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The effect of Ta and Ti additions on the strain sensitivity of bulk Niobium-Tin

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Abstract

The effect of tantalum and titanium additions on the composition, the superconducting properties, and their sensitivity to strain of bulk Nb₃Sn is investigated. Using heat capacity analysis and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX), it is found that the binary Nb₃Sn bulk and Nb₃Sn bulk with added titanium and tantalum consist of stoichiometric Nb₃Sn and niobium(-oxide). Furthermore, it is found that the niobium-to-tin ratio decreases in the presence of tantalum and increases in the presence of titanium, which suggests that tantalum is replacing niobium and titanium is replacing tin in the A15 crystal structure. Using a 10% resistivity criterion, it is observed that the critical magnetic field of unstrained binary bulk is 26.7 T, while the presence of tantalum and titanium raises the critical magnetic field to 29.3 and 30.1 T, respectively. The curves of normalized critical magnetic field as function of strain of all three samples nearly overlap, a strong indication that the variation in strain sensitivity observed in wires is not caused by the titanium and tantalum additions. Understanding the effect of additions on the composition, superconducting properties, and strain sensitivity of Nb₃Sn is important for optimizing Nb₃Sn conductor technology.

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1. Introduction

The superconducting properties of Nb₃Sn, an important superconductor for high field magnet applications, are strongly reduced when the conductor is strained [1]. Nb₃Sn wires are inhomogeneous in their strain-state, exhibit tin gradients and also include various materials beside niobium and tin, making examination of the relationship between composition and strain sensitivity exceedingly difficult. In this paper Nb₃Sn bulk samples are investigated, of which the composition, morphology, and strain-state are more easily controlled.

A binary bulk sample is compared to bulk samples with titanium and tantalum additions, in terms of composition, superconducting properties, and strain sensitivity. The effect of additives on the critical temperature (T_c) distribution is investigated through heat capacity analysis. Using automated SEM-EDX characterization, the phase separation in binary Nb₃Sn as well as the effect of tantalum and titanium on the local

Table 1. The nominal composition of investigated samples

Bulk sample identification	Nominal composition
Nb-Sn binary	76 at% Nb + 24 at% Sn
Nb-Sn + Ta	4.05 at% Ta + 71.95 at% Nb + 24 at% Sn
Nb-Sn + Ti	1.52 at% Ti + 74.48 at% Nb + 24 at% Sn

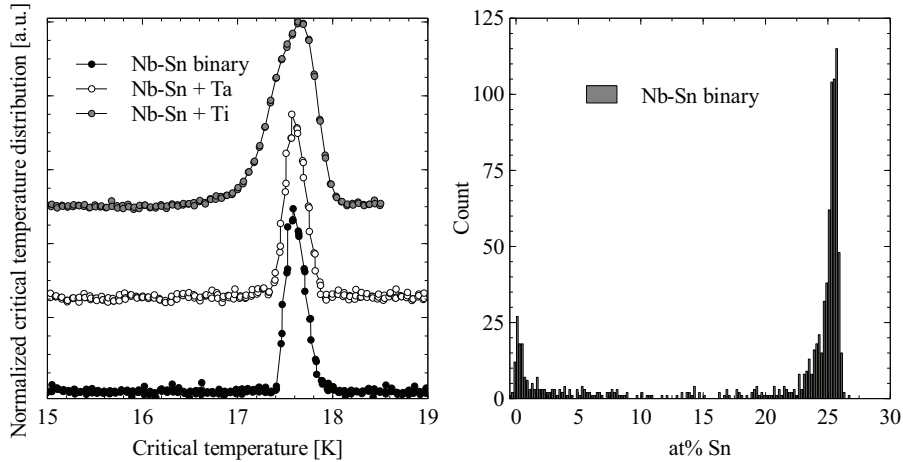


Fig. 1. (a) T_c distribution of bulk samples, derived from heat capacity analysis (b) Composition distribution of the Nb-Sn binary bulk sample, determined using automated SEM-EDX analysis.

niobium to tin ratio is investigated. From resistivity measurements as a function of temperature, magnetic field, and uni-axial strain the $T_c(H, \epsilon_a)$ phase boundary and the strain sensitivity of the normalized upper critical magnetic fields H_{c2} are compared.

2. Samples

Bulk samples were fabricated using the hot isostatic pressure (HIP) technique, which involves reacting powders at 1100 °C, under a pressure of 100 MPa. Details of this process, as well as X-ray diffraction (XRD), SEM, and vibrating sample magnetometer (VSM) measurements are found elsewhere [2, 3]. The nominal compositions of the investigated bulk samples are listed in table 1.

3. Heat capacity

The T_c distribution of the bulk samples is derived from the temperature dependence of the heat capacity. A detailed description of the experimental procedure, can be found elsewhere [4]. Figure 1a shows the T_c distributions of the three investigated bulk samples. The onset temperature of 18 K is consistent with the critical temperature of binary stoichiometric Nb_3Sn [5].

4. Automated SEM-EDX analysis of bulk samples

4.1. Experimental details

SEM-EDX is a well-known tool for determining the atomic composition of samples. This involves directing an electron beam to a spot and determining the local composition from X-rays emitted at that particular spot, with a typical spot size of a few micrometer. An uncalibrated automated SEM-EDX is used to determine the composition of 900 spots in a 80x60 μm^2 sample area, where every spot is located 2-3 μm away from the nearest spot.

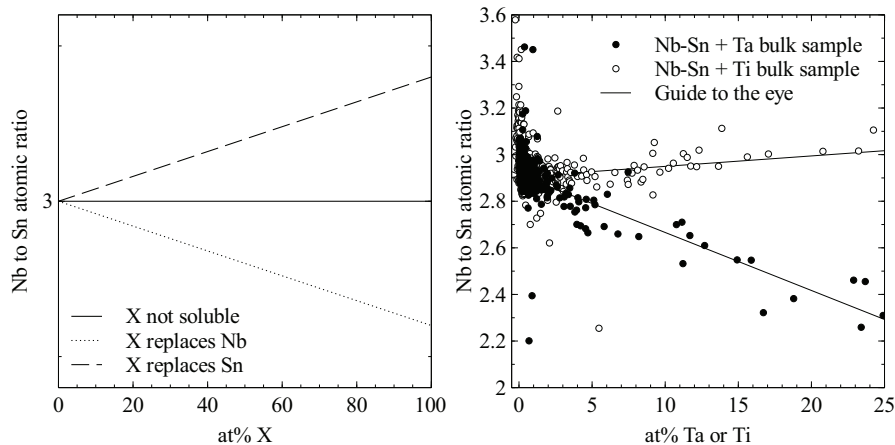


Fig. 2. (a) Expected effect of an addition on the local niobium-to-tin ratio, which dependent on the solubility of X in the Nb_3Sn A15 crystal structure (b) SEM-EDX measurement of local niobium to tin ratio as a function of local additive concentration.

4.2. Nb-Sn binary sample

Figure 1b shows the composition distribution of the Nb-Sn binary bulk sample. The majority of the sample is close to stoichiometry, with a maximum count at 25.5 at% Sn. As the nominal tin concentration in the sample is lower than stoichiometry (see table 1), the excess niobium is concentrated in pure niobium regions (see figure 1b). A significant amount of oxygen is observed as well, particularly in the pure niobium regions. A proprietary process is used to prepare oxygen-free powder, and it is therefore assumed that most of the oxygen is introduced during polishing of the sample and exposure to air. Therefore, oxygen counts are not included in the analysis for the remainder of this paper.

It was previously observed in XRD analysis of binary samples with varying nominal tin concentrations that the fraction of pure niobium increases with decreasing nominal tin concentration [3], which is consistent with the two distinct phases of stoichiometric Nb_3Sn and niobium observed here.

4.3. Effect of tantalum and titanium on the local niobium-to-tin ratio

While there is consensus that tantalum replaces niobium in the A15 crystal structure [6, 7], the effect of titanium is controversial. Tafto [6] et al. claim that titanium replaces niobium and Flükiger [7] et al. claim that titanium replaces tin in the A15 crystal structure. Using the automated SEM-EDX analysis, these hypotheses are investigated.

As a thought exercise, a bulk sample is considered, that includes Nb-Sn and metal X (see figure 2a). The Nb-Sn is preferably stoichiometric, with excess niobium contained in pure niobium regions. Three cases can be distinguished with regards to the effect of X on the Nb-Sn composition. In the first case, X does not replace either Nb or Sn, so whenever any niobium atoms are detected, a three times lower amount of tin atoms is detected, regardless of the local amount of X atoms. In the second case, X replaces niobium atoms in the A15 crystal structure. In regions of the sample where no X is present, the niobium to tin ratio is once again 3, but in the presence of more X atoms, the niobium to tin ratio decreases. In the third case, the niobium to tin ratio increases with increasing X concentration when X replaces tin in the A15 crystal structure.

Automated SEM-EDX measurements are performed on the Nb-Sn + Ta and Nb-Sn + Ti bulk samples, which are shown figure 2b. Using the model shown in figure 2a as reference, it is clear that this result is consistent with Flükigers hypothesis, i.e. figure 2b suggests that indeed Ta replaces Nb and Ti replaces Sn.

The samples with additions include regions of pure niobium, pure tantalum and pure titanium. In the regions where no tin is present, no mixtures of niobium and tantalum or niobium and titanium are observed, leading to an asymptotic increase to infinite niobium to tin ratio near the y-axis in figure 2b. The median compositions of the samples (sorted per element and derived across all 900 analyzed spots) are 74.0 at%

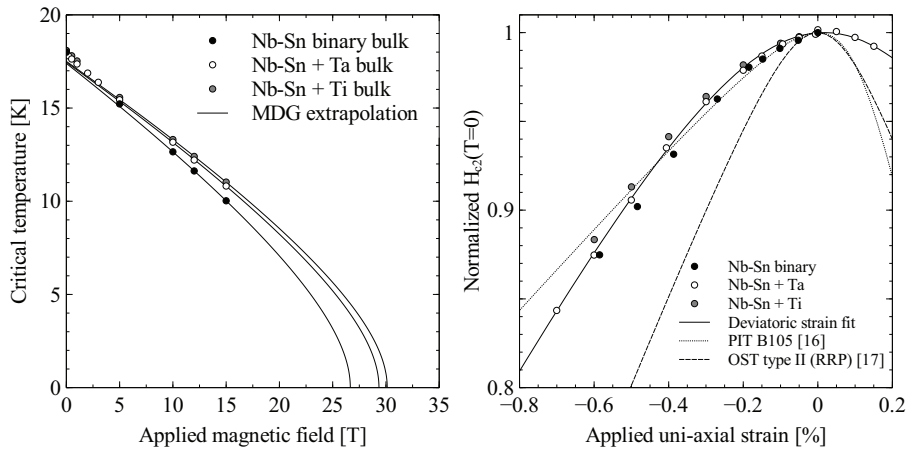


Fig. 3. (a) $T_c(H, \epsilon_a = 0)$ of bulk samples, using 10% criterion and Maki DeGennes fit, only fitting $T_c(\mu_0 H \geq 10, \epsilon_a = 0)$ (b) Normalized $H_{c2}(0)$ vs ϵ_a of bulk samples, deviatoric strain fit of Nb-Sn + Ta bulk sample and selected strain fits for two Nb_3Sn wires.

Nb, 25.4 at% Sn, and 0.6 at% Ta for the Nb-Sn + Ta bulk sample, and 74.1 at% Nb, 25.3 at% Sn, and 0.5 at% Ti for the Nb-Sn + Ti bulk sample.

5. Resistance measurements as a function of temperature, magnetic field, and uni-axial strain

5.1. Experiment

The resistance as function of temperature, magnetic field and uni-axial strain is measured using a U-spring sample holder in vacuum [4, 8]. The accessible temperature, magnetic field, and uni-axial strain range is $T = 4.2 - 325$ K, $\mu_0 H = 0 - 15$ T and $\epsilon_a = -1\% \dots 1\%$ strain, where the negative sign indicates compression. Exemplary resistivity measurements for the Nb-Sn binary bulk sample discussed here are found elsewhere [8].

5.2. Field-temperature phase boundary at $\epsilon_a = 0$

The critical temperature at a given strain state and magnetic field is determined using a resistivity criterion [8]. In order to make a comparison to the superconducting properties of Nb_3Sn wires, where a low electric field criterium is used [9], a 10% criterion is applied. Figure 5 shows $T_c(H)$ of the unstrained samples, which is fitted with the Maki-DeGennes relationship [11, 12], only fitting the critical temperatures measured at 10 T and higher to mitigate low-field deviation due to inhomogeneity [8]. The measured $T_c(0)$ are 18.0, 18.0 and 18.1 K, whereas the fitted T_c values are 17.4 K for the Nb-Sn binary sample and 17.5 for the Nb-Sn + Ta and Nb-Sn + Ti samples. The extrapolated $\mu_0 H_{c2}(0)$ are 26.7, 29.3 and 30.1 T for the Nb-Sn binary, Nb-Sn + Ta and Nb-Sn + Ti bulk sample respectively. Using a 90% criterion, 28.8, 30.4 and 31.0 T is found respectively, where 28.8 T is consistent with the results of other recent binary Nb_3Sn bulk analysis, that also used a 90% criterion [10].

5.3. Normalized strain dependence of the zero-temperature upper critical magnetic field

Per strain state, $H_{c2}(0)$ is determined using the Maki-DeGennes extrapolation as discussed in section 5.2, and the normalized result is shown in figure 6. Consistent with fitting the strain related properties of Nb_3Sn wires [1], the ratio $T_c(0)^3$ to $H_{c2}(0)$ is fixed as an additional fitting constraint. The deviatoric strain equation (equation 13 in [1]) is fitted to the normalized $H_{c2}(0, \epsilon_a)$ of the Nb-Sn + Ta bulk sample with optimal fitting parameters $C_a = 33.4$, $\epsilon_{0,a} = 0.44\%$, $\delta = -0.02\%$. It should be noted that the deviatoric strain equation is equivalent to more recent wire models [14, 15], with parameter C_{a2} set to 0. As an indication of the strain range observed in wires, the normalized $H_{c2}(0, \epsilon_a)$ of two wires, those with the smallest and largest strain sensitivities that were found in the recent literature and for which fit parameters from the same model are given, are also shown in figure 3b [16, 17].

6. Discussion

The T_c distributions shown in figure 1a, as well as the composition distribution shown in figure 1b and X-ray diffraction spectra of Nb-Sn binary bulk samples [3] consistently illustrate that the binary Nb-Sn bulk as well as the Nb-Sn bulk with added titanium and tantalum consists of stoichiometric Nb₃Sn and niobium (-oxide) regions, under the HIP reaction conditions as discussed in section 2. Thus, the basic assumptions of the model discussed in section 4.3 are justified.

It is not clear, however, what the exact tin concentration of the stoichiometric Nb₃Sn phase is. While the SEM-EDX measurement indicates a concentration of 25.5 at% Sn, the peak at $T_c = 17.6$ K observed in figure 1a is consistent with a tin concentration of 24.5 to 25 at% [5]. Presumably the uncalibrated SEM-EDX measurement is 0.5 at% above the correct value. It should be noted that the T_c of 18.0 K, determined from the resistivity measurement (see figure 3a), is consistent with the onset of superconductivity observed in the heat capacity measurement, as only a fraction of the sample needs to be superconducting to form a superconducting path and short out the resistivity measurement.

A useful reference on how additions affect $H_{c2}(0)$ is given by Suenaga [18], who finds a $\mu_0 H_{c2}(4.2K)$ of 23.4 T for binary Nb₃Sn and $\mu_0 H_{c2}(4.2 K)$ up to 27 T for Nb₃Sn with optimized amounts of tantalum and titanium additions. Extrapolating to $T = 0$ K [9] yields $\mu_0 H_{c2}(0)$ of 26 and 30 T for the binary sample and the samples with additions respectively, which is consistent with our observation, when using a 10% resistivity criterion. However, it should be emphasized that the phase boundary as well as the compositions that are probed depend strongly on the applied criterion [11].

The strain range of the bulk samples is within the indicated wire strain range, but above the average wire strain sensitivity. Furthermore, the strain sensitivity of the three bulk samples is nearly the same, compared to the large variation in strain range between wires (see e.g. [14, 15]). This indicates that titanium and tantalum additions do not contribute in a significant way to variations in the strain sensitivity and some factor not present in these bulk samples causes the variation in the strain sensitivity in wires.

7. Conclusion

HIP fabricated Nb₃Sn bulk samples have been investigated in detail to determine the effect of titanium and tantalum on the composition, superconducting properties, and strain sensitivity of Nb₃Sn.

Using heat capacity analysis and automated SEM-EDX analysis, it is determined that all investigated Nb₃Sn bulk samples consist of two distinct phases, which are stoichiometric Nb₃Sn and niobium(-oxide). The correlation between the local niobium-to-tin ratio, and the local tantalum and titanium concentrations, measured with SEM-EDX, yields strong evidence that indeed tantalum replaces niobium and titanium replaces tin in the A15 crystal structure.

The presence of titanium and tantalum cause a significant increase in $H_{c2}(0)$, from 26.7 T for the Nb-Sn binary bulk sample to 29.3 T and 30.1 T for the Nb-Sn + Ta and Nb-Sn + Ti bulk samples respectively, using a 10% criterion. Despite this difference, the normalized strain sensitivities of the three samples are nearly identical, which implies that the spread in strain sensitivities in wires is related to another effect that is not yet clarified.

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