Investigations of Bronze Processed Nb₃Sn Wires With Enhanced Characteristics

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Abstract. The bronze processed Nb₃Sn strands differed by specific layouts and the matrix and filament composition were investigated. Two ways of alloying were used: artificial alloyed filaments by Ti and use of alloyed bronze. By means of optical and electron microscopy the features of wire microstructure were explored. The dependences of critical current density from magnetic field and temperature have been determined. It is established that in explored alloyed wires the critical current density (Jc) is higher than 800 A/mm² (non-copper, diameter 0.82mm, 4.2K, 12T).

1. Introduction
The bronze processed Nb₃Sn superconductors with high value of critical current density are required for the creation of the large magnetic systems [1]. Particularly the necessity of the increase of the Nb₃Sn superconductors critical current density for non Cu section from 550 (initial requirement) up to 750 A/mm² (at 12T, 4.2K; 0.1μV/cm) and higher are considered for the construction of the International Thermonuclear Experimental Reactor [2].

In this connection the investigations directed on the increase of current-carrying ability without damping of the processing workability and mechanical properties are taking on special topicality and importance.

The current-carrying ability of the composite superconductors produced by bronze technology in the first place depends from such parameters as the Bronze/Nb ratio, content of tin in bronze matrix, alloying of Nb filaments or/and matrix, the peculiarity of filaments distribution and shape, the strand manufacture regime and so on.

Therefore in this work the task has been assigned to investigate the Nb₃Sn strands critical characteristics with different Bronze/Nb ratio, different Ti content in Nb filaments and also with alloyed bronze matrix with the aim of creation the optimized layout of strand with increased critical current density.

2. Experimental procedure
In this work stabilized Nb₃Sn composite strands were manufactured by bronze route, including hot extrusions of initial materials and composite billets, drawing, rolling and intermediate heat treatment.

Samples of the strands were heat treated for the formation of Nb₃Sn at 575°C (150h) + 650°C (200h) on the Ti mandrels for further current measurements and on quartz-glass mandrels for hysteresis losses measurements.
Critical current of strands was measured by the standard four-probe technique in fields from 8 to 12T at 4.2K, 0.1μV/cm. Hysteresis losses $Q_h$ were measured by the vibrating magnetometer method in alternating magnetic field $\pm$ 3T at 4.2K. Parameter "n", which characterize the steepness of V-A curve correlated in certain extent with the Nb$_3$Sn phase quality and with the uniformity of Nb filaments along the conductor, were calculated in accordance with the formulae:

$$n = \frac{1}{\lg (I_1/I_2)}$$

where $I_1$ and $I_2$ - critical currents, measured at the sensitivities of 1.0 and 0.1μV/cm respectively.

Scanning electron microscopy (SEM) by Hitachi S-2300 with EDX analyzer Oxford Instruments Link ISIS-300 and optical microscopy by Leica DM-IRM were used for analyzing the microstructure of strand specimens. The fine structure of composites was studied by transmission electron microscopy using a JEM – 200 CX instrument.

3. Results and discussion

The universal layout of strand has been developed for solution of this task. The layout was characterized that some small change in distribution or in quantity of filaments inside of one group of them let us to vary the Bronze/Nb ratio in desired range. But this does not lead to change of the filament size. The artificial doping has been used for the filaments by the introduction of the Nb-Ti alloy (NT-47) insert inside the Nb filament. In addition the strands with doped bronze matrix and non doped Nb filaments have been manufactured.

In strand layout the external copper stabilization has been separated from the superconducting core by Nb barrier with Ta inserts-separators. The Cu/non Cu ratio was equal 1.0±0.2 for all strands investigated.

Nb$_3$Sn strands with Bronze/Nb ratio equal 2.72, 2.57, 2.44 have been manufactured to get the dependence connecting Bronze/Nb ratio and critical current density. The content of Sn in bronze matrix was in the range 14-14.3wt%. The calculated size of binary filament in cross section (reduce to ellipse) in strands of 0.82mm in dia of all layouts ($d \times 1.785d$) was equal 1.79 x 3.20mk.

The analysis of dependence of a critical current density from the value of Bronze/Nb ratio has shown that the optimal values for this strand layout are in range 2.5-2.57.

The Nb$_3$Sn strands characterized of the equal and fixed value of Bronze/Nb ratio have been manufactured to reveal the dependence of critical current density from the Ti content in the Nb filaments. The rest parameters of layout were identical with strands described before. After reaction and current-carrying ability measurements the dependence of critical current density from the Ti content in filament has been obtained (Figure 1). The analysis of it has shown that under the decrease of Ti contain in filaments (up to ~1wt%) the critical current density of strand increases up to 880A/mm$^2$.

In this work the current-carrying ability under doping of bronze matrix has been studied. It was calculated that in bronze matrix has to contain about 0.25wt% of Ti in order to achieve the same level of Ti content ~ 1wt% converting to Nb filament. The bronze ingots with 14.3 - 14.5wt% Sn and 0.25wt% Ti have been manufactured by double vacuum melting. It was determined at microstructure study that particles of cupper-tin eutectoid and round particles of compound enriched by Sn and Ti are in the material. It was also established that particles of compounds Cu$_3$Ti and Ti$_5$Sn$_3$ were in bronze matrix.
Figure 1. Dependence of the critical current density (at 12T, 4.2K) vs the Ti content in Nb filaments.

On figure 2 the experimental dependencies \( J_c(T,B) \) of strands are presented.

Figure 2. Experimental dependencies \( J_c - T \) for strand with doped filaments at different values of magnetic fields.

The study of some mechanical properties of the doped bronze samples has been done to develop regimes of their deformation. The regimes of deformation and heat treatment of bronze semi products for the first composite assemble have been optimized on base of the analysis of results obtained.
In principal the further technological process did not differ from the used one before for strand with non doped matrix.

On base of results obtained the layout with Bronze/Nb ratio equal 2.45% has been selected for the production of strand with doped matrix. The rest parameters of layout were identical with above mentioned strands. The experimental batch of Nb₃Sn strand of 0.82 mm in dia with doped matrix and with unit length more than 3km that meet ITER requirements have been produced.

It was noticed under comparison of the cross section microstructures of strands with doped and non doped matrix (Figure 3) that filaments have higher size homogeneity than in strands with non doped matrix.

The study of current-carrying ability of strand of 0.82mm in dia with doped matrix has shown that the critical current density reached the value higher than 900A/mm² at 12T and 4.2K (Figure 4). In addition, as seen on the graph, the value of Jc of strands with doped matrix are higher in compare with Jc for strands with non doped matrix and doped filaments in the range of studied fields.

![Figure 3](image-url)

*Figure 3. Typical fragments of the strands obtained with non doped matrix (a), with doped matrix (b).*

In addition the study of field dependencies of critical current density of strands of different diameters (Figure 5) has shown that they have high critical current density in all range of fields and diameters investigated. The character of Jc from strand diameter dependence for fields investigated is the same: Jc increases under the diameter reduction.

The calculation of n parameter has been carried out at analysis of VAC of strand obtained. It has been determined that strands with doped matrix characterized considerably higher values of “n” (38-40) than strands with doped filaments (usually about 30). In addition, in spite of more high current-carrying ability, these strands characterized rather low level of hysteresis loss (Table 1).

|                      | With doped matrix and non doped filaments | With doped filaments and non doped matrix |
|----------------------|------------------------------------------|------------------------------------------|
| Hysteresis Loss, mJ/cm³ | 344                                      | 313                                      |
| “n”                  | 43                                       | 30.5                                     |
Figure 4. Dependence of critical current density vs magnetic field.

The study of microstructure of strand cross section by MRS-analysis and TEM methods have shown that after reaction particles containing Ti do not observed in bronze matrix. Apparently Ti practically completely goes into superconducting filament. By date of MRS-analysis Ti content in filament is about 1wt%. By TEM study filament structure the particles of Ti₆Sn phase of 2nm in size have been found out (Figure 6a).

Apparently these particles present the additional centers of flux pinning of magnet flow – it is fasten of the force lines of magnetic field and they are able to increase of critical current density such way.
In addition the study of grain structure of Nb₃Sn layer has been carried out by TEM method (Figure 6b). As seen from histogram of grains distribution by sizes the Nb₃Sn layer characterized by fine equal axis grains, their average size not more then 69nm. Under that ASD (average standard deviation) is rather narrow - less than 21, i.e. structure of layer is rather perfectly.

While the grain boundaries are the main centers of pinning it can be surely proposed that high value of critical current density in strand samples with doped bronze are stipulated by formation comparably fine and uniform structure of superconducting layer.

4. Conclusion
In the work the influence of doping and layout peculiarities of Nb₃Sn strands produced by bronze method on their current-carrying ability has been investigated. It was shown that optimal value of Bronze/Nb ratio is 2.5-2.57. Maximum value of critical current density is reached under Ti content in filaments about 1 wt%. The dependencies of critical current density from magnetic field, temperature and mechanical stress have been determined.

It was shown that in the strands investigated with non doped matrix and doped filaments of 0.82mm in diameter the critical current density exceeds 800A/mm² in field 12T at 4.2K and under application of the doped bronze and non doped filaments it exceeds 900A/mm².

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