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FIELD ION MICROSCOPY AND ATOM PROBE MICROANALYSIS OF Nb_3Sn WIRES

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Abstract - Nb_3Sn compound superconductor wires have been imaged in the field ion microscope for the first time. Comparison of the observed images with computer-simulated patterns indicates that tin atoms image more brightly than niobium in the ordered structure. Atom probe microanalysis of a grain boundary region showed enrichment in both tin and copper, the latter element being present as an impurity from the "Bronze Process" route used in fabrication. The results are important for understanding both the method of flux pinning and also the mechanism of crystal growth of the material.

1 - INTRODUCTION

Nb_3Sn composite wires are used extensively in superconducting applications. Fabrication is by a method called the "Bronze Process". This involves the insertion of niobium rods into holes drilled in a bronze block. This composite is then swaged and drawn, rebundled and further reduced to a final filament diameter of 2 to 5 μm , the final wire having an overall diameter of about 1mm and containing around 6000 individual filaments. This is then formed into its final shape and partially reacted, at 700°C for 2 to 3 days, to produce Nb_3Sn by solid state diffusion.

Recent work by Suenaga et al. [1] and Taftø et al. [2] has indicated that the grain boundary regions of Nb_3Sn wires contain amounts of copper significantly above that in the grain interior. The level of tin is also suggested to be higher in the region of the boundaries. Both these results, if confirmed, would have implications for the mechanism of flux pinning, and also for the mechanism of growth of the material. This paper reports a first investigation of Nb_3Sn in the FIM and subsequently in the time of flight atom probe with the objective of clarifying the composition at and near grain boundaries.

2 - EXPERIMENTAL PROCEDURE

In the production of Nb_3Sn for its usual applications, the wire is not fully reacted, so as to leave a central core of niobium for strength and stabilisation. For this investigation, however, fully reacted wire was required otherwise only the central core of niobium would have imaged. To achieve full reaction, times of around 28 days at 700°C were required. The production of tips by standard FIM preparation techniques [3] proved to be impossible for these composite wires. The technique developed was to mount a 1cm length of wire in a nickel tube, and to dissolve away some of the matrix using dilute nitric acid. Then a 90%/10% HNO_3/HF chemical polish was used, in conjunction with a micropolishing technique, so that only one of the filaments was left standing out from the rest. The very fine diameter of the wires meant that the end form of the protruding filament was difficult to resolve optically, so TEM was used to assess the quality of the tips. Polishing of these ultra fine wires was very difficult, and only a limited proportion of specimens imaged. However, the specimens that imaged successfully began to appear at around 1-3kV. The polishing conditions were such that regions

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further back down the tip were thinned, often causing premature fracturing, although the specimens would usually still image again at a higher voltage.

The new Oxford atom probe [4,5] (VG Scientific FIM100) was used for the atom probe work. This was because of its superior mass resolution (FWHM 1/2000), compared to the older instrument. The greater resolution was needed so that the niobium peak at $m/n=31.0$ did not obscure low concentrations of copper (if present) at $m/n=31.5$.

3- FIELD ION MICROSCOPY AND COMPUTER SIMULATION OF IMAGES

Field ion micrographs were recorded with neon imaging gas at a pressure of about 10^{-5} torr, 50K tip temperature and at a voltage of about 13kV. A typical image is shown in fig.1a.

The texture of Nb_3Sn wires produced by the "Bronze Process" is known to be strongly $\langle 110 \rangle$ [6], so the central pole on the images was provisionally identified as $\langle 110 \rangle$. The images show a regularity of rings and also signs of alternately bright and darker rings, both of which are indications of an ordered phase. Striking features of the images are the parallel rows of atoms lying transverse to the zone lines which radiate away from the central pole.

The structure of Nb_3Sn is classified as being of the Cr_3Si type. Interpretation of FIM images from such a complex structure is not straightforward, and computer simulations were required to help in the indexing. Simulations were carried out on a Sirius computer using a shell model [7]. Patterns were generated with only tin atoms imaging, fig.2, or with both species imaging, fig.3. (In each case only a quadrant of the simulated image is shown, with the $\langle 100 \rangle$ pole located at the bottom left, and $\langle 101 \rangle$ and $\langle 011 \rangle$ planes at the top left and bottom right respectively). The best match with the FIM micrographs was obtained for both species imaging, but with the tin atoms brighter than the niobium atoms, fig.4. The simulations show that the most prominent rows of tin atoms lie between the $\langle 110 \rangle$ and $\langle 211 \rangle$ poles so the indexing of fig.1b is done in accordance with this assumption.

4 - MICROANALYSIS RESULTS

The atom probe analysis of the material was done at 50K and 3.10^{-11} torr with a pulse fraction of 20%. Analysis of the bulk material gave at most 1 copper ion in 1000, fig.5, the overall stoichiometry corresponding to 78.4% niobium ($\pm 3.1\%$), and 21.6% tin ($\pm 1.6\%$). Some hydrogen and oxygen ions were also recorded, but it is believed that these were artifacts of the technique rather than being genuine features of the specimen composition. Only one grain boundary region was found and analysed, fig.6. The composition it gave was 7% copper ($\pm 2\%$), 65% niobium ($\pm 6\%$) and 28% tin ($\pm 4\%$) (all results are to one standard deviation). In the matrix close to the boundary, the copper level decreased to zero leaving 81% niobium ($\pm 6\%$) and 19% tin ($\pm 3\%$). The anomalously low value of tin concentration that is obtained from the matrix is probably due to the different evaporation potentials of Nb and Sn. This suggests that the pulse fraction of 20% is still not high enough to prevent the D.C. standing voltage from removing some tin atoms in the intervals between the high voltage pulses. The relative differences in tin content between the matrix and the boundary are probably still significant, however.

5 - DISCUSSION AND CONCLUSIONS

The previous work carried out on grain boundaries in this material was by Auger spectroscopy and ALCHEMI (atom location by channelling enhanced microanalysis), and indicated approximately 25% and 1.2% copper respectively, preferentially at the grain boundaries. Bulk analysis [8] has shown that there is usually about 0.5% copper in the Nb_3Sn . If it is assumed that a grain boundary has a width of 2nm and the Nb_3Sn has an average grain size of about 100nm, then if all the copper is preferentially in the boundary about 6% atomic concentration should be found in this region. This compares very well with the results found from the present investigation. The work by Suenaga and Jansen [1] also indicates a 5% higher concentration of tin in the grain boundary region which also compares well with the results found in this investigation.

Grain boundaries have recently been recognised as effective flux pinning sites [8]. Copper segregation to boundaries can have two effects on this pinning. Firstly the copper can Zener pin the boundaries during reaction to help maintain a small grain size. Secondly by creating a local chemical inhomogeneity, it can increase the effectiveness of the boundary as a flux pinner (as also could a locally higher concentration of tin). Controlled use of such phenomena may prove to be of value in the further development of superconducting materials.

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(a)

(b)

Fig.1 (a) Neon field ion micrograph of a Nb₃Sn specimen containing a grain boundary (50K, 13kV).

(b) Crystallographic indexing of (a), showing location of grain boundary.

Fig. 2 Computer simulation of Nb₃Sn FIM image with only the tin atoms appearing.

Fig.3 Computer simulation of Nb₃Sn FIM image with both tin and niobium atoms appearing equally bright.

Fig. 4 Computer simulation of Nb₃Sn FIM image in which the tin atoms appear brighter than the niobium atoms.

Fig. 5 Atom probe mass spectrum of matrix region. (1000 ions).

Fig. 6a Atom probe mass spectrum of grain boundary region. (280 ions).

Fig. 6b Enlargement of fig.6a, showing resolution of copper isotopes.