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CHARACTERIZATION STUDIES OF A FULLY REACTED HIGH

BRONZE-TO-NIOBIUM RATIO FILAMENTARY Nb₃Sn COMPOSITE

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ABSTRACT

An attempt has been made to increase the chemical homogeneity of Nb₃Sn layers in a conventional bronze-process composite with excess Sn through extended time reaction heat treatments at high temperature (> 750°C). This study has included measurements of J_c, B_{c2}, local chemical composition, and grain size and morphology. The local bronze/Nb ratio has been found to influence the local chemical composition even after extensive reaction times. The dependence of B_{c2} on local composition variation is uncertain. Critical current densities at high magnetic fields have been improved up to 50% over those obtained for heat treatments at 700°C. These increases are attributed to increased values of B_{c2} but they are accompanied by a reduction in J_c below 12 T. Drastically reduced J_c is found with over-aging, despite a quite high value of B_{c2}. Grain size is found to increase strongly with heat treatment temperature and a large variation is found above 750°C. Equiaxed morphologies have been found at all temperatures between 650°C and 800°C.

INTRODUCTION

The critical current density (J_c) of bronze-process Nb₃Sn composites in low magnetic fields depends directly on grain size and morphology, the peak pinning force being proportional to grain boundary area or the inverse grain size.¹ In high fields the pinning force (and hence J_c) are less sensitive to the microstructure, and the upper critical field (B_{c2}) is important in determining J_c.² B_{c2} has been shown to vary with crystallographic order and chemical composition in thin Nb₃Sn films³ and in bulk samples.⁴ However, there is little direct evidence to substantiate a variation of B_{c2} with chemical composition in bronze-process composites.

Because Nb₃Sn layers in these wires are grown by solid-state diffusion, a Sn concentration gradient across the layer is typically present.⁵ This varying composition, together with the small thickness of the layers (< 3 μm), makes quantification of the chemical state difficult. Some success in measuring the relative composition across these layers has been achieved, both with the scanning Auger microprobe (SAM)⁵⁻⁷ and with x-ray analysis on

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the scanning transmission electron microscope (STEM).⁸ However, there are problems in obtaining absolute concentrations from both of these techniques.

An additional problem involved with a quantitative characterization of these composites is that the local bronze/Nb ratio can vary significantly with position in a wire.⁹ This variation can affect the local grain size and morphology, as well as the local composition of the layer. This presents problems for the correlation of high-resolution analysis of the microstructural and chemical state with measurements of the superconducting properties, which are generally interpreted as bulk averages for the wire.¹⁰ Convincing correlations must depend on an appropriate average of the locally varying structure and composition. A first step toward such a process may be taken by identifying and characterizing the local environment in which the high-resolution analysis is made.

In fact, the situation appears to be even more complicated. Evetts has pointed out that common techniques for measurement of T_c , B_{c2} and J_c do not generally give bulk averages.¹¹ He suggests that the appropriate program to pursue is the development of higher resolution techniques for the determination of local superconducting property variation within a layer.¹¹

This work is a subset of a broader program to characterize the local composition and morphology, and to explore the extent to which such microstructural measurements can be correlated with conventional measurements of J_c and B_{c2} . A series of extended time heat treatments at a range of temperatures has been given to an excess Sn composite in an attempt to react it as fully as possible and to achieve as uniform a composition as possible. We report here some of the results to date.

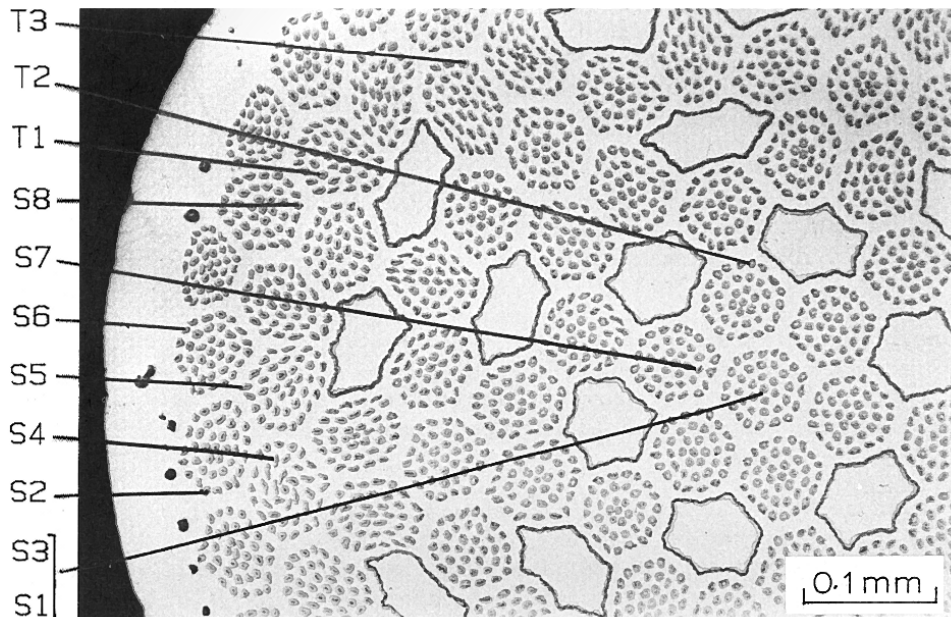


Fig. 1. Segment of the cross-section of a wire reacted for 191hr/800C. Filament labels show the location of filaments studied with SAM and TEM (compare Table 2, Fig. 5).

EXPERIMENTAL DETAILS

The Composite and Its Reaction Heat Treatment

The composite discussed here was fabricated at AERE, Harwell, England, and is a conventional bronze composite with a bronze/Nb ratio design of 4.1:1 and a bronze composition of 14 w/o Sn. Full reaction of the Nb to stoichiometric Nb₃Sn from a 13.5 w/o Sn bronze matrix requires a ratio of 3:1. Fig. 1 shows a segment of a cross section of the wire at 1 mm diameter. The stabilizing copper is internally located in 24 larger filaments protected by Nb diffusion barriers. The 5143 filaments have an average diameter of 7 μm and are grouped in bundles of 37. A series of reaction heat treatments have been done in 1 atmosphere of Ar for various times and temperatures from 24 to 1000 hours and 650 to 800°C.

Superconducting Properties

I_c was measured resistively at 4.2 K on 0.6 m samples wound helically on 35 mm diameter stainless steel barrels. The tap length varied from

B_{c2} was measured resistively on 10 mm samples at 4.2 K. Measuring current densities varied between 0.01 and 1.2 A/mm² over the wire cross-section. This corresponds to estimated Nb₃Sn current densities between 0.06 and 6 A/mm². We also calculated values of the critical field, B^*_{c2} from the $J_c(B)$ data using the Kramer $J^{3/4}B^{1/4}$ extrapolation.

Concentration Profiles

Reacted filaments were chemically analyzed for Nb, Sn, Cu, O, and C using line scans and multiplexed point analyses on a Physical Electronics 595 scanning Auger microprobe. The samples were polished transverse sections of whole wires. Experimental details were similar to those previously reported.⁵ The major difference from our past experiments was that these results were obtained while continuously ion-etching at a very slow rate (~ 5 Å/min on a Ta₂O₅ standard). This reduced the effect of residual oxygen and carbon in the system, which can strongly affect the sensitivity factors of Nb and/or Sn. This problem was particular to the machine used, since the sample chamber pressure was higher than normal, ranging between 6 and 10 x 10⁻¹⁰ Torr. The results obtained on a thick layer tape standard showed less statistical error and greater reproducibility from run to run using this technique. The disadvantage of data acquisition during sputtering was decreased signal-to-noise ratio. Since higher beam currents were required to obtain good signal-to-noise ratios in a reasonable time, some spatial resolution was lost. The probe size used for these measurements was ~ 0.3 μm.

Microstructure

The grain size and morphology were studied using a JEOL 100B or 200CX transmission electron microscope. Transverse section foils were thinned electrolytically. Details of the sample preparation are similar to those used previously for transverse sections of filamentary NbTi composites.¹² Average grain sizes were determined by the linear intercept method.

RESULTS

Attempts to fully react the filaments in this composite have been only partially successful. Fig. 1 shows that the outermost filaments in the composite are reacted to a greater extent than the inner filaments. Nb₃Sn

area measurements are being made but are unavailable at this time. We can comment that complete reaction in the outermost filaments of the wire has been achieved at all reaction temperatures between 650 and 800°C. Nearly complete reaction in the filaments at the wire center required 636 hours at 800°C.

Results for the critical current density (bronze plus Nb area) are shown in Fig. 2. These results are for those reaction times that produced essentially complete reaction at the outside of the wire at 650, 700, 750 and 800°C. Additionally we show results for a 636 hr/800°C sample. Above 16 T, J_c increases with higher reaction temperature. At 16 T the J_c for 191 hr/800°C is 118 A/mm², 7% more than with 672 hr/700°C. At 19 T the J_c is 22 A/mm², for an increase of 83%. At fields below 10 - 12 T the trend is reversed, with lower reaction temperature resulting in higher J_c . An obvious exception is the 636 hr/800°C sample, which had quite low J_c at all fields.

In Fig. 3 the Kramer extrapolations to B^*_{c2} are plotted. Some of the lower field data is not linear; our extrapolations emphasize the linear high field region, as the model predicts linearity only at fields well above the field at which the pinning force peaks ($0.2 B_{c2}$).²

Fig. 4 shows the resistive B_{c2} as a function of measuring current density in the whole wire. The inset shows the definition of B_{c2} used for these results. B_{c2} increased with decreased measuring current. In most cases the slope of the B_{c2} -J curve decreased with decreasing current as well, the 650°C sample being an exception. Table 1 lists the values obtained at the lowest measuring currents and compares these with the extrapolated B^*_{c2} values. The two sets of values are consistent in rank, with the resistive values varying from 2.1 to 2.8 Tesla higher than the extrapolations. In both cases B_{c2} increases with increasing reaction temperature. The highest value is for the 636 hr/800°C sample, which reaches 24.9 T. The transition widths in Table 1 are from B_{c2} to the midpoint, as defined by the half voltage point. These

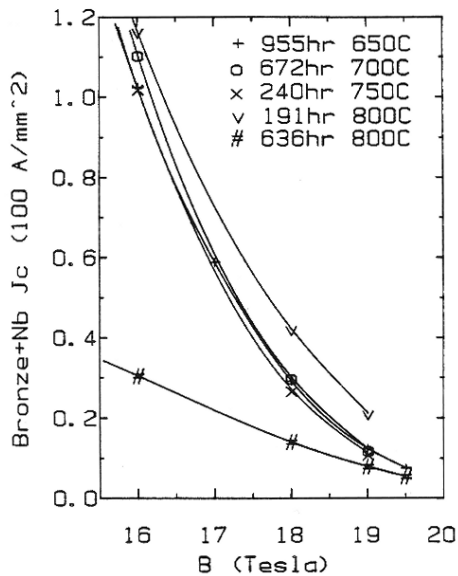


Fig. 2. Critical current density in the bronze + Nb area. Criterion for I_c is 10 μ V/m.

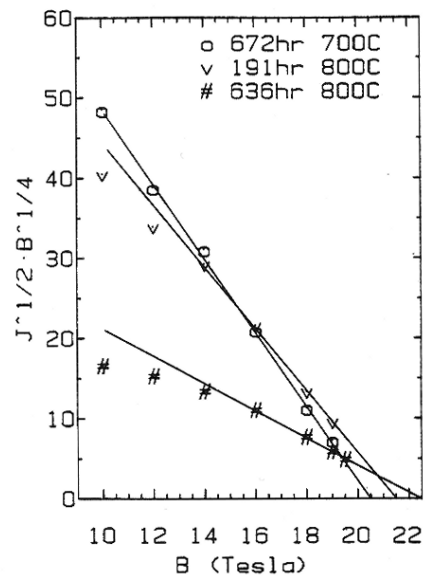


Fig. 3. Kramer plot showing extrapolated B^*_{c2} for three of the samples studied.

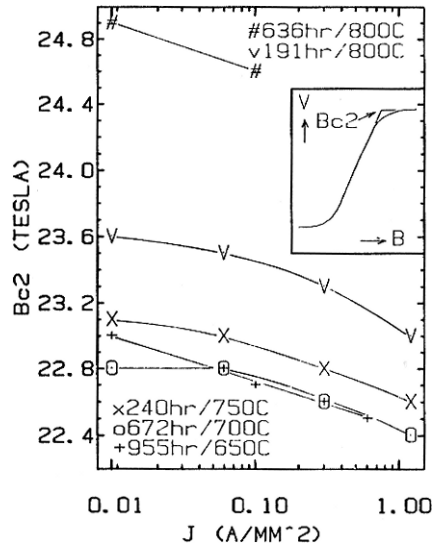


Fig. 4. Upper critical field measured resistively as a function of measuring current density. The inset shows the definition of B_{c2} used.

Table 1. Comparison of Critical Field Values Measured Resistively with Extrapolated Values

Sample	B_{c2} (T)	$\Delta B_{c2}/2$ (T)	B^*_{c2} (T)
955hr/650C	23.0	0.7	20.2
672hr/700C	22.8	0.4	20.5
240hr/750C	23.1	0.5	20.5
191hr/800C	23.6	0.4	21.5
636hr/800C	24.9	0.5	22.3

Table 2. Maximum Sn Contents and Estimated Gradients Found in Fully (Right) and Partially Reacted (Left) Filaments.*

Sample	955hr 650°C	672hr 700°C	240hr 750°C	191hr 800°C	955hr 650°C	672hr 700°C	240hr 750°C	191hr 800°C
Fil.#	S1	S3	S5	S7	S2	S4	S6	S8
Max Sn at%	23.0	23.4	26.0	21.0	23.0	25.3	26.0	25.9
Gradient at%/ μm	5	1	3	2	4	0	0	0.3

*Locations of these filaments in the wire are shown in Fig. 1, referenced by filament number.

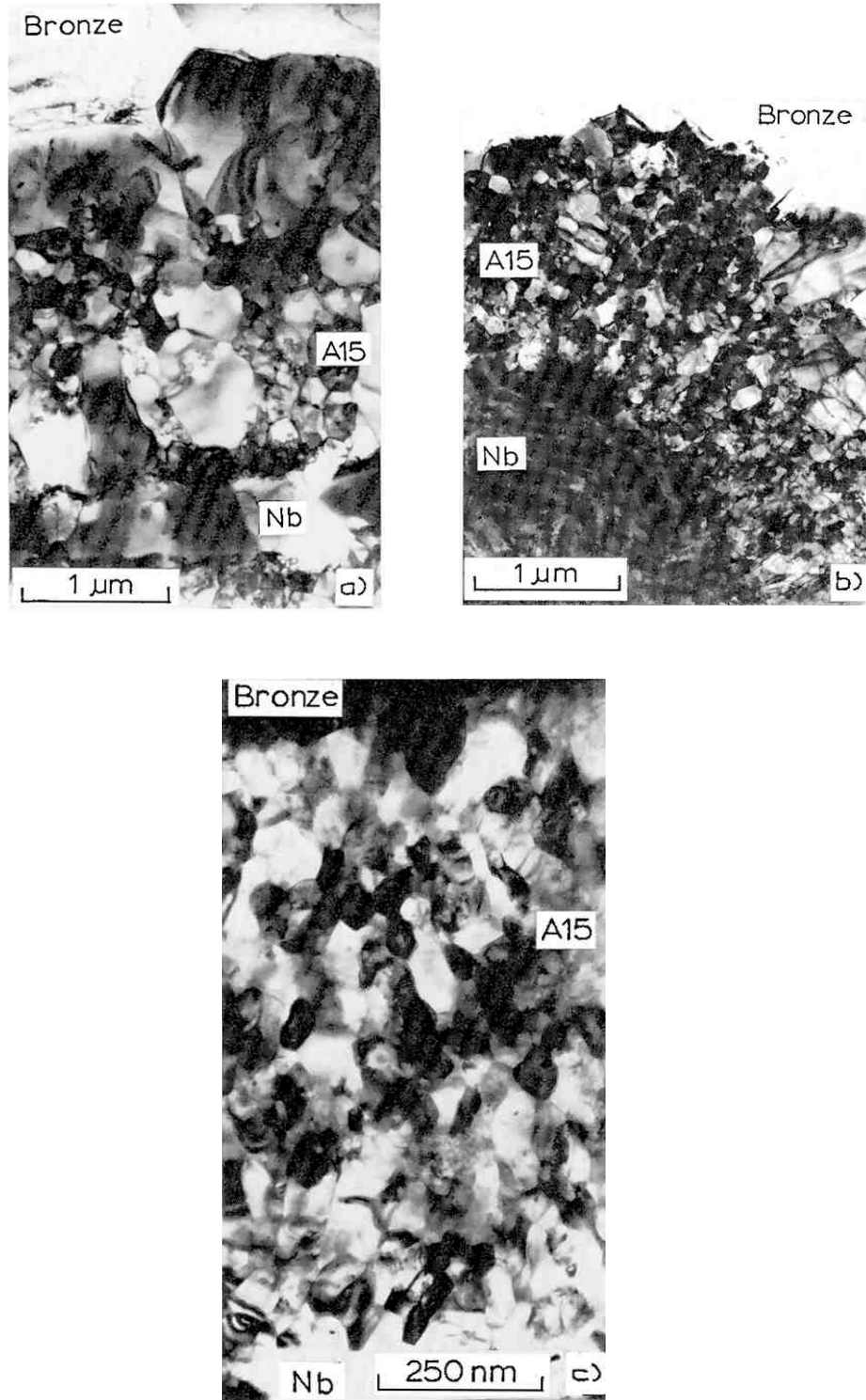


Fig. 5. Transverse section TEM micrographs showing the complete reaction layer at three temperatures. Locations of these filaments in the wire are shown in Fig. 1, referenced by Fil. # a) Fil. T1, 120hr/800°C; b) Fil. T2, 240hr/750°C; c) Fil. T3, 935hr/650°C.

widths are all close to 0.5 T.

Preliminary composition measurements were made on one filament at the wire edge and one at the wire center for each sample. Locations of measured filaments are shown in Fig. 1. Results are summarized as a function of temperature in Table 2. The maximum Sn concentrations measured are shown; in all cases these were measured nearest the bronze interface. The tabulated gradients are estimates only, since in most cases point analyses were not done at the minimum Sn concentration points. The filaments from the wire center had unreacted Nb cores, strong composition gradients, and low maximum Sn concentrations, regardless of reaction temperature. In contrast, the filaments at the wire edge were completely reacted (except for the 650°C sample) and the line scans showed relatively constant Sn concentration across the layers, with maximum Sn contents between 25 and 26 a/o.

Typical grain morphologies found in this composite are shown in Fig. 5 in TEM micrographs from samples reacted for 955 hr/650°C, 240 hr/750°C, and 120 hr/800°C. These are transverse sections that show the entire reaction layer. The location of these filaments in the composites is given in Fig. 1. An equiaxed morphology was found in this composite at all reaction temperatures from 650°C to 800°C. A few aspected grains were observed, occurring at random locations within the layers. Average grain size measurements are presented in Table 3. The size increased strongly with increasing temperature; the spread in size increased with temperature also.

DISCUSSION

The radial dependence of the extent of reaction is explained by the radial bronze/Nb ratio variation of the wire. There is a significant Sn reservoir in the extra bronze at the outside of the wire, and the fully reacted filaments are all found within a few rows of the outside. In all cases the central filaments are the least fully reacted. There is also a variation in bronze/Nb ratio from outside to inside each bundle. However, the extent of reaction does not appear to vary significantly within a bundle at these long reaction times.

The capability of the SAM to probe whole wire cross sections is a real advantage for the study of these radial variations. The exact location in the composite of the filament under study is apparent, and the layer can be analyzed along the direction of growth. The initial composition results, while not extensive enough to be statistically representative of the whole sample, do suggest the range of variation within a composite for a given heat treatment. The results suggest that this range is about the same for

Table 3. Average Grain Size Results

Sample	Size (nm)
955hr/650°C	60
672hr/700°C	115
240hr/750°C	102
120hr/800°C	187
636hr/800°C	542

temperatures between 700°C and 800°C at these extended times. All of these samples had high, uniform Sn concentrations across outer filaments, and lower concentrations with a strong gradient in the inner filaments. This means that the bronze/Nb ratio variation across the wire strongly affects the local composition, even after extended time and high temperature heat treatments. It is not clear why the measured Sn concentration reaches 26% Sn. This may be a standardization problem; however, Smathers has also measured high Sn concentrations at the bronze-Nb₃Sn interface.¹³

There is a consistent difference between the measured and extrapolated B_{c2} values, the measured values being about 3 T higher. A difference of 2 T was found by Suenaga and Welch in a bronze process monofilamentary wire.¹⁶ They suggested this difference was due in part to composition gradients across the Nb₃Sn layer or to variations in strain. In our samples there is only an approximate correlation between the B_{c2} values and the composition measurements. B_{c2} is almost constant from 650 to 700°C (22.8 - 23.1 T), rising to 23.6 and 24.9 T at 800°C. The Sn composition is low at 650°C (23 at%), the maximum value being fairly constant between 25.3 - 26.0 at% Sn above 700°C. It seems unlikely then that radial composition variation alone can account for the 3 T difference. It is possible that this difference is due in part to the distribution of critical current values in the wires, caused by structural or chemical variations along the length of the filaments. A sensitive measurement of I_c probes the low end of this distribution. On the other hand, a low current density resistive B_{c2} measurement samples the best material present.

The grain morphology is notable for its equiaxed nature over a wide temperature range (650 - 800°C). Transverse sections allowed complete layers to be examined along the growth direction. The results of this study are quite different from recent reports of two and three shell layer morphologies.^{8,14} The difference may be due to the high bronze/Nb ratio of this composite. However, we have also found uniform columnar layers in a composite with a low bronze/Nb ratio.¹⁵ We have found no dependence of morphology on position in this composite. The grain size measurements are complicated by the wide variation in size throughout the layer, especially at temperatures above 750°C. However, the average sizes measured are comparable to averages measured by West and Rawlings on a similar composite.¹

The J_c results suggest that B_{c2} is a major determinant of high field current density for most typical reaction conditions. The increased high field J_c of the 191 hr/800°C sample is, however, at the expense of J_c below 15 T, indicating that heat treatment for optimum J_c is different for different field ranges. The low J_c in the 636 hr/800°C sample indicates over-aging is possible in this composite. The sample shows no signs of damage, having sharp transitions and little I_c variation along its length. Since B_{c2} is high, the implication is that the large grain size has depressed J_c even at very high fields.

CONCLUSIONS

1. Transverse wire sections are important for the study of composites with radial structure and property variations.
2. Even after extended time, high temperature heat treatments the bronze/Nb ratio variation across the wire has influenced the local composition of this excess Sn composite.
3. The grain morphology of this composite is equiaxed across the reaction layer, independent of location in the wire and reaction temperature.
4. Over-aging is possible in this high bronze/Nb ratio composite. This appears to occur for grain sizes between 0.19 and 0.54 μm .

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