JOURNAL OF MATERIALS SCIENCE 15 (1980) 1907–1914

The morphology and grain size of Nb_3Sn filaments in *in situ* prepared multifilamentary Nb_3Sn–Cu composite wire

J. D. VERHOEVEN, J. J. SUE, D. K. FINNEMORE, E. D. GIBSON,
J. E. OSTENSON
Ames Laboratory-USDOE, Department of Materials Science and Engineering and Department of Physics, Iowa State University, Ames, Iowa 50011, USA

Multifilamentary Nb_3Sn–Cu wire was prepared from chill-cast Cu–20 wt % Nb ingots by drawing 12.5 mm ingots to 0.15 mm diameter wire, plating with 9 vol % Sn and reacting at temperatures ranging from 450 to 725° C. The morphology and grain size of the as-cast Nb filaments and the Nb_3Sn filaments formed on heat treatment were characterized by TEM and SEM studies, and the Sn diffusion process was evaluated using electron microprobe analysis. The as-drawn Nb filaments had a cross-section typically 50 Å by 2500 Å and were generally convoluted in the wide direction. Tin diffusion produced Nb_3Sn filaments with an essentially equi-axed cross-section having diameters of around 800 Å for the 550° reaction temperature and grains extending across the diameter. It was shown that the change in cross-sectional shape is produced largely by coarsening of the thin Nb filaments prior to diffusion of Sn to form the Nb_3Sn. Optimum J_c values at both 1 and 8 T were found to occur for diffusion temperatures of 550° C and times of 3 to 6 days where the grain size was 750 to 800 Å.

1. Introduction

The *in situ* process for preparing multifilamentary Nb_3Sn superconducting wire consists of preparing a cast alloy containing Nb dendrites in a copper or bronze matrix, mechanically deforming the casting into wires thereby forming the Nb dendrites into elongated filaments, and finally converting the Nb filaments into Nb_3Sn by diffusing tin to the filaments. Development of this process has been carried out independently by three groups, all of whom have recently shown high-field (10 to 14 T) critical current data as good or better than that of wire prepared by the bronze process [1–6]. The MIT-Quebec group [1, 2] prepared the wire from Cu–Nb alloys cast from graphite crucibles into graphite moulds. The Harvard group [3, 4] prepared their wire from bronze–Nb alloys produced by levitation melting followed by rapid cooling. In our initial work at Ames [5, 6], the alloys have been prepared by melting in either Y_2O_3 or ThO_2 crucibles and casting into a water-cooled copper chill mould. Our material differs from the MIT-Quebec group [1, 2] in two principle ways: (a) our as-cast Nb dendrites are smaller, around 1 μm diameter versus 2 to 20 μm diameter, and (b) the carbon content of our castings are much lower, around 60 parts per million atomic (ppma) versus 2000 ppma. Our material differs from the Harvard group [3, 4] also in two principle ways: (a) our as-drawn Nb dendrites are much smaller, primarily because larger area reductions were used, 7000 versus 40 to 160, and (b) the Sn is introduced by external diffusion rather than from the as-cast bronze. There may also be some subtle differences which arise due to the fact that their Nb dendrites form in the ternary alloy and such as-cast dendrites are encased in a thin Nb_3Sn layer [7].

In this paper we present an analysis of the morphology of our as-drawn Nb dendrites and the Nb_3Sn filaments formed from them by external diffusion of Sn into the wires. The study was done on 0.15 mm (6 mil) wires prepared from 12.5 mm diameter castings, an area reduction of about 7000. These small diameter wires were used to facilitate diffusion of Sn into the wire and to reduce the

0022–2461/80/081907–08$02.80/0

current requirements in the measurement of J_c at zero magnetic field. All of the data reported here are for castings of Cu–20 wt % Nb.

The wires were coated with Sn by electroplating and the vol % Sn was controlled to 9% by plating a slight excess and then drawing through a die. Heat treatment was done for various times and temperatures under 1 atm helium, utilizing tantalum as a "gettering" material to reduce any oxygen contamination.

2. Morphology of Nb and Nb_3Sn filaments

The wires were examined using optical microscopy and it was clear that the filaments were too small to be resolved. Therefore the wires were examined using various electron microscopy techniques. Attempts were made to thin samples for TEM analysis using both ion milling and electrochemical polishing, but these were only partially successful, primarily because of the very small diameter, 0.15 mm, of the wire. However, it was fairly easy to remove the filaments by selectively etching away the Cu or bronze matrix in a solution of 55% phosphoric acid, 25% acetic acid, 20% nitric acid. The filaments were collected on folding grids and TEM analysis revealed that they were thin enough for successful analysis by both TEM and STEM techniques.

Samples were prepared for SEM analysis by first embedding several wires inside a copper tube using a lead–tin soft solder. Transverse sections of the wire were then prepared by polishing through 600 grit SiC followed by hand lapping successively through 9, 6, 3 and 1 μm diamond powder on nylon cloth. The surface was then etched for 15 sec in a Nb etchant, 10 parts HF, 10 parts HNO_3, 10 parts H_2SO_4 and 50 parts H_2O, and again polished with 1 μm diamond. After repeating this etch–polish step three times in order to eliminate any smearing of the Nb filaments, final polishing was done with 0.25 μm diamond, and the sample was given a final etch of anywhere from 5 to 15 sec in the 55% phosphoric acid solution.

2.1. As-drawn Nb filaments

Fig. 1 shows a TEM photo of the extracted Nb filaments as they appeared on the folded grids. It is seen that the filaments have a ribbon shape. Estimates were made of the aspect ratio of these ribbons by examining many twisted ribbons at higher magnifications as shown in Fig. 2. The dark band at the side of the filament is assumed to be an edge-on view of the filament and indicates a maximum filament thickness of 50 Å. The projected filament width is 2000 Å at its largest point indicating an aspect ratio of 40 or more for the filament width-to-thickness dimension. Examination of many filaments revealed these numbers to be typical.

Figure 1 Extracted Nb filaments from a Cu–20 wt % Nb alloy after an area reduction of 7000.

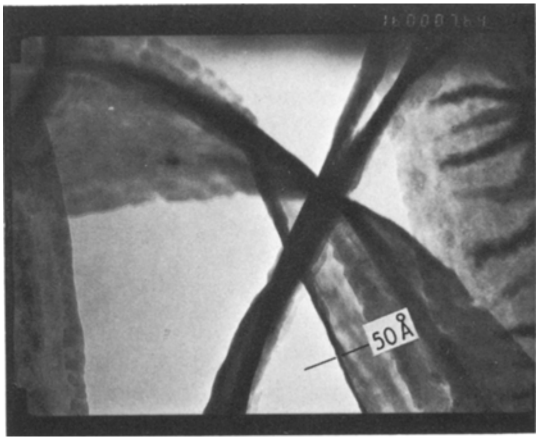

Figure 2 An individual Nb filament at high magnification, × 160 000.

Typical SEMs of polished surfaces are shown in Figs. 3 and 4. Fig. 3 is a lower magnification picture showing a larger view revealing the overall filament shape and packing arrangement. It is seen that the filaments are not flat but have a convoluted shape along their wide dimension, and this feature was consistently found in examination of many SEM pictures. Many extracted filaments also displayed this feature in the TEM examination. It is difficult to obtain high-resolution SEMs of the

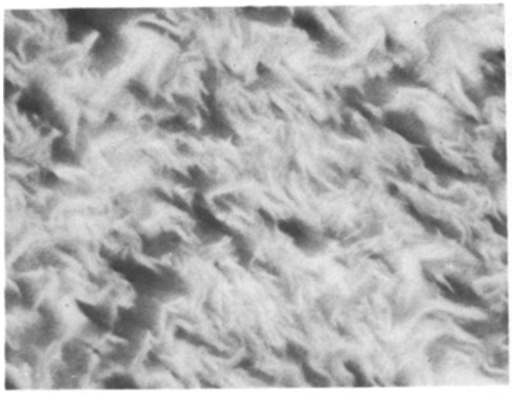

Figure 3 Polished and etched surface of transverse section of 0.15 mm wire in as-drawn condition, × 30 000.

filament edge because the beam penetrates the filaments and the large secondary yield from both surfaces plus the edge surface produces a flaring effect at the edges. Nevertheless, from pictures such as Fig. 4 it was possible to establish that the filament thicknesses are under 70 Å. The SEMs also confirm an aspect ratio on the order of 40 and higher.

Assuming an aspect ratio of 40 and an area reduction of 7000, a simple volume balance predicts that the 1 μm diameter as-cast Nb dendrites would draw down to a thickness of only 17 Å. Even if the aspect ratio were 10, the calculated thickness is only 33 Å. Hence, either the area reduction of the Nb is less than that of the wire, or the Nb filament thicknesses are less than the value of 50 Å estimated here. There are more accurate TEM techniques [8] for measuring foil thicknesses which we intend to use to determine the Nb filament thicknesses.

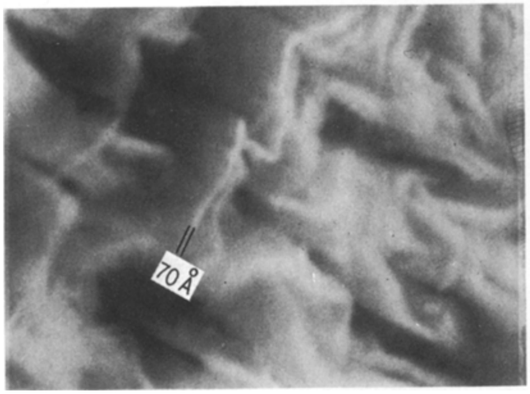

Figure 4 A higher magnification of lower portion of Fig. 3 showing individual filament thicknesses on the order of 70 Å.

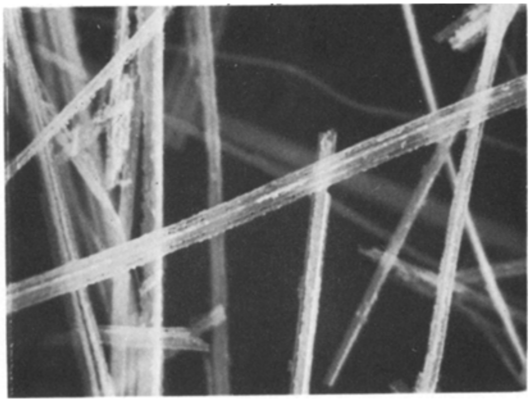

Figure 5 Extracted Nb_3Sn filaments from a Cu–20 wt % Nb alloy after plating with 9 vol % Sn and heating 6 days at 550° C, × 4000.

2.2. Nb–Sn filaments

Figs. 5 and 6 show SEMs of extracted filaments after a heat treatment which was found to produce optimum critical current properties, 6 days at 550° C. Views of the extracted fibres, such as Fig. 5, show clearly that the filaments were much straighter and hence much stiffer after reaction. Higher magnification pictures, as Fig. 6, show that the filaments had broken up into columns of connected cylindrically shaped granules on the order of 800 Å in size. TEMs of the individual cylindrical granules of Fig. 6 suggested that each one was an individual grain, and microdiffraction in the STEM mode confirmed crystallographic orientation differences between the grains.

Typical SEMs of polished and etched surfaces are shown in Figs. 7 and 8. The view at lower magnification, Fig. 7, reveals that the high aspect ratio

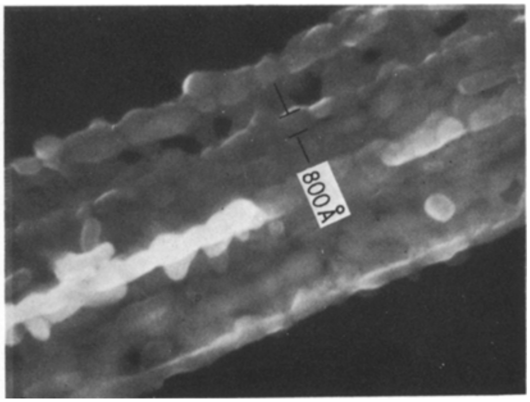

Figure 6 An enlargement of the central portion of Fig. 5 illustrating the granular surface structure of the reacted filaments, × 40 000.

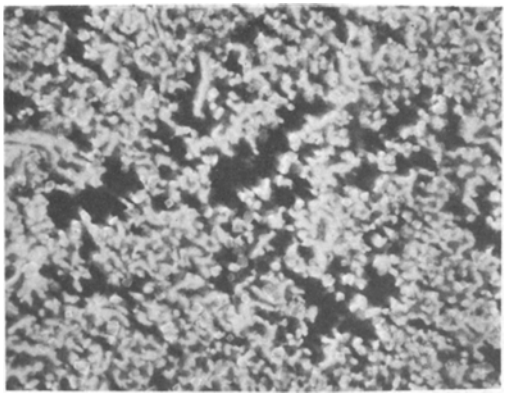

Figure 7 Polished and etched surface of transverse section of 0.15 wire after heating at 550° C for 100 h, × 10 000.

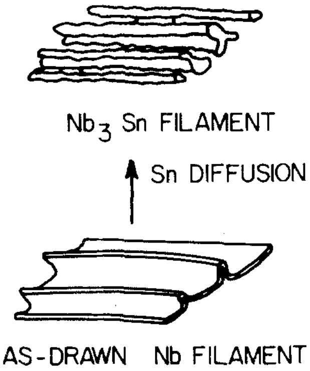

Figure 9 A sketch of the morphological change which occurs between the as-drawn Nb filaments and the Nb_3Sn filaments produced by reaction with Sn.

of the original Nb filaments is almost completely lost, with most filaments appearing to be nearly cylindrical. The higher magnification view of Fig. 8 shows the nearly equi-axed cross-section of the Nb_3Sn filaments to have a dimension of the order of 800 Å.

Based upon examination of many photographs similar to those presented here, our view of the morphology of the Nb and Nb_3Sn filaments is presented in Fig. 9. The as-reacted Nb filaments are very thin, of the order of 50 Å, and are generally convoluted in their wide direction. It seems probable that the shapes of columns of Nb_3Sn grains formed from the Nb filaments are related to the shapes of the convolutions, as is suggested by the drawing of Fig. 9.

2.3. Coarsening of Nb filaments

Because the as-reacted Nb filaments are so thin, it seemed likely that they might be coarsening at the reaction temperatures due to shape instabilities, a phenomenon recently reviewed by McLean [9]. To evaluate this possibility, samples of as-drawn Cu–Nb wires without addition of Sn were heated to 450 to 550° C for various times and the extracted filaments examined as above. Fig. 10 shows typical extracted Nb filaments after 5 h at 550° C, and it is seen that the filaments have coarsened to sizes on the order of 600 to 800 Å. Examination of filaments heated to 550° C for only 0.5 h shows similar shapes with the filaments coarsened to sizes on the order of 300 to 500 Å. Comparision of Figs. 6 and 9 suggests that the morphology of the Nb_3Sn filaments is produced by coarsening of the Nb filaments followed by conversion to Nb_3Sn with only a small change in morphology occuring in the latter step. Examination of the Nb filaments heated to 450° C for 5 h reveals that even at this low temperature the Nb filaments had coarsened significantly, to sizes on order of 200 to 300 Å.

TEM examination of coarsened filaments, simi-

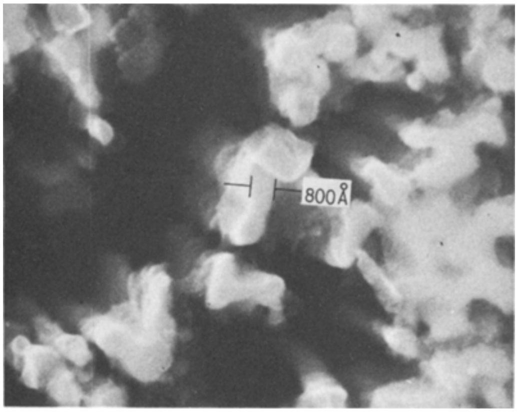

Figure 8 Enlargement of central portion of Fig. 7 illustrating the roughly equi-axed cross-section of reacted fibres, × 71 000.

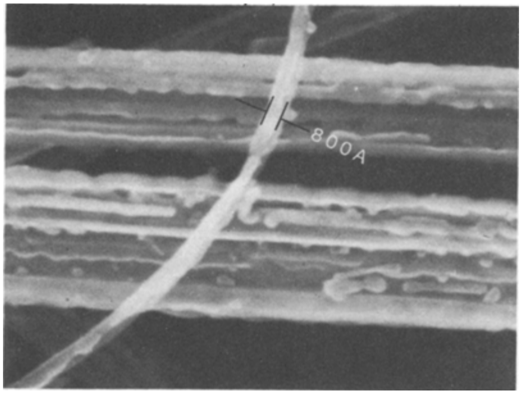

Figure 10 Extracted Nb filaments from Cu–20 wt % Nb wires heated to 550° C for 5 h with no Sn added, × 40 000.

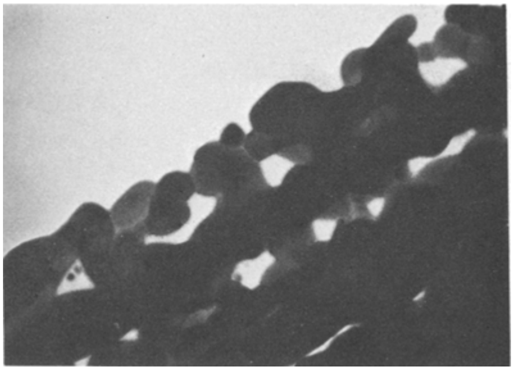

Figure 11 A TEM picture illustrating the grain structure within the filaments.

lar to those shown in Fig. 10, revealed that they remained single crystals during the coarsening in contrast to the polycrystalline nature of the Nb_3Sn filaments. This result seems reasonable as one would not expect recrystallization of the Nb filaments at 550° C during coarsening, but a crystal structure change necessarily occurs upon formation of Nb_3Sn. Apparently the development of the Nb_3Sn grain structure does not alter the external shape of the Nb filaments very significantly.

3. Nb_3Sn grain size

The Nb_3Sn grain size was determined from TEMs of extracted filaments, which clearly revealed the grain boundaries on individual filaments as shown in Fig. 11. In order to obtain good statistical averaging 10 grains were measured on each of 13 to 15 filaments for a total of 130 to 150 measurements per data point. The grains were observed to be larger along the direction of the filament axis than at right angles to the filament axis, as seen in Fig. 11. Fig. 12 presents a plot of the time dependence of the minor axis of the grains at reaction temperatures ranging from 500 to 750° C. The data are correlated with time, t, by an equation of the form $G = G_0 t^n$ where n was found to be 0.12 ± 0.01 averaged over all temperatures. The major axis was consistently found to be larger than the minor axis by a factor of around 2, and plots similar to Fig. 12 gave $n = 0.11 \pm 0.02$ for the major axis data.

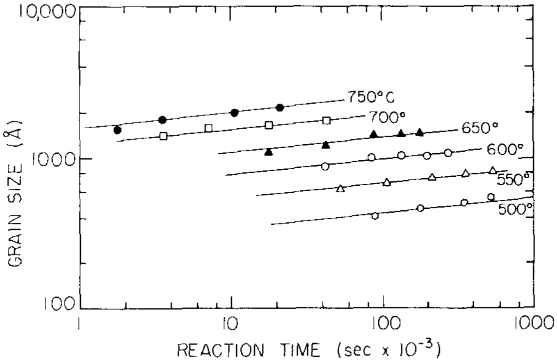

Figure 12 The minor axis of the Nb_3Sn grains as measured from TEM images of extracted fibres.

The temperature dependence of the grain size was determined from the data of Fig. 12 and was found to follow the usual Arrehenius form, $G = G_0 e^{-Q/RT}$, where Q was independent of reaction temperature and had a value of $11\,100\,\text{cal mol}^{-1}$. The value of G_0 varied with time as $G_0 = 1.93 \times 10^5 t^{0.10}$, where t is in seconds and G_0 in Å. It is interesting to point out that the activation energy found here, $11.1\,\text{kcal mol}^{-1}$, is quite similar to that found by Old and Macphail [10], $9.7\,\text{kcal mol}^{-1}$, for Nb_3Sn layer growth in Nb–Sn diffusion couples. Perhaps the same mechanism is operative in the layer growth as in the grain growth study of this work.

The SEMs of Figs. 6 and 8 on filaments of wires reacted at 550° C show granular dimensions on the order of 800 Å, which agrees well with the grain size data of Fig. 12 taken on extracted fibres using TEM imaging.

The only other reported data on Nb_3Sn grain size in *in situ* wire are those of Bevk and Harbison [3, 4] and they report a grain size of 400 Å for a heat treatment of 48 h at 650° C. Under these conditions our wires produced a transverse grain size of 1300 Å. The main differences in these studies are that Bevk and Harbison introduced the Sn from an as-cast bronze matrix and used much larger filament sizes. It is not possible to determine which of these differences accounts for their smaller grain sizes, and additional research will be required to resolve this difference.

4. Tin diffusion

In order to evaluate the Sn diffusion process, transverse sections of the 0.15 mm wires were mounted as described above for the SEM study, except that the final etch was not employed, so that as-polished surfaces were examined. The composition profile of Sn, Nb and Cu were then determined using a non-dispersive X-ray analyser in an SEM. In order to average over both the Nb_3Sn and the bronze phases, the analyses were made with the electron beam scanning a 0.6 μm by 1.8 μm raster. Analyses were made at various points along a radius, and re-

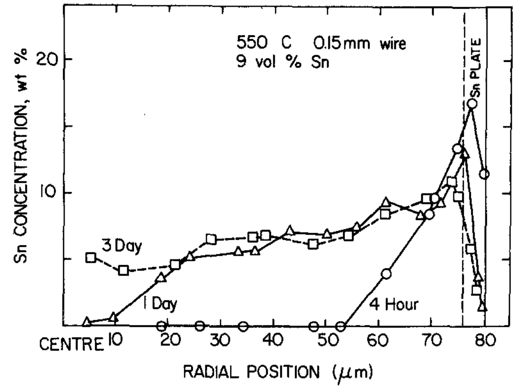

Figure 13 Microprobe results on transverse sections of 0.15 mm diameter wire of Cu–20 wt % Nb plated with 9 vol % Sn and heated to 550° C for various times.

sults on wires heat treated at 550° C for 0.17, 1 and 3 days are shown in Fig. 13. The % Sn was determined from the *k* ratios using a standard ZAF programme. No account was taken of the fact that the samples are two phase alloys so that some small undetermined error is involved here. Analyses on a sample heated for 6 days gave a profile identical to the 3 day profile within the scatter of the data. Hence it is seen that the Sn advance into the 0.15 mm wire is essentially completed between 1 and 3 days at 550° C.

One would not expect a simple linear diffusion model to describe the present diffusion problem for several reasons, but primarily because the continual formation of Nb_3Sn throughout the volume would require a sink term in the diffusion analysis. Nevertheless, the simple approximate volume diffusion equation, $Z = \sqrt{(Dt)}$, gives a D value of $3.8 \times 10^{-10} cm^2 sec^{-1}$ for the 4 h data of Fig. 13, where Z is taken as the point of furthest advance of the Sn front into the wire. Values of 5.5 and $5.8 \times 10^{-10} cm^2 sec^{-1}$ were obtained from 16 and 24 h data. It is surprising, but literature data on the diffusion coefficient of Sn in bronze are quite limited and vary considerably. At 7 wt % Sn and 550° C the data of da Silva and Mehl [11] extrapolate to a D of $2.6 \times 10^{-10} cm^2 sec^{-1}$ while the data of Matano [12] at 7 to 10 wt % Sn and 550° C give a D value of $2.1 \times 10^{-11} cm^2 sec^{-1}$. The values measured here are close to the average of these literature values and indicate that one may make a good first order guess at the diffusion depth in the present case using the simple volume diffusion equation.

The diffusion data indicate that the Sn front has advanced about half way into the 0.15 mm diameter wires after 5 h, while the above coarsening study shows that the Nb filaments were already heavily coarsened after 5 h. This means that in the centre of the wires the Sn diffuses into the Nb filaments after they have already coarsened. Near the outside of the wire the coarsening and Sn diffusion should be occurring simultaneously and this might have some effect on the filament morphology and grain size there. However, careful examination of deep etched specimens showed the filament morphology to be essentially the same at the centre and near the outer edges of the wire, and it seems likely that the grain sizes are also the same, but this result has not been experimentally confirmed.

5. Critical current measurements

The details of the critical current, J_c, measurement procedures have been reported elsewhere [5, 6]. Results showing J_c at a magnetic field of 1 T versus annealing time for various reaction temperatures are shown in Fig. 14. At this low field the critical currents are controlled by flux pinning at grain boundaries and one expects smaller grain sizes to enhance J_c. However, it is apparent from the data of Fig. 14 that the smallest grain size samples do not have the maximum J_c values. The maximum J_c values for the 500 and 550° C heat treatment occurred at 2 to 6 days and were essentially the same, even though the grain sizes were around 500 and 800 Å, respectively. Also, essentially the same J_c values were obtained for the 11 day 450 and 550 °C samples even though the measured grain sizes were 550 and 870 Å, respectively. It may be that the smaller grain size of the lower temperature samples does not produce higher J_c values because the Nb_3Sn formed at the lower temperature is defective with respect to composition or structure. In an attempt to answer this question, the transition temperatures were measured and it was found that T_c for the 450 and 500° C samples were significantly lower than for a 550° C reaction temperature as shown on Fig. 15. This depression of T_c probably reflects an Sn deficiency in the Nb_3Sn lattice. The reduced J_c values at 600 and 725° C must be due to a combination of increased grain size and loss of filament continuity due to coarsening.

There have been several recent studies of the effect of grain size upon J_c in bronze-processed Nb_3Sn wires. These have been summarized by Madsen and Hill [13] in a plot of the critical current per area of Nb_3Sn at 4 T versus reciprocal

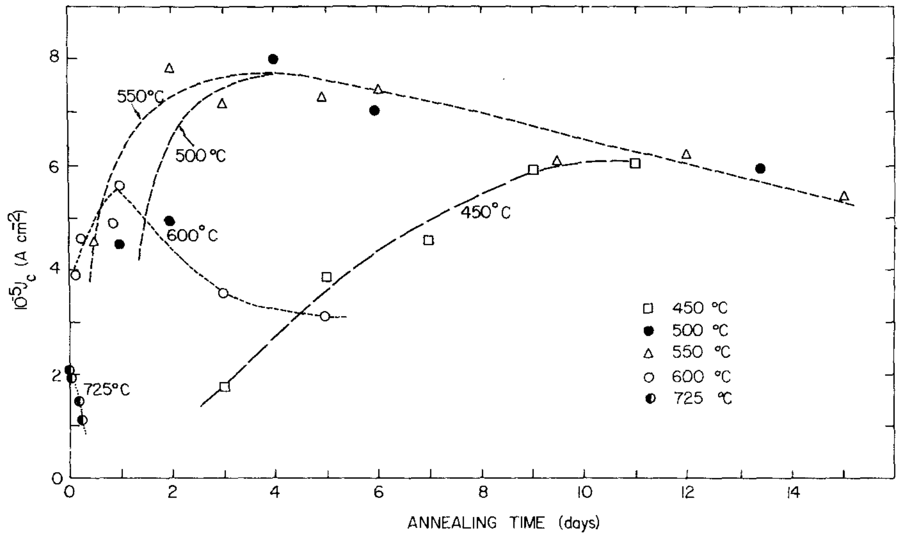

Figure 14 Critical current measurements at 1 T versus annealing time on Cu–20 wt% Nb wire plated with 9 vol% Sn and heated at various temperatures. The 450° C data were taken on 0.10 mm wire and the remaining data on 0.15 mm wire. J_c calculated using total wire area prior to Sn plating.

grain size. Fig. 16 presents such a plot of our 4 T data on samples heat treated to optimum J_c values, where the area of Nb_3Sn has been estimated by assuming the Nb_3Sn occupies 20% of the wire cross-section. The data of Fig. 16 for samples heat treated at 550° C and above agree well with the literature data [13], indicating similar flux pinning characteristics of these *in situ* processed wires with bronze processed wires. The data at 500 and 450° C do not correlate with the linear increase of J_c with reciprocal grain size, and this probably results from the defective character of the Nb_3Sn formed at these lower temperatures, as mentioned above.

Measurements of J_c versus annealing time at 8 T give results similar to Fig. 14 except that now the 550° C data lie significantly above the 500° C data. Our data on H_{c2} versus annealing temperatures as well as data on bronze processed wire [14] indicate that H_{c2} may be improved by reaction at higher temperatures. It appears then that there may be some distinct advantages of using smaller reduction ratios than employed here in order to increase the as-drawn filament sizes. This would allow reaction at higher temperatures with less coarsening of the filaments. Also, based on the study of Bevk and Harbison [3, 4] it might even produce smaller Nb_3Sn grain sizes, and, as seen in Fig. 14, a significant improvement of J_c could be expected if smaller grains sizes could be achieved at higher annealing temperatures.

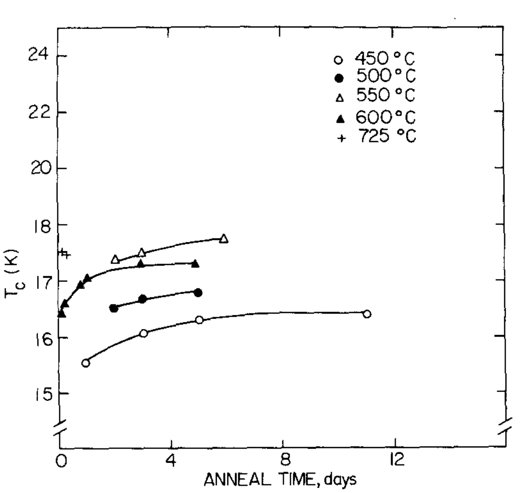

Figure 15 Transition temperature measurements on wire heat treated at various temperatures and times.

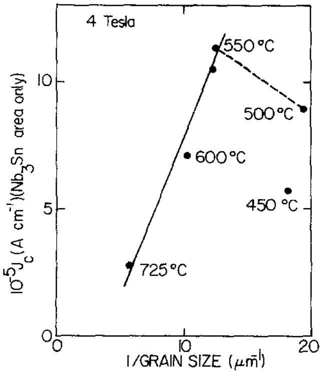

Figure 16 Critical current versus reciprocal grain size.

6. Conclusions

(1) The Nb filaments of the 0.15 mm diameter Cu–20 wt % Nb wires produced by an area reduction of 7000 are of the order of 50 Å thick by 2500 Å wide. The filaments generally contain several convolutions across the wide dimension.

(2) When an individual Nb filament is converted to Nb_3Sn it breaks up into several parallel columns of grains. These grains are slightly elongated in the drawing direction and are equi-axed in the transverse direction, with diameters 10 to 15 times larger than the original 50 Å thickness of the Nb filaments.

(3) The formation of Nb_3Sn from these very thin Nb filaments is accomplished in the central wire area by coarsening of the Nb filaments followed by formation of Nb_3Sn form Sn diffused from the outside Sn plate. At the outside area of the wire both processes must occur simultaneously but no difference in Nb_3Sn filament morphology is found between the centre and outside of the wires.

(4) The progress of the Sn front into the wire appears to be reasonably approximated by the simple linear volume diffusion equation, $Z = \sqrt{D}t$.

(5) Optimum J_c properties for the 0.15 mm wires at both 1 and 8 T are produced by a heat treatment of 3 to 6 days at 550° C.

(6) The optimum size of the as-drawn Nb filaments is probably larger than the very thin filaments studied here. Larger filaments would reduce coarsening kinetics and allow higher diffusion temperatures which might increase H_{c2} and decrease grain size. Larger Nb filament sizes could be produced by lower reductions on drawing and by increasing the as-cast dendrite size through the use of slower solidification rates in production of the Nb–Cu castings.

Acknowledgements

This work was supported by the US Department of Energy, contract No. W-7405-Eng-82, Division of Materials Science (budget code AK-01-02).

References

1. S. FONER, E. J. McNIFF, Jr., B. B. SCHWARTZ and R. ROBERGE, *Appl. Phys. Letters* **31** (1977) 111.
2. R. ROBERGE, S. FONER, E. J. McNIFF, Jr. and B. B. SCHWARTZ, *ibid.* **34** (1979) 111.
3. J. P. HARBISON and J. BEVK, *J. Appl. Phys.* **48** (1977) 5180.
4. J. BEVK and JAMES P. HARBISON, *J. Mater. Sci.* **14** (1979) 1457.
5. J. D. VERHOEVEN, D. K. FINNEMORE, E. D. GIBSON, J. E. OSTENSON and L. F. GOODRICH, *Appl. Phys. Letters* **33** (1978) 101.
6. D. K. FINNEMORE, J. D. VERHOEVEN, E. D. GIBSON and J. E. OSTENSON, *IEEE Trans. Mag.* **MAG-15** (1979) 693.
7. J. D. VERHOEVEN, E. D. GIBSON, D. FINNEMORE, J. OSTENSON and L. GOODRICH, *Fabrication of Superconducting Wire Composites by Directional Solidification*, IS-4698, Ames Lab., Ames, Iowa (1979).
8. G. LOVE, M. G. COX and V. D. SCOTT, *Inst. Phys. Conf. Ser.* **36** (1977) 347.
9. M. McLEAN, *Met. Sci.* **12** (1978) 113.
10. C. F. OLD and I. MACPHAIL, *J. Mater. Sci.* **4** (1969) 202.
11. L. C. C. DA SILVA and F. MEHL, *Trans. AIME* **191** (1951) 155.
12. C. MATANO, *Jap. J. Phys.* 9 (1934) 41.
13. P. E. MADSEN and R. F. HILLS, *IEEE Trans. Mag.* **MAG-15** (1979) 182.
14. J. W. EKIN, private communication, National Bureau of Standards, Boulder, Colorado (1979).

Received 14 November and accepted 17 December 1979.