JOURNAL OF MATERIALS SCIENCE 23 (1988) 1961–1966

Tin supply and microstructure development during reaction of an external tin process Nb_3Sn multifilamentary composite

B. A. GŁOWACKI*, J. E. EVETTS
Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK

The class of "high tin" multifilamentary Nb_3Sn superconducting composites depends on the diffusion of tin from a high tin reservoir to the niobium filaments where the superconducting A15 phase grows by solid state reaction. In particular, external tin composites are fully fabricated as niobium filaments in a copper matrix and the wire is subsequently coated with tin prior to reaction. In the work reported a detailed study is made of tin diffusion and microstructure development during the reaction of a 1369 filament external tin composite wire consisting of 37 × 37 bundled filaments of 3.5 μm diameter. During the initial low-temperature anneal stage the formation and evolution of copper–tin intermetallic phases is followed. High-temperature reaction anneals were then carried out at 755 and 588° C. The rapid conversion of ε-phase to α-Cu is accompanied by diffusion of tin towards the centre of the composite and the growth of Nb_3Sn A15 phase layers on the niobium filaments. The variation of tin composition and layer thickness is reported for different stages of reaction. In addition, the average composition of the A15 layer is measured as a function of the radial position of the filament, and the tin concentration gradient is measured within the A15 layer for the outermost filaments of the composite. The results show clearly the very strong dependence of the A15 layer growth rate on the tin concentration in the matrix. As a result, for an isothermal anneal at 755° C the layer growth is highy non-uniform across the composite. Furthermore it can be seen that additional inhomogeneity of the layer composition arises as a consequence of the bundled geometry of the composite. An important practical observation is that when the layer thickness approaches the filament radius the A15 compound is still far from stoichiometry particularly for filaments near the centre of the composite. The results overall emphasize the need for a detailed understanding of tin supply and compound growth before optimum heat-treatment procedures can be prescribed for a particular external tin design. A comparison of anneals at 755 and 588° C indicates that the relative rates of tin diffusion and A15 layer growth changes strongly with temperature; this suggests that a combination of anneals at different temperatures might be necessary for the optimization of the superconducting properties of high tin composites.

1. Introduction

Multifilamentary superconducting composites based on the high-field A15 compound Nb_3Sn are always fully fabricated into wire prior to undergoing solid state reaction to form the brittle A15 phase. There are a number of possible fabrication routes; however, they all depend on the mechanical reduction of niobium or ductile niobium alloy distributed in a suitable matrix which must also have reasonable ductility. Such composites have to fulfil two critical design features. Firstly, they must be capable of supporting a huge reduction in area, often in excess of 10^6; a composite in its final form after one or more rebundling operations may contain upwards of 10 000 highly uniform niobium filaments a few micrometres in diameter. Secondly, after fabrication it must be possible to present a sufficient supply of tin to each filament to react a layer of A15 compound of the required thickness and quality.

The majority of first generation Nb_3Sn commercial conductors was fabricated by the so-called bronze route, in which niobium filaments are supported in a copper-tin bronze matrix during fabrication; subsequently during solid state reaction tin diffuses from the bronze into the niobium. The bronze route has many drawbacks, and it has been evident from some time that lower production costs, higher yields and improved specification and wire quality are offered by other production routes that avoid using a bronze as the tin-bearing alloy during fabrication.

---

*On leave from the Technical University of Wroclaw, Wroclaw, Poland.

0022–2461/88 $03.00 + .12

The main disadvantages of bronze are its low ductility and the very limited amount of tin that can be incorporated into a single phase solid solution bronze. The low ductility necessitates frequent intermediate annealing treatments to soften the bronze, this has to be done after every 40 to 60% reduction in area. The large number of anneals are costly and lead to the undesirable formation of small amounts of brittle A15 phase which reduce composite uniformity during subsequent processing. The limited amount of tin in the bronze also affects the composite specification because in order to ensure adequate tin supply during reaction, a large fraction of the composite cross-section must consist of bronze which plays no useful part in the specification after reaction. This consideration has recently become more important with the appreciation that A15 compound reacted in the presence of a high tin concentration forms more rapidly and is of higher quality.

An attractive alternative to the bronze route is to support the niobium in pure copper and supply tin from a source of pure tin or high tin-bearing alloy. When the tin is incorporated at an early stage in the fabrication process this is termed an "internal tin" route. If, instead, the tin is incorporated on to the composite after fabrication, it is called an "external tin" route. In such high-tin composites the solid state reaction process is complex involving a low-temperature reaction stage to convert the initial low melting point tin-bearing region to a higher melting point copper–tin intermetallic, this must be followed by one or more reaction stages at higher temperatures in order to form the A15 phase. An understanding of microstructure development and tin supply during each stage is essential for the design of a practical composite. The phases present determine both the safe upper annealing temperature and the dimensional changes that distort different regions of the composite at each stage of the reaction, while tin supply is perhaps the single most important factor determining the rate and uniformity of layer growth and the quality of the Nb_3Sn layer formed. If the filament reaction rate is uneven those filaments completing their reaction early in the anneal will undergo grain growth and consequent degradation of their critical currents.

Although the importance of the overall tin concentration has long been recognized as affecting layer growth [1, 2] the consequences of considerable variations in the availability of tin to filaments in different parts of the composite has not been observed until recently [3–5]. In a previous study of growth rates and tin supply in a Vacuumschmelze Gmbh bronze route rebundled composite, Pugh *et al.* [3] identified three distinct A15 growth stages for filaments belonging to the central bundles of the composite. If high-quality conductors are to be fabricated by the new high-tin routes it is important to understand changes in the tin composition during different reaction stages and relate such changes to A15 layer growth. In this paper we present the results of an investigation of microstructure development and changes in tin concentration during low- and high-temperature annealing of an external rebundled composite.

2. Experimental procedure

The composite investigated was a 1369 filament conductor fabricated using the tube technique [6]. The final Cu/Nb composite wire was 0.32 mm diameter and consisted of 37 bundles each of 37 filaments with mean diameter 3.5 μm. A 16 $\pm$ 1 μm surface coating of pure tin was electrodeposited from an acid tin sulphate bath (26 $\mathrm{g\,l^{-1}}$ $SnSO_4$, 125 $\mathrm{g\,l^{-1}}$ H_2SO_4 with 4 $\mathrm{g\,l^{-1}}$ Polux 6 brightener). The tin thickness was calculated to be sufficient to fully react the filaments to an average concentration of 30 wt% (25 at.%) and simultaneously provide a residual concentration of close to 13 wt% (7 at.%) in the copper matrix.

Short lengths of wire were annealed in a vacuum of 1.33×10^{-3} Pa. A first-stage low-temperature anneal (LTA) was performed to convert the tin coating to a uniform surface coating of ε-phase. Previous experience with external tin composites [7, 8] has indicated that tin layers thicker than 6 to 10 μm cannot be reacted above the melting point of tin (232° C) to give uniform intermetallic layers. Two alternative LTA were performed; the samples were either annealed at a constant 225° C for 800 h, or they were annealed for 200 h at 225° C followed by 20 h at 350° C. Second-stage high-temperature anneals (HTA) were performed at either 588 or 755° C for times between 1 min and 200 h.

The chemical composition of matrix and filaments was determined using scanning electron microscopy (SEM) with X-ray microprobe (EDAX), and scanning transmission electron microscopy (STEM) with *in situ* energy dispersive X-ray spectroscopy (EDS). TEM foils were prepared by grinding 50 μm discs, and then argon-ion milling the discs until perforated. Lattice parameters were determined using an X-ray diffractometer with Cu$K\alpha$ radiation.

3. Results

3.1. Phase and microstructure development

During the first stage LTA the tin layer is consumed while layers of roughly equal thicknesses of ε-phase and η-phase grow. As soon as the tin is exhausted the η-phase shrinks rapidly, see Fig. 1. The velocity of the interface between the ε- and η-phases, $V_{\eta\varepsilon}$, can be expressed in terms of the diffusive flux to the interface,

$$V_{\eta\varepsilon} = \frac{D_\eta(\partial c_\eta/\partial x) - D_\varepsilon(\partial c_\varepsilon/\partial x)}{\Delta c_{\eta\varepsilon}}$$

where D_η and D_ε are the diffusivities and $(\partial c_\eta/\partial x)$ and $(\partial c_\varepsilon/\partial x)$ are gradients of concentration in the η- and ε-phases, respectively; and $\Delta c_{\eta\varepsilon}$ is the change in tin concentration across the interface. When the pure tin layer is fully consumed $(\partial c_\eta/\partial x) = 0$ and $V_{\eta\varepsilon}$ takes a large negative value indicating the rapid growth of the ε-phase to the wire surface.

At the end of the LTA the 31 to 34 μm reaction layer consists almost entirely of columnar grains of ε-phase as shown in Fig. 2. A band of α-Cu is also present; however, this region is extremely narrow because below 225° C the diffusion coefficient in α-Cu is very small and the solubility of tin in copper is low [9]. If the initial composite is fabricated with niobium filaments too close to the wire surface, the ε-phase region

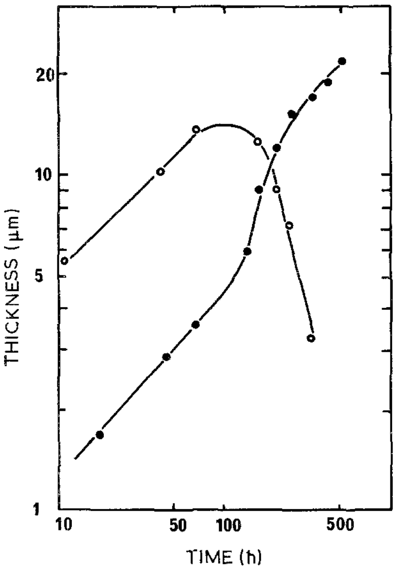

Figure 1 Thickness of (●) the ε-Cu_3Sn and (○) η-Cu_6Sn_5 phases plotted against time of LTA at 225° C.

extends to fill the space between the outer niobium filaments [6]; such a tin-rich region has a strong influence on the kinetics of A15-phase formation during the HTA stage. The composites used in this investigation had sufficient copper in the outer regions for this not to occur.

On increasing the temperature to 755° C for the second stage HTA, the thickness of the band of α-Cu increase rapidly. Above 676° C the ε-phase transforms to γ-phase. However, although the solidus line at 25 at.% Sn is only at 720° C, it appears that for normal heating rates tin diffuses so rapidly that the γ-phase remains below the solidus line. This is confirmed by the observation that after HTA for times of ~ 1 min samples examined at 20° C invariably contained only α-Cu and δ-phases. The development of phases and microstructure during HTA can only be inferred from the distribution of the α-Cu and δ-phases because the high temperature γ-phase transforms to the lower temperature δ-phase by a rapid diffusionless transition [10]. The β-phase also appears to decompose rapidly to α-Cu and δ-phase at a eutectoid at 586° C. In contrast, the δ-phase, although only stable above 350° C, decomposes extremely slowly at 20° C especially in massive specimens [9].

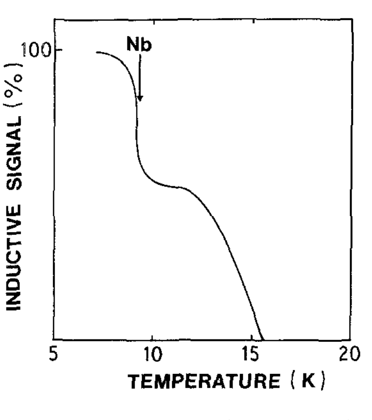

Figure 2 Columnar grain structure in the ε-Cu_3Sn phase after LTA at 225° C.

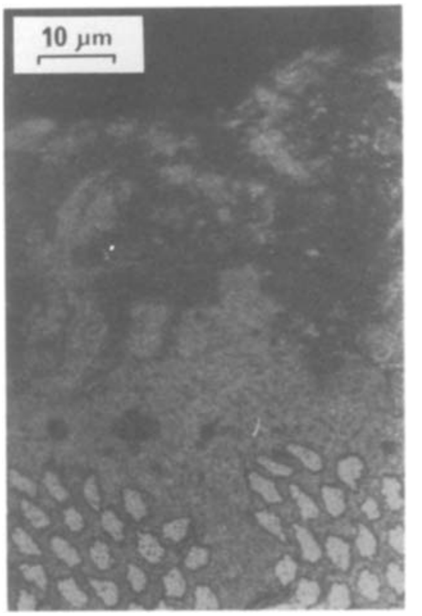

Figure 3 An optical micrograph revealing the decomposition of γ-phase in the outer region of the wire after HTA for 20 min at 755° C; dark areas represent the δ-phase with finely distributed precipitates of α-Cu; light areas represent the α-Cu phase.

Samples examined during the early stages of HTA display two characteristic reactions, see Fig. 3. The inner region consisted of single-phase α-Cu with a lattice parameter 0.3697 nm which corresponds to a composition near the saturation limit, measured as 15.3 wt % Sn using SEM with X-ray microprobe analysis. Secondly there was an outer two-phase region consisting of a fine distribution of α-Cu in δ-phase (Fig. 3). The δ-phase lattice parameter was 1.785 nm which is low compared to the value of 1.795 nm that is quoted for the copper-rich side of the δ-phase; the discrepancy is likely to be related to the process of decomposition of copper-rich γ-phase. This is supported by the measurement here of a characteristic composition of about 29 wt % Sn for the δ-phase while the reported minimum tin concentration on the copper-rich side is 32 wt % Sn [9].

As the HTA proceeds the α-Cu region spreads throughout the composite, at the same time the two-phase region becomes limited to the outermost part wire taking an increasingly more fragmented form until it finally disappears.

During annealing and reaction the composite macrostructure undergoes complex geometrical distortion due both to the expansion caused by diffusive flux divergence and to the differing densities of the different phases formed. This distortion is of technological importance, it can lead to high stresses within reacting layers that can affect the layer growth morphology [11, 12], also relative displacement of individual filaments and bundles of filaments can lead to undesirable interfilament contact. The dimensional changes after full HTA reaction at 755° C were investigated. The original 3.5 μm niobium filaments were found to have expanded to a mean diameter of 4.0 ± 0.1 μm. This confirms the observation of Cave and Weir [12] that the 37% expansion of the filament on conversion to A15 phase is accommodated fully as an increase in filament area cross-section. The linear dis-

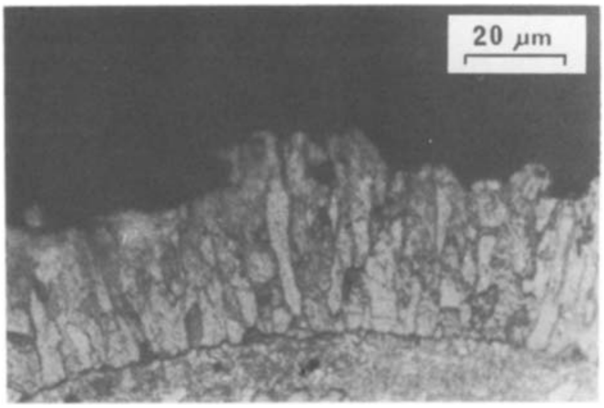

Figure 4 Inductive transition for the 1369 filamentary wire after HTA at 755° C for 12.5 min.

tance between bundle centres was also found to increase by 7 to 8%, this can be explained as a straightforward combination of the above filament expansion and the expansion of the pure copper matrix resulting from the solution of 14 wt % Sn.

3.2. Variation of tin composition and concentration gradient during HTA

In the early stages of the HTA at 755° C the tin composition is highly non-uniform with a steep radial concentration gradient. Initial tin diffusion is extremely rapid and after only a few minutes there is evidence from SEM observation for A15 formation on niobium filaments in the outer bundles. This is confirmed by the inductive transition measurement shown in Fig. 4. After 12.5 min reaction the trace shows [12] that approximately half of the filaments are effectively shielded by a high T_c layer with the maximum T_c approaching 15.5 K.

At different stages of the anneal the radial tin concentration in the bronze was determined at points midway between successive bundles (Fig. 5). In addition, the average thickness of the reacted A15 layer was measured for filaments along the wire radius (Fig. 6). After 4 h at 755° C the tin concentration was significant across 90% of the wire cross-section, increasing approximately linearly with radial distance (Fig. 5, curve a). In contrast the A15 thickness was considerably more non-uniform (Fig. 6, curve a), confirming the strong dependence of the A15 compound growth rate on tin concentration [1, 2].

The outer two filaments of the outer bundles are already fully reacted, whereas only half of the filaments in the next ring of bundles centred on an 80 µm radius show significant reaction. The tin concentration falls from 10 to 5.5 wt % across these bundles after 4 h at 755° C. This clearly indicates that there is a very sharp drop in A15 reaction rate at 755° C for tin concentrations below 10 wt %.

After 18 h at 755° C the tin concentration was almost uniform (Fig. 5, curve b), and all the filaments gave the appearance of being fully reacted (Fig. 6, curve b). However, the mean tin concentration in the bronze is still near 15 wt %, considerably greater than the designed final concentration of 13 wt % for a fully reacted wire with stoichiometric Nb_3Sn. Measurements of the tin concentration (EDAX) in the reacted filaments is shown in Fig. 7 for filaments along a radius passing through the centre of successive bundles as indicated. Two features can be seen, firstly, all of the reacted material has a low average tin concentration compared to the stoichiometric concentration of 30 wt %, and secondly, within each bundle there is a difference in the tin concentration between filaments at the surface of the bundle and at the centre. It is clear that the detailed geometry of the composite determines tin supply and compound reaction rate in a similar way to that reported previously for a bronze route bundled composite [3]. The microprobe EDAX results give an average composition within the reaction

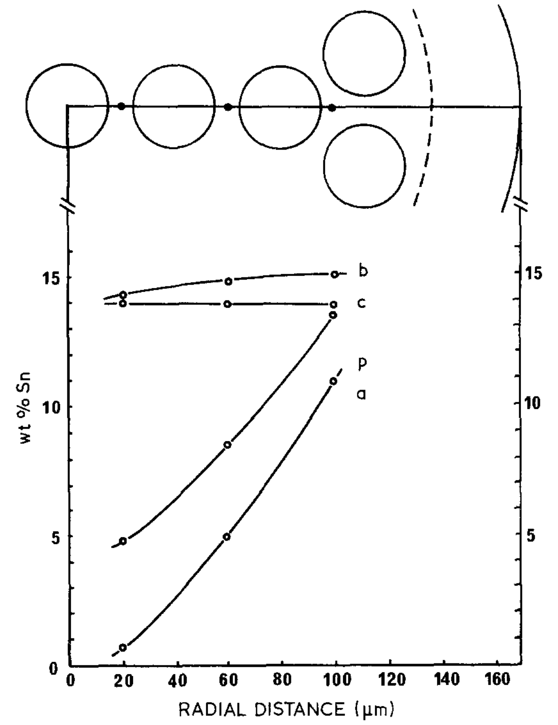

Figure 5 Tin concentration profiles in MF wire between the bundles of the filaments along a radius of the wire; (a) HTA 755° C, 4 h; (b) HTA 755° C, 18 h; (c) HTA 755° C, 200 h; (p) HTA 588° C, 108 h. (Inset at the top of the figure is a schematic representation of the MF wire along its radius: large circles, bundles of 37 filaments; (●) places of analysis; (— — —) primary boundary between ε phase and copper matrix; (———) outer surface of wire.)

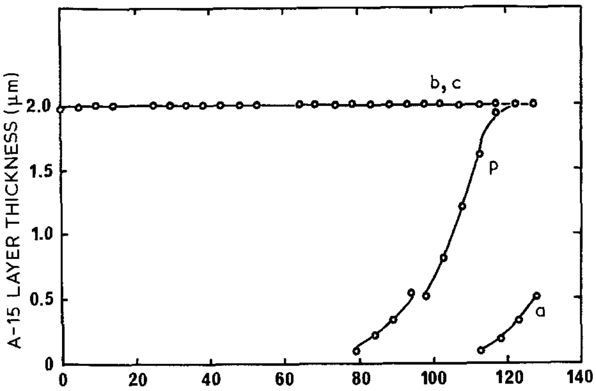

Figure 6 Average thickness of the Nb_3Sn layer along a radius of the wire. In this figure and in Fig. 7 each point represents data for a reacted filament at the radial position indicated; (a) HTA 755° C, 4 h; (b) HTA 755° C, 18 h; (c) HTA 755° C, 200 h; (p) HTA 588° C, 108 h.

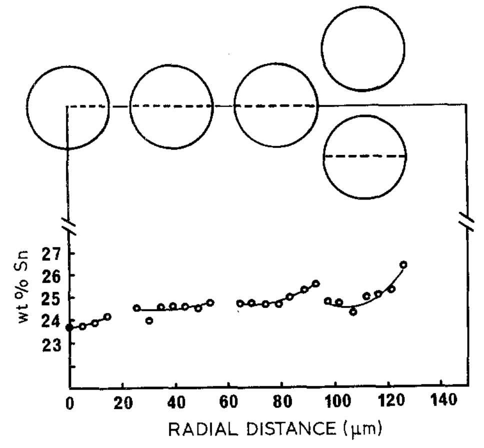

Figure 7 Tin concentration in the filaments along the radius of MF wire HTA 755° C, 18 h. (Dashed lines over the figure represent the lines of analysis in bundles.)

layer; in addition the tin concentration within the A15 layers of filaments from outer bundles was determined using transverse STEM with EDS. The tin concentration was found to vary by 3 wt % across the reaction layer; a similar variation has been observed in partially reacted bronze route conductors [3, 13, 14].

After completing a 200 h HTA at 755° C the tin concentration in the bronze is a constant 14 wt % (Fig. 5, curve c); while the average tin concentration in the A15-phase varies from 28 wt % for filaments at the centre of the wire to 30 wt % for those at the wire surface.

An alternative HTA at 588° C for 108 h was investigated in an attempt to distribute the tin more uniformly prior to reacting the A15-phase. The tin concentration was raised to a relatively high level (see Fig. 5, curve p) without reacting large amounts of A15-phase (see Fig. 6, curve p). The A15 layer thickness was about an order of magnitude less than that formed in 4 h at 755° C even though the final tin concentration was everywhere higher and exceeded 10 wt % Sn over more than 50% of the composite cross-section. The changes in the relative rates of tin diffusion and A15 layer formation arises because the two processes have different activation energies. This result has important implications for the selection of optimum heat-treatment conditions for high tin composites.

4. Discussion and conclusions

The sole objective of the successive heat-treatment anneals is to facilitate the transport of tin from a high tin reservoir to the niobium filaments in such a way as to form uniform layers of fine grain Nb_3Sn with a composition close to stoichiometry. The critical temperature and upper critical field of Nb_3Sn vary strongly with tin concentration [15]; as a consequence, regions with a composition more than 2 wt % off-stoichiometry are likely to have poor high-field performance. To obtain a high critical current density it is necessary to grow the A15-phase with a fine grain size and avoid as far as possible grain growth during subsequent annealing. Problems of grain growth are most severe when non-uniform tin supply results in filaments in certain regions of a composite becoming fully reacted much more rapidly than those in other regions. Within one filament the relative rate of layer growth and grain growth depend on the interaction of a number of metallurgical factors such as grain size, grain-boundary energy, tin concentration and tin diffusivity. In many composites it is also necessary to take account of the effect of additives such as titanium, tantalum or magnesium on grain-boundary energy and diffusivity [11, 16, 17].

It is apparent that for isothermal annealing at 755° C, layer growth is highly non-uniform across the composite. Measurement of the tin concentrations in reacted filaments after 18 h (Fig. 7) provides confirmation that there is a strong geometrical factor controlling layer growth in bundled composites. In addition to the overall radial tin concentration gradient inherent in an external tin process there is evidence for a secondary radial gradient centred on each bundle of filaments and also a tertiary radial gradient within each filament.

The effect of gradient in tin concentration on the Nb_3Sn layer thickness is attributable to the strong dependence of compound growth rate on tin concentration in the bronze. Previous work on bronze route multifilamentary composites and on monofilamentary wires [1–3] has also given an indication of the sensitivity of compound growth rate to tin concentration in the bronze. In each case, however, there are special factors that make quantitative comparisons difficult. Work on monofilamentary wires is complicated by recrystallization of the bronze during the reaction anneal. Because the bronze grain size in a multifilamentary composite is determined by the interfilament spacing, there is likely to be a significant "short-circuit" or grain-boundary component to the tin diffusivity. After recrystallization bulk diffusion will predominate. The resultant differences in diffusivity will be accentuated at lower temperatures. The work on bronze route multifilamentary composites and particularly on bundled composites is complicated by the rapid drop in the local tin concentration within the bundles and to a lesser extent in the channels between bundles [3, 13]. In both cases described the result is that the strength of the variation of compound growth rate with tin concentration is masked.

The variation of layer thicknesses and corresponding tin concentration reported here after 4 h anneal at 755°C (Figs 5 and 6, curve a) shows clearly the strong dependence of layer growth rate on tin concentration. If the composite is reacted isothermally at 755° C the outer filament will be fully reacted early in the anneal and suffer extensive grain growth, with consequent reduction in their critical current density. An alternative strategy is to take advantage of the relative reduction in compound growth rate at low temperature in order to diffuse tin more uniformly throughout the composite prior to extensive reaction of the A15-phase. The results shown in Figs 5 and 6, curve p, indicate in a preliminary way that this is possible.

Finally, the result of layer thickness and tin concentration measurements after 18 h at 755° C show that the filaments give the appearance of full reaction whilst still being seriously off-stoichiometry. The critical current at high fields for a composite at this stage of reaction is likely to be poor because of depression of the upper critical field and critical temperature.

In conclusion, it is evident that the variation of tin concentration during reaction of high tin composites is complex and has serious implications for reaction rates in different parts of the composite and the final properties of the composite. There are, however, a number of possibilities for optimizing the reaction heat treatment to achieve rapid growth of reasonably uniform A15 layers. The design of such optimized anneals depends on obtaining a detailed knowledge of diffusion rates and layer growth rates in composites of different geometrical construction.

Acknowledgements

This work was supported by the Science and Engineering Research Council and the British Council. The authors wish to thank Dr E. R. Wallach, Dr J. R. Cave, J. L. M. Robertson and Z. M. Kosek for helpful discussions.

References

1. M. SUENAGA, O. HORIGAMI and T. S. LUHMAN, *Appl. Phys. Lett.* **25** (1974) 624.
2. B. V. REDDI, V. RAGHAVAN, S. RAY, A. V. NARLIKAR, *J. Mater. Sci.* **18** (1983) 1165.
3. N. J. PUGH, J. L. M. ROBERTSON, E. R. WALLACH, J. R. CAVE, R. E. SOMEKH and J. E. EVETTS, *IEE Trans. Mag.* **21** (1985) 1128.
4. M. SUENAGA, C. J. KLAMUT, N. HIGUCHI and T. KURODA, *ibid.* **21** (1985) 305.
5. D. R. DIETDERICH, J. GLAZER, C. LEA, W. V. HASSENZAHL and J. W. MORRIS Jr., *ibid.* **21** (1985) 292.
6. B. A. GŁOWACKI and Z. M. KOSEK, *Cryogenics*, **27** (1987) 551.
7. J. D. VERHOEVEN, E. D. GIBBSON and C. C. CHENG, *Appl. Phys. Lett.* **40** (1982) 87.
8. S. F. COGAN, S. KWON, J. D. KLEIN and R. M. ROSE, *IEE Trans. Mag.* **19** (1983) 1139.
9. M. HANSEN (ed.), "Constitution of Binary Alloys" (McGraw-Hill, New York, Toronto, London, 1958) p. 634.
10. F. A. SHUNK, *ibid.*, second supplement, (McGraw-Hill, New York, 1985) p. 295.
11. E. R. WALLACH and J. E. EVETTS, *Adv. Cryog. Eng. Mater.* **32** (1986) 911.
12. J. R. CAVE and C. A. F. WEIR, *IEEE Trans. Mag.* **19** (1983) 1120.
13. I. W. WU, D. R. DIETDERICH, J. T. HOLTHUIS, M. HONG, W. V. HASSENZAHL and J. W. MORRIS, *J. Appl. Phys.* **54** (1983) 7139.
14. N. J. PUGH, J. E. EVETTS and E. R. WALLACH, *J. Met. Sci.* **20** (1985) 4521.
15. H. DEVANTARY, J. L. JORDA, M. DECROUX and J. MULLER, *J. Mater. Sci.* **16** (1981) 2145.
16. I. W. WU, D. R. DIETDERICH, J. T. HOLHUIS, W. V. HASSENZAHL and J. W. MORRIS, *IEEE Trans. Mag.* **19** (1983) 1437.
17. K. OSAMURA, S. OCHIAI, S. KONDO, N. NAMATAME and M. NOSAKI, *J. Mater. Sci.* **21** (1986) 1509.

Received 2 July
and accepted 9 October 1987