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A transmission electron microscopy study of bronze-processed Nb_3Sn and $(Nb, Ta)_3Sn$ multifilamentary superconducting wire

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The morphology, grain size and composition of A15 diffusion layers produced on heat-treating Nb–bronze and (Nb, Ta)–bronze multifilamentary composites over the temperature range 650 to 800° C have been investigated and compared using transmission electron microscopy with energy dispersive spectroscopy. A characteristic two-fold layer structure of columnar and equiaxed grains has been confirmed in both cases at all temperatures while tantulum was shown to be incorporated into the A15 phase and to retard grain growth. A model for evolution of the microstructure is proposed and discussed.

1. Introduction

It is widely known that the microstructure of a superconducting material has an influence on the attainable critical current density. Several studies have been carried out on A15 niobium–tin (Nb_3Sn) superconductors to identify those microstructural features that behave as flux pinning centres and hence determine the critical current [1–4]. Generally, grain boundaries have been found to have the major flux pinning effect and, in the case of superconductors fabricated by the so-called Bronze Process [5, 6] in which tin diffusing from a bronze matrix reacts with embedded niobium filaments to form encircling layers of Nb_3Sn, attention has been focused on determining the annealing temperature and time dependence of grain size and morphology in the diffusion layers [7–9]. Examination of the grain structure by scanning electron microscopy is usually unsatisfactory in that no information is obtained concerning defects and often only the largest grains are revealed with any clarity, thus making accurate assessment of grain size difficult. Transmission electron microscopy (TEM) studies, until fairly recently, have been hampered by problems of foil preparation; the differential electropolishing or chemical thinning rates of the three components – bronze, niobium and the A15 phase – making it almost impossible to obtain acceptable foils. The use of ion bombardment techniques have, however, considerably improved the success rate and, with care, foils of both single and multifilamentary wires may be prepared in which large areas of all components are penetrable by a 100 kV electron beam [10].

The inclusion of small quantities of other elements alloyed with the bronze or niobium components before reaction is known to influence both the layer growth kinetics and the grain size and morphology within the layer (see, for example, [11]). Of these additives, tantalum is potentially of commercial interest since it is completely miscible with niobium without adversely affecting ductility and hence drawability during fabrication, and small additions to niobium filaments have been shown to increase the critical current density at high fields [12, 13]. Tantalum reduces the electron mean-free path and hence the superconducting coherence

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length, and for small additions can significantly increase the upper critical field without seriously depressing the critical temperature. If the grain morphology and flux pinning force were unchanged, an overall increase in critical current density at all fields might be expected. In practice, tantalum additions also modify the layer structure and growth kinetics and this can lead to a reduction of the critical current density at lower fields.

In this paper, the grain structure and composition of the A15 diffusion layer in two types of commercial bronze process multifilamentary wire, one a plain niobium–bronze and the other containing 7.5 wt % (4.0 at %) tantalum addition to the niobium, are investigated using TEM, and compared as a function of annealing temperature and time. The results are discussed and a model for the evolution of the A15 microstructure is proposed.

2. Experimental methods

The wire containing plain niobium was provided by Imperial Metal Industries and consisted of approximately 3000 niobium filaments of diameter 5 μm embedded in a 13.5 wt % (7.7 at %) tin–bronze matrix of overall diameter 0.6 mm. The sample with tantalum alloyed to the niobium was of overall diameter 0.4 mm and contained 3721 filaments of diameter 3.85 μm in a bronze matrix of the same composition as before; this wire was supplied by Vacuumschmelze GmbH, Hanau. Samples of both wires were sealed in quartz tubes under argon and annealed for periods of 49 and 100 h at several constant temperatures in the range 650 to 800° C. The A15 diffusion layers so formed had thicknesses in the range 0.55 to 1.65 μm as determined by scanning electron microscopy (SEM) of polished cross-sections.

Foils for transmission electron microscopy were prepared as follows. Longitudinal sections of reacted wire were mechanically ground from both sides in turn to a final thickness of about 30 μm and then further thinned by ion-milling using an accelerating potential of 5 kV and an initial beam incidence angle of 15°. When small holes began to appear in the foils, generally first in the bronze areas, the angle was reduced to about 8° and the thinning allowed to continue for a further 2 to 4 h. Transverse sections of wire were also prepared after having initially electroplated the wire with copper to a thickness of about 3 to 4 mm to facilitiate handling. The plated wire was cut into discs and thinned as before with the exception that a chemical etch, a mixture of 70% nitric acid and 30% hydrofluoric acid, prior to the ion-milling stage proved useful in preferentially pre-thinning the filaments. Generally the transverse sections proved less successful with many filaments tending to detach and be lost during the ion thinning, and the subsequent thin areas of those that remained being too limited in extent for accurate mean grain size determination.

The foils were examined in a Philips EM400 transmission electron microscope equipped with tilt and energy dispersive analysis facilities and operated at an accelerating voltage of either 100 or 120 kV. Mean grain sizes were determined by the linear intercept method from at least ten representative micrographs per data point averaging over between 1000 and 2000 grains. Chemical analyses were carried out using an electron probe diameter of about 60 nm to give a statistically acceptable count rate (over 500 cps), and relative concentrations were calculated by comparison with standard profiles.

3. Results

Samples of both types of wire prepared and thinned in the as-received state showed the presence of very irregular A15 layers of fine grains 20 to 40 nm diameter formed during the intermediate anneals which are required in the fabrication process. An example from the tantalum alloyed wire is shown in Fig. 1. Energy dispersive analysis of these areas gave a tin

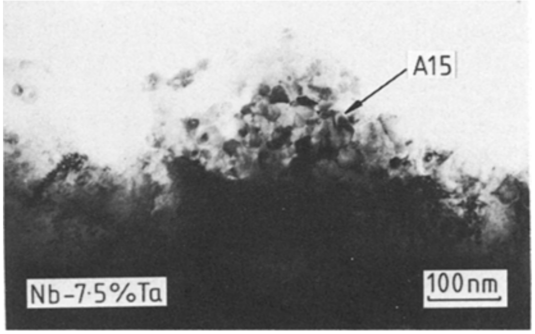

Figure 1 Longitudinal section of unreacted (as-received) niobium–7.5 wt % tantalum multifilamentary wire showing the presence of A15 grains.

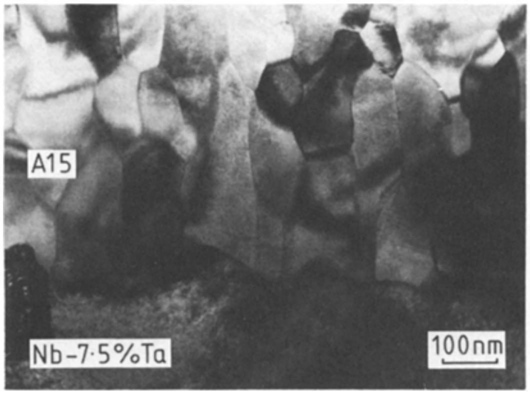

Figure 2 Longitudinal section of niobium–7.5 wt % tantalum multifilamentary wire annealed for 49 h at 700° C showing columnar grains at the A15 layer growth front.

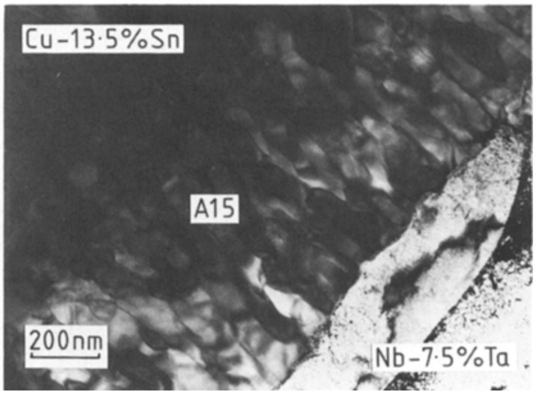

Figure 3 Longitudinal section of niobium–7.5 wt % tantalum multifilamentary wire annealed for 100 h at 650° C illustrating the typical morphology of the diffusion layer.

concentration in the range 17 to 20 at %, i.e. less than stoichiometric, for both types of wire and, in the case of the tantalum additive, a tantalum concentration roughly the same as in the bulk filaments.

None of the filaments in any one of the heat-treated samples had reacted to completion, i.e. there was always some residual niobium or niobium–tantalum forming a sharp and unconvoluted boundary with the diffusion layer. Both kinds of wire exhibited a diffusion layer grain morphology similar to that previously observed by several other workers for plain niobium filaments [7–9]. Thus grains at or close to the niobium or niobium–tantalum interface were invariably of the columnar type (see Fig. 2), with the longer axes radiating away from the interface, and an axial ratio generally within the range 2 to 8. Further out in the bulk of the layer, the grains tended to become more equiaxed in shape and of diameter comparable to or slightly larger than the shorter dimension of the columnar grains. This transformation is illustrated in Fig. 3 which also shows the interfaces of the A15 diffusion layer with both bronze and niobium–tantalum components. The volume fractions of the two types of grain were difficult to estimate in the absence of good cross-sectional foils since the plane of the longitudinal section seldom coincided exactly with the filament axes and hence the columnar nature of some grains was not always apparent. Nevertheless, samples annealed at lower temperatures appeared to contain a greater proportion of columnar grains and, in the case of wires heated for 100 h at 650° C, these possibly accounted for up to one-half of the layer. A few anomalously large grains, often occurring in isolation, with diameters several times that of the bulk average were generally observed at the bronze interface, but as these represented a neglibible percentage of the total number of grains in the layer, they were not included in the grain size measurements. Schelb [8] has suggested that such grains arise from the abnormal growth of either the fine grains formed during the drawing process anneals or certain favourably orientated grains with high grain-boundary energies. Very few dislocations were observed in these studies, most of the grains apparently being defect-free within the limits of resolution.

The structural features of the diffusion layers in the two types of wire were virtually identical, as far as could be discerned from TEM examination, with the important exception that the tantalum additive wire generally yielded somewhat smaller mean grain diameters for a given anneal. Grain size measurements are listed in Table I and displayed graphically in Fig. 4. Micrographs illustrating the difference in grain size after 100 h at 800° C are shown in Fig. 5. Some considerable variation in grain diameter was observed within any one heat-treated sample, most noticeably from filament to filament, ranging from roughly 3.5 times the mean for the largest equiaxed grains present to about 0.3 times for the smallest, and may relate to variations in the supply of tin according to filament position in much the same way as layer thickness has been observed to vary [14].

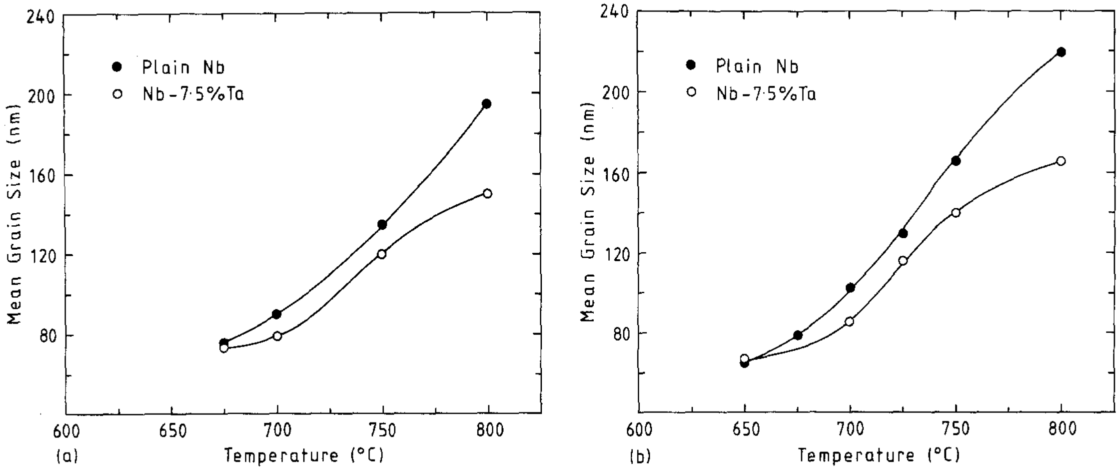

Figure 4 Relationship between mean equiaxed grain size and annealing temperature for the two filament compositions investigated: (a) after 49 h; (b) after 100 h.

Energy dispersive analysis indicated a steadily decreasing tin concentration across the layer towards the niobium interface, starting from a value close to stoichiometry in grains immediately adjacent to the bronze interface. Little variation was observed between different heat treatments and generally the fall in tin concentration across the whole layer amounted to about 3 to 4 at %. A similar variation in tin content was observed for the tantalum alloyed wire, together with an increase of 1 to 2 at % in tantalum concentration across the layer towards the niobium interface, which was otherwise comparable to the concentration in the unreacted filaments.

4. Discussion

The general observations of grain morphology confirm the findings of other workers. Thus West and Rawlings [7] reported that after annealing at 600° C columnar grains accounted for most of the layer but that at higher temperatures (750, 780° C) the structure became progressively more equiaxed. Schelb [8] studied a wider range of annealing temperatures and times and found a two-fold structure in all cases together with anomalously large equiaxed grains at the bronze interface. Wu *et al.* [9] and Okuda *et al.* [15] have reported similar observations, so that the division of the layer into regions of columnar and equiaxed grains is a feature now fairly well established. Various mechanisms have been proposed to account for this pattern. Okuda *et al.* have suggested that the tin concentration at the growth front is responsible for the type of morphology adopted, arguing that a low tin concentration favours radial growth of existing grains rather than the nucleation of new ones. They maintain that at the higher temperatures, when tin depletion is more rapid, the

TABLE I Annealing conditions and grain size measurements

Annealing conditions		Mean grain size (nm)	
Temperature (° C)	Time (h)	Plain niobium	Niobium–7.5 wt % tantalum
650	100	65	67
675	49	77	74
675	100	79	–
700	49	91	79
700	100	103	85
725	49	–	–
725	100	129	116
750	49	135	121
750	100	166	141
800	49	195	150
800	100	219	165

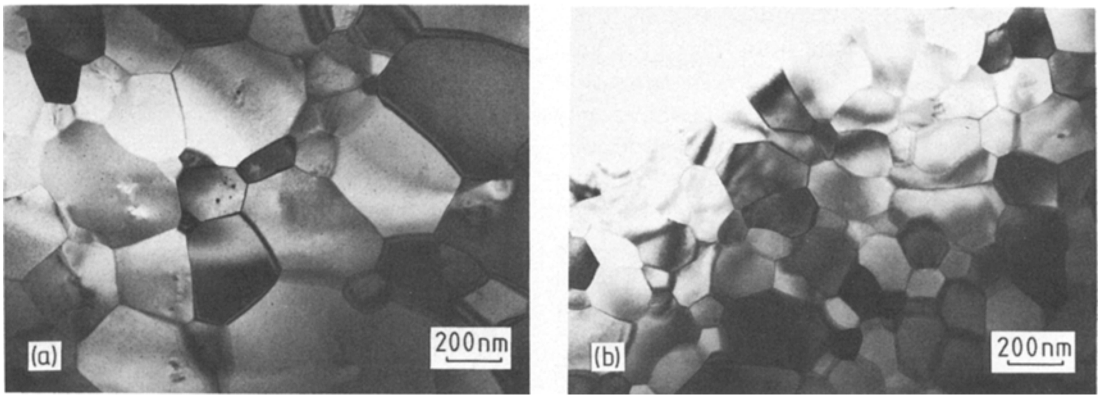

Figure 5 Comparison of grain size in the equiaxed region of the layer for samples annealed for 100 h at 800° C: (a) plain niobium filaments; (b) niobium–7.5 wt % tantalum filaments.

columnar morphology should predominate. This, however, does not seem to be the case in practice and Okuda *et al.* suggest that the reason may lie in the temperature dependence of the relative diffusivities of tin and niobium in the layer.

An alternative explanation proposed by Wu *et al.* [9] and Cave and Weir [16], and developed by Pugh *et al.* [14], is that as growth of the A15 layer proceeds, a considerable stress builds up during annealing as a result of the 37% volume expansion of Nb_3Sn over the original niobium. This stress promotes the successive breakdown of those portions of the columnar grains furthest from the growth front, probably via the action of accumulated dislocations, to form the fine-grained portion of the layer. While the present observations have shown both columnar and equiaxed grains to be remarkably free from dislocation structures, this is not entirely incompatible with the above argument since dislocations generated under such stresses might be expected to be of high instability and activity and to lead to almost spontaneous breakdown of the columnar grains. Moreover, Moiré fringes were frequently observed at the boundaries of overlapping adjacent columnar and equiaxed grains indicating low angle relationships and giving support to this idea. Cave and Weir have shown, from inductive and resistive T_c transition measurements, that the volume increase is accommodated entirely as an area expansion, i.e. there is negligible change in the length of a sample on annealing. Their measurements indicate that the layers grow without cracking, and this is substantiated by the present electron microscope observations; thus the stress must be relieved by internal modification of the microstructure. In light of the current work, it is proposed that, following the breaking of grains in the outermost portion of the columnar shell, the newly formed equiaxed grains undergo a process of mutual sliding and rotation in a manner analogous to the superplastic behaviour shown by many alloys with grain sizes on the micron or sub-micron scale under the action of a tensile stress. A model for this kind of deformation has been described by Ashby and Verrall [17] in which grains mutually translate while ultimately preserving their shape via a process of grain-boundary sliding coupled with diffusional accommodation.

Columnar grains nucleated in niobium–tin and vanadium–gallium tapes produced by diffusion from surface coatings have been shown by Togano and Tachikawa [18] to be highly textured, and this is confirmed by Schelb [8] for the case of columnar grains nucleated at the niobium interface in bronze processed multifilamentary wire. The subsequent formation of an outer layer of fine equiaxed grains via the process outlined above would be expected to result in a loss of texture, though this has yet to be experimentally verified.

Activation energies for A15 grain growth were calculated from the measured mean grain sizes and found to be 66 kJ mol^{-1} in the case of plain niobium filaments, and 52 kJ mol^{-1} for the tantalum alloyed wire; the former comparing well with Schelb's [8] value of 63 kJ mol^{-1} for plain niobium filaments.

To date, no other detailed measurements by transmission electron microscopy of A15 grain size in tantalum alloyed multifilamentary wires have been made. Livingston [12] postulated from enhanced critical current measurements at high field that small additions of tantalum may inhibit the coarsening of grains when annealing. Suenaga *et al.* [13] have examined, by scanning electron microscopy, layers formed around niobium filaments containing different starting concentrations of tantalum and reported a slightly larger grain size for a composition of 20 wt % (11.6 at %) tantalum, but admitted difficulty in evaluating differences in grain sizes between samples of different tantalum concentrations by this method. The present work has shown that, over the range of temperatures and annealing times studied, the tantalum alloyed Vacuumschmelze wire had a smaller A15 mean grain size than the corresponding IMI sample. While it should be noted that the nominal as-received filament diameters of the two wires were similar but not identical (and some evidence has been found for a variation of grain size with filament diameters for larger differences [15]), the grain refining effect is almost certainly attributable to the presence of tantalum.

5. Conclusions

A two-fold morphology of the diffusion layer in multifilamentary bronze-processed wire has been confirmed for both plain niobium filaments and niobium containing a 7.5 wt % (4.0 at %) tantalum addition, the volume fraction of columnar grains apparently decreasing with increasing annealing temperature for a given time. A two-stage mechanism is proposed in which initially the columnar portion of the layer close to the growth front undergoes a process of stress-driven recrystallization to the equiaxed morphology, followed by deformation involving mainly grain rotation and mutual sliding with associated diffusional accommodation.

An increase in mean equiaxed grain size as a function of annealing temperature has been observed, with generally a smaller grain size in the tantalum alloyed wire for a given annealing temperature and time, which consequently might be expected to exhibit improved critical current density characteristics.

Elemental analysis has revealed a diminishing tin concentration across the layer towards the growth front and shown that tantalum is incorporated into the A15 compound with a concentration approximately equal to that in the unreacted filaments.

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