JOURNAL OF MATERIALS SCIENCE 17 (1982) 1579–1584

Influence of oxygen content on some properties of Nb_3Sn tape used for superconducting transmission lines

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The influence of the presence of oxygen in the Nb–Zr substrate upon some physical and mechanical properties of the Nb–ZrO_2 substrate and/or Nb_3Sn tape superconductor prepared from such a substrate has been studied. The results have shown that the Nb_3Sn grains are much finer in the case of Nb–ZrO_2, than those obtained on Nb–Zr substrate. As a result, both the electrical and mechanical properties have been substantially improved. The critical current at a field of 5 T increased by between 100 and 200 %, the alternating current losses decreased by about one order of magnitude, the tensile strength increased by about a factor of three and the microhardness value also increased by about a factor of three for oxygen contents in the range 0.03 to 0.70 wt%. The specific resistance of this substrate increased at the same time from 17 to 22 $\mu\Omega$ cm and the relative elongation decreased from 5 to 3 %.

1. Introduction

At present, one of the most commonly used technical superconductors is Nb_3Sn. Although the discovery of this material took place twenty years ago [1], its development is still not complete. The high current-carrying capacity of Nb_3Sn suggests the use of this superconductor for the construction of alternating current/direct current (a.c./d.c.) transmission lines and today many laboratories are involved in this type of research.

Two modes of energy transmission (a.c. or d.c. power transmission) are generally considered with the transmission cables being either in flexible or rigid form. For all the types of cables mentioned, Nb_3Sn in the form of a tape prepared by the diffusion process is preferably used. Besides having a high current-carrying capacity, such a Nb_3Sn tape for transmission line applications must also have low a.c. losses. Both these properties are influenced by the manufacturing process which, in turn, has a great influence on the internal microstructure of the Nb_3Sn superconducting layer. Thus, the superconducting performance of diffusion-processed Nb_3Sn is substantially influenced by its microstructure.

The widely-used techniques of the diffusion process consist of hot-dip coating the Nb tape substrate with molten tin followed by heat-

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treatment in a vacuum. It is already well-known that the current-carrying capacity of Nb_3Sn diffusion-processed tape may be substantially increased either by doping the Nb substrate with zirconium oxide [2, 3] or by the addition of a third component (for instance copper) into the tin bath [4]. Data concerning the doping of Nb substrate by zirconium without oxidation are also reported [5] but the presence of ZrO_2 precipitates has one of the most significant effects upon increasing the current density value of Nb_3Sn tape. The ZrO_2 particles within the Nb_3Sn layer are formed by internal oxidation of Nb–Zr substrate [6].

The results of our experiments have shown that the presence of ZrO_2 influences not only the value of the critical current density, J_c, in the Nb_3Sn layer but also the value of the a.c. losses as well as of the other physical and mechanical properties of the superconductor.

This work shows the results of our experimental investigation of the influence of oxygen presence upon some of the physical and mechanical properties of the substrate, as well as those of the produced Nb_3Sn ribbon conductor, which are of interest from the point of view of their applications in the construction of transmission line cables [7].

2. Experimental procedure

2.1. Preparation of Nb–Zr substrate for the diffusion and oxidation processes

As a starting material, Nb tape of width 10 mm and thickness 40 μm with a zirconium content of 1.5 wt% has been used. To clean the substrate before treatment, the surface layer of the tape has been etched-off by a slightly modified process described in [8] to a final thickness of 34 to 36 μm. After rinsing the etched tape with distilled water and alcohol, the process of external and internal oxidation of zirconium was followed, forming precipitates of ZrO_2 within the Nb–Zr substrate. The external oxidation was performed in a gas atmosphere containing oxygen, following by the internal oxidation of zirconium [2, 3] to a degree of 0.03 to 0.70 wt% O_2 in the substrate. It was found that the properties of prepared Nb_3Sn tape are optimal for oxygen contents from 0.30 to 0.40 wt% O_2. The specific resistance, ρ, microhardness, HV, specific elongation $\Delta l/l$ and tensile strength, σ, for both Nb–Zr as well as Nb–ZrO_2 types of substrates have been measured.

2.2. Hot-dipped coating and heat treatment

Both Nb–Zr and the prepared Nb–ZrO_2 substrates were then passed through a crucible containing molten tin and 25 wt% Cu, in a vacuum of 5×10^{-5} Torr. The temperature of the bath was 700° C and the speed of the moving tape was 30 m h^{-1}. The thickness of the coating was about 5 μm on each side of the tape.

The reaction was performed by passing the coated tape continuously through a tube furnace in a vacuum of 5×10^{-5} Torr. The temperature of heat treatment was 750° C to 900° C with the reaction time being 30 to 120 min. The length of the samples prepared by the described procedure was of the order of 100 m.

2.3. Sample testing and structural analysis

The d.c. critical current of the tape samples was measured by the standard four-probe procedure in the usual manner at a temperature of 4.2 K in a background transverse magnetic field of 5 T with the magnetic field vector perpendicular to the width of the tape. Measurements of the a.c. losses has been performed using a magnetic method. All loss data reported here pertain to a frequency of 50 Hz and a temperature of 4.2 K.

The oxygen content of the Nb–ZrO_2 substrate was determined by gas chromatography. To investigate the macro- and/or the microstructure of the substrate and the prepared samples a combination of both scanning electron microscopy (SEM), to show the surface morphology, and transmission electron microscopy (TEM), to show the internal structure, were used. The surface roughness, as a function of oxygen content in the Nb–Zr substrates, has also been studied. The structural analysis has been completed by Mössbauer spectroscopy giving quantitative information about the Nb_3Sn-phase content in the Nb–Sn system.

3. Results and discussion

The results of our investigation have shown that the presence of oxygen content has a substantial effect upon the properties of the Nb–Zr and/or $NbZrO_2$ substrates, as well as upon the behaviour and properties of the prepared Nb_3Sn superconductor.

Some physical and mechanical properties of the substrate used for production of the Nb_3Sn, as a function of the oxygen content, are presented in Fig. 1. For oxygen contents from 0.03 to 0.70 wt%, the specific resistance increased from 17 to

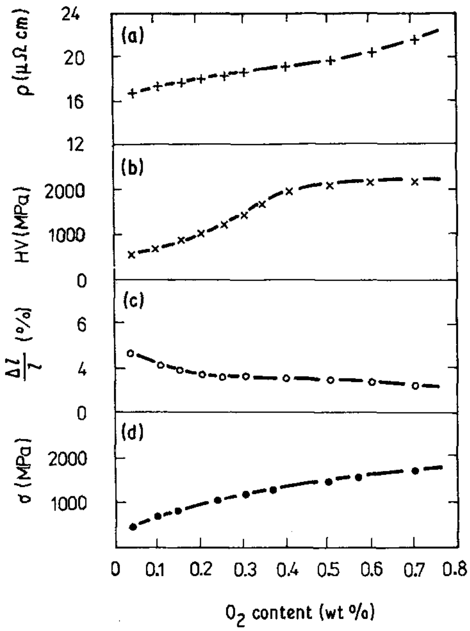

Figure 1 Influence of oxygen content upon some properties of the Nb–Zr and Nb–ZrO_2 substrates: (a) specific resistance; (b) microhardness; (c) specific elongation; (d) tensile strength.

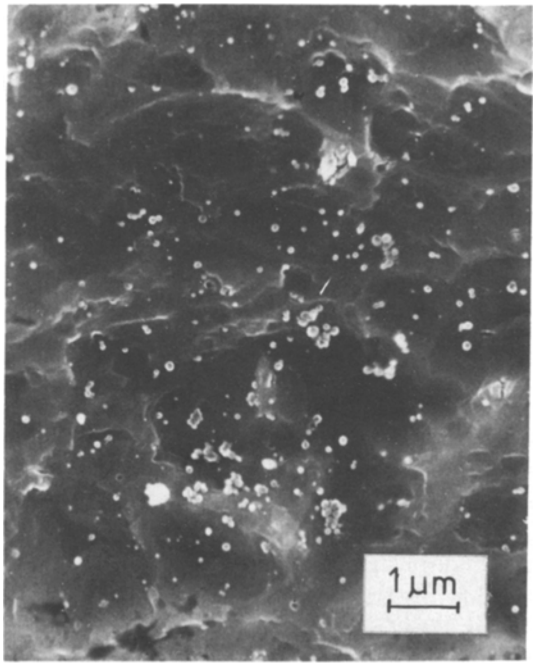

Figure 2 **ZrO_2 precipitates in the oxidized Nb–Zr substrate (white dots).**

22$\mu\Omega$ cm (1), the microhardness increased from 685 to 2160 MPa (2), the specific elongation decreased from 5% to 3% (3) and the tensile strength increased from 590 to 1815 MPa (4). Evaluating the structural properties of the prepared Nb_3Sn samples by SEM and TEM it was found that the ZrO_2 precipitates more easily in samples with higher O_2 contents. The layout, shape and size of these particles can be seen in Fig. 2. From Fig. 2 it can be seen that the precipitates are approximately spherical in shape and are relatively uniformly arranged within the matrix. The size of the ZrO_2 precipitates is not larger than 0.5 μm with the majority of particles being of

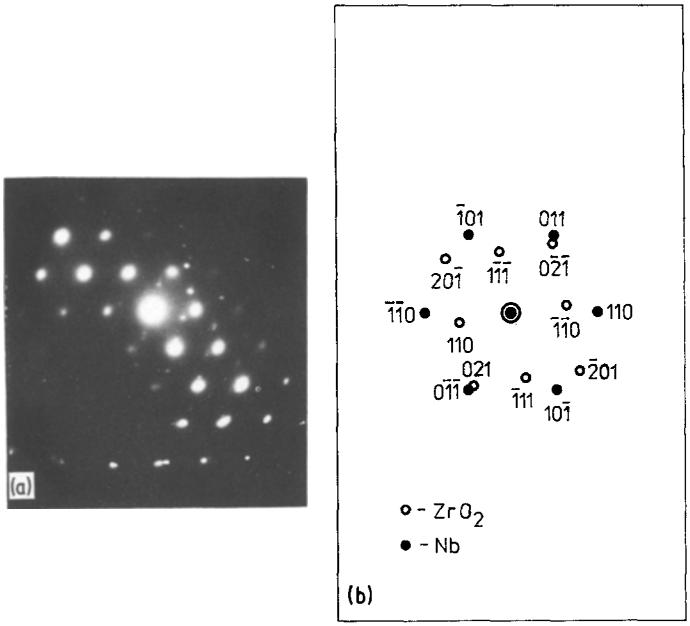

Figure 3 Diffraction patterns obtained from Nb–ZrO_2 foil: (a) directly observed; (b) calculated.

TABLE I The influence of O_2 content and heat treatment conditions (temperature, T_h, and time t_h) upon the Nb_3Sn critical current value, I_c

Sample number	O_2 content (wt%)	Heat treatment		I_c (A)	Sample supplier
		T_h (° C)	t_h (min)		
13048	0.03–0.08	920	11	300	Kablo
05058	0.03–0.08	870	11	250–350	Kablo
1	0.32–0.34	750	120	600–700	AUICI
2	0.32–0.34	850	30	600	AUICI
3	0.32–0.34	900	20	700–800	AUICI
4	0.32–0.34	900	30	800–1000	AUICI

size less than 0.1 μm. The existence of these ZrO_2 precipitates has also been confirmed by selective electron diffraction (SED) from a thin foil of the oxidized Nb–ZrO_2 substrate, Fig. 3a and b. The microdiffraction analysis has revealed that the ZrO_2 crystallites are of cubic modification. It is rather difficult to determine exactly the volume-fraction of ZrO_2 particles in the Nb–ZrO_2 substrates. The quantitative information concerning the surface densities of the ZrO_2-precipitates has been obtained by means of comparison analysis (using a Hitachi 720 Quantimet machine). This density was 3×10^6 part mm^{-2} and 1×10^6 part mm^{-2} for oxidized and non-oxidized substrates respectively.

The influence of heat-treatment parameters upon the critical current value of Nb_3Sn samples prepared from Nb–Zr as well as of Nb–ZrO_2 substrates is shown in Table I.

A typical dependence of critical current on the induction of the external magnetic field value for one of the better Nb_3Sn samples is plotted in Fig. 4. Curve a is for the Nb–Zr substrate and Curve b is for the Nb–ZrO_2 substrate. Mössbauer spectroscopy has revealed that the relative content of the Nb_3Sn-phase in the superconducting layer is directly proportional to the critical current value, and is independent of the heat-treatment conditions, with the other Nb–Sn phases being Nb_6Sn_5, $NbSn_2$ and/or unreacted Sn, Cu_3Ns and Cu_6Sn_5 respectively.

One of the most important properties, the extent of the a.c. losses, is illustrated in Fig. 5 for the Nb_3Sn samples of Fig. 4. As can be seen from this diagram, the a.c. losses are substantially lower for Nb_3Sn prepared on a Nb–ZrO_2 substrate.

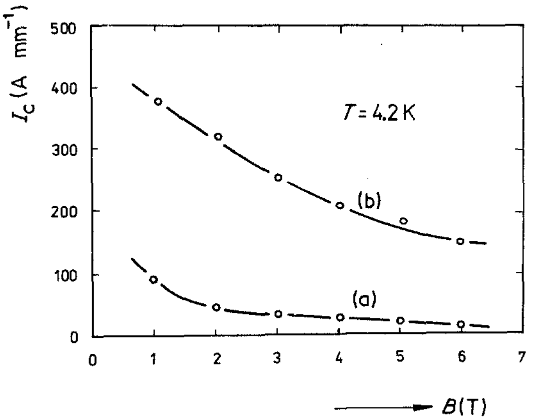

Figure 4 The critical current (I_c)–field (B) characteristics of Nb_3Sn tape prepared on: (a) Nb–Zr substrate (Sample number 13048, Table I); (b) Nb–ZrO_2 substrate (Sample number 3, Table I).

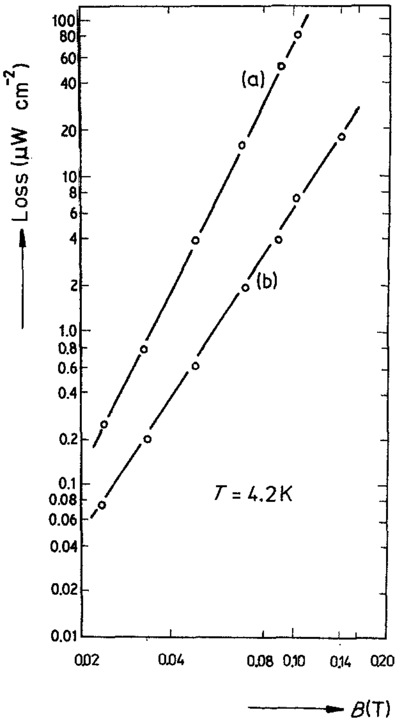

Figure 5 The a.c. loss characteristics of Nb_3Sn tape, from Fig. 4: (a) Nb–Zr substrate; (b) Nb–ZrO_2 substrate.

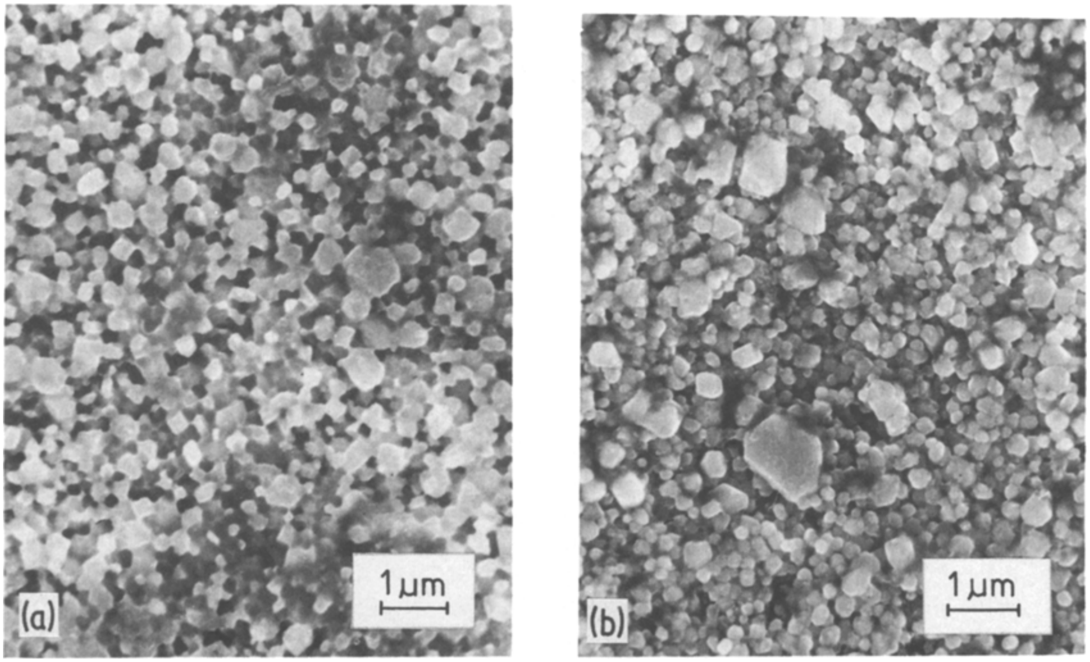

Figure 6 The surface and grain size of the Nb_3Sn layer: (a) Nb–Zr substrate; (b) Nb–ZrO_2 substrate. (The dark areas of Fig. 6a are probably the areas (or volumes) of other Nb–Sn phases which were etched-off when preparing samples for SEM.)

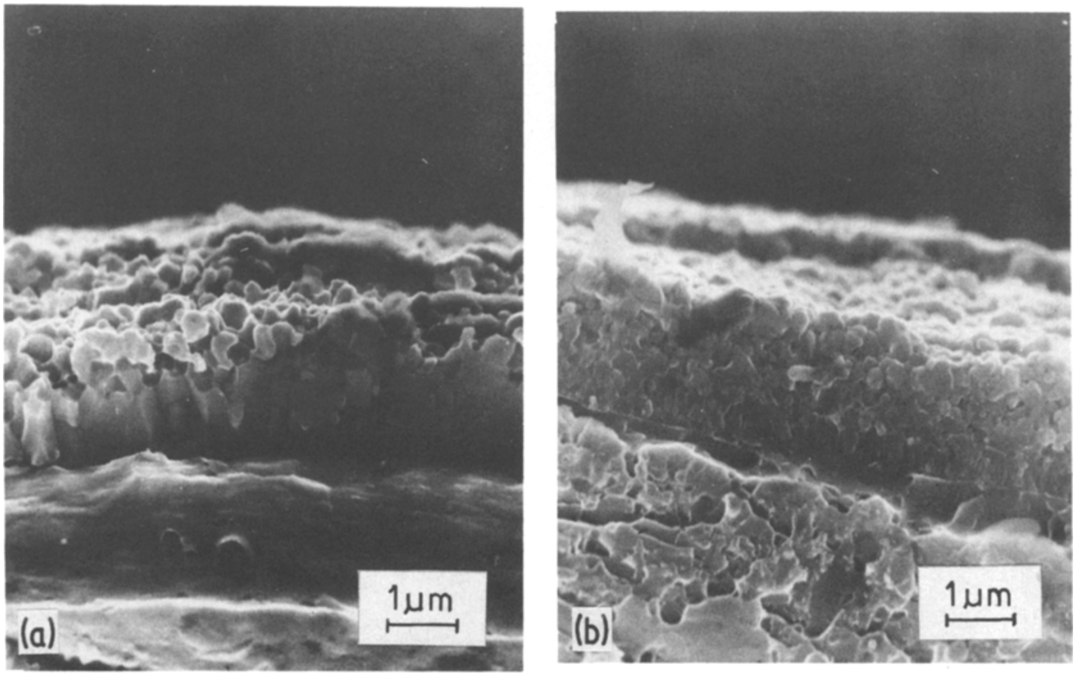

Figure 7 The cross-section and grain size of the Nb_3Sn layer: (a) Nb–Zr substrate; (b) Nb–ZrO_2 substrate.

TABLE II Dependence of surface micro-roughness, R_a, value upon the oxygen content in the Nb–Zr substrate

O_2 content (wt%)	R_a (μm)
0.03–0.08	0.7–0.8
0.15–0.20	0.5–0.6
0.32–0.34	0.4–0.5

The very good properties of Nb_3Sn tapes prepared on Nb–ZrO_2 substrates are determined by their microstructure, as is demonstrated in Figs 6 and 7. One may see that the surface Nb_3Sn grains are smaller when oxidized substrates are used, Fig. 6b, than those when non-oxidized are used, Fig. 6a. This effect may be seen more clearly within the cross-section of the Nb_3Sn layer. The length of the Nb_3Sn grains is identical to the total thickness of the Nb_3Sn layer when a non-oxidized substrate is used, Fig. 7a, but the presence of oxygen decreases the Nb_3Sn grain dimensions, Fig. 7b. As a result, more pinning centres from ZrO_2-precipitates and grain boundaries are created which, in turn, increases the critical current density, J_c, values, as it is already well-known.

The finer microstructures of the Nb_3Sn layers obtained for samples with oxygen additions have also influenced the surface roughness, R_a, values. The relationship between oxygen content in the Nb–Zr substrate and the measured R_a value may be seen from Table II. Prior to the, R_a, measurement the remaining Sn was etched-off in a Sn–25 wt% Cu bath. Thus, the addition of oxygen into the Nb–Zr substrate lowers the R_a value which, in turn, also lowers the a.c. losses, as has been shown in Fig. 5.

4. Conclusions

It has been confirmed that the presence of oxygen in the Nb–Zr substrate has a substantial effect upon the physical and mechanical properties of the Nb_3Sn tape superconductor produced from such an oxidized substrate. In this work the oxygen content in the Nb–ZrO_2 substrate was varied in the range 0.03 to 0.70 wt% and the following results have been obtained. For the substrate the specific resistance increased from 17 to 22 μΩ cm, the microhardness also increased from 685 to 2160 MPa, the specific elongation decreased from 5 to 3% and, the tensile strength increased from 590 to 1815 MPa. ZrO_2 precipitates in the microstructure of the Nb–ZrO_2 substrate were clearly identified using SEM and SED techniques and, together with increased grain boundary density, they are primarily responsible for the physical and mechanical changes described.

For Nb_3Sn prepared on an oxidized substrate it has been seen that there is an increase of about 100 to 200% in the critical current, I_c, value at a field of 5 T, compared with Nb_3Sn tape prepared on a non-oxidized Nb–Zr substrate. A.c. losses were decreased by one order of magnitude, being approximately 2 $\mu W\,cm^{-2}$ at 500 $A\,cm^{-1}$ and 4.2 K. The technique of Mössbauer spectroscopy was used and it was found that the critical current value is directly proportional to the relative content of the Nb_3Sn-phase in the superconducting layer. Microstructure analysis has revealed that the Nb_3Sn layer consists of fine equiaxed grains in case of Nb–ZrO_2 substrates but that the length of the grains is identical to the layer thickness in the case of the Nb–Zr substrates. The surface roughness, R_a, value is lower in case of the oxidized substrates which accounts to a large extent for their lower a.c. losses.

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Received 3 July 1980
and accepted 20 May 1981