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INFLUENCE OF Nb₄O SUBOXIDES IN THE SUBSTRATE UPON PROPERTIES OF Nb₃Sn TAPE SUPERCONDUCTOR

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Résumé - Nous décrivons les propriétés d'un ruban supraconducteur de Nb₃Sn préparé par la diffusion de Sn dans un ruban de NbZr. Par un traitement thermique approprié en plus des particules de ZrO₂ le sous-oxyde Nb₄O a été formé. En conséquence, l'épaisseur de la couche de Nb₃Sn et le courant critique ont augmenté, et les propriétés mécaniques ont été améliorées par rapport aux propriétés d'un ruban de Nb₃Sn sans Nb₄O.

Abstract - The properties of tape diffusion processed Nb₃Sn superconductor prepared on NbZr substrate are described. By appropriate heat treatment besides the ZrO₂ particles the Nb₄O suboxides are formed too. Consequently, the values of the Nb₃Sn layer thickness and that of the critical current have increased and some mechanical properties are being improved, when compared with properties obtained on substrates without Nb₄O particles.

I. INTRODUCTION

It is already well-known that high $J_c$ values in the diffusion processed Nb₃Sn tape may be obtained by using the oxidized Nb-Zr substrate as well as by adding mainly Cu into the Sn bath. The ZrO₂ particles in the substrate serve then as new pinning centres. As a result, both the electrical and mechanical properties of Nb₃Sn superconductor may be improved substantially [1].

In our previous experiments using the pure Nb substrate [2] we have observed by SEM, that the Nb-suboxides (content of $O_2 < 0.25$ wt.%) and the NbO particles (content of $O_2 > 0.25$ wt.%) may be formed. As a result, the thickness and the $I_c$ values of Nb₃Sn layer have increased in optimal case up to 100%. The presence of $O_2$ in the Nb-lattice causes increased strength and microhardness of substrate. In most cases the ductility is decreased but by suitable heat treatment it may be increased again from about 4% - 6% to more than 10% and, the strength from 600 MPa - 650 MPa to about 750 MPa - 900 MPa. Plausible explanation is the presence of Nb-O phases. The diffusion activation energy
of Sn on the grain boundaries of these particles is much lower than that of the volume diffusion [3].

In the following part we tried to repeat our previous results obtained on the Nb-substrate [2] also on Nb-ZrO₂ substrate.

II. EXPERIMENTAL

As a tape substrate the Nb-1.5 wt.% Zr alloy (the O₂ content being (0.01 to 0.02) wt.% O₂) has been used with the dimension 10 mm x 0.02 mm. Samples of the substrate were externally and internally oxidized. After that a secondary heat treatment has been applied in vacuum of 5x10⁻⁷ kPa at temperatures 200°C to 700°C during 5 hours. The Nb₃Sn layers were prepared by hot-dipping the substrates in molten Sn-25 wt.% Cu bath followed by heat treatment in vacuum of 10⁻⁶ kPa at 900°C during 20 min.

Critical currents were measured in transverse magnetic field of 5 T, perpendicular to the broad side of the sample at 4.2 K. The substrate specific resistance was measured at room temperature and, for the microhardness Hₘ measurement the test load of 10 g was used. The value of strength G₀₂ and the Nb₃Sn layer thickness were also measured.

III. RESULTS

As the investigation by SEM has shown, the substrate structure may be influenced substantially by the secondary heat treatment.

In the samples without secondary treatment globular ZrO₂ particles may be found in the α-Nb (solid solution) matrix, with diameter 30 nm to 200 nm. Also traces of Nb-0 particles may be seen with dimensions 0.2 µm to 1.0 µm, Fig. 1a. The heat treatment up to 250°C does not cause any substantial change in the structure except that the boundaries of Nb-0 particles are more visible. At temperatures 250°C to 400°C a quantity of new particles with dimensions 0.1 µm to 0.5 µm may be seen, Fig. 1b. We have found by selective electron diffraction that the particles are Nb-suboxid Nb₄O, which is in agreement with Niebuhr [4]. The Nb₄O cubic lattice parameter is a₀ = 0.69 nm. The number of smallest ZrO₂ particles has decreased and, on the other hand, the number of larger ZrO₂ particles, 100 nm to 200 nm in diameter has increased. For temperatures more than 400°C the Nb₄O phase is unstable and it is decomposed. As a result, the O₂-concentration gradient is lowered in the substrate. The number of larger ZrO₂ particles is rising with their nonuniform distribution within the substrate, because of their clustering on the energetically favourable places - the Nb₄O particles boundaries, Fig. 1c.
The described change in the substrate structure has also influence upon formation and growth of the Nb$_3$Sn superconducting layer, Fig. 2.

During the heat treatment at $T < 250^\circ$C the O$_2$-content is lowered in the $\alpha$-Nb matrix and it is trapped on the boundaries of Nb$_4$O particles. The value of specific resistance $\rho$ decreases. For $T = 250^\circ$C to $400^\circ$C new Nb$_4$O particles are formed. Because of precipitation hardening the strength $\sigma_{0.2}$ and microhardness $H_m$ increase with further lowering of $\rho$. Boundaries of Nb$_4$O particles serve as diffusion paths for Sn and consequently the Nb$_3$Sn layer thickness and critical current values increase. For $T > 400^\circ$C, O$_2$ diffuses into inside parts of the substrate, Nb$_4$O particles are decomposed and new ZrO$_2$ particles are formed. The values of $\sigma_{0.2}$ and $H_m$ decrease and that of $\rho$ increase at the same time. The activation energy of Sn-diffusion is increased and, therefore, the values of layer thickness and $I_c$ decrease.
Figure 3 shows fractures of Nb$_3$Sn samples, 3a - without secondary heat treatment, 3b - sample heat treated at 400°C. The Nb$_3$Sn layer thickness is 3.5 μm to 4.0 μm in the first case but about 6.0 μm in case b. The dimension of the Nb$_3$Sn grains is changed slightly from 0.2 μm to 0.4 μm towards direction substrate - Nb$_3$Sn layer interface to Nb$_3$Sn layer surface.

![Fractures of Nb$_3$Sn samples (5000x)](image)

**IV. CONCLUSION**

By appropriate heat treatment besides ZrO$_2$ particles also Nb$_4$O suboxides may be formed in the Nb-ZrO$_2$ tape substrate. The presence of Nb$_4$O particles influences substantially the properties of substrate as well as those of Nb$_3$Sn layers prepared on such substrates. The critical current values increased from (100 - 120) A/mm at 5 T to (160 - 180) A/mm at 5 T. Besides, some mechanical properties are improved. The preparation procedure described above is now commercially utilized in the production of Nb$_3$Sn tape superconductor.

**References**


