Influence of small additives of Si, Sc, Cu on properties of Nb-48.5 wt.% Ti superconductor

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Abstract. A study was made on the effect of small quantities of doped elements Si, Sc and Cu on the microstructure, mechanical and superconducting characteristics of the alloy Nb-48.5 wt.% Ti.

1. Introduction

Addition to a binary alloy of a third element in small quantities can well exercise a considerable influence on the mechanical, electrophysical, magnetic properties of material. In this way, the doping of superconducting niobium-titanium alloy with a number of additives acts to improve the critical current density $J_c$ and increase the critical field $B_{c2}$. For example, the addition of heavy additives (Ta, Hf) enable to increase the values of $B_{c2}$ up to 14 T at 2K owing to the decreased paramagnetic confinement in the superconducting state [1].

In order to ameliorate the current-carrying characteristics under different applied magnetic fields, a number of additives were introduced, including Cu and Si [2–4]. The better current-carrying characteristics in the doped alloy-based superconductors can be attributed to the processes of intensification of the oversaturated solid solution diffusion decomposition of $\alpha$-phase and, appropriately, an accelerated growth of the particles of $\alpha$-Ti phase. The higher is the content of this non-superconducting phase, the larger is the magnetic flow pinning force and, respectively, the higher are the values of $J_c$ [5,6]. Over and above, with an increased content of the dopant another possibility appears to have the pinning force increased due to formation of a high fine-particle dispersion eutectoid mixture.

However, the complete realization of potential possibilities of the growth of $J_c$ in the doped alloys is rather hard to make. As a matter of fact, the plastic characteristics in those alloys are lower than usual, and they keep deteriorating with a growing concentration of the third element up to the brittle failure of the material. Considering as well the complicated deformation route of manufacture of the superconductor, the problem transpires in all its clarity of search for how to improve the plasticity characteristics of the doped alloys. It is understood as well that the data on a rather low $J_c$ available from literature as regards the alloys containing a third element have to do with employment of the simplified production schemas of those superconductors.

The traditional way of amelioration of the mechanical properties is pounding of the microstructure of material cast. With the aim of creation of the fine-grain structure, we have tested a method of
differently-directed deformation (DDD) of ingots of niobium-titanium alloy [7]. This method enables to form the homogeneous thin subgrain structure and promotes the characteristics of plasticity in the binary alloy [8].

The choice of additives (Si, Sc, Cu) studied in this research was prompted by the similitude of the state diagrams: judging by their effects on titanium polymorphism, these additives should be the β-eutectoid stabilizers. In addition, those additives that are different from the main alloy components in their electronic structure can exert their influence on the value of surface energy of the matrix and precipitate.

All considered, the objective of this research was to make the study on the influence of introduction of additives Si, Sc and Cu on the microstructure, mechanical and current-carrying characteristics of Nb-48.5 wt.% Ti alloy, as produced via the differently-directed deformation of ingot.

2. Materials and Research Techniques

Methods of the production and research of the composition, microstructure and properties of a niobium-titanium alloy with additives of the third element are described earlier in detail quite enough [9]. Here we note only, that ingots of the alloy NT50 (Nb-48.5±1.5 wt. %Ti) with additives Si, Sc and Cu have been obtained as in the laboratory frame of reference and under the conditions of plant (Ul’ba Metallurgical Works). Diameters of these ingots made approximately 20 and 90 mm, respectively. The concentration range of the additives in the alloys was 0.1-1.0 wt.%.

In order to form the homogeneous subgrain structure in the doped alloys a treatment was made such as to have those ingots deformed in different directions, first, via the upsetting in closed container (Ø20→Ø30 or Ø90→Ø130 mm) followed up by their extrusion out of this container until they had reached the initial diameter of the ingot. The alloy plastic strain value in its true magnitudes was ~1.5 per one cycle of such treatment. The treatment temperature was ~600 °C. Then, following different schemas of the deformation route, single-filament and 2970-filamentary superconductors were manufactured on the base of the doped alloys.

3. Experimental Results and Discussion

The metallographic analysis of the initial binary alloy ingot comes up with rather coarse grains with the size 350-400 microns (Fig.1a). The addition of the research additives acts to decrease slightly the size of grain structure (Fig.1b), although not to such degree as with B or Be, which, owing to a big difference in their atomic dimensions, are more effective modifiers [9]. As the content of the dopants in the ingots increases, especially on the grain boundaries, some supplementary phases come into being. After the high-temperature annealing and quenching, the grain structure size somewhat increases, the monophase homogeneous state being stabilized.

Figure 1. Microstructure of cast alloy NT50 (a), alloy with additive 0.18 wt.% Cu (b), after differently-directed treatment of alloy (c) with additive 0.26 wt. %Sc.
After the differently-directed treatment of ingot, there appear clear-cut undulating lines of the flow that traverse several grains and are distributed uniformly over the cross-section of the material (Fig. 1c). As indicated in work [8], the DDD of niobium-titanium alloy promotes formation of a homogeneous strongly dispersed subgrain structure. The sizes of subgrains are 0.3 to 0.5 microns, their disorientation being several degrees. This kind of reduction to fine state is very propitious for enhancement of the technological parameters of the doped alloys.

The current-carrying characteristics of single-filament superconductors obtained via the simplified deformation route without intermediate anneals, but with the only heat treatment at $T=375 \, ^\circ C$, are given in Fig 2. The deformation pressing stage-to-annealing interval is $4.6 \, (\mathcal{Q}10 \, mm \rightarrow \mathcal{Q}1.0 \, mm)$. After the annealing at $\mathcal{Q}1.0 \, mm$, the samples were drawn until they had been $\mathcal{Q}0.3 \, mm \left(\varepsilon_{\text{fin}}=2.4\right)$. With short annealing times, the difference in $J_c$ for the binary and doped alloys was rather substantial, although in its absolute magnitude the critical current density was low. With increasing duration of the treatment, the level of the current-carrying characteristics grows, the values of $J_c$ converging for all samples. This experiment also indicates that, with increasing content of the doping elements, the values of $J_c$ tend to become higher as well, especially in the region of the short annealing duration.

![Figure 2. J_c vs. treatment duration relationship in field 5T.](image)

![Figure 3. Variation of J_c vs. final deformation degree in magnetic field 5T.](image)

The growth of the current-carrying characteristics in the doped alloys at the early stages of oversaturated solid solution decomposition can be associated with the process of heterogeneous nucleation of this phase on impurity atoms and, as well, with an increased diffusion mobility of atoms of the precipitate phase. This kind of mobility can be caused, for instance, by the difference between atomic dimensions of the matrix and dopant, their electronic structures, their levels of defects present in material, etc. In addition, if the additives act to decrease the level of surface energy on the matrix-precipitate interface, the size of the critical precipitate nucleus decreases while the density of those precipitates grows. Finer precipitations of $\alpha$-Ti phase in Nb-Ti alloy have been observed for example when Cu atoms were diffused through the thin Nb barrier [1]. The increasing density level of non-superconducting precipitates and their volume content acts to increase $J_c$ in the doped alloys.

When approaching the equilibrium, the process of decomposition slackens quite naturally. This slackening is more pronounced in the doped alloys, which can be attributed to a great amount of $\alpha$-Ti phase precipitated in them owing to the heterogeneous nucleation occurring at the inchoate stage of the process of decomposition. Besides, the additives may act to bring down the surface energy of the interface thereby decreasing the average size of the precipitates on account of the concomitant process of precipitate particle coalescence (Ostwald ripening). Those post-long anneal structural transformations result in convergence of the levels of the current-carrying characteristics of the superconductors based on the doped and binary alloys.

The intensification of the process of solid solution diffusion decomposition due to increasing of the number of intermediate anneals and plastic strain degree enables to increase drastically the level of the
values of $J_c$ for all alloys under consideration. Fig. 3 gives the typical dependence of $J_c$ on $\varepsilon_{\text{fin}}$ for certain single-filament superconductors obtained via 6 heat treatments at 390°C for the duration of 72 hours. The deformation interval prior to the last anneal was 7.0 (ø10 mm → ø0.3 mm). The highest value of $J_c$ which is equal to 3.1 kg/mm$^2$ in the applied field of 5T was obtained for the alloy with copper additives. Noteworthy is the fact that the peak of $J_c$ in the doped alloy-based superconductors shifts toward smaller values of $\varepsilon_{\text{fin}}$. It is generally considered that, in current-optimized samples of the binary alloy, the thickness of ribbon precipitates of $\alpha$-Ti phase that stretch over the length of the wire should be 1-4 nm [1]. For this reason, to achieve the same structural state in the doped alloys, a lesser degree of deformation is needed on account of a finer size of the precipitates of $\alpha$-Ti phase after the last annealing.

Considering the rather high level of current-carrying characteristics of the single-filament superconductor on the base of alloys with small additives of copper, their good strength properties and appropriate engineering relevance, a 2910-filament superconductor was produced of the same material at the Metallurgical Works. The number of intermediate anneals made at $T$=390°C for the total duration of 50 hours was 5. The current-carrying and mechanical properties of those superconductors are presented in Table.

Table. Critical current density and mechanical properties of 2910-filament SC ø0.85 mm.

| Additive content, wt.% | $J_c$ (5T, 4.2K), kA/mm$^2$ | Ultimate strength, MPa | Relative elongation, % | Volume part SC, % |
|------------------------|-------------------------------|------------------------|------------------------|-------------------|
| NT50                   | 2.18                          | 835                    | 1.5                    | 41.5              |
| NT50-0.23 Cu           | 2.38                          | 843                    | 1.5                    | 41.7              |
| NT50-0.64 Cu           | 2.48                          | 854                    | 1.0                    | 39.9              |

From this Table it can be gathered that the level of the values of $J_c$ is higher by 10–15% in the doped alloy-based superconductors, their strength and plastic characteristics being approximately the same as those of the binary alloy-based ones, while the statistical evaluation made over the quality assurance factor supports the good prospects for manufacturing these superconductors.

4. Conclusions
1. In order to have the homogeneous strongly dispersed microstructure formed in niobium-titanium alloys with small additives of 0.1-1.0 wt.% Si, Sc and Cu, the differently-directed treated was made of initial ingots, the superconductors manufactured on the base of those alloys.
2. It is demonstrated that small additives promote betterment of the current-carrying characteristics of the superconductors, especially so at the early stages of diffusion decomposition.
3. The peak value of the critical current density achieved in the doped alloys is as high as 3.1 kg/mm$^2$ in applied magnetic field of 5 T at 4.2 K.
4. At the Metallurgical Works, the pilot industrial-scale batch of 2970-filament superconductor was produced on the base of niobium-titanium alloy with small additives of copper.

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