known that in filaments of composites produced according to the bronze technology, there arise concentric zones of Nb$_3$Sn grains of different morphology [6]. A zone of equiaxed grains adjoined the bronze matrix has a certain gradient in the sizes of grains from the fine ones in the middle to the coarse ones near the bronze matrix; the zone of columnar grains is contiguous with the residual niobium. It has been well established that tin concentration is different in the Nb$_3$Sn grains of different morphology, decreasing from 24.5–21 at.% in equiaxed grains to 21–18 at.% in columnar grains from the outside to inside of the Nb$_3$Sn layers forming in Nb filaments under heat treatment [6–8]. Based on this, it can be concluded that the smaller fraction of columnar grains provides the higher average tin concentration in the superconducting layers.

The critical current density, in its turn, is determined by the pinning force. As has been well established, the main pinning centers in multifilamentary Nb$_3$Sn-based composites are grain boundaries [9, 10]. The Nb$_3$Sn phase grain refinement results in larger area of grain boundaries, and, thus, in higher pinning force and $J_c$ [11]. Of not less importance than the grain sizes proper is the morphology of superconducting layers, because in equiaxed grains the pinning centers are distributed more uniformly than in columnar ones. Because of the variety of parameters that determine the properties of a superconductor, it becomes necessary to thoroughly investigate the microstructure of the Nb$_3$Sn layers under various conditions.

2. Materials and experimental procedure

2.1. Samples

The samples studied are composite wires of overall diameter of 0.82 mm manufactured by bronze technology as mentioned above. They consist of 13,212 coupled niobium filaments artificially doped with 1.55 wt.% Ti and embedded in a bronze matrix (Cu–14%Sn). This assembled billet is surrounded with a niobium barrier with tantalum inserts and placed in a tube of stabilizing copper. Under the diffusion annealing superconducting Nb$_3$Sn layers are formed starting from interfaces of niobium filaments and bronze matrix.

Different temperatures and times of annealing were applied to samples studied in this work. The first group of composite wires was annealed at 575 °C during 10, 50 and 100 hours (samples 1, 2 and 3, respectively). The second group (samples 4–6) was annealed at 650 °C for the same annealing times. The annealing temperature of the last group (samples 7 and 8) was increased up to 750 °C and the heat treatment was carried out for 10 and 50 hours.

Composites of this design with other regimes of the diffusion annealing were investigated in our previous studies [12–15].

2.2. Experimental methods

For scanning electron microscopy (SEM) polished transverse sections and fractures of strands were used to determine the thickness of the superconducting layers. SEM images were obtained in Inspec F (FEI) and Quanta–200 (FEI) microscopes in the Secondary Electrons and Back-scattered Electrons modes. Polished sections were produced by standard metallographic procedures. The morphology of grains in Nb$_3$Sn layers was determined using SEM images of Nb filaments on transverse fractures of the wires prepared in liquid nitrogen. Quantitative image analysis was performed on SEM images of several Nb filaments from different (central and peripheral) areas of the strands.
The relative fractions of the zones of different morphology in the superconducting layers were determined by the program of image treatment ImageMagick (GNU). The areas of different morphology were painted in various colors, and the ratio was calculated from the relationships of pixel proportions of every color.

The Nb₃Sn layers structure was also studied by transmission electron microscopy (TEM) of longitudinal foils in JEM-200CX electron microscope. The foils were prepared by a standard method of mechanical thinning of longitudinal sections with further chemical polishing in a mixture of HNO₃, H₂SO₄ and HF acids. TEM (longitudinal foils) and SEM (transverse fractures) images obtained were treated with the help of specialized program of statistical analysis of images SIAMS-600 (SIAMS) to calculate the average grain size of the Nb₃Sn phase.

3. Results and discussion

An overall view of multifilamentary ITER-type composite is shown in figure 1a. As it is shown in figure 1b, after multiple cold drawing and diffusion annealing the coupled filaments retain their dumbbell shape, but the filament diameter varies along the wire axis and the thicker filaments have wider areas of the residual niobium.

**Figure 1.** SEM images of polished transverse sections, sample 3 (575 °C, 100 h): (a) an overall view of multifilamentary ITER-type composite; (b) a group of filaments with different degree of Nb transformation into Nb₃Sn.

For each sample, fracture images were obtained, on which the boundary of the residual niobium is clearly visible, as well as the morphology of the grains of the superconducting phase. Thus, in the layers we can distinguish zones of different morphology and determine the ratio of columnar and equiaxed grains. An example of such an image is shown in figure 2. The proportion of grains of certain morphology was calculated as the area of this zone in the cross section of the filament reduced to the area of the entire filament. The values obtained were averaged over several filaments in order to reduce the error. In general, from the data obtained, it can be seen that the columnar grains account for slightly more than a third of the volume of the superconducting layer at all the temperatures studied, which is a common ratio for bronze-processed composites [14]. A slight increase in the fraction of columnar grains is observed with an increase in the annealing time at a temperature of 575 °C (figure 3). For more definite conclusions about the effect of temperature and time of single-stage annealing on the fraction of columnar grains, further investigations with a larger number of points, both over the temperatures and the annealing durations, will be required.
The thickness of the superconducting layer is usually determined on the cross sections of the composite as the shortest distance between the phase boundaries "bronze matrix–Nb₃Sn" and "Nb₃Sn–residual Nb". Exact thickness measurements are complicated by irregularities of the Nb filaments surface. The error due to these irregularities is minimized by averaging a number of thickness measurements made on several cross sections of a composite wire. When the boundaries of the phase sections are strongly distorted and the thickness of the layer reaches the entire volume of the material, the task becomes much more complicated. Since two hexahedral rods are used as a billet for the creation of coupled filaments, the final dumbbell-shaped Nb filament can be approximated by two hexahedrons. SEM images of fractures of Nb filaments with Nb₃Sn layers after the annealing at 575°C, 650 °C and 750 °C during 10 hours are shown in figure 4. The calculated values of the average layer thickness, \( L \), with the standard deviation (SD) of this value, obtained during the processing of images, are presented as a graph in figure 5a.

It can be seen from figures 4 and 5a that at 750 °C the superconducting layer growth is much faster. After a short annealing (10 hours), slightly thicker layers are formed in sample 4 (650 °C) than in sample 1 (575 °C), but at the same time almost complete Nb transformation into Nb₃Sn is achieved in sample 7 (750 °C) in the majority of filaments. At lower annealing temperatures, even after 100 hours exposure, a full transformation of niobium filaments is not achieved (although at 650 °C there are not many filaments with the residual niobium).
Figure 5. Parameters of Nb₃Sn layers: (a) Layer thickness versus the annealing time. Wide bars show standard deviation of values obtained, narrow bars mark standard error of mean. Dashed lines demonstrate the allometric fittings $L(t)=bt^m$ for different temperatures. (b) Average size of equiaxed grains of the superconducting Nb₃Sn phase as a function of the annealing time at different temperatures (according to SEM). Vertical bars indicate the standard deviation of the grain size distribution.

The common used fitting for time dependence of layer thickness $L(t)$ is $L=bt^m$, in which $m$ is a growth exponent, and $m = 1$ for a reaction-rate limited dependence and $m = 0.5$ for a diffusion-rate limited case. The SD of the data obtained in this system is very high, so it is very difficult to find the exact growth exponent. Nevertheless, an attempt was done, and the layer thickness data is shown in figure 5a with the fits of $bt^m$. Such a rough estimate shows that the layer growth at 575 °C corresponds most completely to a parabolic law ($m = 0.45$). At higher temperatures (650 °C and 750 °C) there is a significant deviation from this law ($m = 0.35$ and 0.23, respectively). It is known that a time-dependent increase in grain size can suppress the intermetallic layer growth below a parabolic rate when grain boundary diffusion is important [16]. This factor along with the depletion of bronze matrix can be a reason for the deviation of the layer growth from the parabolic law.

The results of grain size distribution were obtained according to the transmission and scanning microscopy. In the first case, we studied the grains from the images of longitudinal foils of composites. In the second case we used images of fractures of the cross sections. The calculated values of the average size of equiaxed grains (with the SD of this value) obtained during the processing of images are presented in figure 5b. The data from longitudinal foils reflect similar trends, except for the fact that the average grain size according to SEM data is slightly increased due to the fact that more large grains are counted in this calculation. As can be seen from the presented data, at a temperature of 750 °C, even with short annealing at 10 h, the average size of equiaxed grains considerably exceeds those after long low-temperature annealing.

The data obtained are of importance for the optimization of current-carrying capacity of the wires under consideration. As mentioned in the Introduction, columnar grains are undesirable for two reasons. Firstly, their composition is farther from stoichiometry, which results in lower upper critical field and, thus, in their poorer performance in high magnetic fields. Secondly, in grains of such shape the grain boundaries are distributed non-uniformly, which may cause current instabilities. The equiaxed grains are much more preferable as their composition is closer to stoichiometry and thus they have higher critical characteristics. Of not less importance than composition is grain size, for, as mentioned above, grain boundaries in such superconductors are the main pinning centers, and grain refinement is the crucial factor for the enhancement of the current-carrying capacity. As seen from the results obtained, some factors (higher annealing temperature) are beneficial for an improvement of
composition and an increase of the total amount of superconducting phase. On the other hand, grain growth at high temperatures results in lower pinning force. At longer low-temperature annealing the relative fraction of columnar grains is increasing, which results in poorer performance of a composite for the reasons mentioned above. Thus, based on the data obtained one can find a reasonable compromise in annealing temperature and duration in order to achieve the best performance of the Nb3Sn strands.

4. Summary
Since at high annealing temperatures (750 °C) there is no increase in the fraction of columnar grains in the layer, we can expect that the average concentration of tin in this layer in these samples is not lower than in samples with a lower annealing temperature. This makes the high-temperature annealing regime preferable because of more complete transformation of the filaments. However, in the sample annealed at 650 °C, 100 h almost complete processing of niobium filaments is also observed, but the grain size of the superconducting phase is much smaller. This means that the pinning force is higher, which is also significant for an achievement of high critical characteristics. In high fields the current carrying capacity is determined mainly by the value of the upper critical field of the Nb3Sn intermetallic compound, whereas in intermediate fields the main role is played by pinning force, and thus the grain size is of great importance.

Therefore, when choosing the annealing regimes, different trends should be taken into account: on the one hand, the possibility of approaching stoichiometry and ensuring the maximum amount of the superconducting phase, and on the other hand, the growth of grains and the loss in the pinning force. The knowledge of these trends will allow finding optimal trade-offs to ensure the best current-carrying capacity of conductors, which makes the ongoing research of great importance.

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References
[1] Pantsyn Y, Shikov A and Vorobieva A 2008 Cryogenics 48 354
[2] Tronza V I et al. 2016 IEEE Trans. Appl. Supercond. 26 (4) 4200105
[3] Ballarino A and Bottura L 2015 IEEE Trans. Appl. Supercond. 25 (3) 6000906
[4] Popova E N, Deryagina I L, Valova-Zakharevskaya E G and Patrakov E I 2016 Phys. Met. and Metallogr. 117 (10) 1028–37
[5] Flükiger R, Uglietti D, Senatore C and Buta F 2008 Cryogenics 48 293–307
[6] Uglietti D, Abächerli V, Cantoni M and Flükiger R 2007 IEEE Trans. Appl. Supercond. 17 (2) 2615
[7] Abächerli V, Uglietti D, Lezza P, Seeber B, Flükiger R, Cantoni M and Buffat P-A 2005 IEEE Trans. Appl. Supercond. 15 3482
[8] Senatore C, Abächerli V, Cantoni M and Flükiger R 2007 Supercond. Sci. Technol. 20 S217
[9] Luhman T, Pande C S and Dew-Hughes D 1976 J. Appl. Phys. 47 (4) 1459
[10] Lee P J and Larbalestier D C 2008 Cryogenics 48 283
[11] Larbalestier D C 1995 Cryogenics 35 S15–8
[12] Deryagina I L, Popova E N, Patrakov E I and Valova-Zaharevskaya E G 2017 J. Magn. Magn. Mater. 440 119-122
[13] Deryagina I, Popova E, Patrakov E and Valova-Zaharevskaya E 2017 J. Appl. Phys. 121 233901
[14] Popova E N, Deryagina I L and Valova-Zaharevskaya E G 2014 Cryogenics 63 63
[15] Popova E N and Deryagina I L 2015 Diff. Found. 5 199
[16] Farrell H H and Gilmer G H 1974 J. Appl. Phys. 45 4025