The study of Nb₃Sn phase content and structure dependence on the way of Ti doping in superconductors produced by bronze route.

Elena Dergunova, Alexandra Vorobieva, Ildar Abdyukhanov, Konstantin Mareev, Semen Balaev, Ruslan Aliev, Alexander Shikov, Alexander Vasiliev, Mikhail Presnyakov, Andrey Orekhov, a*  

a Bochvar Research Institute of Inorganic Materials, Rogova St. 5a, Moscow, 123060, Russia  
NRC Kurchatov Institute, Academic Kurchatov Sc., 1, Moscow, 123182, Russia

Abstract

One of the most effective ways to increase the current-carrying ability of Nb₃Sn superconductor is doping of the superconducting phase by Ti, since it leads to Hc₂ increase due to the rise of Nb₃Sn phase electrical conductivity in normal state, and also to acceleration of the Nb₃Sn layer growing during reaction and to critical current density increasing. The investigations of structure and composition of Nb₃+xSn superconducting strands by SEM, TEM and EDXS microanalysis have been carried out. The structure and composition of Nb₃Sn superconducting phase of the strands after reaction at 575°C 150 h + 650°C 200 h have been studied. The dependence of Ti content in Nb₃Sn phase from the amount of Ti introduced in Nb filaments or in bronze matrix has been also studied. It was found, that the lowest Ti content corresponds to introduction of it through the matrix doping. It has been established that Nb content in Nb₃Sn essentially exceeds the stoichiometric one (3:1). The Nb₃Sn lattice parameters have been defined by XRD. It was found, that the lattice parameters in the samples with Ti doped matrix were the closest to the stoichiometric Nb₃Sn. The correspondence between grain morphology and composition of superconducting phase and critical current density of studied strands has been established.

© 2012 Published by Elsevier B.V. Selection and/or peer-review under responsibility of the Guest Editors.

Open access under CC BY-NC-ND license.

Nb₃Sn; superconductors; doping; ITER; bronze route; grain structure

* Corresponding author.
E-mail address: vor@bochvar.ru
1. Introduction

The Ti doping of Nb\textsubscript{3}Sn superconducting phase commonly used to increase the stability and high repeatability of the Nb\textsubscript{3}Sn strands current carrying capability, especially under operation at high magnetic field. It is known that the presence of Ti in Nb\textsubscript{3}Sn compound affects on superconducting layer grain structure and critical characteristics of strands [1, 2]. Earlier it was found [3], that Ti suppress the martensitic cubic- tetragonal phase transformation in Nb\textsubscript{3}Sn that possible has positive influence on current-carrying ability of this phase. Therefore, the optimization of the Ti concentration in Nb\textsubscript{3}Sn strands along with determination of the effective doping method is still actual ones. Another important goal is the identification of Ti influence on Nb\textsubscript{3}Sn microstructure and physical properties, especially on critical current density. In previous study [4] we found that the critical current density could decrease when Ti concentration in the superconductor arise (Fig 1 a). The aim of this work was to establish correlation between the current carrying ability and microstructure (grain structure, composition and lattice parameter) of Nb\textsubscript{3}Sn strands differed by Ti content.

2. Materials and methods

The comparative investigations of structure and content of Nb\textsubscript{3}Sn phase in bronze strands differed by the method of Ti doping have been carried out: artificial doping of Nb filaments and/or doping of bronze matrix. The strands formation was considered in more details in [5]. A cross-section view of the wires produced in Bochvar Institute (JSC “VNIINM”) c is shown in Fig. 1 b. These wires consisted of bronze matrix with Nb coupled filaments, Cu stabilization, Nb diffusion barrier with Ta inserts. The Ti concentration and doping methods are presented in Table 1.

The microstructure and composition of superconducting filaments and matrix after reaction at 575\textdegree{}C-150 h + 650\textdegree{}C-200 h have been studied by scanning electron microscopy (SEM) in Helios (FEI, USA) dual beam electron microscope (DB EM), equipped with energy dispersive X-ray spectrometer (EDXS) (EDAX, USA), operated at 2-30 kV accelerating voltage. The grain structure and composition of Nb\textsubscript{3}Sn layer has been studied in scanning transmission electron microscope (STEM) Titan 80-300ST with attached (EDAX, USA) EDXS, Gatan image filter (GIF) and high angle annular dark-field (HAADF) detector operating at 300 kV. Samples for TEM/STEM were prepared by focus ion beam (FIB) in the Helios DB EM. Thin cross-sections of wires 15x10x0.1 \textmu{}m in size were cut out from the mechanically grinded (along the wire axis) wires. Final polishing of the FIB cross-sections were performed by 2 kV Ga\textsuperscript{+} ions using low ion current.

![Graph](image)

**Fig. 1.** a) dependence of critical current density from the Ti content in Nb\textsubscript{3}Sn strands [4]; b) light microscope image of cross-section of Nb\textsubscript{3}Sn superconductor of 0.82 mm in diameter
Table 1. Ti content in samples of Nb₃Sn strands

| Sample № | Ti concentration, wt.% (Doping method) |
|----------|--------------------------------------|
| 1        | 0.25 (Matrix)                        |
| 2        | 1.11 (Filament)                      |
| 6        | 1.75 (Filament)                      |

To define the lattice parameter of Nb₃Sn phase X-ray analysis after reaction had been done on diffractometer DRON-3M at Cu-Kα radiation and graphite monochromator maintained in front of detector. The lattice parameter of superconducting phase have been defined for samples (N 1-6) prepared of Nb₃Sn filaments etched out of strands and glued to an organic glass by varnish. The values of the lattice parameter have been calculated by angle positions of lines (400) and (600) situated in precessional area of angles 2θ by Nelson-Raily formula and compared with the lattice parameter of the stoichiometric Nb₃Sn phase equal 0.529 nm.

3. Results and discussion

3.1. Microstructure of Nb₃Sn superconductors by SEM analysis

The microstructure of Nb₃Sn superconductors cross section view has been obtained in secondary (SE) and backscattered electrons (BSE) in Fig 2 a and b respectively. The Nb, Sn, Ti and Cu distribution along the line across a group of filaments have been studied in samples 1, 2 and 6 and one example is shown in Fig 2 b. In all samples Ti distribution followed Sn declining almost to zero at the filament-matrix interface. The averaged results of semi-quantitative composition microanalysis of samples 1, 2 and 6 are presented in Table 2. It was found that Nb and Sn concentration is not uniform: as a rule Sn content is higher closer to the edges of filaments. The Nb content in the filaments exceeded 3:1 stoichiometric ratio, especially in the areas close to the filament centre. Moreover, we observed the nonreacted Nb in a number of filaments. The diffusion of Ti from the bronze matrix towards the filament after heat treatment was found in sample 1. EDXS study demonstrated that after heat treatment the Ti content in bronze matrix was close to zero. Ti content in the filaments arises along with Ti content in the strands. Maximum quantity of Ti was obtained in superconducting phase of the sample N6. It is possible that little part of Ti could be remaining in the central Nb part of filament.

Fig. 2. The microstructure of Nb₃Sn superconductors by SEM in second (a) and backscattering (b) electrons and qualitative results of EDXS by line
Table 2. The results of Nb₃Sn filaments composition in studied samples by EDXS analysis, at % (the rest up to 100 % is Cu)

| №  | Nb    | Sn    | Ti |
|----|-------|-------|----|
| 1  | 68-70 | 23-25 | 0.78 |
| 2  | 60-74 | 16-19 | 1.0 |
| 6  | 69-71 | 18-20 | 1.48 |

3.2. The investigation of grain structure and composition of Nb₃Sn phase by TEM with EDXS analysis.

The HAADF cross-section STEM image of superconducting filaments of the sample N1 after reaction is presented in Fig 3. As far as essential Z-contrast technique was used, Sn enriched areas exhibited brighter contrast. TEM analysis of enlarged area of filaments cross section has shown the presence of dark contrast in the center of some filaments: unreacted Nb is clearly visible in the central parts in few filaments. Cross section bright field (BF) TEM images of sample 1 and sample 6 filaments are shown in Fig 4 a and b correspondingly to compare the morphology of intermetallic phase of both samples. The morphology of the intermetallic phase grains was found to be different in the areas close to bronze/Nb₃⁺⁺Sn interface towards the center of the filament: small equiaxed grains in peripherals areas and columnar grains closer to the center. There are also large grains of size 130±50 nm at the boundary between a filament and a bronze matrix. The mean diameter of equiaxed grains in sample 1 was about 70 nm. However, few grains were up to ~300 nm in diameter. The central part of filament (the sample N6) consists of unreacted Nb grains of similar orientation and high density of dislocations. The area of column grains marked more strongly in sample N6.

![Fig. 3. HAADF cross-section STEM image image of sample N1: superconducting coupled filaments in bronze matrix after reaction](image1)

![Fig. 4. TEM image of grain structure of Nb₃Sn filaments in samples: a) N1; b) N6](image2)
It was shown that equiaxed grains situated close to bronze matrix is about 70 nm in diameter (it is ~1/9 of ones for N1). But it is possible to find single grains by size of ~300 nm in dia. Typical aspect ratio of columnar grains for sample N2 is presented in Fig 5.

It follows from point-by-point EDXS analysis (Fig 6) that the ratio Nb:Sn is close to stoichiometric one only on the boundary between the bronze and the filament in area of large grains. In the area of column grains this ratio is shifted to large content of Nb. EDXS elemental line profiles (Fig 6 a and b) consisted with EDS SEM results: Sn content fell down from ~25 at% at the bronze/filament interface to ~15 at % in the areas close to the center. As it was observed by HAADF STEM, the central area consisted of Nb, Sn content was ~0.2 at%. Nb content has opposite tendency: it grows up from 56 to 75 at % in grains situated close to the edge of filament and rises sharply up to 90 at% in central part of it.

Ti content was ~1 at% inside sample 1 filaments, however, there were no Ti in the central (Nb) part of the filament (Fig 6).
3.3. X-ray definition of Nb$_3$Sn lattice parameter of samples differed by Ti content.

The lattice parameters of Nb$_3$Sn in samples N 1-6 have been defined in present work. Analysis of the results obtained has shown the tendency to decrease of lattice parameter value under increase of Ti content in filaments (Fig 7). That can be due to the substitution of Nb or Sn by Ti in A15 Nb$_3$Sn lattice [6]. The changes of chemical content could follow by decrease of critical current density in the samples observed earlier (see Fig 1).

![Graph showing dependence of Nb$_3$Sn phase lattice parameter from Ti content in samples N1, 2 and 6](image)

Fig. 7. Dependence of Nb$_3$Sn phase lattice parameter from Ti content in samples N1, 2 and 6

4. Conclusion

The SEM, TEM/STEM and EDXS study of microstructure, grain morphology and elemental composition of Nb$_{3+x}$Sn filaments have been carried out for 3 bronze strands with different method and amount of Ti doping after reaction. It was shown that the sample with the highest critical current density value has the lowest Ti content and the smallest grain size of Nb$_3$Sn in filaments. The Nb: Sn ratio is the most close to stoichiometric one in the same sample.

Acknowledgements

The authors are indebted to O. Krimskaya, M. Isaenkova and U. Perlovich (NRNU MEPHI) for X-ray definition of Nb$_3$Sn lattice parameter.

References

[1] Goldacker W and Flukiger R. Phase transition and superconductivity properties of binary and Ti, Ta, Ga and H alloyed Nb$_3$Sn. Physica B+C V.135 issues 1-3, 1985, p. 359-363.
[2] Popova E, Popov V, Romanov E, Sudareva S, Dergunova E, Vorobyova A, et al. Ti Redistribution in Multifilamentary NbCu-Sn Composites. Defect and Diffusion Forum. 2009. V. 283-286. p. 649-656.
[3] Sekine H, Iijima Y, Itch K. Effects of Titanium Addition to the Matrix of Nb$_3$Sn Composites. Proc, Intern, Cryog, Mater, Conf, Kobe, 1982, p. 86-89.
[4] Shikov AK, Vorobieva AE, Dergunova EA, Balayev SM. Technology production of Nb$_3$Sn superconductors for ITER project researching. Non-Ferrous Metals №7, 2010, p. 84-85.
[5] Nikulin A, Shikov A, Vorobieva A, Khlebova N, Malafeeva O, Pantsyny V, et al. The investigation of the effect of niobium artificial doping with titanium on Nb$_3$Sn superconductors properties. Adv. Cryog. Eng. Mater. 1996; 1337-1342.
[6] Flukiger R, Uglietti D, Senatore C, Buta F. Microstructure, composition and critical density of superconducting Nb$_3$Sn wires. Cryogenics, V.48, issues 7-8, 2008, p. 293-307.