Analysis of Bulk and Thin Film Model Samples Intended for Investigating the Strain Sensitivity of Niobium-Tin

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***Abstract*—Bulk samples and thin films were fabricated and characterized to determine their suitability for studying the effect of composition and morphology on strain sensitivity. Heat capacity and resistivity data are used to determine the critical temperature distribution. It is found that all bulk samples contain stoichiometric Nb_3Sn regardless of their nominal Nb to Sn ratio. Furthermore, in bulk samples with Cu additions, a bi-modal distribution of stoichiometric and off-stoichiometric Nb-Sn is found. Thus the nominally off-stoichiometric bulk samples require additional homogenization steps to yield homogeneous off-stoichiometric samples. A binary magnetron-sputtered thin film has the intended off-stoichiometric Nb-Sn phase with a mid-point critical temperature of 16.3 K. This type of sample is a suitable candidate for investigating the strain sensitivity of A15 $Nb_{1-\beta}Sn_\beta$, with $0.18 < \beta < 0.25$. The strain sensitivity of Nb-Sn as a function of composition and morphology is important for an in-depth understanding of the strain sensitivity of composite Nb_3Sn wires.**

***Index Terms*—Bulk, composition, heat capacity, Nb_3Sn, strain sensitivity, superconductor, thin film.**

I. Introduction

AFTER its discovery in 1954 [1], the superconductor Nb_3Sn has sparked considerable scientific interest because of its ability to carry large currents at magnetic fields H and temperatures T where Nb-Ti is no longer superconducting [2]. Continuous development has resulted in wires that carry 2500–3000 A/mm^2 at 12 T and 4.2 K in the non-Cu fraction [3], [4].

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Unlike Nb-Ti, however, the critical properties of Nb_3Sn are highly sensitive to the strain-state of the material [5]. Furthermore, the origin of the strain sensitivity is still poorly understood and the effect of composition and morphology on the strain sensitivity of Nb_3Sn is unknown.

The strain dependence of the critical current of Nb_3Sn wires with their inherent inhomogeneity in composition and morphology has been investigated thoroughly, and accurate scaling models are readily available [5]–[8]. These models suggest that strain sensitivity mainly originates from a strain-induced shift of the effective magnetic field-temperature phase boundary [5]. Probing the strain-induced change in the critical temperature T_c and the critical magnetic field $\mu_0 H_{c2}$ therefore allows for parameterization of the overall strain-related behavior of the material.

To investigate the effect of composition and morphology on the strain sensitivity, homogeneous and well defined model samples are required that include both stoichiometric and off-stoichiometric A15 $Nb_{1-\beta}Sn_\beta$, where stoichiometry means $\beta = 0.25$ and off-stoichiometry means $0.18 \leq \beta < 0.25$. The unavoidable inhomogeneity in composition, morphology and strain state of Nb_3Sn wires [9] makes them unsuitable for this type of research. Bulk and thin film samples were fabricated as possible candidates and the T_c distribution of a selection of samples is presented as investigated through resistivity ρ and heat capacity C measurements.

II. Experiment and Data Reduction

A. Sample Manufacture

Bulk samples were fabricated with a hot isostatic pressure (HIP) process, which involves heat-treating a mixture of powders at 1100 °C under a pressure of 100 MPa [10]. In this way, dense bulk samples are produced with varying nominal Nb to Sn ratios. Some samples are binary, while others contain Cu, Ti and Ta additions. Needles were cut from the bulk samples with electrical discharge machining.

Thin films were magnetron-sputtered. The method is based on previous research [11], [12] that resulted in a T_c distribution range of 0.3 K to 1.5 K for nominally stoichiometric films and a T_c distribution range of 2 K to 6 K for nominally off-stoichiometric films, measured using heat capacity. Nb and Sn are co-sputtered onto a heated A-plane sapphire substrate. Insufficient thermal conduction between heater and substrate resulted in a substrate temperature between 600 and 700 °C.

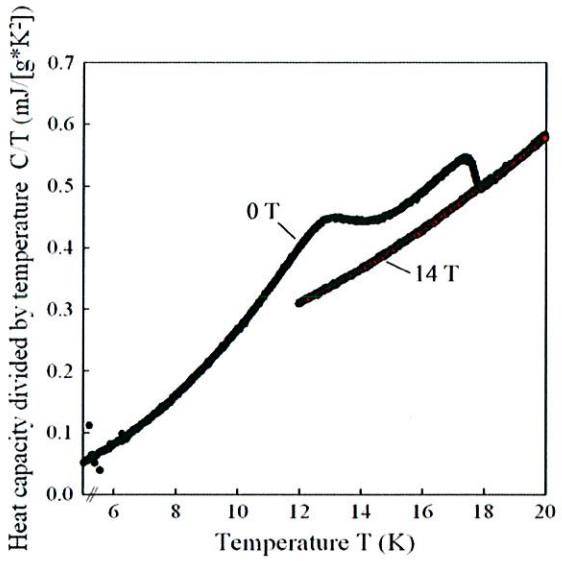

Fig. 1. Heat capacity divided by temperature versus temperature at magnetic fields of 0 and 14 T, of a (76 at% Nb + 24 at% Sn) + 5 wt% Cu bulk sample.

At this deposition temperature, the T_c distribution width is expected be 1 K in case of a nominally stoichiometric film and 4 to 6 K in case of a nominally off-stoichiometric film [11], [12].

The deposited film has a thickness of ~250 nm. The positioning of the Nb and Sn targets during the deposition results in an 18 to 25 at% Sn composition gradient across the 25 mm wide substrate. The substrate was cut into strips of 2 mm width, so that multiple samples with different nominal composition are fabricated in one deposition run.

B. Heat Capacity Measurements

Heat capacity measurements were performed with a Quantum Design Model 6000 Physical Property Measurement System. Grease thermally connects the samples to the sample holder. The heat capacity of the holder itself is pre-determined and corrected for. Heat capacity versus temperature data were collected at 0 and 14 T, which allows for a comparison between the superconducting and normal states (see Fig. 1).

As the critical temperature of stoichiometric Nb_3Sn can be as high as 11.5 K at $B = 14$ T, the normal-state heat capacity is only measured down to $T = 12$ K. The normal-state heat capacity at lower T is estimated through the extrapolation

$$\frac{C_{fit}}{T} = \gamma + \alpha_3 T^2 + \alpha_5 T^4, \tag{1}$$

where C_{fit} is the fitted heat capacity, α_3 and α_5 are fit parameters, and γ is the electronic specific heat coefficient.

Using the derivation as reported in [13], the T_c distribution of the sample is related to the heat capacity through

$$f(T_c) = \left(\frac{1}{(n-1)\cdot\gamma\cdot T}\right) \cdot \left(\frac{n\cdot(C_{0T} - C_{fit})}{T} - \frac{d(C_{0T} - C_{fit})}{dT}\right), \tag{2}$$

where $n = 3$ follows from the two-fluid Gorter-Casimer model [14]. $f(T_c)$ indicates the sample fraction with critical temperature T_c and C_{0T} is the heat capacity at $B = 0$ T.

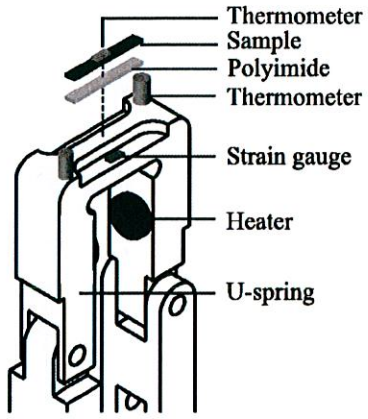

Fig. 2. "U-spring" sample holder with sample and instrumentation.

C. Resistivity Measurements

Resistivity measurements as function of temperature were performed using two different methods. In one method, samples are thermally connected to a copper block in vacuum [15]. In the other method, samples are glued to a U-spring sample holder [5] and electrically insulated with polyimide foil (Fig. 2). The second method is of particular interest, as it allows measuring resistance as function of temperature, magnetic field and longitudinal strain.

To validate both methods, $\rho(T)$ resistivity measurements on needles cut from the same bulk sample are compared to magnetization as a function of temperature $M(T)$ measurement performed in a commercial vibrating sample magnetometer (VSM). The onset temperature as determined from the three methods is found to be consistent with an uncertainty of 50 mK.

Both $\rho(T)$ methods use a bipolar four-probe technique. In the current range of 10^{-6} to 10^{-4} A, ρ is current-independent so that a standard measuring current of 10^{-4} A was selected.

As in a parallel resistor network, a single superconducting path percolating through a sample is sufficient for the overall sample resistivity to be zero: Once a certain sample fraction with the highest critical temperatures is superconducting, the resistivity no longer changes with temperature.

An analytical model is developed, which assumes that the electrical behavior of the sample is dominated by a single, effective, percolating path. In this path, the various compositions with varying T_c are connected in series, so that the current density through all of them is the same. The change in sample resistivity as a function of temperature is thus proportional to the volume, and the normal-state resistivity of Nb-Sn that transitions from normal to superconducting state at that temperature.

Using the resistivity data (see Fig. 3), the T_c distribution and composition distribution of the sample can then be derived from

$$f(T_c) = \frac{d\rho}{dT}\cdot\frac{1}{\rho_n(T_c)}, \tag{3}$$

where $\rho_n(T_c)$ is the normal state resistivity as found in literature [2]. It is unknown how the normal state resistivity of Nb-Sn is affected by Cu and Ta additions, which is a possible source of error for this model.

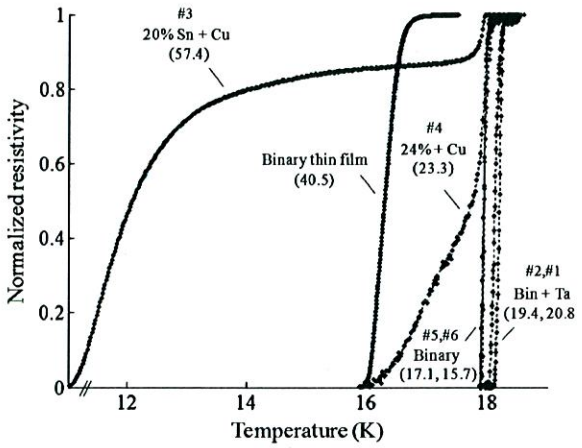

Fig. 3. Normalized resistivity as a function of temperature at 0 T and no externally applied longitudinal strain. The bulk sample compositions are: #1. 75.7 at% Nb + 20 at% Sn + 4.3 at% Ta ($\rho_n = 20.8\ \mu\Omega$cm), #2. 72 at% Nb + 24 at% Sn + 4.0 at% Ta ($\rho_n = 19.4\ \mu\Omega$cm), #3. (80 at% Nb + 20 at% Sn) + 5 wt% Cu ($\rho_n = 57.4\ \mu\Omega$cm), #4. (76 at% Nb + 24 at% Sn) + 5 wt% Cu ($\rho_n = 23.3\ \mu\Omega$cm), #5. 78 at% Nb + 22 at% Sn binary ($\rho_n = 17.1\ \mu\Omega$cm), #6. 76 at% Nb + 24 at% Sn binary ($\rho_n = 15.7\ \mu\Omega$cm). The normal state resistivity of the thin film is 40.5 $\mu\Omega$cm.

The T_c distribution can be converted to a composition distribution $f(\beta)$ through

$$f(\beta) = f(T_c) \cdot \frac{dT_c(\beta)}{d\beta}, \tag{4}$$

where $f(\beta)$ is the composition distribution. $T_c(\beta)$ is given in the literature [2].

To validate this rather simple analytical description, the concept of percolation is explored in more detail using a three-dimensional percolative model. This model is a FEM simulation of a bulk sample that consists of cubes. Each cube is assigned a unique composition with related critical temperature and normal state resistivity. The electric potential of each cube is related to that of its six nearest neighbors, using Kirchhoff's point law. The resistivity of simulated bulk samples containing up to 10^6 cubes can be calculated using finite element analysis.

The three-dimensional percolation model is physically more correct but also significantly more complicated. It is found that the outcome of the two models is qualitatively the same, although quantitatively the analytical model overvalues the lowest observable tin concentration, on the order of 40%.

As a qualitative analysis is sufficient, the analytical expression is used to derive the T_c distribution of the samples.

III. Results

A. T_c Distribution From Heat Capacity

Using (2), the T_c distribution of the various bulk samples is derived from the heat capacity data (see Fig. 4). Each of the samples contains a stoichiometric phase, with a T_c around 18 K, regardless of the nominal Nb to Sn ratio of the sample.

Of particular interest is the comparison between a 76 at% Nb + 24 at% Sn and a (76 at% Nb + 24 at% Sn) + 5 wt% Cu sample. In the presence of Cu the T_c distribution is bi-modal with both a stoichiometric and an off-stoichiometric phase, as follows from the well-established dependence of T_c on composition [2].

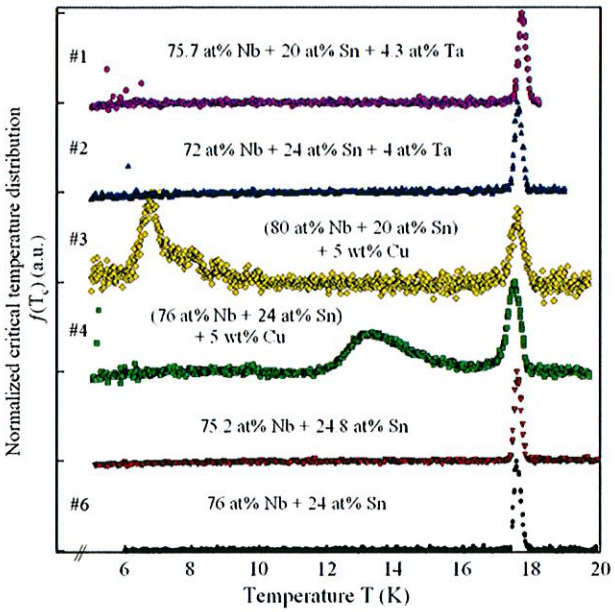

Fig. 4. T_c distributions as determined from heat capacity analysis.

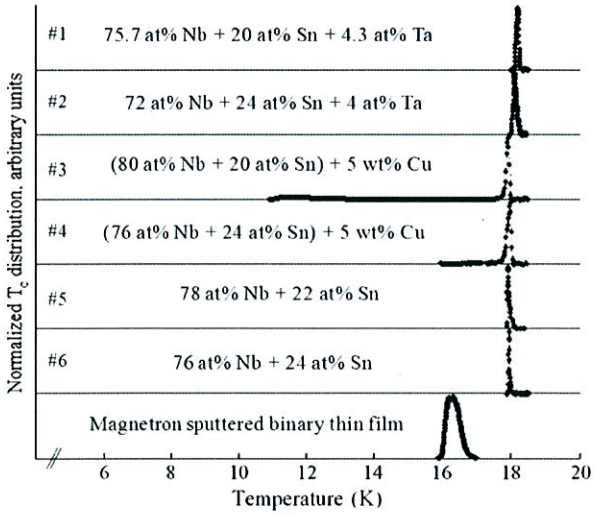

Fig. 5. T_c distributions as derived from resistive analysis.

B. T_c Distribution From Resistivity

The T_c distribution as derived from the resistive data (using (3) is shown in Fig. 5. Since the electrical behavior of the sample is dominated by the fraction with the highest T_c, only this fraction is revealed in the resistivity analysis. In other words, off-stoichiometric Nb-Sn with a T_c-value below the temperature where the overall resistivity of the sample becomes zero is hidden in this analysis. An composition distribution, calculated using (4) is plotted in Fig. 6.

IV. Discussion

It is evident from Fig. 4 that binary Nb-Sn and Nb-Sn with Ta addition is predominantly stoichiometric at the temperature and pressure at which the bulk samples were fabricated. However, this is not true for the bulk samples with Cu additions. In these

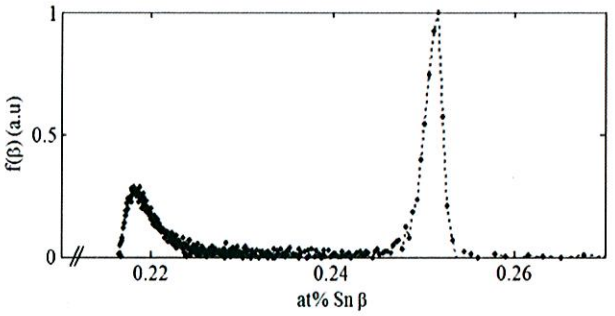

Fig. 6. Composition distribution of (80 at% Nb + 20 at% Sn) + 5 wt% Cu sample extracted from resistivity as a function of temperature data.

samples, distinct peaks in the temperature range 6-17 K are observed (Figs. 4 and 6), which is the T_c range for off-stoichiometric Nb-Sn [2]. Therefore, it is concluded that the presence of Cu triggers the formation of off-stoichiometric Nb-Sn under the conditions at which the bulk samples were fabricated. If Cu is not homogenously distributed in the samples, then the sample may be regarded as a mixture of binary Nb-Sn, and Nb-Sn+Cu, which could explain the observed bi-modal distribution (see Figs. 4 and 6). It is interesting to note that this bi-modal distribution was also recently observed in Nb_3Sn wires [16].

It is interesting to note that the 75.7 at% Nb + 20 at% Sn + 4.3 at% Ta bulk sample consists primarily of stoichiometric Nb_3Sn while the nominal Nb to Sn ratio dictates the presence of excess Nb. Presumably, a phase is present in this sample with a T_c value below the investigated temperature range. Possible candidates are A15 Nb_3Nb (T_c = 5.2 K [17], [18]) or bcc $Nb_{1-\beta}Sn_\beta$ with $\beta < 0.05$ (T_c = 4 K in case of 95 at% Nb + 5 at% Sn [17]).

The T_c distributions in Fig. 5 are significantly sharper than the T_c distributions in Fig. 4. For the binary bulk samples and the bulk samples with tantalum addition, this is to be expected as Nb-Sn with the highest T_c shorts out the Nb-Sn with slightly lower T_c and thus the single T_c distribution peak is only partially revealed.

However, for the bi-modal samples with Cu addition this argument doesn't hold. A possible explanation is that the strain-state of the samples is not the same in the two methods used to determine the T_c distribution. This could account for both the difference in width of the peak and the fact that the critical temperatures that are measured resistively are relatively high in comparison to what is found through the heat capacity measurements. A second possible cause is a small error in the temperature measurements.

Unlike in the heat capacity measurements, the T_c distribution from resistivity is limited by the fact that only the fraction with highest critical temperature is observable. Heat capacity measurements are preferable, but the strain state cannot easily be varied in such measurements. Heat capacity measurements on thin films are also far from trivial. Literature heat capacity results on co-evaporated thin films deposited at temperatures between 600 and 700 °C indicate a distribution width of 4 to 6 K [11], [12]. A sharper T_c distribution can be expected with some improvement in fabrication method, i.e. a higher substrate deposition temperature [11], [12], which would make these samples suitable for the investigation of strain sensitivity in off-stoichiometric Nb-Sn.

V. Conclusion

The proposed T_c distribution analysis based on resistivity measurements is consistent with an analysis based on heat capacity data for the overlapping range.

A stoichiometric phase is found in all investigated bulk samples. In the binary bulk samples and the bulk samples with added tantalum, no off-stoichiometric A15 Nb-Sn is observed. The bulk samples with Cu addition have a bi-modal T_c distribution with both stoichiometric and off-stoichiometric Nb-Sn.

Unlike the bulk samples, in the investigated thin film only the intended off-stoichiometric composition is detected in a resistive analysis. Therefore, this sample type appears to be a suitable candidate for studying the effect of composition on the strain sensitivity of Nb-Sn.

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