

SCANNING AUGER INVESTIGATION OF COMMERCIAL
MULTIFILAMENTARY Nb₃Sn CONDUCTORS

D. B. Smathers, K. R. Marken, and D. C. Larbalestier, Applied Superconductivity Center, University of Wisconsin-Madison, Madison, Wisconsin 53706

J. Evans, NSF Regional Instrumentation Facility, University of Minnesota, Minneapolis, Minnesota 55455

Abstract

A Physical Electronics 595 Scanning Auger Microprobe was used to study etched filaments and transverse sections of variously reacted commercial bronze matrix multifilamentary Nb₃Sn conductors. Using beams as fine as 100 nm, tin concentration profiles were observed in polished samples. Differences were noted in the shape of the tin gradient as a function of the location of the reacted filaments within the wires. The tin content of the bronze was also measured between pre-reacted filaments in an unreacted composite and found to be about 1 at.% lower than in the large bronze reservoirs. In a Harwell composite with P-poisoned niobium diffusion barriers, P was detectable in the Nb₃Sn formed on the barrier but not on the filaments.

Introduction

There is, at present, a great deal of variability in the critical current density (J_c) performance of multifilament Nb₃Sn composites.¹ The two principal influences on the J_c are the upper critical field (H_{c2})² and the grain size.^{3,4} The composition affects J_c through the normal state resistivity (ρ_n) and the critical temperature (T_c) dependences of H_{c2} .⁵ One of the reasons for this variability is that there are no standard production specifications for the bronze process. The bronze to niobium ratio, the tin content of the bronze, the number and distribution or spacing of filaments, the method of electromagnetic stabilization (internal or external copper, niobium or tantalum diffusion barrier), the addition of third elements, and the reaction conditions (time and temperature) are variables which are, currently, all imperfectly understood. When the processing variables are different, the variability of J_c between composites may not be too surprising. There is, however, often variability even when the processing variables are kept the same. A recent example of this phenomenon is the great variability in J_c of production lengths of the compacted monolith conductor for the High-Field Test Facility (HFTF).⁶ Not all composites show such wide variability, however. The Large Coil Project conductor (LCP) showed good uniformity in J_c over many long lengths.⁷ Both of these conductors were manufactured by the same company. To understand why these conductors behave as they do, detailed correlations of the design, processing and properties need to be done.

The effects of bronze content, bronze to niobium ratio, and alloying element additions have been studied more frequently with single core wires or tapes^{8,9} than with filamentary composites.¹ The effect of grain size and influence of reaction conditions have also been studied in multifilamentary conductors.^{3,4} The influences of filament spacing, bronze to niobium ratio, impurity poisoning of niobium diffusion barriers, and the local tin content of the bronze are just beginning to be studied in multifilamentary conductors. Many conventional composites have filaments with about 3 micron diameters, spaced about one and half diameters apart. Thus, the chemical analysis of either the Nb₃Sn formed, or the bronze between filaments is not possible with conventional techniques such as the electron microprobe. At present, there are two options being pursued; the

scanning Auger electron spectrometer (SAM) and the scanning transmission electron microscope equipped with characteristic X-ray emission analysis (STEM/EDX).¹⁰ Applying our experience with the Auger technique on tape samples^{11,12,13}, we have extended our work to multifilamentary samples using the SAM technique.

Experimental Details

Fine beam scanning Auger uses the high surface sensitivity of Auger electrons to get high spatial chemical resolution. The penetration of the electron beam into the sample is the same as for the electron probe but the mean free paths of the Auger electrons are less than 5 nm, whereas the mean free paths of characteristic X-rays are greater than 2 microns. Thus, the spatial resolution will be determined largely by the width of the electron beam within the first 5 nm of penetration into the sample. The finest electron beams are about 1 nm diameter.

A Physical Electronics Industries (PHI) fine beam scanning Auger spectrometer (model 595) was used in this study. The diameter of the electron beam can be reduced to about 100 nm. This and the associated low beam current (0.5 nA) combine to produce a small signal-to-noise ratio. The emitted electron distribution ($N(E)$) is measured directly, multichannel analyzed (MCA), and stored digitally. If desired, the stored data can be smoothed, differentiated and expanded to reveal the fine features. The small signal-to-noise problem is partially compensated for by multichannel averaging, at the expense of the time needed for effective signal averaging.

The PHI 595 fine beam scanning system has both advantages and disadvantages compared to a broad beam AES instrument; the experience gained from our tape studies^{11,12,13} has helped identify the potential disadvantages. The sample is not sputtered during the data collection period, the length of which determines the signal-to-noise ratio. Oxygen and carbon collect on the surface when the sample is not being sputtered and this influences the effective sensitivity ratios.¹¹ Samples to be point, area or line scanned must be first sputter cleaned, which introduces two problems. The sputter cleaning preferentially etches the tin out of the Nb₃Sn and copper out of the bronze, requiring the use of sputter corrected (effective) sensitivity ratios. A directly related problem is that the different sputter rates for bronze, niobium and Nb₃Sn cause surface relief at the interfaces. These effects can be kept to a minimum by maintaining constant collection conditions and by limiting the sputter cleaning to a minimum necessary to remove the surface adsorbed layer.

Single filaments were extracted from multifilamentary composites by chemically removing the bronze with a 50% mixture of nitric acid and water. A smooth, clean surface with well defined interfaces is desired for examination of transverse sections. This was achieved by mechanically polishing thin sections of the composite. Wire samples for polishing were mounted in copper blocks using a high vacuum (low vapor pressure), thermo setting, conductive resin (type N microcircuit silver). After polishing, a short etch (1/8 HF, 3/8 HNO₃, and 1/2 H₂O) was used to

distinguish the Nb_3Sn from the niobium.

Results

Extracted Filaments

The fine beam Auger technique makes it possible to place the entire electron beam on a single extracted filament so that it can be sputter/depth profiled in the same way as were tape samples.^{11,12,13} One of the advantages of Auger electron spectroscopy is the ability to easily detect the light impurities.^{11,12,13} As we have indicated, the quantification of detected oxygen and carbon levels in the SAM is very difficult since the sample is not sputtered during the data collection. Other impurities which are not adsorbed from the vacuum environment, however, may be detectable if the signal-to-noise ratio permits.

We are able to detect phosphorus in the reacted Nb_3Sn in a multifilamentary composite made with a phosphor bronze. We extracted both the filaments and niobium diffusion barriers (used to protect the stabilizing copper) from an AERE Harwell composite, CF-99, reacted for 50 hours at 700°C. The bronze next to the niobium diffusion barrier had been doped with phosphorus in order to inhibit the formation of Nb_3Sn on the barrier.

The determination of the phosphorus level is tedious since the only two peaks in the 0 to 2000 eV range lie at, or near, the same energy as niobium peaks, and require some form of subtraction routine.¹³ The stronger of the two phosphorus peaks (LMM) is located at 120 eV. To determine the phosphorus content, the filament data was subtracted from the barrier data. The reduced data for an extracted filament and an extracted diffusion barrier are plotted as a function of the sputtered depth in figure 1. The 10 keV Nb/P sensitivity ratio was taken from the PHI Auger Handbook¹⁴ and the oxygen was corrected for the level on the composition standard. The tin level in the filament is high near the bronze- Nb_3Sn interface and then decreases into the layer. The tin level in the barrier begins to decrease strongly after only about 250 nm have been sputtered. Both samples appear to contain significant levels of oxygen extending over 100 nm into the Nb_3Sn layer. This may be contained in surface cracks. The phosphorus level was detectable only in the Nb_3Sn layer formed on the diffusion barrier and was found with concentrations greater than 6 at.%. These points will be considered further in the discussion.

Transverse Sections

An important advantage of using the SAM on polished cross-sections is the ability to study any filament and its local matrix in the composite. Studies of the bronze composition on a fine scale can be useful when correlated with the composition data obtained from reacted filaments.

We examined a polished cross-section of an unreacted HFTF conductor and found that the bronze matrix tin composition within a sub-bundle was about 1 atomic percent lower than the surrounding matrix reserve. The missing tin was consumed in the premature reaction to Nb_3Sn during the cold work anneals.¹⁶ We also examined the bronze in several Modified Jelly Roll (MJR) samples¹⁷ both before and after a series of heat treatments. When the filament spacing was small (bronze to niobium ratio of 2.3:1), the tin composition decreased rapidly from the central core level, approaching a limiting value of about 1 atomic percent

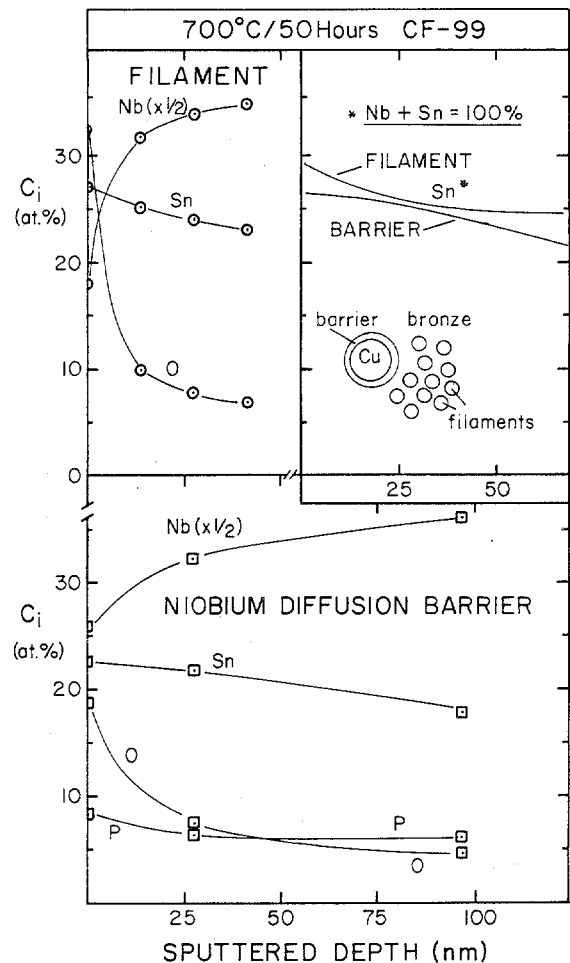


Fig. 1. Derived composition/depth profiles from multiplexed SAM data for a filament and a barrier extracted from the AERE Harwell composite, CF-99. The inset in the upper right hand corner shows the renormalized tin content in both cases (tin plus niobium equals 100%).

at the outer edge for all reaction times over 48 hours at 700°C. For larger filament spacings (Br:Nb ratio > 3) the tin level fell off more gradually (see reference 17). Since the wires studied were only lightly pre-reacted ($T_c < 10.5$ K),¹⁶ it is not surprising that there was not a strong gradient in the matrix composition found across the wires in the unreacted condition.

The fine beam in the SAM can be scanned across individual filaments and the spatial distribution of particular elements determined. We examined a number of samples for Nb, Sn, Cu, O and C. In our earlier studies on reacted HFTF samples we observed asymmetric tin composition gradients on filaments located at the edge of sub-bundles¹³, as opposed to symmetric tin composition gradients on interior filaments. This was interpreted as a bronze to niobium ratio effect. We have since observed similar features in the MJR wires in data taken with improved signal-to-noise ratio. A line scan for tin across an incompletely reacted filament in the M68L composite (48 hours at 700°C) is shown in figure 2. On the core side of the filament the tin level is essentially flat while there is a steep gradient on the opposite side. The reacted layer varies in thickness along the perimeter; the

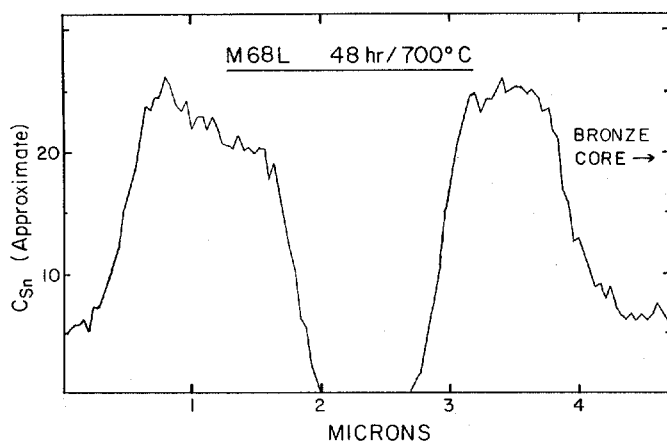


Fig. 2. Tin Auger line scan of a reacted Nb_3Sn filament at the edge of the central bronze core.

line scan happened to cross a thick section on one side and a thin section on the other. A fully reacted filament next to the one shown in figure 2 had a flat gradient over the whole thickness. A filament located about half way through the wire is shown in figure 3. The tin gradients are very similar to those we observed in broad beam Auger tape studies.^{11,12,13} After 168 hours at 700°C, a fully reacted filament in the M68L composite showed a composition gradient of about 2 to 3 at.%, with the core composition being close to 25 at.% tin. A fully reacted filament near the outside edge of the wire had a steeper gradient but the core composition was closer to 21 at.% tin (figure 4).

The tin concentration gradients in the reacted Nb_3Sn in MJR samples made with Nb 0.8 at.% Ti cores were very similar to those observed in the M68L wires. The growth rate was accelerated, however. Many filaments next to the bronze cores showed features similar to figure 2; there was usually no unreacted niobium left but the reacted layer on the bronze core side was flat while there was a distinct gradient on the opposite side of the filament.

Discussion of Results

The use of the fine beam scanning Auger instrument to study multifilamentary Nb_3Sn composites is practical. The SAM makes the determination of the composition of Nb_3Sn layers on a scale as fine as 100 nm possible. In polished cross-sections, filaments can be studied in their local environment and the bronze content measured between filaments. Filaments with diameters on the order of microns can also be extracted and sputter/depth profiled. The absolute uncertainty of the tin contents, estimated by the comparison of broad beam and SAM depth profiles is about 1.5 to 2.0 at.% for point or area depth profiles and a little larger for line scans. This uncertainty includes the plus or minus 0.5 at.% uncertainty in our composition standard,¹¹ as well as the uncertainties resulting from the low signal-to-noise ratio.

The lateral spatial resolution should be principally determined by the beam diameter for well prepared surfaces with sharply defined interfaces. In figures 2 - 4 the beam diameter was 150 nm. The additional width of the bronze- Nb_3Sn interfaces in the line scans shown for the reacted filaments is due to instabilities in the SAM electronics which cause a steady, slow drift of the analysis area across the sample at a rate of about 10 nm/minute.

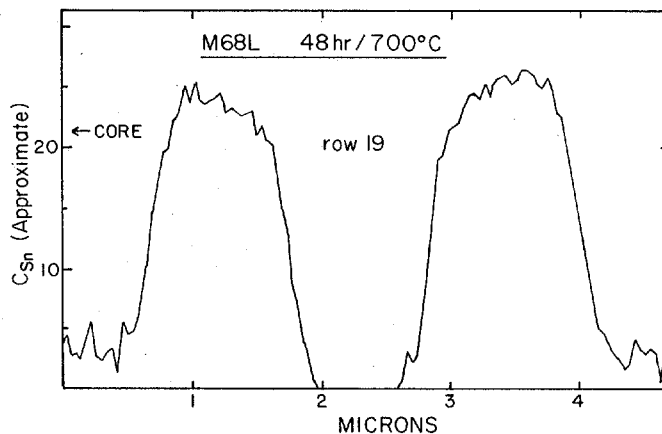


Fig. 3. Tin Auger line scan of a reacted Nb_3Sn filament in the middle of the filament distribution.

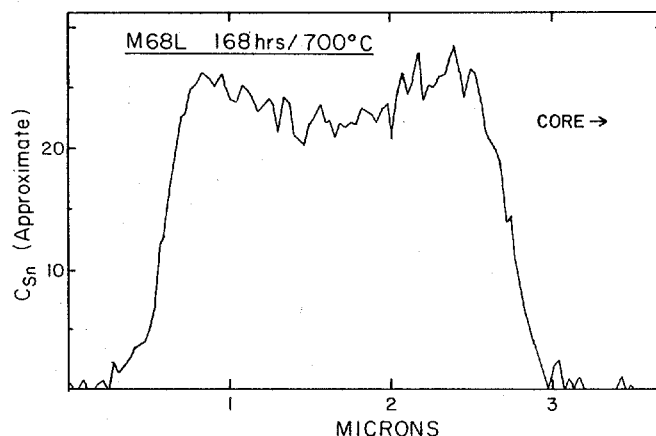


Fig. 4. Tin Auger line scan of a reacted Nb_3Sn filament at the outer edge of the filament distribution.

A potential bonus of Auger spectroscopy is the ability to detect impurities in the Nb_3Sn . The small signal-to-noise ratios obtained so far with the SAM, however, make the detection of any element in concentrations less than about 2 at.% very difficult. No copper was detected in samples determined to contain 1.5 at.% using the broad beam AES.^{13,15} Carbon and oxygen, though detected, are hard to define quantitatively, since the steady state residual levels under sputter conditions cannot be measured. If the concentrations are high enough, impurity levels can be measured in sub-micron thick layers. We were able to detect phosphorus in the niobium diffusion barriers, but not the filaments, of a composite known to contain phosphor bronze. The minimum detectable level of phosphorus is higher than that for most elements since the peak height determination requires subtraction of two small signal-to-noise ratio signals. The filaments were thought to contain some level of phosphorus since the (bronze-on) H_{c2} of the composite was only 13.2 Tesla, compared to the usual 18 to 22 Tesla, and the intrinsic T_c (bronze-off) was only 17.3 K. The Nb_3Sn layer on the diffusion barrier contained about 6 at.% phosphorus and had a T_c of about 15.5 K. It is not clear whether this amount of phosphorus can be dissolved in the Nb_3Sn . There is some evidence of binding to the niobium since a small additional niobium peak at 166 eV appears after deconvolution. The possibility of binding to the tin also cannot be

ruled out.

Using the SAM, we were able to measure the tin content of the bronze between filaments spaced about a micron apart, with a precision of about one atomic percent. The ability to study the diffusion of tin through the bronze matrix as a function of filament spacing is an important contribution. Our studies indicate that the tin supply is definitely affected by the filament spacing and that this results in variations in the characteristics of the reacted layer (extent of reaction and the shape of the concentration gradient). Within a given composite, the further a filament is from an adequate tin supply, the lower will be the highest tin level in the reacted layer and the layer thickness. This was not only observed in the MJR wires in which a large proportion of the filaments were located far from the major tin source, but also in double extruded composites in which the major tin source was located between large sub-bundles of filaments. As the line scans shown demonstrate, a filament taken at random from a composite will not, in general, be representative of the whole composite. It is also necessary to know the geometry of the composite and the relationship of the filament studied to that geometry. This is an important advantage of the SAM technique which is not possessed by STEM/EDX studies where there is, in general, no control over the specific area which ends up thin enough for examination.

One of the reasons for studying the characteristics of the reacted layers within composites is to understand how these affect the J_c properties. As indicated, the MJR wires studied had very inhomogeneous reaction characteristics but they also had exceptional J_c properties.¹⁷ These results, however, do not imply that such characteristics are necessary for good J_c performance. Rather, further studies of the MJR composites indicate that the uniformity of the filaments along their length ensures that most of the Nb_3Sn is available to carry the current.¹⁶ In one MJR composite (M66) which had a more uniform tin supply, the J_c in the $Nb + Nb_3Sn$ was about 10% higher than composites with the simpler design illustrated in reference 17.

Acknowledgements

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