Study of the superconducting layer microstructure and (Nb,Ti,Ta)$_3$Sn bronze strands properties

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Abstract. Superconducting materials with high current carrying capacity operating in magnetic fields up to 18 T at 4.2 K are required for promising applications in magnetic systems of high-energy physics devices, NMR-spectroscopes and others. The paper presents the study results of the Nb$_3$Sn strands manufactured by the bronze route differed in the filament composition. The filaments were made from the alloys Nb-3.5 wt. %Ta and Nb-7.0 wt.%Ta and the matrix was produced from the Cu-15.5 wt.%Sn-0.25 wt.%Ti alloy. To form the superconducting Nb$_3$Sn phase a series of reaction heat treatements of conductor samples were carried out by two-stage regimes with the temperature of the second stage varying from 650 to 720 °C. The microstructure of the Nb$_3$Sn layer was studied by scanning electron microscopy and their electro-physical characteristics were also measured. It was shown that after reaction at 575 °C, 100 h + 650 °C, 200 h samples with different Ta content had almost the same current carrying capacity in the field range 12-18 T at 4.2 K. The critical temperature of superconductors decreased from 17.5 to 16.5 K with an increase of the second stage of reaction temperature from 650 to 720 °C.

1. Introduction

Superconducting materials with high current carrying capacity in magnetic fields up to 18 T at 4.2 K are required to create magnetic systems of high-energy physics devices, such as accelerators of elementary particles or NMR spectroscopes. Nb$_3$Sn superconductors manufactured by the bronze route are widely used to operate in magnetic fields up to 12 T. Ti or Ta doping are widely used to increase current-carrying capacity of Nb$_3$Sn superconductors in higher fields, wherein the alloying element may be introduced into Cu-Sn matrix and into starting filament material.

It is shown in paper [1], that a small amount of alloying additives of transition elements significantly increases the value of the upper critical field ($B_{C2}$) of Nb$_3$Sn superconductors. Thus, the maximum value of $B_{C2}$ achieved as a result of conductor doping was 27 T at 4.2 K (with the addition of ~1.5at.%Ti or ~4at.%Ta) compared to 23.5 T for undoped one. Other studies [2-5] were aimed at determination an optimal Ti content in the conductor also doped of 7.5 wt. %Ta. The authors of [2] showed that superconductors with adding of 7.5wt.%Ta in Nb filaments and 0.25wt.%Ti in bronze matrix had a maximum critical current density (Jc) and $B_{C2}$.

It was noted that the value of $B_{C2}$ and the current carrying capacity of superconductors decreased with an increase of the Ti content up to 1wt.% in filaments or at simultaneous use of 0.75wt.%Ti both
in filaments and matrix. The critical temperature (Tc) of the samples was also reduced by increasing the Ti content in the superconductor filaments up to 2wt.% at 2.2 K, the Ta content was 7.5wt.%. Joint doping of 0.25wt.%Ti and 7.5wt.%Ta also reduced the Tc of 0.7 K compared to the only Ta doped superconductor. It was shown in [2] that the optimal regime of reaction heat treatment of conductors with joint doping of 0.25wt.%Ti and 7.5wt.%Ta was 600 °C, 100 h+670 °C, 150 h. In work [4] it was shown that at joint alloying of 1wt.%Ti+7.5wt.%Ta the value of $B_{C2}$ was lower than at doping of 0.25wt.%Ti+7.5wt.%Ta. Jc of such conductors reached a maximum during reaction at 670 °C, 100 h. The value of Tc also reached a maximum in this case. $B_{C2}$ reached 27.5 T in wire doped with 7.5wt.%Ta by reducing Ti content up to 0.18wt.% [5]. It was also found that the distribution of alloying elements varies in the width of the layer. Minimal Ti content and the maximum content of Ta were in the center of it, but at the periphery the situation was reversed: the Ta content decreased and the mass fraction of Ti increased. The authors of this work also pointed to the decrease of $T_c$ with increase of mass fraction of alloying elements and they associated it with the presence of inhomogeneity in the superconducting layer and the formation of zones with too high or insufficient content of alloying elements.

Thus, the analysis of previous works showed that the optimal content of Ti in the bronze matrix was 0.25 wt. %. However, data on the effect of Ta content in filaments on the electrophysical properties of the wire was not enough.

The aim of this work was to study the effect of different Ta content in filaments on the Nb$_3$Sn layer microstructure in wire doped of Ti and Ta simultaneously, and the dependence of the microstructure on the reaction heat treatment regime, as well as to determine the electrophysical properties of these superconductors.

2. Experimental

2.1. Strands manufacture and reaction heat treatment

Nb$_3$Sn superconductor samples of 1 mm in diameter with 68406 Nb filaments differed by the Ta content (T3 and T7) were manufactured by the bronze route. Figure 1 shows the structure of sample T3 cross section with Nb-Ta filaments uniformly distributed in the bronze matrix doped with 0.25wt.%Ti. Copper stabilization is separated from the superconducting core by Nb diffusion barrier with Ta inserts.

![Figure 1](image)

**Figure 1.** Optical micrograph of the wire cross section at ø 1mm (a) and fragment (b).

Table 1 shows the characteristics of the two experimental strands investigated.

The reaction heat treatment for the superconducting phase formation was performed under vacuum ($<10^{-5}$ Torr) by a series of two-stage treatments: $575^\circ$C/100h+(650;680;700;720)$^\circ$C/100h and $575^\circ$C/100h+650 $^\circ$C/200h.
Table 1. Nb₃Sn strands 1 mm in dia parameters.

| Type of sample | T3 | T7 |
|----------------|-----|-----|
| Bronze composition, wt. % | Cu-15.5Sn-0.25Ti | Cu-15.5Sn-0.25Ti |
| Filament composition, wt. % | Nb-3.5Ta | Nb-7.0Ta |
| Number of doubled filaments in group | 39 | 39 |
| Number of filaments | 68406 | 68406 |
| Volume fraction of Cu in strand, % | 12 | 12 |
| Volume fraction of Nb in superconducting core (calculated), % | 32 | 32 |

2.2. Investigation of the superconducting phase microstructure and critical characteristics measurements

The fractured cross sections of reacted samples T3 and T7 were observed in scanning electron microscope (SEM) for microstructure investigation of the superconducting phase. The quantitative analysis of the grain structure morphology and average grain size was carried out by the method of random secants from SEM micrographs.

For superconducting phase composition study the micro-x-ray spectral analysis was carried out on polished conductor cross sections.

The critical current (Ic) of the conductor samples was determined on the base of transport measurements (by the criterion of 0.1 µV/cm) at 4.2 K in a magnetic field of 12-18 T in SC"VNIINM" and in the High Magnetic Field Laboratory (Grenoble, France). Measurements were performed on the ITER-VAMAS type holder 32 mm in diameter.

Critical temperature (Tc) was determined by the volt - temperature characteristics (VTC) of the samples in accordance with the recommendations of the standard IEC-61788-10 using device SR-SC-05 of Sniper-Researches production. VTC were measured on samples of 60-70 mm in length which were soldered to the current and potential contacts on the substrate of the probe equipped with a temperature sensor Cernox CX-1030-SD-4B. The total temperature measurement error (taking into account the sensor error and temperature fluctuations) for the range of 20-40 K was ~30 mK.

3. Results and discussion

The microstructure of the superconducting layer of conductors T3 and T7 samples after reaction heat treatment by different regimes (Table 2) has been studied in this work. As one can see in figure 2, the Nb₃Sn layer structure of studied samples is characterized by the presence of the equiaxed and columnar grain zones and the residual Nb zone.

Table 2. Results of quantitative analysis of Nb₃Sn grain structure morphology and average grain size of conductor after different reaction heat treatment regimes.

| Regime of reaction heat treatment | T3 | T7 |
|----------------------------------|----|----|
|                                 | Fraction of equiaxed grains, % | Fraction of columnar grains, % | Average grain size, nm | Fraction of equiaxed grains, % | Fraction of columnar grains, % | Average grain size, nm |
| 575°C-100h+650°C-200h            | 44.4 | 49.5 | 84±10 | 54.5 | 40.6 | 84±10 |
| 575°C-100h+650°C-100h            | 55.0 | 36.5 | 71±8  | 55.6 | 39.1 | 75±9  |
| 575°C-100h+680°C-100h            | 59.0 | 35.9 | 96±3  | 57.3 | 36.6 | 77±4  |
| 575°C-100h+700°C-100h            | 65.4 | 33.9 | 107±7 | 75.6 | 22.9 | 93±11 |
| 575°C-100h+720°C-100h            | 72.7 | 26.2 | 111±14| 80.1 | 19.4 | 107±13|
Figure 2. Microstructure of the Nb₃Sn superconducting phase of strands samples with different Ta content in filaments (T3 and T7) after reaction by different regimes.
It was established that the residual fraction of Nb in both samples decreased after increase of the second stage temperature from 650 to 720 °C, but the fraction of equiaxed grains increased (table 2). At the same time there is a noticeable decrease of the fraction of columnar grains: in the T7 sample from 39.1 to 19.4 % and in the T3 sample from 36.5 to 26.2 %.

Herewith in the T3 strand the columnar grains fraction is higher or at the same level in comparison with T7 after reaction by all regimes (table 2). The increase of the superconducting phase average grain size of both samples was observed at the increase in the temperature of the second stage treatment. The maximum difference in grain size was found after reaction in temperature range 680-700°C. Despite the different content of Ta in the filaments a significant difference had not been found in the fractions of columnar and equiaxed grains in the studied samples.

The results of X-ray analysis of the superconducting layer composition after different heat treatment regimes are presented in table 3.

| Regime of reaction heat treatment | T3 Sn content in superconducting layer, at.% | T7 Sn content in superconducting layer, at.% |
|----------------------------------|---------------------------------------------|---------------------------------------------|
| 575 °C, 100 h + 650 °C, 100 h    | 20.2±2.8                                    | 20.3±2.1                                    |
| 575 °C, 100 h + 680 °C, 100 h    | 20.2±2.6                                    | 20.9±2.3                                    |
| 575 °C, 100 h + 700 °C, 100 h    | 22.5±1.1                                    | 21.9±2.0                                    |
| 575 °C, 100 h + 720 °C, 100 h    | 22.1±2.8                                    | 21.2±2.2                                    |

Despite the different Ta content in the filaments of T3 and T7 samples no difference in the amount of Sn in the superconducting layer was found. It was noted that the Sn content in the superconducting phase of both samples was slightly increased from 20.2-20.3 up to 21.2-22.1 at.% after increase of reaction temperature up to 720 °C.

The dependence of Jc on the magnetic field of T3 and T7 samples is shown in figure 3. As one can see, both samples of 1.0 mm in diameter had almost the same value of Jc in the field range from 12 to 18 T at 4.2 K after heat treatment at 575°C, 100 h + 650 °C, 200 h. Analysis of the results showed that the increase in Ta content from 3.5 to 7.0 wt. % had no noticeable effect on the current carrying capacity of these conductors.

![Figure 3](image3.png)

**Figure 3.** J_{nonCu} Versus magnetic field (at 4.2 K) for the T3 and T7 strands 1 mm in diameter.

The Tc dependence on the temperature of the second stage of reaction heat treatment of the studied samples is shown in figure 4.
Figure 4. $T_c$ dependence on the reaction heat treatment second stage temperature of the T3 and T7 samples.

Analysis of the results showed that the increase of the heat treatment second stage temperature from 650 to 720°C led to the decrease of the strands T3 and T7 $T_c$ value by 0.38 and 0.8 K (from 17.6 and 17.7 K to 17.2 and 16.9 K), respectively. This may be due to the heterogeneity of the alloying elements distribution in the superconducting phase. It is known [1] that a small amount of Ti additive (~1 at.% or Ta (~3 at.%) provides a slight increase of the $T_c$ value compared to pure Nb$_3$Sn. However, the increase of alloying elements amount can significantly reduce the value of $T_c$. The maximum values of $T_c$ 17.6-17.7 K were achieved on the samples after the reaction heat treatment at 575 °C, 100 h + 650 °C,100 h.

4. Conclusion
The microstructure and electrophysical characteristics of the bronze route Nb$_3$Sn strands with filaments containing 3.5 or 7.0 wt.% Ta in the matrix doped by 0.25wt.%Ti have been studied. Analysis of the superconducting layer microstructure in strands with filaments differed by Ta content showed that the increase of the second stage temperature from 650 to 720 °C led to columnar grains and residual niobium fraction decrease and equiaxed grains fracture increase. The average grain size increased from 71 to 111 nm in the strands of both types.

It was found that the value of $T_c$ of the investigated strands decreased with the increase of the heat treatment second stage temperature. At the same time $T_c$ value is reduced for the strands with 3.5 and 7.0 wt.% Ta content by 0.38 and 0.8 K, respectively, that could be connected with the greater heterogeneity of the superconducting layer composition of the conductor with a higher content of Ta.

It was shown that the current carrying capacity of these superconductors in the range of magnetic fields 12 - 18 T practically did not depend on the amount of Ta in the filaments. It was found that the increase in Ta content from 3.5 to 7 wt.% did not lead to a significant change in the microstructure of the superconducting layer and an increase of Jc in the magnetic fields of more than 12 T, which indicated the possibility of reducing content of Ta down to 3.5 wt.%.

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