Influence of Ta and Ti Doping on the High Field Performance of (Nb,Ta,Ti)3Sn Multifilamentary Wires based on Osprey Bronze with High Tin Content

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Abstract. Ta and Ti are the most widely used additions for technical Nb,Sn multifilamentary superconductors. These elements are known to influence grain growth, grain morphology and chemical composition in the A15 layer, hence the current carrying properties of the wires over a wide magnetic field range. So far only few studies tried to compare systematically Ta and Ti doped and undoped Nb,Sn wires in the frame of the same work, down to a nanometric scale. We present an investigation on several multifilamentary (Nb,Ta,Ti),Sn bronze route wires, fabricated at a laboratory scale, with various amounts of additives. The wires consist of fine filaments embedded in a Cu-Sn or Cu-Sn-Ti Osprey bronze with > 15 wt.% Sn and an external Cu stabilization. Microstructural observations are compared with the results of $J_c$ and $n$ values measured up to 21 T at 4.2 and 2.2 K, and for longitudinal strains up to 0.5%. Non-Cu $J_c$ values up to 300 Amm$^{-2}$ and $n$ values up to 50 at 17 T and 4.2 K show clearly that wires with Ti addition to the bronze have a better performance with respect to wires with Ti additions to the filaments.

1. Introduction
Bronze Route processed multifilamentary Nb,Sn superconducting wires are presently the most appropriate conductors to meet the demanding conditions required by NMR magnet constructors. Homogeneously distributed filaments of 4 - 5 μm size are necessary to reach an extremely high time stability in the persistent mode as well as a low flux jump energy release during magnetic field change (adiabatic stabilization). But also a high RRR value of the Cu (dynamic) stabilization and a precise knowledge of the mechanical properties, especially of the compressive prestrain on the superconducting filaments, are very important to reach high field homogeneity and working reliability of superconducting magnet systems. At fields exceeding 21 T, the main drawback of bronze processed wires turns out to be their critical current density, which is currently limited by the Nb,Sn fraction, typically being at ~28 % of the total cross section for technical conductors using bronze with 15-16 wt.% Sn.
It is well known that alloying Nb3Sn with elements like Ta or Ti enhances its current carrying capacity, the positive effect becoming more relevant at high magnetic fields. While Ta is usually added to the filament material by metallurgical alloying prior to wire processing, Ti is added separately to conductor elements adjacent to the filaments, due to processing difficulties with Ti alloyed filaments [1], [2]. In this work we tried to find out how and why the two different ways of Ti addition in quaternary (Nb,Ta,Ti),Sn bronze route wires influence the superconducting properties.

2. Experimental

2.1. Conductor fabrication

Three different bronze route wires of 100 m length were fabricated by hot hydrostatic extrusion and cold drawing [3]. The Ø 1.25 mm wires consist of an external Cu stabilization (20 %), a Nb diffusion barrier (10 %) and 14,641 filaments of 4.5 μm diameter embedded in a Cu-Sn(-Ti) bronze (70 % non-Cu part). Table I summarizes the composition of the 3 conductors. For conductors #18 and #21, a Cu15.4Sn (wt.%) Osprey processed bronze from Swis smetal (Dornach, CH) was used, whereas for conductor #24, a Cu15.5Sn 0.25Ti bronze was applied, also manufactured by the Osprey procedure at Wieland Werke AG (Ulm, D). Ti was added to conductor #21 by introduction of a Nb47Ti rod into a Nb7.5Ta tube for the first extrusion step of the monofilament [3].

Table 1. Wire composition, all contents in wt.%.

| #18   | #21          | #24          |
|-------|--------------|--------------|
| bronze composition | Cu15.4Sn | Cu15.4Sn | Cu15.5Sn 0.25Ti |
| filament components  | Nb7.5Ta | Nb7.5Ta / Nb47Ti | Nb7.5Ta |
| Ti content of filaments   | 0     | 1.0 wt.% | 0     |
| $\alpha_{local}$ (filament group) | 2.0   | 2.2   | 2.2   |
| $\alpha_{global}$ (non-Cu part) | 2.7   | 2.5   | 2.5   |

The wire samples were reacted under vacuum (<10^{-5} mbar), the heat treatments being optimized for the ternary conductor #18 (695°C/100h-730°C/50h) and for the quaternary conductors #21 and #24 (600°C/100h-670°C/150h).

2.2. Superconducting properties and microanalysis

Critical current density measurements were performed in our laboratory at 4.2 and 2.2 K up to 21 T on a recently installed 21 T shielded magnet. Additional measurements on conductor #24 have been performed with the modified Walters Spiral (WASP) by applying longitudinal strains up to 0.5 % [4]. The Lorentz force on the conductor was applied towards the coil axis, and a 0.1 μV cm⁻¹ criterion was applied for the $I_c$ determination. The resistive transition index (also called exponential factor) $n$ was calculated as the slope of the logV-logI plot between 0.1 and 1 μV cm⁻¹ using a least mean square fit.

In order to observe the surface roughness of the filaments, the bronze was etched off, the free filaments being observed by SEM.

3. Results and Discussion

3.1. Transport properties and critical temperature

Figures 1 and 2 show the non-Cu $J(B)$ and $n(B)$ values at 4.2 K for the wires #18, #21 and #24, respectively. Wire #24 has clearly the highest $J_c$ and $n$ values for the entire field range. The upper critical field $B_{c2}^*$, extrapolated from the $J_c$ values in the range 17T • $B$ • 21T indicates 24.8 T for #18, 25.5 T for #21 and 27.1 T for #24, respectively.
Figures 3 and 4 show the non-Cu $J_c(B, \epsilon)$ and $n(B, \epsilon)$ values of wire #24. The maximum values occur at $\epsilon_m = 0.21 \%$, which is a moderate value in accordance with the relatively low Residual Tin Content (RTC) of about 1 – 3 wt. Sn in the depleted bronze (corresponding data not shown here).

Figures 5 and 6 compare the non-Cu $J_c(B=21T, \epsilon)$ and $n(B=21T, \epsilon)$ values, measured at 4.2 K and 2.2 K on conductor #24. The empirical “2T rule” applies quite well to these results: the $J_c(T=2K, B=21T, \epsilon)$ and the $J_c(T=4K, B=19T, \epsilon)$ values coincide almost perfectly, but the $n(T=2K, B=21T, \epsilon)$ values are even higher than the $n(T=4K, B=19T, \epsilon)$ values, which demonstrates that bronze route wires still exhibit high $n$ values at fields exceeding 21 T.
The results of $T_c$, measured by AC susceptibility on filaments either embedded in the bronze matrix (under precompression) or after etching off the bronze matrix (with released precompression) have already been reported in a former paper [5]. A slight decrease of $T_c$ was observed, due to higher Ti contents and to a higher precompression exerted by a higher Sn content in the depleted bronze.

3.2. Microanalysis
Residual Niobium Ratio ($RNR$), Residual Tin Content ($RTC$), FE-SEM images of the fractured filament cross sections and (S)TEM/EDX observations on filament cross sections by Focused Ion Beam (FIB), also been reported in [5], do not show significant differences between the 3 wires.

Fig. 7 shows SEM micrographs of free 4.5 $\mu$m thick filaments of wires #18, #21, #24, extracted from unreacted wire samples. The surface roughness of #24 seems to be smaller compared to the other 2 wires, which is a possible explanation for the high $n$ values of #24. From the viewpoint of wire processing, this result is surprising since the (cold) work hardening of Cu-Sn-Ti bronze is higher compared to that of a Cu-Sn bronze with the same Sn content. Therefore the co-deformation of Cu-Sn-Ti bronze together with the soft filament material is expected to be the more difficult one.

4. Conclusions
A bronze route wire processed with Ti alloyed bronze yields clearly better transport properties compared to a wire where the Ti is introduced by a NbTi alloy into the filaments. The large differences in $J_c(B)$ and $n(B)$ values can be explained by the smaller surface roughness of the filaments in the Cu-Sn-Ti bronze processed wires. The concentration profile in the A15 layer and the A15 grain size are of a minor importance.

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