JOURNAL OF MATERIALS SCIENCE 21 (1986) 1914–1918

The microstructure of Nb_3Sn in modified jelly roll superconducting composites

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Transmission electron microscopy (TEM) has been used to characterize the microstructure of the Nb_3Sn layers developed during heat treatment of two superconducting wires, with and without 0.8 wt% titanium addition to the niobium, manufactured by the modified jelly roll (MJR) process. The composites in the as-received state are shown to contain pre-reacted layers formed during fabrication anneals, while heat treatments over the range 650 to 750° C yield a two-fold layer structure of columnar and equiaxed grains. Examples of both transverse and longitudinal TEM micrographs are given. The addition of 0.8 wt% titanium to the niobium before fabrication leads to coarsening of the equiaxed grains after identical reaction times. The results are discussed in terms of a recently proposed model for the development of microstructure in A15 multifilamentary composites.

1. Introduction

Modified jelly roll (MJR) superconducting composites [1] are currently gaining much interest as viable alternatives to the more conventional multifilamentary wires for commercial application. The fabrication technique is a variant of the well-known bronze process [2] and involves the wrapping of alternate sheets of bronze and expanded niobium mesh (which may be alloyed to incorporate third element additions) around a copper core rod to form the "jelly roll" configuration, the whole being inserted into a copper can and then extruded and drawn down to wire with overall reduction in area of typically 10^4. The result is an array of numerous interconnecting niobium filaments of uniform cross-section in a bronze matrix. Conventional composites, extruded and drawn from bronze billets inserted with niobium rods, frequently suffer from distortions of filament geometry, particularly near the periphery of the wire, and a radial variation in tin supply [3]. While this may not necessarily degrade overall superconducting properties, it introduces extra variables into an already complex system.

The advantages of the MJR process include (i) greater ease of production incorporating fewer intermediate steps, (ii) the versatility of the approach which allows for considerable flexibility in the design of filament dimensions, filament arrangement and bronze to niobium ratio, and (iii) the possibility (with the inclusion of tantalum diffusion barriers) of achieving greater homogeneity across the composite with minimal variations between filaments and their local environments [4]. Thus the MJR process should lead to more uniform and predictable superconducting properties. For example, after heat treatment of the present wires, the thickness of the Nb_3Sn layers developed as a result of tin diffusion largely independent of filament position in the composite, while critical current (J_c) values are comparable to those obtained with conventional multifilamentary composites [4]. However, the microstructural characterization of these materials is still in its early stages with consequent little understanding of the effects of the novel filament geometry, composition and stress state developed during heat treatment on the diffusion layer morphology. Furthermore, the premature and unavoidable formation of some Nb_3Sn during production annealing and its ultimate effect on the structure and properties of the wire has received only limited attention [5].

Addition of titanium in small quantity to the niobium (up to about 2 wt%) before fabrication is known to have a beneficial effect on J_c at high field whether the composites be single core, conventional multifilamentary or MJR [6, 7], though the effect on the layer growth kinetics and microstructure as reported in the literature is somewhat unclear and sometimes conflicting (see Section 4).

In this paper, we describe a TEM examination of two MJR composites supplied by Teledyne Wah Chang, Albany, Oregon, USA and investigate the effect on microstructure of 0.8 wt % titanium addition to the niobium.

2. Experimental details

The given specifications of the two composites investigated, designated M88L and M94-1, were as follows. The core and can material was copper and the bronze in both cases contained 13.8 wt % tin. Plain niobium mesh of aspect ratio 1 : 1.25 was used for M88L while that for M94-1 contained 0.8 wt % titanium and was of the same aspect ratio. Light microscopy of polished sections revealed 28 "jelly roll" wrappings in the case of M88L and 37 for M94-1. The overall

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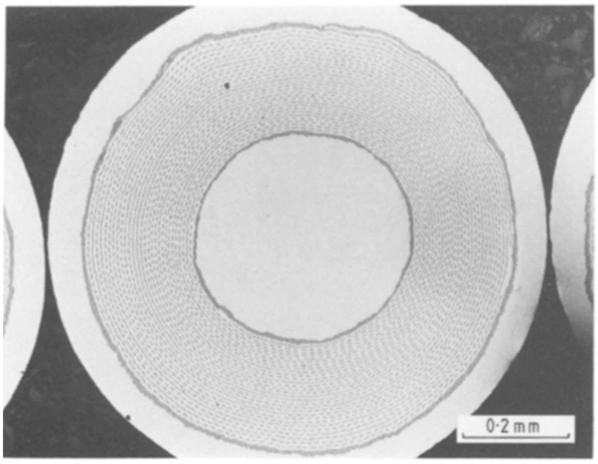

Figure 1 Light micrograph showing plain niobium composite (M88L) in cross-section before reaction.

bronze to niobium ratio was 3.17 : 1 in the former and 2.57 : 1 in the latter. Tantalum diffusion barriers, incorporated as tantalum sheets interleaved in the wrapping, separated the bronze/superconducting components from the core and outer can in each case. Both composites had undergone fabrication anneals for a total period of about 24 h, mainly at 450° C after initial large diameter reduction anneals at 550 and 500° C. The final diameter of the wires was approximately 0.93 mm. Fig. 1 illustrates the plain niobium composite (M88L) in cross-section. Short lengths of each wire were sealed in quartz tubes under reduced pressure of argon and then heated at constant temperatures in the range 650 to 750° C for 49 h. Some were also heated for periods of only a few minutes in order to observe the early stages of layer growth.

Preparation of TEM foils was based on the method developed for standard multifilamentary wires published elsewhere [8], and is similar to that described by Pande *et al.* for vanadium–gallium MJR composites [9]. Essentially, material for transverse sections is first electroplated with copper for ease of handling, then cut into discs which are subsequently metallographically polished from both sides in turn to a final thickness of between 35 and 50 μm. Samples for longitudinal sections need not be plated before polishing.

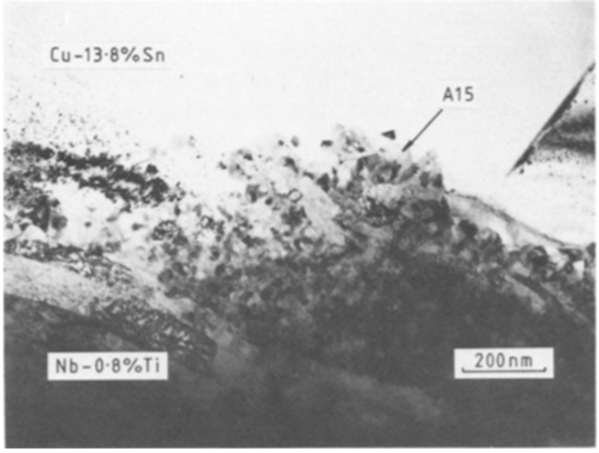

Figure 2 Longitudinal section of the titanium alloyed composite (M94-1) showing presence of "pre-reaction" layer.

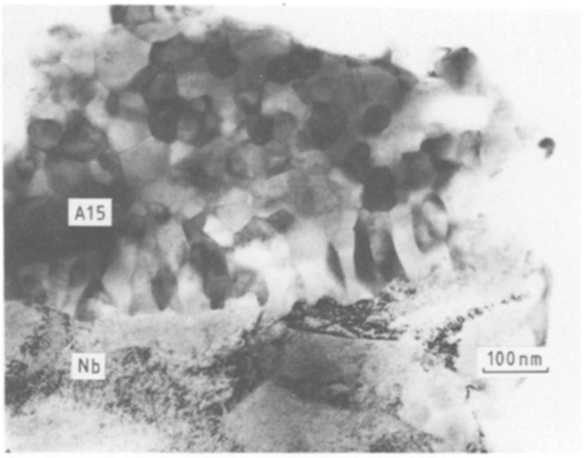

Figure 3 Longitudinal section of the plain niobium composite (M88L) after 10 min heat treatment at 700° C showing coarsened equiaxed grains arising from the "pre-reaction" layer, and columnar grains at the niobium–A15 interface.

The thin sections are placed in copper folding electron microscopy grids and ion thinned at an incident angle of 15°, reduced to about 7° for the final few hours. Use of a grid helps to hold the foil together as copper thins preferentially, and is particularly important for transverse sections where thinning tends to attack the join between the copper can and copper plate. Virtually all longitudinal foils prepared in this way yielded areas thin enough for TEM characterization. The success rate with transverse sections was lower with suitable areas of filament located only at the extreme edges of the foil: the likelihood of finding an entire single filament thin enough for TEM was quite low; consequently, for a comprehensive investigation, it was necessary to repeatedly re-thin a given foil between successive examinations. All micrographs were obtained with a Phillips EM400 transmission electron microscope operated at 100 kV.

3. Results

As with conventional multifilamentary composites [5], substantial A15 phase is already present in the MJR material as a result of premature reaction during fabrication anneals prior to the final heat treatment. Transmission electron micrographs indicate that the layer is highly irregular and may be up to 0.3 μm thick in places. It consists of a debris of fine grains 20 to 30 nm in diameter and often showing evidence of dislocations, which result from cycles of growth of Nb_3Sn and subsequent fracture during drawing. An example of as-received titanium alloyed wire (M94-1) is shown in Fig. 2.

After heat treatment at 700° C for 10 min, the layer thickness was still fairly irregular but had increased to a mean of about 0.6 μm, as measured from ten filaments, and in a very few places exceeded 0.9 μm. The majority of grains were equiaxed and of mean diameter about 50 nm and, in contrast to the "as-received" layer, defect free. In all cases in which a clear niobium–A15 interface was apparent, a single row of columnar grains existed at the growth front. An example for the plain niobium wire (M88L) is shown in Fig. 3. The columnar nature was often quite

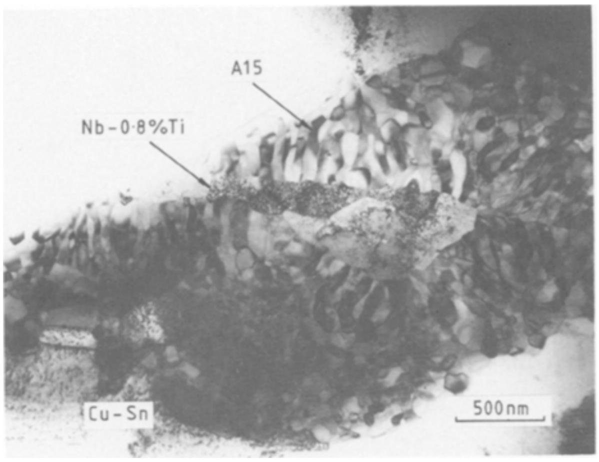

Figure 4 Composite M94-1 in transverse section after heat treatment for 49 h at 650° C. Both the niobium–A15 and A15–bronze interfaces are clearly shown.

marked, with axial ratio of grains ranging between 2 and 5 and a mean columnar length of about 0.12 μm. Moiré fringes were very frequently observed between adjacent overlapping columnar grains indicating low-angle boundaries.

Typical micrographs obtained for the longer heat treatments are presented in Figs. 4 to 7. Transverse sections for periods of 49 h at 650 and 750° C, respectively, are shown in Figs. 4 and 5. Here the pattern, familiar from studies on conventional multifilamentary material [8, 10], of a region of columnar morphology close to the growth front yielding to a more equiaxed state nearer the bronze–A15 interface, is again apparent, though in the present work the columnar grains seem to comprise the greater portion of the layer. The radial boundaries of such grains often have an unusually undulating character which contrast with the more normal straighter boundaries of the equiaxed grains. There was no obvious difference in the layer morphologies of the two composites for any given heat treatment. In Fig. 4 some residual niobium grains remain; these are of diameter about 0.5 μm and are highly defective as a consequence of the extreme area reduction during wire fabrication. Work is in progress to investigate the orientation relationships between the A15 phase and the niobium and also between individual A15 grains. A noticeable feature of the material heated for 49 h at 750° C (Fig. 5), in which reaction has proceeded to completion, is the preservation of a vestige of the two impinging growth fronts in the form of an uninterrupted grain-boundary line along the centre of the filament. This is a clear indication of the uniformity of growth rate of the columnar grains.

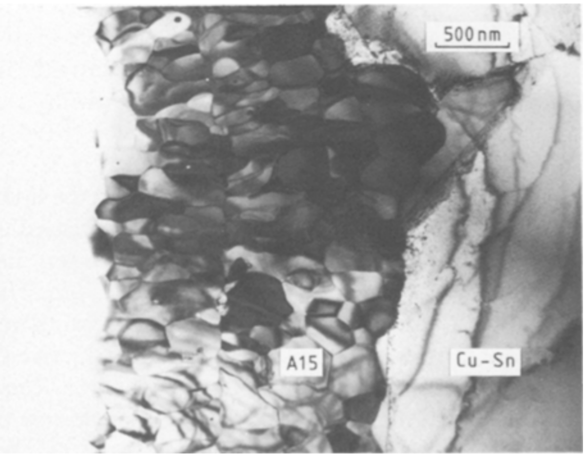

Figure 5 Transverse section of composite M94-1 after heat treatment for 49 h at 750° C, showing almost complete reaction.

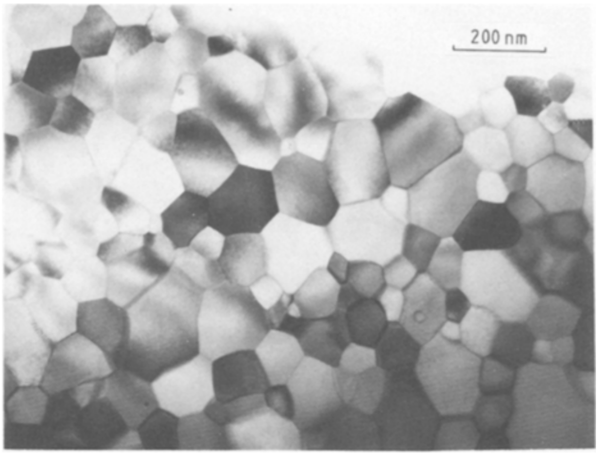

Figure 6 Longitudinal section of composite M94-1 after heat treatment at 700° C for 49 h showing equiaxed grains.

Micrographs of longitudinal sections are shown in Figs. 6 and 7. Longitudinal sections were used as the basis for determinations of mean equiaxed grain sizes by the linear intercept method; it was generally found impractical to use micrographs of transverse sections for this purpose. The results are listed for the two composites in Table I where each figure represents a mean diameter of between 800 and 1000 grains taken from at least ten micrographs. In all cases, grain sizes were larger for the titanium additive wire. Equiaxed grains closest to the ends of the columnar grains tended to be of similar width to the latter, and a slight increase in grain diameter across the equiaxed portion of the layer toward the bronze–A15 interface was noticeable. Measurements of the columnar grain widths, made on transverse sections, immediately adjacent to the niobium–A15 interface showed no clear systematic difference between the two composites, but this may have been partly due to the comparatively small number of grains available.

4. Discussion

The question of the generation of the characteristic microstructure found in reacted multifilamentary composites has been addressed elsewhere [8, 11], where the stress induced by the volume increase as the diffusion layer grows was considered to play the dominant role in microstructure evolution. Cave *et al.*

TABLE I Mean grain size measurements on equiaxed portion of layer

Heat treatment		Mean grain size (nm)	
Temperature (° C)	Time (h)	M88L	M94-1
650	49	64	82
700	49	79	96
750	49	132	149

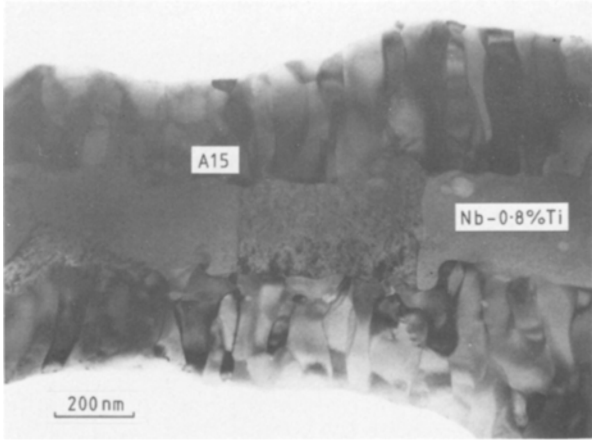

Figure 7 Composite M94-1 after heat treatment at 650° C for 49 h, in longitudinal section showing columnar grains at the niobium–A15 interface.

[12] have developed a model to predict the stresses produced in growing layers surrounding filaments of various geometries, taking as a starting point the 37% volume expansion of stoichiometric Nb$_3$Sn over the original niobium. Assuming that formation of columnar grains is the natural mode of growth of Nb$_3$Sn at the niobium surface, they estimate a maximum allowable columnar shell width before the material degrades to equiaxed grains. For filaments of circular cross-section, this is of the order of 0.3 to 0.6 μm, given an initial filament radius of 2.5 μm, which is in good agreement with experimental data [11]. These present MJR materials are of interest because of their somewhat elliptical filament geometry compared to the nominally circular cross-section of filaments in conventional multifilamentary composites. The consequent difference in stress-state during reaction would be expected to lead to a perceivable difference in the diffusion layer microstructure. The observations presented in this paper suggest that columnar growth is more prominent in the MJR composites than in the conventional material, at least at the flatter portions of the filaments. This is in accordance with the model of Cave *et al.* where the maximum permissable width of the columnar shell is shown to vary approximately as the local radius of curvature of the niobium–A15 interface. However, it should also be borne in mind that the differing geometries and arrangements of filaments in the two types of design may result in different diffusion characteristics of tin, and it has been suggested that local tin availability is also a factor controlling microstructure [4, 13].

A further effect to be considered is that of the pre-formed fabrication layer. Subsequent heat treatment will result in competition between growth of the existing grains and the nucleation of new ones at the niobium interface. The present study has shown that after only 10 min heat treatment, the pre-formed grains have coarsened appreciably and form the bulk of the layer, the newly nucleated columnar grains accounting for only about 15% of the overall layer thickness at this stage. More prolonged heat treatment results in rapid growth of the columnar region leading to the final mature layer structure described. Nevertheless, part of the equiaxed portion of the mature layer must have had its origin in coarsened preformed grains. The above result is important in another respect; Nb$_3$Sn forming at the niobium–A15 interface appears always to adopt the columnar morphology, even at the earliest stage of layer growth, when tin concentration in the vicinity of the growth front is presumably at its highest (see Fig. 3). This conflicts with the proposal that a high matrix concentration of tin leads to the nucleation of a layer consisting predominatly of small equiaxed grains [13].

The present investigation into the effect of 0.8 wt % titanium addition to the niobium clearly indicates a coarsening of A15 grains after constant reaction times and temperatures, even given the difficulty of interpreting grain size measurements made on planar sections where the layer structure is duplex. Furthermore, grain growth is greater between 700 and 750° C than between 650 and 700° C. These observations are consistent with those of Suenaga *et al.* [14] and Johnson-Walls *et al.* [15] on internal tin route and conventional multifilamentary composites, respectively. Tachikawa *et al.* [16] and Takeuchi *et al.* [7] obtained grain refinement (as measured from scanning electron micrographs) for core titanium concentrations of 1 or 2 at % in single core wire and tape, which they state was most noticeable after high temperature anneals (800° C). Improvement in J_c at high field (> 12 T) for titanium additions in multifilamentary materials is thought to be due to an increase in the normal state resistivity. At fields less than about 12 T, the grain coarsening observed in the present study would be expected to reduce J_c below that for pure niobium composites.

5. Conclusions

Sustantial pre-reaction was found in both MJR composites in the as-received state. Heat treatment for only a few minutes resulted in coarsening of these grains together with the growth of a single row of columnar grains at the niobium–A15 interface. Prolonged heat treatment yielded the characteristic two-fold layer structure of columnar grains near the niobium and of equiaxed grains near the bronze, part of the latter portion being considered to have had its origin in the pre-formed grains. The radical dimensions of the columnar grains are consistent with the microstructural model of Cave *et al.* The addition of 0.8 wt % titanium to the niobium before fabrication leads to a coarsening of the equiaxed portion of the layer for constant reaction times and temperatures which may cause a degradation in J_c at fields below about 12 T, in common with similar results for conventional composites.

Acknowledgements

The authors are grateful for many helpful discussions with Dr J. R. Cave and Miss J. L. Robertson, who also provided the light micrograph in Fig. 1. We also thank Professor D. Hull for provision of research facilities and SERC for financial support.

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Received 1 May
and accepted 12 June 1985