Influence of Two-Step Heat Treatments on Bronze-Route (NbX)₃Sn Conductors

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Abstract. To increase the field strength of superconducting High-Field-Magnets, it is necessary to improve the physical properties critical current and upper critical field of the superconducting materials. For (NbX)₃Sn this can be done partly by optimising the heat treatment, which is necessary to form the superconducting phase. In this paper we will present results of two-step heat treatments on a Ta and Ti alloyed bronze route Nb₃Sn conductor. Special attention will be focused on the growth of the Nb₃Sn layer as well as on the influence of the heat treatment temperatures and times on the upper critical field and the maximum pinning force. The differences between one- and two-step heat treatments will be discussed.

1. Introduction
(NbX)₃Sn- wires become superconducting only after a heat treatment (HT) in which the superconducting phase is formed. The temperature and time of the heat treatment strongly influences the critical current and n-value of the conductor. This is due to the influence of the HT on Nb₃Sn layer thickness, grain size and Sn content of the reacted layer which determine the upper critical field and the maximum pinning force (e.g. [1]).

On the other hand, ternary or quaternary alloying elements, the manufacturing route, the initial Sn content and the layout of the conductor also influence the HT. This requires in principle a separate HT optimisation for each conductor and also for each magnetic field in which a conductor operates.

In recent years we have carried out quite detailed experiments on one-step HTs for differently alloyed bronze-route conductors [2],[3], that serve as starting point for the investigation presented in this paper, which concern two-step heat treatments of a Ta and Ti doped bronze route conductor manufactured by European Advanced Superconductors (EAS).

From the literature it is known that two-step HTs, i.e. heat treatments with two different temperatures and times, result in higher critical current values than HTs with only one temperature and time step [4],[5]. The main focus is not to give the optimum heat treatment for this wire and a specific background magnetic field but to get some insight into the physical mechanisms behind the heat treatment.

2. Experimental
The experiments were carried out with the Vacyrfux NSTT 10000 conductor by EAS. This wire has a diameter of 0.9 mm and contains 10000 filaments of 3.5 µm diameter embedded in a bronze matrix.
For the heat treatment the wire is wound to one layer coils of 33.3 mm diameter on a stainless steel cylinder. After HT the wire is transferred to a glass fibre reinforced mandrel.

The one-step heat treatments are described elsewhere [2]. The temperatures and times of the two-step heat treatments are shown in Fig. 1.

Two kinds of measurements have been performed. The first was the determination of the E(I)-characteristic. These experiments were carried out in the JUMBO test facility at liquid helium temperature (4.2 K) and in external magnetic fields up to B=15 T. The E(I)-curve was examined resistively by a four point measurement where the current is increased in discrete steps. From the E(I)-curves the critical current is determined using an criterion of E_c = 10µV/m. The slope of the E(I)-characteristics in double logarithmic scale gives the n-value. A detailed description of the method can be found in [6].

As well as the E(I)-measurements, optical measurements with a scanning electron microscope (SEM) were carried out. Backscattering images were taken of polished cross sectional areas of the differently reacted samples to investigate the Nb_3Sn layer thicknesses.

3. Results

3.1. Critical current
The critical currents of the differently heat treated samples were determined for magnetic fields up to 15 T. The results for 10 T are shown in Fig. 2. As well as the two-step heat treatments, one-step heat treatments with same end temperatures have been included for comparison.

As expected, the critical current is higher for most of the two-step HTs. The maximum enhancement is about 29% for a HT of 635°C 160h and 750°C 160h at 10 T.

3.2. Cross sectional Areas and Nb_3Sn layer thicknesses
From the optical measurements the layer thickness s could be determined.

A diffusion-like function was fitted to the layer thicknesses of not fully reacted samples according to

\[ s = b_3 \cdot t^{b_1} \cdot \exp \left( -\frac{b_2}{T_{abs}} \right) \]  \hspace{1cm} (1)
for one-step HTs and

\[ s = b_1 \left( t_2 + \exp \left( \frac{b_1}{b_2} \left( T_{\text{abs}} - T_{\text{set}} \right) \right) \right)^{b_3} \]  

for two-step HTs. With (2) the influence of the first HT step is transferred into a correction time for the second HT step, i.e. the two-step HT is treated as a one-step HT with time \( t_2 + t_{\text{corr}} \) and \( T_2 \).

The resulting fitting parameters for (1) and (2) were \( b_1 = 0.375 \), \( b_2 = 9378 \) and \( b_3 = 4861 \). The time dependence \( b_1 \) agrees well with literature data of about 0.35 [4].

### 3.3. Upper critical field and maximum pinning force

From linearised Kramer plots the upper critical field \( B_{c2} \) and the maximum pinning force \( F_{p,\text{max}} \) of the conductor can be obtained [3]. Furthermore the pinning force density \( f_{p,\text{max}} \) can be calculated since the superconducting cross sectional area \( A_{sc} \) is known.

This description of the results is independent of the external magnetic field and therefore well suited for investigating the influence of the HT on the physical properties of the conductor. The results of \( B_{c2} \) and \( f_{p,\text{max}} \) for one and two-step HTs are shown in Fig. 3.

The value of \( B_{c2} \) is mainly determined by the maximum temperature of the HT, and it does not matter whether this temperature is reached in the first or second step. This can be clearly seen for the heat treatments with 600°C as second step temperature where the \( B_{c2} \) values change strongly depending on the temperature of the first HT step.

The maximum temperature seems to play an important role for the pinning force density as well, but here the values decrease with increasing temperature.

### 4. Discussion

The above results for \( f_{p,\text{max}} \) are qualitatively in good agreement with literature data. The higher the maximum temperature of the heat treatment, the higher the grain size and the lower \( f_{p,\text{max}} \) should be since it is known to scale with the inverse grain size [7],[8].

For \( B_{c2} \) the data fit quite well with previous results from single step HTs, where we found a correlation between the grain size and \( B_{c2} \), i.e. for bigger grains \( B_{c2} \) was also higher [4]. New literature data suggest a correlation of the measured \( B_{c2} \) with deviations of Sn from stoichiometry within the Nb filaments [9]. This would imply a correlation between the maximum heat treatment temperature and the Sn content in the superconductive layer in a way that higher temperatures would result in layers with higher Sn content and higher homogeneity.
Table 1 shows $I_c$ for a field of 10 T, $B_{c2}$, and $F_{p,max}$ for some one-step and two-step HTs. The values are normalised to the one-step values. It can be clearly seen that the differences in critical current are due to differences in the maximum pinning force or rather the maximum pinning force density.

What really causes the enhancement of $F_{p,max}$ is not quite clear at the moment. It is certainly not due to an enhancement of the superconductive layer since for all HTs given in table 1 the filaments are fully reacted. Whether the enhancement is due to a finer grain structure cannot be decided with the data so far. Here additional SEM images of the grain structure itself are necessary.

5. Conclusions

For the investigated bronze route conductor an enhancement in critical current of about 30% could be achieved by two-step heat treatments compared to one-step HTs with same maximum temperature and overall HT time. Analysing the results with the help of Kramer’s relation shows that upper critical field and pinning force density are mainly influenced by the maximum temperature during heat treatment. Furthermore, the differences between one- and two-step HTs are mainly due to different values of the pinning force density. To explain the reason for these differences, further investigations are necessary, for example taking SEM images of the grain structure.

Table 1. Influence of two-step heat treatment on $B_{c2}$, $f_{p,max}$ and $I_c$ at 10 T normalised to the corresponding one-step heat treatment

| Heat Treatment | $I_c$ (B=10 T) | $B_{c2}$ | $f_{p,max}$ |
|----------------|----------------|----------|-------------|
| 750°C 350 h    | 1              | 1        | 1           |
| 570°C 20 h / 750°C 300 h | 0.98          | 1.00     | 0.97        |
| 570°C 300 h / 750°C 20 h    | 1.30          | 0.96     | 1.33        |
| 675°C 350 h    | 1              | 1        | 1           |
| 570°C 160 h / 675°C 160h    | 1.14          | 0.99     | 1.15        |

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