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A transmission electron microscopy investigation of filamentary superconducting composites

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The microstructure of the Nb_3Sn grains in commercially produced superconducting filamentary composites has been studied using transmission electron microscopy. The mean grain size increased with annealing time and temperature while the degree of columnar growth decreased at higher temperatures. Correlation of grain size and superconducting properties showed that the maximum pinning force was obtained for a grain size of about 800 Å.

1. Introduction

The use of superconducting materials in the manufacture of laboratory solenoids, beam-handling magnets and plasma containment systems in fusion reactors enables high magnetic fields to be produced at great energy savings.

The superconducting materials in commercial use at present include the A 15 compounds such as Nb_3Sn, which is produced in both tape and wire form. In the wire form, the Nb_3Sn is divided into discrete filaments of $< 20\,\mu m$ diameter inside the wire in order to prevent flux-jumping and subsequent adiabatic instability of the superconductor during service. Owing to the brittle nature of Nb_3Sn, specialized fabrication techniques must be used in the manufacture of the filamentary wire since Nb_3Sn itself cannot be drawn down to the small filament diameters required. One method used to prepare the wires is to embed rods of niobium in a tin–bronze matrix and to swage down the composite, cut and re-bundle, and then drawn down the reassembled rod to wire containing niobium filaments of the required diameter. The composite wire is then heat-treated in the temperature range 600 to 800° C to allow diffusion of tin from the bronze into the niobium, and hence form Nb_3Sn by solid state reaction. A more detailed description of the fabrication of these composite wires is given in [1].

The critical current density which can be carried by a superconducting material and hence the maximum magnetic field it can produce, is a structure-sensitive property as it is affected by any micro-structural features in the material, such as grain boundaries and precipitates, which can act as flux-pinning centres.

Transmission electron microscopy investigations of Nb_3Sn tape [2, 3] and laboratory-produced multifilamentary ribbon [3] have been carried out, but no similar study on commercially produced filamentary composite wires has been reported. This paper gives the results of a detailed transmission electron microscopy investigation of the commercially produced filamentary composite wires and as such fills a gap in our knowledge of these materials. The microstructure has been determined as a function of time and temperature of heat-treatment and is correlated with the superconducting properties of the wires.

2. Experimental procedure

Nb_3Sn composite wires (approximately 1 mm diameter) containing 5143 filaments in a 7.2 at.% tin–bronze have been fabricated by Dr J.A. Lee and co-workers at AERE, Harwell, and used in the construction of working super-conducting magnets at the Rutherford Laboratory [4, 5]. Samples of the wires, which had been reacted for various times at 600, 750 and 780° C, were kindly supplied by these Laboratories. In order to determine fully the microstructure, thin foils for transmission electron microscopy were prepared from both transverse and longitudinal sections of the wires using an ion-beam thinning technique. Examination of the foils was carried out using a 100 kV electron microscope (Philips 301) and high-voltage electron microscopy (AEI EM 7).

3. Results and discussion

3.1. Examination of microstructure

In contrast to commercial tape, the Nb_3Sn filaments were found to be almost devoid of second phase particles. In addition, very few dislocations, or any other crystallographic defects, were observed within the Nb_3Sn grains. It is concluded that the linear defects previously reported by Hart *et al.* [2] were, as suggested by these workers, the result of the high oxygen or nitrogen contents. It is clear that the only microstructural features that could act as flux-pinning centres in the Nb_3Sn filaments are grain boundaries and consequently the following sections are concerned with grain morphology and size.

3.1.1. Grain morphology

Examination of an unreacted wire sample revealed that very small Nb_3Sn grains were already present in the periphery of the filaments (Fig. 1). These

Figure 1 High voltage electron micrograph (longitudinal section, of unreacted filament showing elongated Nb grains and small reacted Nb_3Sn layer (at top of micrograph).

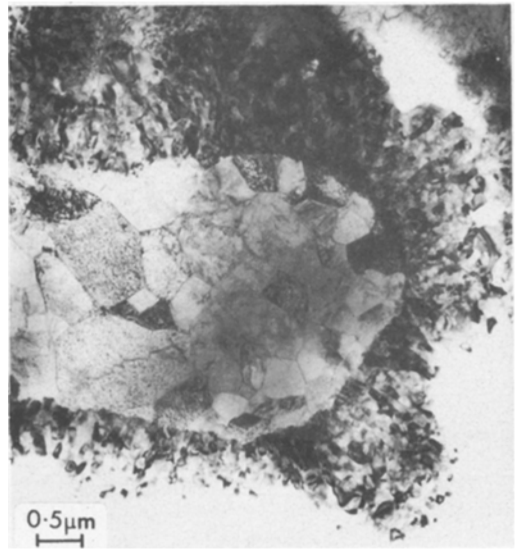

Figure 2 High-voltage electron micrograph (transverse section), reacted 450 h at 600° C showing well-defined interface between Nb_3Sn layer and unreacted Nb core.

grains must have been formed during the intermediate anneals which the wire received between drawing operations.

Comparison of transverse and longitudinal foils from reacted wires showed that the growth morphology of the Nb_3Sn grains was independent of the as-drawn grain structure of the original niobium filament, e.g. the Nb_3Sn grains were not elongated in the drawing direction. Furthermore, foils prepared from wires containing incompletely reacted filaments showed that the Nb_3Sn/Nb interface was very well defined (Fig. 2) and that there was no evidence of any preferential growth of Nb_3Sn along niobium grain boundaries.

All the filaments in the series of specimens heat-treated at 600° C were incompletely reacted and exhibited similar variations in Nb_3Sn grain morphology across the filament diameter. At the Nb_3Sn/bronze matrix interface the Nb_3Sn grains were equiaxed, but towards the centre of the filament, the grains became more columnar in form. There was a marked "radial" growth of columnar grains towards the unreacted niobium core (see, for example, Figs. 2 and 3). The columnar grains extended to the Nb/Nb_3Sn interface (Fig. 4) and in specimens reacted for the shorter times (up to 450 h) at 600° C, they constituted the greater part of the Nb_3Sn layer.

A transmission electron microscopy investigation of the grain morphology of Nb_3Sn pro-

Figure 3 Micrograph (longitudinal section), reacted 160 h at 750° C showing radial growth of columnar grains. Columnar nature of grains less marked near Nb core.

Figure 4 Micrograph (longitudinal section), reacted 450 h at 600° C showing columnar growth extending to unreacted Nb core.

duced by the reaction of Cu–13 wt % Sn bronze within thin niobium cylinders, has been carried out by Shaw [6] using an etching and replication technique. Both Shaw [6] and Scanlan *et al.* [3] observed columnar grains in their respective laboratory systems.

Specimens heat-treated for the shorter times (up to 293 h) at 750° C were incompletely reacted and also showed a "radial" growth of columnar grains on transverse sections. However, the columnar nature of these grains was less marked (Fig. 3), especially at the Nb_3Sn/Nb interface where the grains appeared more equiaxed in character. A completely reacted specimen heat-treated for 2100 h at 750° C only contained some grains which were slightly columnar in appearance. The grains in the centre of the filament were small and equiaxed. All specimens heat-treated at 750° C contained large equiaxed grains at the Nb_3Sn/bronze matrix interface.

The trend towards a more equi-axed grain structure at higher reaction temperatures was confirmed by two specimens heat-treated 25 and 358h at 780° C and an over-aged specimen given a two-stage heat-treatment of 333 h at 780° C and 114 h at 900° C. The grain structure of the 780° C specimens was approximately equiaxed and that of the two-stage heat-treated specimen completely equi-axed.

3.1.2. Grain size

The Nb_3Sn grain size increased with heat-treatment time and temperature (Fig. 5). However, it was difficult to accurately quantify the grain size for two reasons. Firstly, a variation in grain size was observed within each filament. For example, the equiaxed grains at the Nb_3Sn/bronze interface were always larger than the grains in the bulk of the filament. Indeed, for wires heat-treated for long times at or above 750° C there was a general decrease in grain size towards the centre of the filament (Fig. 6). Secondly, there was the complication with specimens heat-treated at 600° C of the change in grain morphology across the filaments from equiaxed to columnar grains.

In spite of these inherent variations in grain morphology and size across the filaments it was considered acceptable to obtain an approximate measure of the grain size by determining the mean

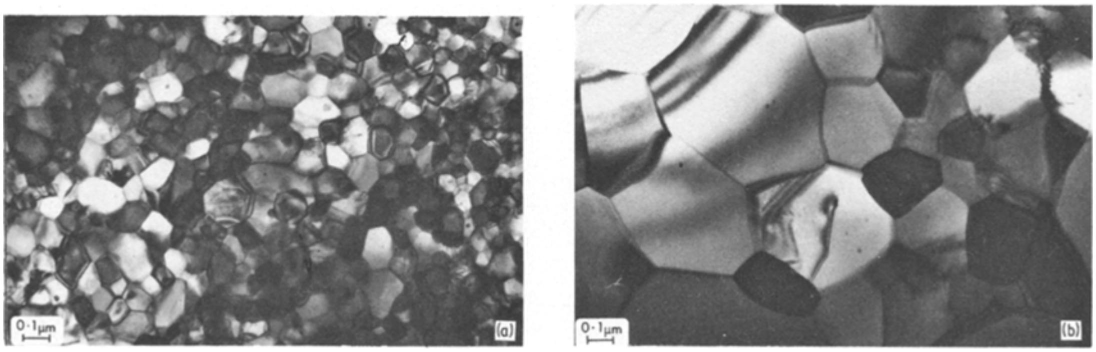

Figure 5 Micrographs (longitudinal sections), showing variation in equiaxed grain size with heat-treatment: (a) reacted 160 h at 750° C; (b) reacted 333 h at 780° C and 144 h at 900° C.

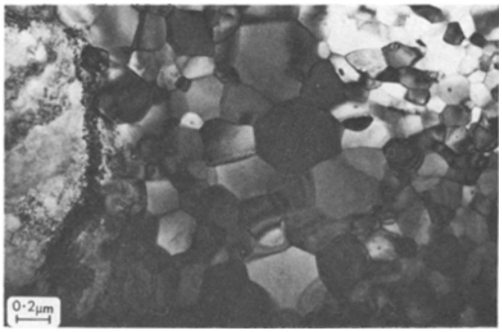

Figure 6 Micrograph (longitudinal section), reacted 2100 h at 750° C showing general decrease in grain size towards centre (right of micrograph), of filament.

TABLE I

Heat-treatment		Grain size (Å)		
Temperature (° C)	Time (h)	Mean	Max.	Min.
600	47	434	2000	127
600	218	610	2600	127
600	450	584	3600	298
600	1250	672	3000	336
750	20.5	911	3900	254
750	160	990	7300	381
750	293	1240	4500	508
750	2100	1710	8400	380
780	25	958	5000	336
780	358	1260	3800	635
780 } 900 }	333 } 144 }	3400	11700	1680

grain size by the linear intercept method. Typically 200 grains were counted and the results of the analysis are presented in Table I. Estimates of the maximum and minimum grain sizes are also given in this table. It can be seen that the maximum grain size, which was associated with the grains at the Nb_3Sn/bronze interface, was 3 to 7 times the mean grain size.

3.2. Relationship between superconducting properties and grain size

A measure of the efficiency of a superconducting material is given by the Lorentz or pinning force, $J_c \times H$, where H is the applied magnetic field and J_c is the critical current density which can be carried by the superconductor in that field.

Critical currents for wires at applied fields up to 10 T were measured at the Rutherford Laboratory [7]. To obtain critical current densities from these critical current values the cross-sectional area for current flow, i.e. the cross-sectional area of Nb_3Sn, had to be determined. The Nb_3Sn layer thickness has been measured by Madsen [8] using light metallography and the thickness values obtained from the electron micrographs in the present investigation were consistent with

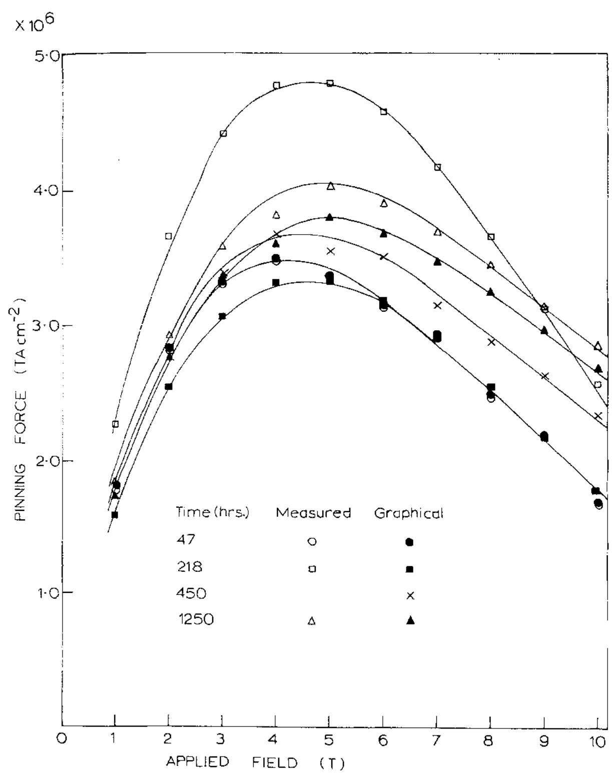

Figure 7 Plots of pinning force against applied field for specimens reacted at 600° C, showing well-defined maxima.

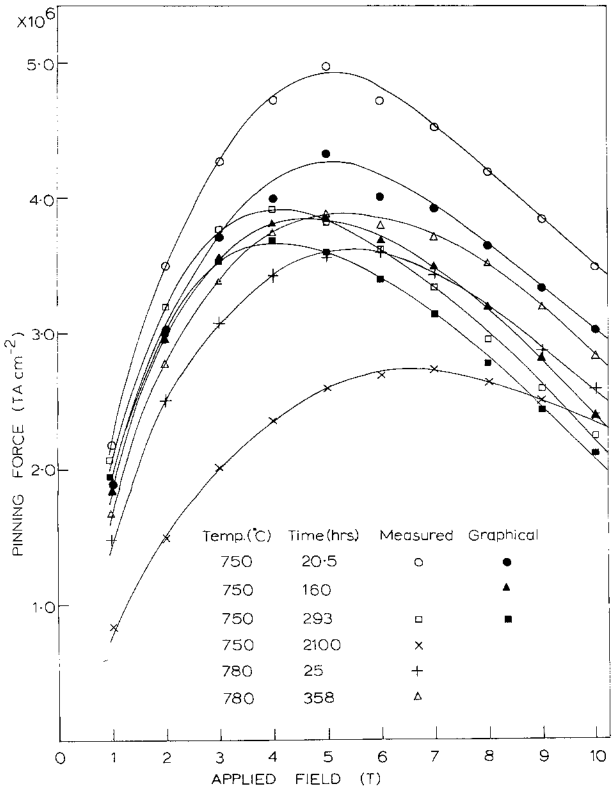

Figure 8 Plots of pinning force against applied field for specimens reacted at 750 and 780° C, showing well-defined maxima.

Madsen's data. Two values for the layer thickness were used to evaluate the critical current density, namely (1) the experimental value due to Madsen for a particular heat-treatment, and (2) the value given by the best fit line of the logarithm of the layer thickness against reaction time. Generally there was little difference between these two values with the exception of 218 h at 600° C where the measured value appears to be an underestimate.

The resulting curves of pinning force against field exhibit maxima in the range 4 to 7 T (Figs. 7 and 8). Plots of pinning force against field have previously been presented by Scanlan *et al.* [3] but their maxima were not so well defined. The general trend shown by both the present results and those due to Scanlan is for the maxima to be at higher fields the greater the grain size.

A plot of the maximum pinning force against reciprocal grain size is shown in Fig. 9. Also included in this figure are the data of previous workers [3, 6], which are in good agreement with the present results. The graph shows a maxi-

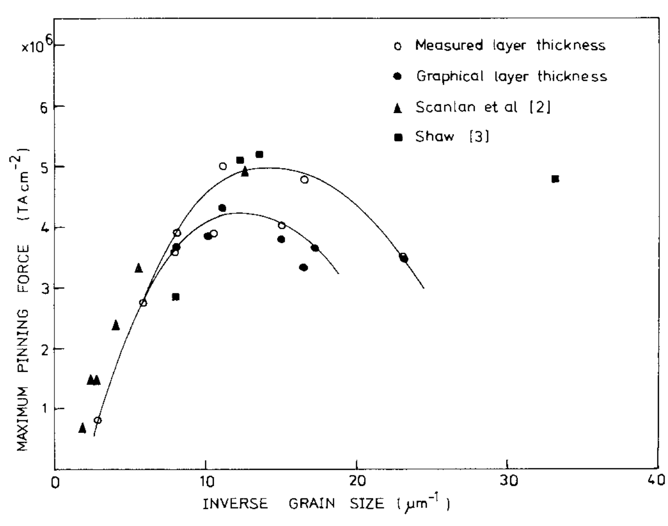

Figure 9 Plot of maximum pinning force against inverse grain size, showing a maximum at a grain size of approximately 800 Å.

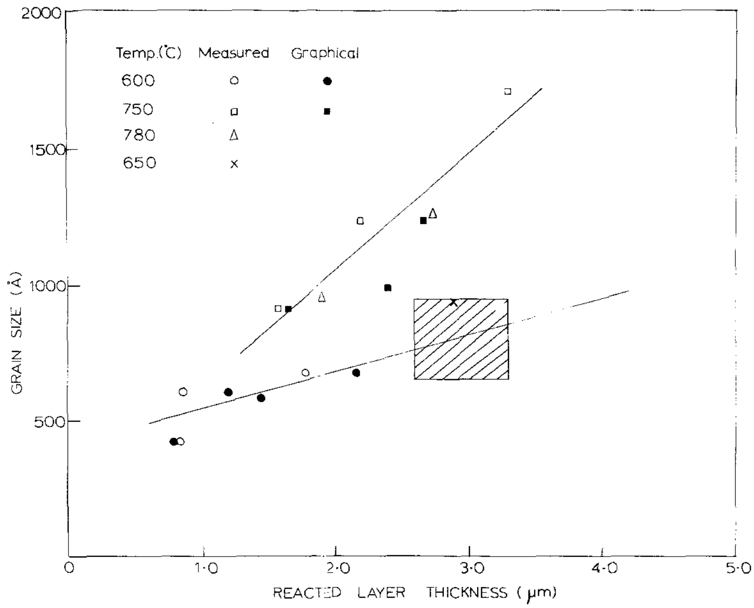

Figure 10 Plot of grain size against layer thickness for all specimens. Specimen within the shaded area should possess good superconducting properties.

mum value of the maximum pinning force for a mean grain size of approximately 800 Å. A similar maximum has been reported for Nb_3Sn tape [9].

Obviously it is advantageous to aim to achieve a grain size of approximately 800 Å, say in the range 650 to 950 Å, in the commercially produced filamentary composite wires. However, it must be remembered that there is the constraint that for a constant filament size, a large layer thickness of Nb_3Sn must be produced in order for the critical current of the wire to be high. The heat-treatments used in this investigation would appear not to be the optimum; reaction at 600° C produced grain sizes and layer thicknesses which are generally too small whereas the layer thickness is satisfactory at the longer times at 750° C but the grain size is too large (Fig. 10). The shaded area in Fig. 10 indicates the range of values of grain size and layer thickness which should give the highest values of critical current density.

A sample heat-treated for 1318 h at 650° C has been quoted as giving good critical current values [4]. The filaments in this sample were >95% reacted, corresponding to a layer thickness of ~ 2.9 μm, and the mean grain size was calculated to be 940 Å. These values of grain size and layer thickness lie within the shaded area in Fig. 10. The grain size was calculated from the results obtained at 600 and 750° C, assuming that the grain size varies exponentially with temperature. From this work, the activation energy for grain growth was calculated to be 266 kJ mol^{-1} while the activation energy for layer growth was 206 kJ mol^{-1}. These values agree well with the activation energy value of 215 to 225 kJ mol^{-1} calculated by Larbalestier *et al.* [4] for layer growth.

4. Conclusions

(1) A transmission electron microscopy investigation of the Nb_3Sn filaments in commercial superconducting filamentary composites has shown that:

(i) there are very few dislocations and second phase particles present;

(ii) columnar grains are formed at the lower annealing temperatures (e.g. 600° C) but the grains become more equiaxed at the higher annealing temperatures (750 and 780° C);

(iii) the mean grain size is greater the higher the annealing temperature. The activation energy for grain growth is 266 kJ mol^{-1}.

(2) Correlating the superconducting properties of the filaments with the grain size measurements revealed that the maximum pinning force is obtained for a grain size of about 800 Å. From the data the ranges of values for the layer thickness and grain size required for good superconducting characteristics of the composites were determined; a commercial composite with a good

critical current value was shown to have a layer thickness and grain size within the predicted ranges.

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