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Filament contact with *in situ* Nb_3Sn superconducting wire

J. D. VERHOEVEN, E. D. GIBSON, F. C. LAABS
Department of Materials Science and Engineering and Ames Laboratory—USDOE, Iowa State University, Ames, Iowa 50011, USA

Experimental evidence is presented which indicates that the Nb_3Sn filaments within *in situ* prepared Nb_3Sn–Cu superconducting wire are welded together at point contacts along a thin annular region which borders the surface of the original tin supply. For wires with tin added from an external plated layer the welded annular region lies near the outside diameter just below the original tin plate, whereas for wires with the tin added from an internal core the annular region lies along the original core hole. This welded region is expected to increase the a.c. loss characteristics of these wires. A possible cause of the welded annular region and methods for its elimination are discussed.

1. Introduction

The Nb_3Sn filaments within *in situ* prepared superconducting wire have generally been assumed to be isolated from each other by the bronze matrix. In this paper, we present evidence that this may not be true throughout the entire wire volume. The *in situ* process consists of essentially three steps: (1) preparation of a cast Nb–Cu alloy; (2) mechanical reduction to wire size; and (3) diffusion of tin into the wire, thereby converting niobium to Nb_3Sn and copper to an α-bronze. Filament contact will now be considered at each of the three steps.

During casting, the niobium filaments form as arrays of side-branched dendrites. The dendrite tips grow towards one another at random locations in the melt and one needs to consider whether contact is likely. At the growth tip, copper is ejected into the melt and the growth velocity is proportional to the normal concentration gradient of the copper into the liquid at the tip. As two tips approach each other, the copper concentration fields will overlap, thereby decreasing the gradient and slowing the growth rate. In the limit where the two tips are about to touch each other this effect is expected to dominate and thereby prevent contact. Hence, in the casting stage one does not expect dendrite-to-dendrite contact unless severe convection currents are present in the casting operation which physically carry the filaments into contact with one another.

In the second step, quite large mechanical reductions are employed. A reduction in area of $\geqslant 99.9\%$ is used in order to achieve good alignment and close proximity of the niobium filaments. Hence, it is possible that the copper may be squeezed from between niobium filaments thereby producing a weld bonding of filaments. However, because the ductility of copper and niobium are not greatly different this possibility seems unlikely.

During the third step, tin diffuses through the copper matrix to the niobium filaments where a chemical reaction converts the niobium to Nb_3Sn. In previous work [1] we have found that the size of the Nb_3Sn filaments may be considerably larger than the original niobium filaments if the diffusion temperature is high ($> \sim 550^\circ$ C) and if the original niobium filaments are small ($< \sim 50$ nm). This increase in filament size is due mainly to coarsening. However, even in the absence of such coarsening effects, the Nb_3Sn filaments are generally found to be 30% to 50% larger than the original niobium filaments. Such an expansion might lead to some contact welding between Nb_3Sn filaments.

2. Experiments

Two types of experiments have been performed to evaluate the connectivity of the filaments: (a)

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SEM examination of deep-etched samples, and (b) dissolution experiments. The experiments were done using wires prepared from Cu–Nb castings having niobium concentrations ranging from 20 to 30 wt%. The niobium dendrite size in these cast alloys was measured to be around $8.0 \pm 1.0\,\mu m$. The reduction in area employed in step 2 was 99.97%. The tin was added by external diffusion from the plated surface or by internal diffusion from a tin core [2]. Wires of both 0.15 and 0.25 mm diameter were studied. In most cases, the amount of tin was that required for stoichiometric conversion of niobium to Nb_3Sn, but in some cases 20% to 30% more tin was utilized. In all cases, the tin diffusion step was carried out at 550° C for periods of 4 to 6 days, a treatment we have found to optimize the critical current density, J_c.

In the SEM study, samples were prepared by soft soldering (a Pb–Sn solder) the wire into slotted copper blocks and then sectioned to expose surfaces transverse to the wire axis. After metallographic polishing the bronze matrix was removed by deep etching with a 55% phosphoric–25% acetic–20% nitric acid solution, and the sections were examined in the SEM.

In the dissolution experiments, short sections of wire were placed in concentrated acids at room temperature for 24 h, followed by a 30 min treatment at the boiling temperature of the acid. The remaining material was then cleaned by a refluxing technique utilizing methanol. Two acid solutions were employed, 50% concentrated HNO_3 plus water, and 100% concentrated HCl. In general, both acids were equally effective at selectively dissolving the copper-rich matrix and not the niobium or Nb_3Sn fibres. In the case of Cu–Nb wires it was necessary to add a few drops of HNO_3 to the HCl in order to initiate the dissolution reaction. After the cleaning operation, the remnants of the wires were examined visually within the liquid carrier. If filament separation had occurred, the filaments were collected on grids and examined by both STEM and SEM techniques.

3. Results

First, the SEM experiments performed on wires following step 3 – the tin diffusion step – will be discussed. The micrograph of Fig. 1a shows the entire transverse section of an external tin wire after deep etching. It was found that after the tin diffusion step the original tin plate was replaced by a low tin content α-bronze rim. The dark outer rim of Fig. 1a resulted from etching away both

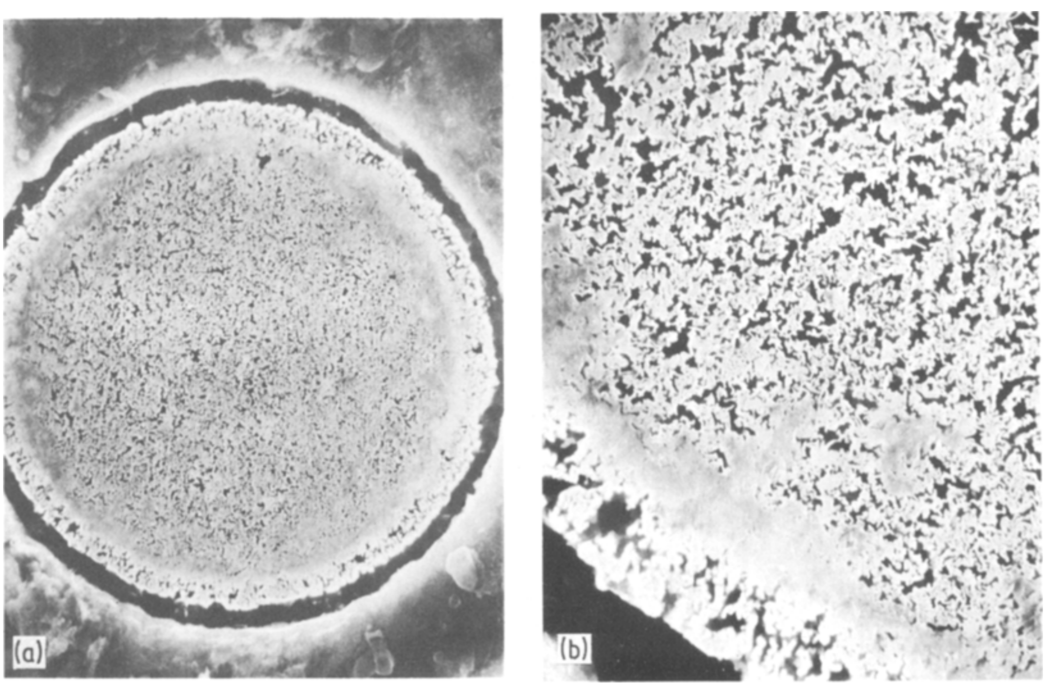

Figure 1 Deep etched transverse sections of Nb_3Sn–Cu wires made from 0.15 mm diameter Cu–22 wt% Nb wire by external diffusion from pure tin plates. (a) ×500, (b) outer edge or wire at the lower left corner of (a), ×1800.

this bronze outer rim and some of the Pb–Sn solder used to hold the wires against the copper block for mounting purposes. At a radius slightly smaller than the outside Nb_3Sn radius of Fig. 1, one sees an annular region where the Nb_3Sn density is significantly higher. Based on the dissolution experiments to be discussed below we believe that the Nb_3Sn filaments are welded together at point contacts within this annular region, but not elsewhere. We will refer to this annular region as the welded region. Examination of the welded region at higher magnifications, such as shown in Fig. 1b, reveals that the Nb_3Sn density is significantly higher within it.

A similar welded region has been found on wires where the tin was supplied from an internal core. Fig. 2a presents a transverse section of a core wire and one sees an annular region of increased Nb_3Sn density lying near the original tin core. Higher magnification micrographs, such as Fig. 2b, reveal a higher Nb_3Sn density in the annular region, but not so much as for externally tin diffused wires.

SEM examination of deep etched surfaces of transverse wire sections after step 2 and of sections of as-cast ingots, step 1, was also carried out. In none of the samples examined was there any clear evidence of regions of increased niobium fibre or dendrite density suggestive of point contact welding.

Dissolution experiments were performed on wires after both steps 2 and 3. In all wires examined after step 2 it was found that complete separation of the niobium filaments was obtained. The wires were converted into expanded cylinders of dark fibres which could be dispersed throughout the solution upon violent shaking of the container. Hence, no evidence of niobium fibre welding was found at the mechanical reduction in areas used here, 99.97%, for niobium compositions of 20% to 30 wt %.

Dissolution experiments on wires following step 3 revealed a completely different result. For wires prepared by external tin diffusion, it was found that the acid dissolution did not cause the wire to separate into a mass of disconnected fibres. Even after violent shaking of the solution inside the glass containers the acid-treated wires maintained their approximate original wire geometry. Occasionally, however, some small fibres of Nb_3Sn would become disconnected from the outer surface and these were examined in the SEM mode of a Jeol 100 CX electron microscope. Fig. 3 shows a typical result and one can clearly see that the

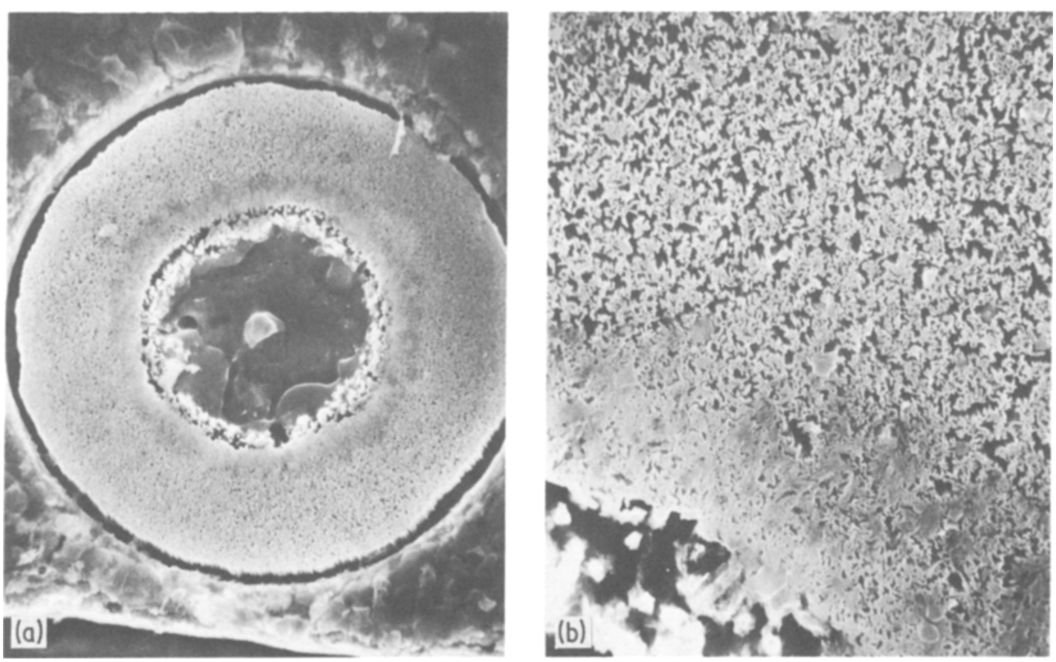

Figure 2 Deep etched transverse sections of Nb_3Sn–Cu wires made from 0.25 mm diameter Cu–20 wt % Nb wire by diffusion of tin from a Sn–5 wt % Cu core. (a) $\times 270$ (b) the boundary between core and matrix at the upper right of (a), $\times 1800$.

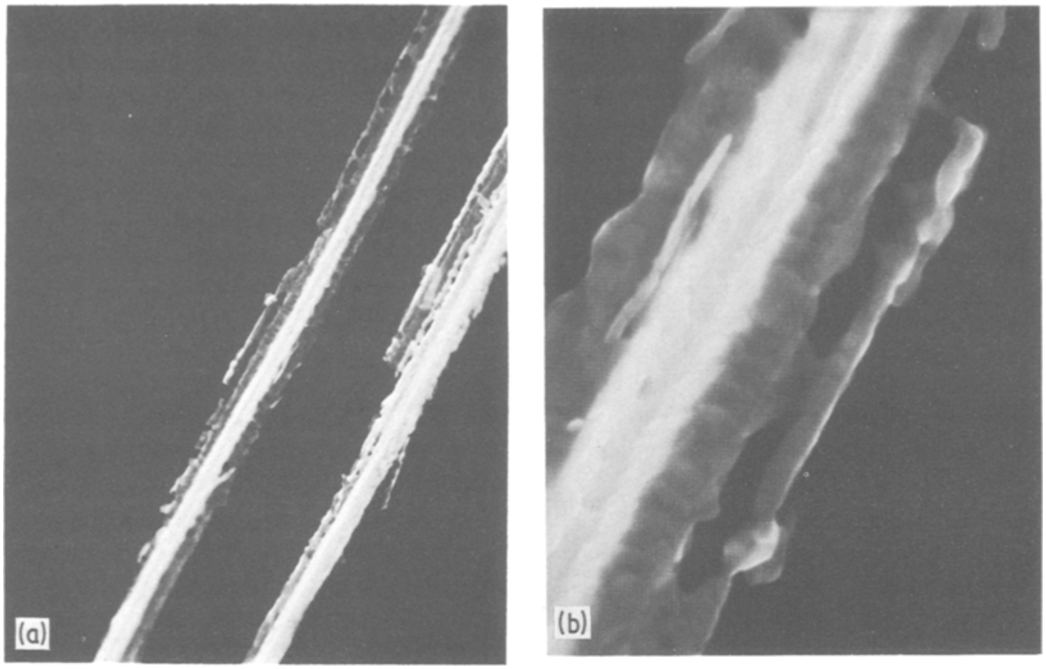

Figure 3 Extracted Nb_3Sn filaments of a Nb_3Sn–Cu wire made from 0.15 mm diameter Cu–20 wt% Nb wire by external diffusion from a pure tin plate. (a) ×9000, (b) ×45 000.

Nb_3Sn fibres appear to be welded together at random points along their length. When these experiments were repeated on the tin core wire it appeared that all of the Nb_3Sn fibres separated into the solution except for a thin central region along the wire axis, which probably corresponded to the dense annular region found near the tin core in Fig. 2.

4. Discussion

Based on the combined results of the dissolution and SEM studies the following picture emerges. No significant welding of niobium fibres occurs during the wire drawing step (step 2) in alloys of 20% to 30 wt% niobium in copper for a reduction in area of 99.97%. This result also implies that no contact welding of dendrites occurs during the casting operation (step 1). However, for the step 3 conditions used here, tin diffusion at 550° C for 4 to 6 days, an annular region is formed near the source of the tin in which the Nb_3Sn fibres are contact welded at random points along their length. For external tin-diffused wires the welded annular region lies at the outer diameter of the wire and, therefore, inhibits separation of the wire filaments after acid dissolution of the α-bronze matrix. However, for internal tin-diffused wires the welded annular region lies at the core of the wire and acid dissolution separates all of the Nb_3Sn filaments except for this small core region.

A qualitative model for the formation of the welded annular region will now be presented. These experiments clearly indicate that the welding of the filaments occurs (a) during formation of Nb_3Sn, and (b) locally in the region near the source of the tin metal. As mentioned above, we find that following the 4 to 6 day treatment at 550° C the original tin-plated region is replaced with a low tin content α-bronze rim. Microprobe analysis on this rim shows that its composition averages around 96% copper/4% tin. This means that during the diffusion step at any volume element in the bronze matrix bordering the original tin-plated region, there must be a net loss of copper atoms into the plated region. This net loss of copper atoms will cause the bronze matrix to collapse unless it is compensated for by a net influx of tin atoms, which seems unlikely because the tin concentration in the bronze matrix is held at a low level set by its chemical potential at the bronze/Nb_3Sn interfaces. Hence, one can explain the welded rim as resulting from the collapse of the bronze matrix due to a net loss of copper atoms into the original pure tin supply region.

After sufficient collapse of the bronze matrix, combined with the 30 to 50 vol % increase in Nb_3Sn fibre size over the original niobium size mentioned in Section 1, the Nb_3Sn fibres make contact at random points and weld together at such points. The collapse of the bronze matrix would be a maximum near the original tin source which accounts for the welded region occurring near the tin source in both plated and cored wires.

It seems clear that a key parameter in determining whether or not the Nb_3Sn filaments make contact is the spacing between the niobium filaments, S, following step 2. Work of several investigators has shown that the niobium filaments become plate-shaped after mechanical reduction of the ingot material. For Cu–Nb alloys with 8 μm dendrites we have found [3] that the niobium filament thickness, t, correlates with the reduction in area ratio, R, as $t = 17\,100R^{-0.421}$. For Cu–Nb ingots with a niobium dendrite diameter, d, the correlation was found to be, $t = 17\,100[R(8/d)^2]^{-0.421}$. Hence, from a simple mass balance, one may approximate S, the average separation distance between niobium filaments after drawing, as,

$$S = 17\,100[R(8/d)^2]^{-0.421}(\%\text{Cu}/\%\text{Nb}) \quad (1)$$

where %Cu/%Nb is the copper/niobium ratio of the starting alloy in wt %. (The densities of copper and niobium are sufficiently close that one may substitute wt % for vol %), S is in nanometres and d in μm. These results indicate:

1. for the conditions of these experiments, 8 μm dendrites and $R = 3900$, the values of S varied from 0.13 μm for the 30 wt % alloy to 0.21 μm for the 20 wt % alloy;
2. in general, the value of S will depend on three variables, the diameter of the niobium particle size, the percentage of niobium in the Cu–Nb billet produced in step 1 and the reduction in area ratio, R, utilized in step 2.

Assuming the above model is correct, one may draw some conclusions regarding the generality of the effect observed here.

(a) The welded annular regions would probably not occur if one were to supply the tin from a plate of α-bronze rather than pure tin, because the copper present in the α-bronze plate would reduce the net loss of copper into the plated region.

(b) The welded annular region would probably not occur if one were to prepare the *in situ* material by including the tin within the original casting, as has been done by Bevk and Harbison [4].

(c) The welded annular region will probably also occur in the Nb_3Sn–Cu wires prepared by powder processes [5, 6]. However, the problem may not be as severe with the powder technique because, in general, larger particle sizes are utilized in the step 1 Cu–Nb billet, which provides a larger d in Equation 1 and will lead to larger S values after step 2.

(d) The extent of the welded annular region will be increased by employment of (i) higher niobium contents in the original Cu–Nb billet, (ii) smaller dendrite sizes in the original Cu–Nb billet, (iii) larger area reduction ratios in step 2, and (iv) thicker tin plates.

As a qualitative check on the proposed model, some additional experiments have been carried out which verify conclusion (a). In a previous study [2], Nb_3Sn–Cu wires were prepared from Cu–20 and 30 wt % castings by plating wires with an α-bronze of composition around 12 wt % Sn. The wires were reacted for 6 days at 550° C and gave excellent J_c values. Fig. 4 is a cross-sectional view of a reacted wire which shows no evidence of a welded annular region. This reacted wire was dissolved in both the HCl and HNO_3 acid solutions and in both cases, complete separation of Nb_3Sn

Figure 4 Deep etched transverse section of Nb_3Sn–Cu wire made from 0.15 mm diameter Cu–20 wt % Nb wire by external diffusion from a ~ 12 wt % Sn bronze plate (×1188).

filaments occurred, thus confirming conclusion (a) above, that no welding occurs when an α-bronze plate is utilized.

This result has important implications for scale-up procedures utilizing external tin plating. In virtually all laboratory scale experiments on *in situ* processed Nb_3Sn–Cu superconducting wire, such as described here, the cast Cu–Nb or Cu–Nb–Sn billets are drawn directly to wire. For industrial scale-up, however, larger billets will be jacketed in copper prior to extrusion and wire drawing in order to reduce galling of the dies by the niobium phase. This means that a thin layer of copper will be present between the Cu–Nb wire and the external tin plate. There are problems during the tin diffusion step if the tin plate is allowed to melt, and so this step is best carried out by a solid state diffusion process [7]. During this process, one converts the tin to layers of various intermetallic Cu–Sn compounds at the Sn–Cu interace region. First, a layer of η-phase forms, followed in sequence by ϵ-, and δ-phases. Conversion of tin to intermetallic phases is completed after formation of the δ-phase, so that one obtains a maximum intermetallic layer thickness, Δ_{max}, after which further diffusion decreases the layer thickness, forming an α-bronze. It is apparent then, that if one adjusts the thickness of the copper jacket, Δ_{Cu}, such that $\Delta_{Cu} > \Delta_{max}$, one will form only an α-bronze at the original Cu–Nb/Cu jacket interface. In this case, the diffusion into the Cu–Nb wire is equivalent to diffusion from a pure α-bronze plate and one would not expect to see formation of a welded annular region. Hence, it appears that one could eliminate the welded region by proper control of the copper jacket thickness.

The major significance of the occurrence of the welded annular region is that it will probably produce an increase in the a.c. loss characteristic of *in situ* and powder-prepared Nb_3Sn–Cu superconducting wires. It seems likely that a.c. losses would be less in core wires because the welded annular region lies near the core and appears to involve a lower volume fraction of the Nb_3Sn filaments than for the externally plated wires.

5. Conclusions

The Nb_3Sn filaments of *in situ* wire, where the tin is supplied by diffusion from a pure tin source, are not isolated from each other by the α-bronze matrix. The Nb_3Sn filaments are welded together at point contacts in a thin annular region which borders the surface of the original tin supply. A model has been presented which explains the welding as resulting from a localized collapse of the α-bronze matrix near the surface of the tin supply. It seems likely that this effect will occur generally in both *in situ* and powder-prepared Nb_3Sn–Cu wire and that it will have a detrimental effect on a.c. loss properties. The problem may be eliminated by utilization of an α-bronze plate or by proper control of the thickness of a copper jacket between the pure tin plate and the Cu–Nb core.

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References

1. J. D. VERHOEVEN, E. D. GIBSON, F. C. LAABS, J. E. OSTENSON and D. K. FINNEMORE, *IEEE Trans. Magn.* **MAG 19** (1983) 563.
2. J. D. VERHOEVEN, E. D. GIBSON, C. V. OWEN, J. E. OSTENSON and D. K. FINNEMORE, *Appl. Phys. Lett.* **35** (1979) 270.
3. J. J. SUE, J. D. VERHOEVEN, E. D. GIBSON, J. E. OSTENSON and D. K. FINNEMORE, *Acta. Metall.* **29** (1981) 1791.
4. J. BEVK and J. P. HARBISON, *J. Mater. Sci.* **14** (1979) 1457.
5. R. BORMANN, *J. Appl. Phys.* **54** (1983) 1479.
6. R. AKIHAMA, R. J. MURPHY and S. FONER, *IEEE Trans. Magn.* **MAG 17** (1981) 274.
7. H. BENZ, I. HORVATH, K. KWASNITZA, R. X. MAIX and G. MAGER, *Cryogenics* **19** (1979) 435.

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