**Influence of the introduction and formation of artificial pinning centers on the transport properties of nanostructured Nb$_3$Sn superconducting wires**

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**Abstract.** The formation of nanostructures projected to act as pinning centers is presented as a highly promising technique for the transport properties optimization of superconductors. However, due to the necessity of nanometric dimensions of these pinning centers, the heat treatment (HT) profiles must be carefully analyzed. The present work describes a methodology to optimize the HT profiles in respect to diffusion, reaction and formation of the superconducting phases. After the HT, samples were removed for microstructural characterization. Measurements of transport properties were performed to analyze the influence of the introduction of artificial pinning centers (APC) on the superconducting phase and to find the flux pinning mechanism acting in these wires. Fitting the volumetric pinning force vs. applied magnetic field ($F_p$ vs. $\mu_0H$) curves of transport properties, we could determine the type and influence of flux pinning mechanism acting in the global behavior of the samples. It was concluded that the maximum current densities were obtained when normal phases (due to the introduction of the APCs) are the most efficient pinning centers in the global behavior of the samples. The use of HT with profile 220°C/100h+575°C/50h+650°C/100h was found as the best treatment for these nanostructured superconducting wires.

1. **Introduction**

Since the discovery of the Nb$_3$Sn superconductors many efforts have been expended to improve the transport properties in these materials. One example for Nb$_3$Sn application is the ITER Project, that uses high current densities to create magnetic fields close to 12 Tesla [1-2].

In previous works [3-4] our group projected and manufactured a Nb$_3$Sn superconductor wire with APC of Cu(Sn), using the solid-liquid diffusion method. The produced wire has 1.0 mm of diameter, 1,451,610 Nb filaments, 36 elements of Sn, internal stabilization of Cu and Ta used as diffusion barrier. These wires showed significant improvement in their transport properties, in comparison to other conventional superconductors produced by the same approach [5]. On the other hand, the superconducting properties of these nanostructured wires can be improved by the optimization of the heat treatment (HT) profiles.

The optimization of the HT profiles is a stage of extreme importance due to the small dimensions of the APCs and Nb filaments. These profiles must be carefully analyzed. The temperatures and times of treatments must permit the diffusion, reaction and formation of the superconducting phases in the

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matrix with nanometric distribution of the initial material preventing, however, the extreme increase of the average grain size. On the other hand, the position of the APCs in the superconducting matrix also depends essentially on the HT profile [3]. This will lead to the optimization of the magnetic flux pinning and, consequently, to the increase of the critical current densities [6].

In this paper, the HT profiles for Nb₃Sn superconductor wires Cu(Sn) APCs in nanometric-scale, produced by RODRIGUES, 2007 [3], were analyzed in an attempt to improve the transport properties by changes in HT. Microstructural characterization and transport measurements were performed in an attempt to find the superconducting properties and the pinning mechanisms acting in the samples.

2. Experimental procedure
For the experiments in the present work, samples of RODRIGUES, 2007 [3] were used. These wires were deformed until 1.06 mm in diameter, which had, before HT, 1,064,514 Nb filaments with average diameter of 410 nm, 36 cores of Sn and internal stabilization of Cu surrounded by Ta diffusion barrier. The APCs had an average diameter of 40 nm. These dimensions were determined by electron microscopy using a Field Emission Gun SEM (FEG-SEM).

Samples were removed for the heat treatment optimization. Cu was electrodeposited on both ends of the samples to avoid leak of Sn during the heat treatments at high temperatures. After that, the samples were encapsulated in quartz tubes under an argon atmosphere of 20 mTorr. The annealing HT already started with the required temperature and finished with quenching to room temperature. The HT profiles were used following the steps showed in Table 1.

| Samples | Temperature/Time              |
|---------|------------------------------|
| 1       | 575°C/200h                   |
| 2       | 650°C/200h                   |
| 3       | 700°C/100h                   |
| 4       | 220°C/100h+650°C/50h         |
| 5       | 480°C/50h+650°C/50h          |
| 6       | 575°C/50h+650°C/50h          |
| 7       | 220°C/100h+480°C/50h+650°C/100h |
| 8       | 220°C/100h+575°C/50h+650°C/100h |

After HT, samples were removed for microstructural characterization using a JSM6330F Field Emission Gun Scanning Electron Microscope (FEG-SEM). These samples were polished and etched with nitric acid.

Superconducting characterization of the samples was performed in order to determine the existence and quality of the superconducting phases, critical temperatures \( T_c \), and critical current densities \( J_c \), consequently determining the influence of the heat treatments on the superconducting phase and on the transport properties.

The critical temperature measurements were performed using the four probe method at the Laboratory of Superconductivity of the DEMAR-EEL-USP. These measurements used the excitation current of 500 mA.

The transport properties were measured also using the four probe method in a magnet capable to generate a continuous magnetic field up to 17 T installed at the Solid State and Low Temperature Laboratory of the Department of Material Physics and Mechanics, Institute of Physics, USP, SP. The criterion of 10 \( \mu V/cm \) was used to determine the critical currents [7]. All measurements were performed at 4.2 K (liquid helium bath). The volumetric pinning force \( F_p(H,T=4.2K)=J_cB \) versus \( \mu_0H \) curves were found using the transport \( J_c \).
3. Heat Treatment Analysis

Figure 1 are micrographs using a FEG-SEM in the secondary electrons mode, comparing the microstructures of the Nb filaments formed before HT (a) and after HT at: (b) 575ºC/200h, (c) 650ºC/200h and (d) 700ºC/100h, samples 1, 2, and 3, respectively. It can be observed the coalescence of the filaments from the first bundling (127 monofilaments) in just one filament with APCs into the superconducting phase. It can be seen a large number of Cu regions used as APCs in the large Nb filament, especially for the sample heat treated at low temperature. For high temperature, the Cu APCs were smaller in number, whereas the average cross sections increased due to the increase of the temperature gradient and, consequently, faster diffusion of Sn into the Nb filaments.

![Figure 1](image.png)

Figure 1. Microstructure of the Nb filaments (a) before HT, and after HT at (b) 575ºC/200h, (c) 650ºC/200h and (d) 700ºC/100h. Scale bars with 1 µm.

4. Superconducting Analysis

Table 2 shows the measurements of critical temperature $T_c$ and the dispersion $\Delta T_c$. The values of $T_c$ were obtained as the middle of the transition, calculated between the 10% and 90% of the transition height. The half-width of the superconductor-to-normal transition defined $\Delta T_c$ [8]. All samples showed almost the same critical temperatures $T_c$ around 17 K. The values of $\Delta T_c$ give the quality of the Nb$_3$Sn superconducting phase formed after HT. These values of $T_c$ around 17 K were expected for Nb$_3$Sn wires due to the differential thermal contraction between Cu, Sn, Nb, and Nb$_3$Sn, increasing the stress on the superconducting phase and decreasing $T_c$ [6].

| Samples | $T_c$ (K) | $\Delta T_c$ (K) |
|---------|-----------|-----------------|
| 1       | 16.6      | 0.4             |
| 2       | 17.3      | 0.5             |
| 3       | 16.4      | 0.3             |
| 4       | 17.1      | 0.3             |
| 5       | 17.3      | 0.2             |
| 6       | 16.6      | 0.3             |
| 7       | 16.5      | 0.5             |
| 8       | 16.7      | 0.3             |

![Figure 2a](image.png)

Figure 2a shows the curve of critical current densities $J_c$ as a function of the applied magnetic field $\mu_0H$ for all samples after heat treatment. These transport measurements describe the global behavior of all samples. It can be observed that the sample 8 (Table 1) had the best $J_c$ behavior for high magnetic fields, while the sample 7 presented the worst result for all magnetic field analyzed.

![Figure 2b](image.png)

Figure 2b shows the curve of pinning force $F_p=J_cB$ as a function of the applied magnetic field $\mu_0H$ for all samples after heat treatment. Table 3 is a compilation of the results from the mathematical fitting of the $F_p$ curves presented in the Figure 2b. These fitting were calculate using the expression

$$F_p = K \left[ x b^{1/2} (1 - b)^2 + (1 - x) b(1 - b) \right]$$

(1)
where $K$ is a constant of proportionality, $b (= B/B_{C2})$ is the reduced magnetic field, and $x$ is the contribution of the flux pinning mechanism due to the grain boundaries. These expressions are adapted from Dew-Hughes original works [9-10], where the first term, $b^{1/2}(1-b)^2$, corresponds to the mechanism of magnetic flux pinning due to the grain boundaries expected for Nb₃Sn superconductors and the second term, $b(1-b)$, is the contribution of the normal phase (or with different superconducting properties) due to the introduction of the APCs into the superconducting phase.

Analyzing the behavior of the curves in Figure 2b and in Table 3, it can be observed that the sample 8, which showed the best values of $J_c$, had flux pinning centers only due to the normal phase. This behavior can also be seen by the values of $x$ and $b(F_{pmax})$, which showed 0% of grain boundaries contribution on the flux pinning and maximum of $F_p$ at reduced magnetic field next to 0.5, expected for pinning centers due to the normal phases. Moreover, this sample showed the highest value of upper critical magnetic field $B_{C2}$. These results can be explained in terms of the HT, where intermediate steps are required to form a homogeneous superconducting phase with APCs in the Nb₃Sn phase.

Observing the values of $x$ in Table 3 and the behavior of the curves in Figure 2, it can be supposed that the high values of $J_c$ for samples 4, 6 and 8 have distinct explanations. Sample 4 had large area of homogeneous Nb₃Sn phases, but without excessive growth of the grains. For this sample the flux pinning had contributions of 50% due to the grain boundaries and 50% due to normal phase. Due to the low value of $x$ it can be supposed that sample 6 presented an excessive increased of the average Nb₃Sn grain size. On the other hand, the introduction of the APCs acted effectively on the flux pinning. Finally, sample 8 showed flux pinning essentially due to the normal phases.

### Table 3. Results from the mathematical fitting of the experimental $F_p$ using equation (1). $F_p$ obtained from the transport properties.

| Samples | $K$ (GN/m³) | $x$ | $B_{C2}$ (T) | $B(F_{pmax})$ (T) | $F_{pmax}$ (GN/m³) | $b(F_{pmax})$ |
|---------|-------------|-----|--------------|-------------------|---------------------|---------------|
| 1       | 93.02       | 0.53| 18.42        | 5.80              | 22.50               | 0.31          |
| 2       | 81.97       | 0.20| 18.32        | 8.08              | 19.51               | 0.44          |
| 3       | 6.09        | 0.18| 17.93        | 7.89              | 15.78               | 0.35          |
| 4       | 114.09      | 0.50| 18.40        | 5.95              | 27.28               | 0.32          |
| 5       | 75.82       | 0.42| 18.67        | 6.47              | 17.93               | 0.35          |
| 6       | 95.24       | 0.17| 18.17        | 8.03              | 22.73               | 0.44          |
| 7       | 56.92       | 0.12| 17.51        | 7.99              | 13.78               | 0.45          |
| 8       | 89.03       | 0.00| 18.88        | 10.36             | 22.20               | 0.55          |

The worst behavior of $J_c$ happened for the samples heat treated with intermediate step of HT at 480ºC and with only one step of HT at 700ºC. These results can be explained by distinct processes: for
samples 5 and 7, the formation of the $\delta$-phase in the Cu-Sn diffusion layer consumes large amount of Sn atoms, changing the availability of Sn atoms and prejudicing the formation of a more homogeneous superconducting Nb$_3$Sn phase [11]; for sample 3, the excessive increase of the superconducting average grain size decreases the grain boundary densities and pinning. The excessive increase of the APCs cross section, like those in Figure 1, decreases the flux pinning due to the difficult for the Cooper pairs to surpass the potential barrier of the normal phases [6].

It could be seen that the HT at 575°C/200h (sample 1) already had enough condition to promote the formation of the superconducting phases capable of transporting high current densities, with high upper critical magnetic field values.

5. Conclusion
During this work it could be observed that conventional heat treatments (HT) [12-13] could not be applied for the nanostructured superconducting wires and news profiles of HTs were required.

All samples showed almost the same critical temperatures next to 17 K, values obtained from transport measurement of the superconducting transition.

It could be seen that the HT at 575°C already showed the formation of the superconducting phase capable of transporting high current densities and with high upper critical magnetic field values. On the other hand, samples heat treated with intermediate step at 480°C or with only 700°C one-step treatment showed the worst results for $J_c$, $F_p$ and $B_{c2}$. These results can be explained by the extreme increase of the average grain size, showed by the microstructures. The sample treated at 220°C/100h+575°C/50h+650°C/100h showed the best results, due to the major contribution of the normal phases in the superconducting phase and, consequently, in the flux pinning.

Furthermore, the 650°C/200h showed to be a good option to heat treat the samples without intermediate steps of diffusion, if a faster HT profile is needed for some application.

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References
[1] Chaowu Z, Sulpice A, Lian Z, Soubeyroux J L, Verwaerde C and Hoang G K 2007 IEEE Trans. Appl. Super. 17 7-12.
[2] Zhang P X, Zhou L, Tang X D, Li C G, Wu Y, Li K, Yan G, Yang M, Feng Y, Liu X H, Weng P D and Lu Y F 2006 Physica C 445-448 819-822.
[3] Rodrigues C A and Rodrigues Jr D 2007 IEEE Trans. Appl. Superc. 17 2627-2630.
[4] Rodrigues C A and Rodrigues Jr D 2006 Journal of Physics: Conference Series 43 43-46.
[5] Rodrigues Jr D, Rodrigues C A, Silveira E B and Romão E G M 2005 IEEE Trans. Appl. Superc. 15 3389-3392.
[6] Suenaga M 1981 In: Schwartz B B and Foner S Eds. Superconductor material science-Metallurgy, fabrication and applications. (New York: Plenum Press) chapter 4 p. 201.
[7] Rodrigues C A and Rodrigues Jr D 2004 Physica C 408-410 921-922.
[8] Murase S, Itoh K, Wada H, Noto K, Kimura Y, Tanaka Y and Osamura K 2001 Physica C 357-360 1197-1200.
[9] Dew-Hughes D 1974 Phil. Mag. B 30 293.
[10] Dew-Hughes D 1987 Phil. Mag. B 55 459.
[11] Yamasaki H and Kimura Y 1982 Cryogenics 22 89-93.
[12] Müller M, Schulz H and Kirchmayr H 2005 Physica C 419 115-120.
[13] Müller H and Schneider Th 2004 Physica C 401 325-329.