Física:

Produção de conhecimento relevante e qualificado 3

Glécilla Colombelli de Souza Nunes
(Organizadora)

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Atena Editora
Ponta Grossa – Paraná – Brasil
Telefone: +55 (42) 3323-5493
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CIÊNCIAS EXATAS E DA TERRA E ENGENHARIAS

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APRESENTAÇÃO

A coleção “Produção de conhecimento relevante e qualificado 4” é uma obra composta por cinco capítulos que possuem como foco principal as Ciências Naturais. Os trabalhos aqui reunidos foram realizados em diferentes instituições de ensino do país e tem como linha central o desenvolvimento de novos materiais, técnicas e instrumentos, em especial, nas áreas de Biofísica, Física e Química.

Essa coleção aborda temas atuais e de interesse da comunidade científica que vão desde a aplicação de sistemas magnéticos à medicina até o impacto da COVID-19 no ensino de Física nas escolas públicas de nosso país. Sendo este último, um tema que contribuirá para que os docentes reflitam e pensem em estratégias (e metodologias) de como suprir os déficits de aprendizagem deixados pela pandemia da COVID-19.

Além disso, esta obra traz uma revisão sobre os avanços que a comunidade científica já conseguiu na produção de supercondutores $Nb3Sn_{(s)}$ e um estudo de caso sobre o comportamento das componentes da radiação solar em um município do Rio Grande do Norte, no qual pesquisou a viabilidade de projetos que envolvem a geração de energia solar na região.

Deste modo, a obra - “Produção de conhecimento relevante e qualificado 4” - apresenta artigos interdisciplinares e que são bem fundamentados nos resultados práticos obtidos. Além do que, as discussões e os dados dos trabalhos desta coleção estão muito bem organizados e os autores conseguiram apresentar seus trabalhos de forma clara e didática.

Por fim, sabe-se o quão importante é a divulgação científica e, por isso, evidenciamos também a estrutura da Atena Editora capaz de oferecer uma plataforma consolidada e confiável para estes pesquisadores exporem e divulgarem seus trabalhos científicos.

Glécilla Colombelli de Souza Nunes

SUMÁRIO

CAPÍTULO 3

CHEMICAL INFLUENCES AND CHALLENGES ASSOCIATED WITH ENHANCED Nb3Sn SUPERCONDUCTOR DEVELOPMENT

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Erick Agnolin
Instituto de Química, Universidade de Passo Fundo
Passo Fundo – RS, Brazil

Ana P. H. Vaniel
Instituto de Química, Universidade de Passo Fundo
Passo Fundo – RS, Brazil

ABSTRACT: $Nb_3Sn_{(s)}$ composites are the go-to superconductors for high magnetic field applications, however, the material is associated with immense difficulty around its manufacturing processes. Different approaches have been taken over the years in order to overcome engineering difficulties regarding superconducting wire production, with two methods being able to successfully provide strands with satisfactory properties, the so- called "Powder-In-Tube" and "Internal-Tin" processes, which utilize optimized heat treatments and stoichiometric composition, since chemical influences can shift the balance between superconducting properties such as critical current density (*Jc*), critical temperature (*Tc*) and upper critical field limit (H_{c2}), all of which act as functions of atomic Tin content (at.% Sn(s)). Since Nb3Sn(s) displays type II superconductor behavior, efforts that lead to increasements in *Jc* values are essential, distinctively by artificial pinning centers (APCs) addition by means of ternary insertions in order to promote greater density of flux pinning centers as deduced from current scientific consensus, however, further research is necessary to determine specific mechanics around pinning centers and grain boundary sizes.

KEYWORDS: Nb3Sn(s), stoichiometry, superconducting properties, artificial pinning centers.

INTRODUCTION

Although the last decades have witnessed the almost homogeneous domination of $NbTi_{(s)}$ superconducting alloys for industrial uses due to better ductility, it was always known that at a certain point in time there would be a need for a material with better superconducting properties, such as a higher upper magnetic critical field limit (H_{c2}) and capacity to withstand bigger electrical currents.

The intermetallic Niobium-Tin alloy, or $Nb_3Sn_{(s)}$, is a $Nb_{(s)}$ based superconductor with an A15 phase in a body-centered cubic lattice, or *bcc* lattice, of $Sn_{(s)}$ atoms with three orthogonal chains of $Nb_{(s)}$ atoms in parallel to the edges of the unit cell that bisect the *bcc* cube faces. [1] It has a critical temperature (T_c) of around 9.2 – 18.3 K (18 – 25 at.% $Sn_{(s)}$), and has regained interest from the scientific community during the past years over the consensus concerning the inevitable exhaustion of the NbTi(s) alloy's intrinsic limits of performance.[2]

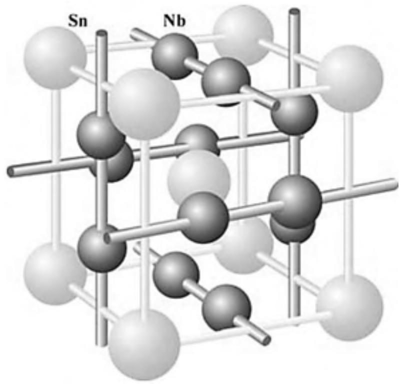

Figure 1. Illustration of the $Nb3Sn_{(s)}$ A15 unit cell, with the $Sn_{(s)}$ atoms forming a bcc lattice and the orthogonal $Nb_{(s)}$ atomic chains on the bcc faces (adapted from reference 8).

The first registered observations of superconductive behavior in $Nb_3Sn_{(s)}$ were reported by Matthias *et al*. in 1954,[3] only one year after the discovery of the first registered A15 phase superconductor, $V_3Si_{(s)}$, by Hardy and Hum, in 1953.[4] The highest reported *T*c for $Nb_3Sn_{(s)}$ was 18.3 K by Hanak *et al*. in 1964,[2] but ever since its discovery, Niobium-Tin alloys have amassed great interest due to the capability to carry very large current densities, at least when compared against the industrially used $NbTi_{(s)}$ alloys, however, the production of $Nb\text{-}Sn_{(s)}$ wires is considerably challenging as consequence of the brittleness of the material, meaning that high strain may thoroughly compromise superconductivity on the sample, and the requirement for high-temperature processing in order to achieve the desired superconducting A15 $Nb_3Sn_{(s)}$ phase.

Although a great extent of current day superconductive material is $NbTi_{(s)}$-based, applications that require high-field electromagnets employ Nb3Sn(s) in their composition (*e.g.,* particle accelerators,[27] tokamak devices and solenoid coils, magnetic resonance imaging [MRI], nuclear magnetic resonance [NMR], as well as non-magnetic applications such as superconducting radio frequency (SRF) cavities[5]), and further enhancement in intrinsic properties such as J_c, better T_c and H_{c2} values are needed for future specific applications, such as the ITER project[6,7]], which keeps $Nb_3Sn_{(s)}$ research an extremely relevant and vital topic for future applications.

Different stoichiometric adjustments regarding the atomic $Sn_{(s)}$ content (β) result in changes for both T_c and H_{c2}, which resulted in extensive research on the correlation between the at.% $Sn_{(s)}$ content and alterations caused in the values for both critical temperature and upper critical field limit,[8] and it is reported that both variables act as functions of stoichiometry, furthermore, since these the critical current density (J_c) is largely dependent of the H_{c2} value, it is also heavily dependent of stoichiometry.[9]

REVIEW ON THE CURRENT STATE OF $Nb_3Sn_{(s)}$ SUPERCONDUCTORS

Despite the fact that $Nb_3Sn_{(s)}$ superconductors display better intrinsic properties when compared to $Nb\text{-}Ti_{(s)}$ alloys, the latter was responsible for overwhelmingly larger practical applications mainly because of the better (and easier to work with) physical properties, resulting in a much easier manufacturing process for electromagnetic wires and coils.

In the present day, two methods of manufacturing are still currently being used in the industry for the creation of $Nb_3Sn_{(s)}$ wires with satisfactory J_c values (for high energy physics uses as well as for sectors with the need for high-fields), they are so called the "Powder-In-Tube" (PIT) and "Internal-Tin" (IT)[22] methods.

Although great progress was reached during the last couple of decades on the matter of $Nb_3Sn_{(s)}$ wires assembly, there is still need for research on the development of wires for high-field applications, such as the Future Circular Collider (FCC)[22,23,27], with specifications for the requirements of higher J_c, as well as the relentless need for a reduction of the manufacturing process cost.

POWDER-IN-TUBE PROCESS

Recent PIT processes consist on the usage of thick Niobium tubes filled with $NbSn_{2(s)}$ powder in a Copper matrix, and the final wire is then extruded from the initial composite.[21,26]

The superconducting wires achieved via PIT process display both good filament sizes, ≤ 50 μm, and high J_c values, however, its production cost is considerably higher than the alternative (IT) method. An illustration of the final PIT composite wire is shown in Figure 2.

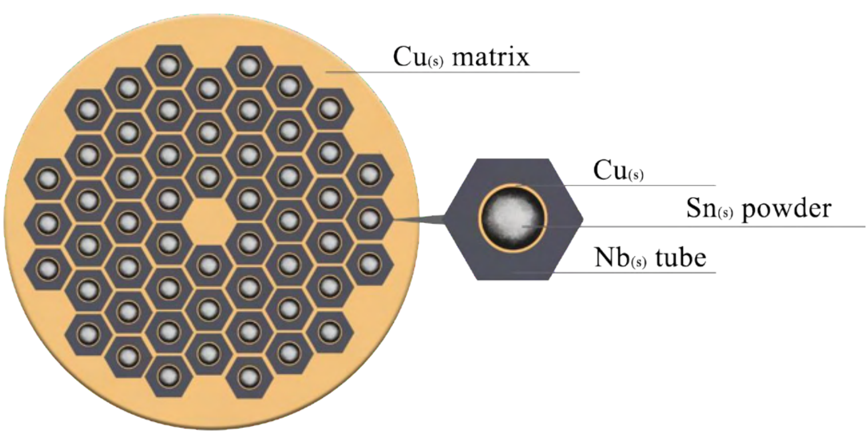

Figure 2. Illustration of a PIT wire, with an $Sn_{(s)}$-rich powder in the $Nb_{(s)}$ tube. The $Cu_{(s)}$ boundary, or barrier, may be adapted according to alternative manufacturing methods.

The A15 $Nb_3Sn_{(s)}$ phase is reached via a solid-state diffusion reaction after several days at a temperature around 675 ºC, in which the $NbSn_{2(s)}$ powder in the $Cu_{(s)}$ matrix is initially converted into $Nb_6Sn_{5(s)}$ and only then into $Nb_3Sn_{(s)}$, with the reaction ceasing after roughly 64 h at ~675 ºC as result of $[Sn_{(s)}]$ exhaustion.[8,22]

INTERNAL-TIN PROCESS (ROD RESTACK PROCESS)

Although IT (RRP) processes may differ widely from each other, the main concept is based upon the assembly of large quantities of $Nb_{(s)}$ filaments and refined $Sn_{(s)}$ (or alloys) rods in a pure $Cu_{(s)}$ matrix enclosed by a boundary, or barrier, made of Niobium in order to prevent Tin diffusion into the matrix, in which the wire is then cold-drawn into the final shape.[26]

An illustration of the final IT composite wire is shown in Figure 3.

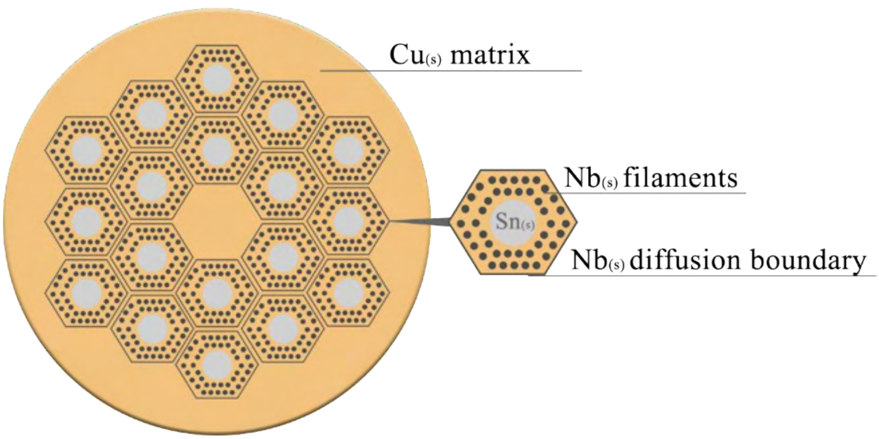

Figure 3. Illustration of an IT (RRP) wire with distributed $Nb_{(s)}$ boundaries, or barriers. An alternative configuration includes a single $Nb_{(s)}$ (or $Nb_{(s)}$ alloy) boundary surrounding the total filament structure perimeter.

Throughout the process, during the heat treatment step, there is a surge of Cu-$Sn_{(sll)}$ phases which are created and annihilated during the solid-state diffusion process and the $Nb_3Sn_{(s)}$ formation, which results in potential hindrance or damage to the wire. The unwanted Cu-$Sn_{(sll)}$ phases issue is solved by applying the heat treatment in different intensities, firstly at just below 227 ºC to create a layer of Cu-$Sn_{(s)}$ with a higher fusion temperature, which works as a container for the fused $Sn_{(l)}$ at >227 ºC, followed by a steady application of ~210 ºC (24-72 h) and ~400 ºC (24-48 h) with the intention of providing enough Tin diffusion into each filament (and to avoid leakage into the Cu(s) matrix). The A15 $Nb_3Sn_{(s)}$ phase is obtained during the third and final step of the heat treatment which varies between ~620 ºC and ~750 ºC, also responsible for the formation of the current optimal material microstructure. It is possible to apply higher temperatures for the reduction of the time required for the process completion, however, higher temperatures usually yield greater grain sizes, which influences the desired superconducting properties of the material as well as possible $Sn_{(s)}$ contamination in the matrix which then results in increased electrical and thermal resistivity.[22,26]

STOICHIOMETRY INFLUENCES ON THE ELECTRON-PHONON INTERACTION

$Nb_3Sn_{(s)}$ can be generally described as a strong coupling superconductor, therefore, the approximation provided by the Bardeen-Cooper-Schrieffer (BCS)[10] theory for the weak coupling energy gap at zero temperature (Δ_0) cannot be valid for Niobium- Tin superconductors.[8,10]

$$\Delta_0 = 2\hbar\omega_c e^{[-\frac{1}{\lambda_{ep}}]} \quad (1)$$

$$T_c(0) \cong \frac{2e^{\gamma E}}{\pi k_B} \hbar\omega_c e^{[-\frac{1}{\lambda_{ep}}]} \quad (1.1)$$

This equation (1) is valid for values that match $\lambda_{ep} << 1$ at Δ_0. With λ_{ep} being a parameter without dimensions for the electron-phonon interaction[8] and $\hbar\omega_c$ as a parameter of energy from the Fermi level (E_F), and outside of which the interactive potential for the electron coupling is equal to zero.[11,18]

With the restriction that the temperature dependency of $\Delta(T) = 0$ at $T \rightarrow T_c$, equation (1) becomes equation (1.1), with γE being the Euler's constant with a value of ≅ 0.577, and k_B being the Boltzmann constant.

The ratio between (1) and (1.1) gives the limit for the BCS theory's weak coupling limit:

$$\frac{2\Delta_0}{k_B T_c} = 3.528 \quad (2)$$

Regarding weak coupling for Niobium-Tin, (1) and (1.1) are no longer valid since they become sensitive to details of the electron-phonon interaction, henceforth, the ratio yields a higher result above the limit for weak coupling interaction ($\lambda_{ep} << 1$) at zero temperature described by $2\Delta_0/k_B T_c$.[8,10,11]

To analyze the superconducting gap and *Tc* in Niobium-Tin films as a function of Sn(s) content, as well as for the ratio between $2\Delta_0/k_B T_c$, Moore *et al.*[12] performed tunneling experiments with the use of a Boltzmann function with a corresponding sigmoidal distribution:

$$y(\beta) = \frac{y_{min} - y_{max}}{1 - e^{(\frac{\beta - \beta_0}{d\beta})}} + y_{max} \quad (3)$$

Where y = T_c or Δ, and β = at.% $Sn_{(s)}$. Results expressed weak coupling for ~20- 24 at.% Sn(s) and strong coupling for ≥24 at.% $Sn_{(s)}$, with Tc and Δ(β) precisely expressed by (3). Results for β ≤ ~24 at.% $Sn_{(s)}$ mean that the electron coupling relation is weakened due to decrease in phonon frequency as a result of softening in the lattice. [8,12,19]

STOICHIOMETRY INFLUENCES ON THE CRITICAL TEMPERATURE AND UPPER CRITICAL FIELD LIMIT

Due to gradients related to composition, T_c and H_{c2} values can fluctuate as a function of atomic Tin content. A few datasets of A15 composition ranges are available in the literature, with the most comprehensive analysis being from Devantey *et al.*[13] which contains values that are expected for the A15 phase.

$$T_c(\beta) = \frac{-12.3}{1 + e^{\left(\frac{\beta - 0.22}{0.009}\right)}} + 18.3 \qquad (4)$$

Utilizing a Boltzmann sigmoidal function similar to (3), with the maximum reported value for Niobium-Tin's T_c of 18.3 K,[2] it was found a correlation for the data provided by Devantey for increasement in T_c as function of atomic Tin content, with the minimum correlation value displayed at ~0.22 K for ~18 at.% $Sn_{(s)}$ and the maximum of 18.3 K for ~24-25 at.% $Sn_{(s)}$.

$$\mu_0 H_{c2}(\beta) = -10^{-30}\, e^{\left(\frac{\beta}{0.00348}\right)} + 577\beta - 107 \qquad (5)$$

Equation (5) represents the function utilized in a display of collected data for H_{c2} variations which demonstrated a linear trend with the $\mu_0 H_{c2}(\beta)$ function, with the maximum H_{c2} value at ~31 T for ~24.5 at.% $Sn_{(s)}$. Equations (3), (4) and (5) demonstrate the variations for values associated with T_c and H_{c2}, as a function of stoichiometry, more specifically, the atomic content of Tin in the samples, therefore, prospects for improvements in these parameters may appear to lie in better stoichiometry adjustments, however, small changes in concentrations may result in unwanted changes in other parameters, with possible decreases in the respective superconductivity properties.[8,13,14,15]

GRAIN BOUNDARIES, PINNING CAPACITY AND J_C

The ($Cu_{(s)}$) matrix is not taken into account when quantization for the critical current density is described by the total ($Nb_3Sn_{(s)}$) filament area. The layer J_c is given by the $Nb_3Sn_{(s)}$ area responsible for the current carriage.[21]

Considering that A15 Nb-$Sn_{(s)}$ shows behavior analogue to type II superconductors (partial penetration of field lines between H_{c1} and H_{c2} at T_c), the main contributing factor for the A15 Nb-$Sn_{(s)}$ capacity to carry current relies on the bulk pinning force (FP), which can be determined by its balance with the Lorentz force: FP = $J_c \times \mathbf{B}$, where **B** (in a dipole cos θ magnet) is the magnetic field generated by the coil: **B** a $W \cdot J_{coil}$. The electronic current density in the coil (J_{coil}) is determined in the material based on its J_c, and W is the coil width. The maximum bulk pinning force, FP, max, is associated with the density of flux pinning centers, which are deduced to be primarily related to grain boundaries in the material.[9,19]

With the assumption that the physical properties are standardized, J_c in Nb3Sn(s) can be mainly described by the current-carrying fractions, H_{c2} and $F_{P,\ max}$, or, in case of property gradient, the maximum J_c of a $Nb_3Sn_{(s)}$ wire is determined by the limits of the weakest part in the composition.[9] These parameters ($Nb_3Sn_{(s)}$ fractions, H_{c2} and $F_{P,\ max}$) are all dependent of the internal structure and chemistry of the materials, with the behavior for H_{c2} being largely dependent on stoichiometry and composition while $F_{P,\ max}$ is greatly related to the flux pinning centers quantized by volume which are, consecutively, dependent of the grain boundary sizes and flux pinning centers in $Nb_3Sn_{(s)}$.

Although specific mechanisms describing the maximum bulk pinning strength in the grain boundaries are not fully comprehended, the maximum bulk pinning force ($F_{P,\ max}$) in addition with temperature phase boundaries and strain effects can determine optimal *J*c values for $Nb_3Sn_{(s)}$ composite wires.[8,9,17]

ARTIFICIAL PINNING CENTERS

Improvements of current density values for superconducting $Nb_3Sn_{(s)}$ composite wires seem to rely on the increasement of bulk pinning force through addition of artificial pinning centers (APCs) in these materials. Improved values for J_c in $Nb_3Sn_{(s)}$ composite wires are obtained by the introduction of APCs based on different ternary materials (*e.g.*, $Cu_{(s)}$) in nanometric scale with matching spacing between flux line lattice.[20,22]

The introduction of different materials for performance enhancing values of J_c is not exclusive to $Nb_3Sn_{(s)}$ superconductors. Da Silva et al.[16] performed measurements with different material additions as artificial pinning centers for $MgB_{2(s)}$ superconductors, such as $VB_{2(s)}$, $SiC_{(s)}$ and carbon doping and reported improvements for the critical current density value in high-field, with more intense flux lines penetration, with the best superconducting performance being attributed to a $MgB_{2(s)}$ sample accompanied by a concurrent addition of 10 wt.% $SiC_{(s)}$ and 2 at.% $VB_{2(s)}$. However, such additions that improve J_c values most likely also result in an unwanted reduction, or alteration, of other superconducting properties (*e.g.,* T_c and H_{c2}) as a result of proximity effects with non- superconducting materials.[16,23,24,25]

CONCLUSIONS AND PERSPECTIVES

With regards to the $Nb\text{-}Sn_{(s)}$ A15 phase, T_c, H_{c2} and J_c, as well as electron-phonon interaction, each can be described as at.% $Sn_{(s)}$ dependent. Cooper pair coupling for microscopic activity in the $Nb_3Sn_{(s)}$ lattice can no longer be defined by the BCS theory weak coupling characterization for atomic Tin content above 23%, which translates to the requirement of certain corrections apropos of strong coupling display.

The superconducting property values for T_c and H_{c2}, much like the electron- phonon interaction, behave as function of atomic Tin content in the sample, with several datasets available in the literature displaying closely related observed results regarding [$Sn_{(s)}$] gradient in $Nb_3Sn_{(s)}$ composition.

Despite the significant accomplishments during the last years with respects to $Nb_3Sn_{(s)}$ superconductor production, notably the development of the Powder-In-Tube and Internal Tin processes, however, since heat treatments and stoichiometry adjustments are nearly achieving maximum practical potential, prospects for further improvements in J_c therefore rely on better comprehension and engineering around artificial pinning centers and reduced grain sizes through addition of artificial pinning centers based on ternary insertions in the composite with the purpose of increasing the density of flux pinning centers.

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