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OBSERVATIONS OF THE EFFECT OF PRE-REACTION ON THE PROPERTIES OF Nb_3Sn BRONZE COMPOSITES

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Abstract

The effect of varying the annealing temperature on the degree of pre-reaction of two Nb_3Sn composites has been investigated. Annealing at 550, rather than 450 C produces noticeably more irregular growth and more uneven Nb_3Sn layers when final reaction occurs. It is believed that this is due to the effect that pre-existing Nb_3Sn nuclei have on subsequent Nb_3Sn growth. In one case the use of four anneals at 550 C, rather than 450 C was found to reduce the J_c by 50%. Results are also presented on some samples of the HFTF conductor. It is concluded that over-annealing of the bronze can be a major cause of reduced J_c in bronze Nb_3Sn conductors.

I. Introduction

The use of Nb_3Sn for large projects has meant that a significant production experience is being obtained for filamentary (FM) Nb_3Sn made by the bronze route. Two projects, the Nb_3Sn LCP coil and the HFTF coils, have required multiple billets of FM Nb_3Sn.[1,2] In view of the many variables of Nb_3Sn manufacture, the initial approach has been to set rather conservative specifications in order to allow for the normal, but not always predictable problems, which arise when a research laboratory scale production is transferred to the full size industrial scale. Among the questions or problems affecting large scale production, we may cite the questions surrounding the choice of impurity specifications for the starting materials, the bronze melting practice (vacuum or air melt) and the problems of filament sausaging and excessive Nb_3Sn pre-reaction brought on by the bronze anneals. This list is purely illustrative and in no way defines all the parameters controlling the design and production of FM Nb_3Sn composites.[3]

Reported critical current densities of Nb_3Sn composites have been rather variable and attempts to understand this variability in terms of such parameters as the bronze to Nb ratio, the filament size, the grain size and the composition gradient across the Nb_3Sn layer have had limited success so far.[2,4-6] An extensive study of the reasons for low J_c in the series of production composites for the HFTF coils uncovered a number of variables, such as Nb_3Sn pre-reaction, strand sausaging and internal strains which could contribute to the degradation of the J_c in the final conductor. It was found that, however, that the variable J_c could be qualitatively correlated with the quality of the Nb_3Sn layer grown during final reaction and the relationship of this to the state of the filament in the (nominally) unreacted condition.[7] The present paper reports on some aspects of these findings, as well as on the effect of increasing the bronze annealing temperature from 450 to 550 C and its influence on the J_c and Nb_3Sn morphology of two high J_c bronze composites. Degradation of the quality of the Nb_3Sn layer and the composite J_c was seen for both composites, the effects being particularly severe for the composite with the finest filaments.

II. The Annealing of Bronze

It has been empirically established that the high Sn bronzes (~ 13 wt.%) used for Nb_3Sn manufacture need to be annealed after every three draw passes, the reduction per draw pass being conventionally 20%. Bronze annealing temperatures undoubtedly vary from manufacturer to manufacturer, with two general approaches having been taken. One approach has been to minimize the time and temperature because of concerns about the formation of even 50 to 100 nm layers of Nb_3Sn. This approach has resulted in anneals of the order of 1 hr at 450°C (or possibly 425°C). A second approach has been to treat Nb_3Sn composites like other Cu-alloy products, annealing them in air or industrially available atmospheres for short periods at higher temperatures (500 - 600°C). As Nb_3Sn composites have increased in size from the initial ~ 100 mm extrusion diameter to ~ 200 mm, there has been a natural tendency to increase the annealing temperatures and to perform the anneals on larger pieceweights in larger furnaces with less stringent atmosphere and temperature control, thus permitting faster throughput.

III. The High-Field Test Facility Conductor

The HFTF conductor is an interesting example of the production of a high current monolith by the assembly of multiple small strands, a method which offers significant economies of scale, as compared to conventional methods of large monolith production. An extensive description of the HFTF conductor development has recently been given.[2]

A significant problem with the HFTF conductors, however, was their low current.[2] The specification of 7500 A at 12 Tesla corresponds to a J_c (bronze + Nb) of 315 A/mm^2, a reasonably conservative value, as compared to the 400 - 450 A/mm^2 values expected of the strands going into the composite.[3] Many of the production lengths had I_c values below 4500 A and some fell as low as 2000 A. Our examination of samples of the conductors showed that the onset T_c values of nominally unreacted monolith conductors were as high as 14 K. These high values were also found for the strands used for the fabrication of the monolith. Metallographic examination of the filaments of nominally unreacted composites showed a significant but variable degree of Nb_3Sn pre-reaction, of which Fig. 1 is an example. The annealing schedule used for the composites had been a nominal 1 hr/520°C; although there was a concern that there could have been significant variation both from batch to batch and from place to place on a given wire spool, associated with

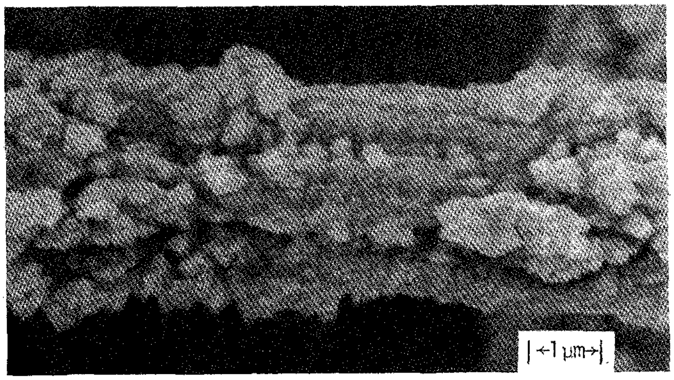

Fig. 1. Unreacted HFTF filament at final size.

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such features as the large batch sizes, the uneven heat-up and cool-down time and the normal temperature gradients found in large furnaces.

The irregular reaction layer shown in Fig. 1 was found to be reproduced in the Nb_3Sn layers of many reacted composites, an example of which is shown in Fig. 2. The J_c value of the composite shown in Fig. 2 was found to be about half that of the prototype conductors, for which compact and uniform layers of Nb_3Sn were found after reaction.[7]

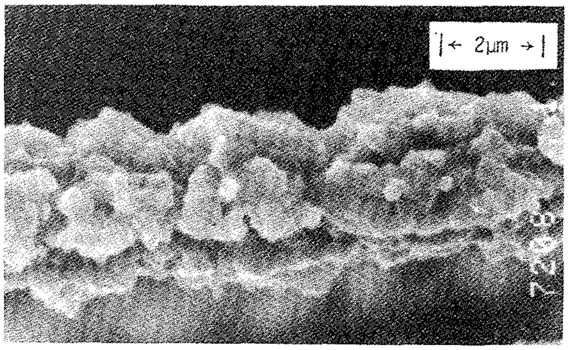

Fig. 2. Reacted HFTF filament.

Although a rather high degree of correlation existed between the degree of irregularity of the Nb_3Sn layer and the value of the critical current density, further investigations uncovered additional contributions to the degradation of J_c. Measurements of the J_c as a function of reduction in area during compaction showed that the J_c declined from 350 A/mm^2 (12 T) at 10% reduction to 250 A/mm^2 at 40% reduction.[2] This reduction had at least two additional causes; the breadth of the T_c transition significantly broadened as the area reduction increased, indicating the presence of a strain induced T_c depression. A second contribution to the reduction in J_c was found after measurements of the variability of the strand cross-section diameter; whereas the ratio ($S/\bar{A}$) of the standard deviation of the strand sizes (S) to the mean cross-sectional area ($\bar{A}$) was 3.4% at the first compaction stage, it had increased to 6.8% at the seventh and final stage. There, thus, were a number of factors contributing to the decline of the J_c in the HFTF conductors, rendering it unclear what the exact effect of the Nb_3Sn pre-reaction was.[7]

IV. Variation of Annealing Temperature and Its Effects

In order to study the effect of varying the annealing temperature on the morphology and the J_c of Nb_3Sn composites, we selected two composites of high J_c whose properties we have already extensively characterized. Both composites were made by the bronze route, one being assembled in the conventional way (CF136), one being made by the modified jelly roll (MJR) process (M68). Composite details are given in Table 1.

Table 1: Composite details.

Composite	Initial/ Final dia (mm)	Initial/ Final fil.size*	Bronze: Nb ratio	Manufacturer
M68	0.91/ 0.267	8x2 μm/ 2.5x0.6	2.96:1	Wah Chang
CF136	1.02/0.267	8/2	4.1:1	AERE

*approximate values

Long sample J_c measurements have shown that J_c values of > 500 A/mm^2 (12 T, 4.2 K, 10^{-14} Ωm) can be obtained from these two composites. T_c measurements on the MJR composite disclosed very little reaction in the as-received condition (T_c onset ~ 11 K), while there was somewhat more for the conventional composite (T_c onset ~ 13 K). The filament morphology confirmed these T_c findings, there being very little Nb_3Sn on the M68 but a little more on the CF136. These findings are consistent with the anneals given the two composites, these being stated to be 1/2 hr/475°C for M68[8] and a dual treatment of 4 hrs/280°C + 2 hrs/475°C for the CF136.[9]

Samples of both composites were then drawn from 1.02 mm (CF136) and 0.91 mm (M68) to 0.27 mm dia, using a 20% area reduction per pass. One set was annealed for 1 hr/450°C, the second for 1 hr/550°C after each three die passes. Long sample critical current measurements at a sensitivity of 10^{-14} Ωm were made on samples taken at various sizes, the reaction times being scaled as the square root of the diameter, in order to obtain a rough equivalence of reaction in the wire at each size, as shown in Table 2. The number of anneals performed varied from 1 to 4. The Nb_3Sn growth morphology was observed using a scanning electron microscope (SEM).

Table 2: Nb_3Sn reaction details.

M68 Wire Size	M68 Reaction	CF136 Wire Size	CF136 Reaction
$\underline{.635}$ mm	96hrs/700C*	$\underline{.711}$ mm	190hrs/700C*
$\underline{.455}$	49/700	$\underline{.508}$	97/700
$\underline{.320}$	25/700	$\underline{.361}$	49/700
.267	17/700	.267	27/700

*An additional 1/2hr/800C was given due to the requirements of other samples in the furnace.

Note: Anneals were performed at the starting sizes (M68, 0.91 mm : CF136, 1.02 mm) as well as the underlined sizes.

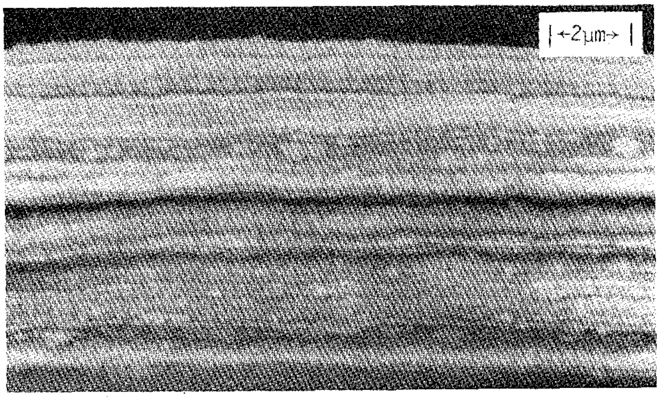

Fig. 3. M68 filament as received. Wire diameter is 0.91 mm.

Examples of the Nb_3Sn morphologies obtained are shown in Figs. 3-6 for the MJR composite M68. The filaments were rather clean and regular in the as-received condition, there being little sign of Nb_3Sn pre-reaction and the composite having the low onset T_c of ~ 10.5 K (Fig. 3). Annealing for 1 hr at 550°C raised the onset T_c to ~ 12.6 K. After four anneals of 1 hr/450°C and drawing to 0.267 mm, the filaments were still quite uniform in cross-section although a few nodules of diameter ~ 0.2 μm could be seen on the filament surface (Fig. 4). The predominating feature visible was, however, the angular ridging, characteristic of the deformation of the Nb filament. Reaction of this composite for 17 hrs/700°C produced a fairly uniform Nb_3Sn layer with a few external nodules of diameter ~ 0.5 - 1 µm (Fig. 4).

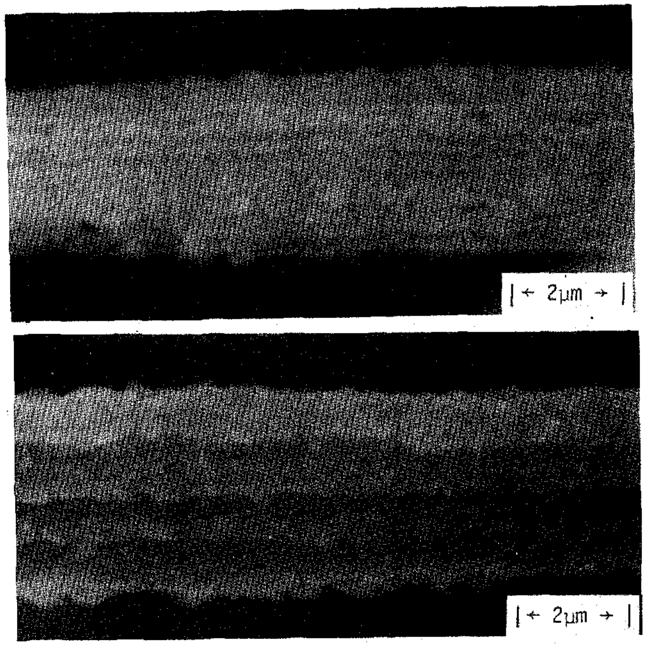

Fig. 4. M68 filaments at wire dameter of 0.267 mm with 450°C annealing temperature. Upper: unreacted; Lower: reacted.

The appearance of the series annealed at 550°C was significantly different. The final anneal (for both series) was performed at 0.32 mm, this producing an irregular reaction on the filaments (Fig. 5) which was noticeably rougher than that following the 450°C *anneal. The roughness was maintained after drawing to* 0.267 mm and a subsequent reaction of 17 hrs/700°C produced an irregular Nb_3Sn layer morphology (Fig. 6). The 550°C anneals clearly produced a significantly more irregular morphology than the 450°C anneals. Qualitatively similar morphologies were seen in the CF136 composite, although the difference between the 450°C and 550°C series was less marked.

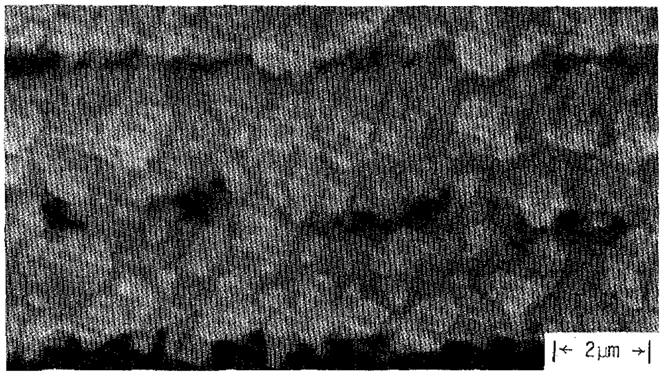

Fig. 5. M68 filaments at 0.32 mm wire diameter after annealing at 550°C; unreacted.

The results of the critical current experiments are shown in Fig. 7. It can be seen that the 550°C anneals exerted a particularly deleterious effect on the J_c properties of M68, the J_c (5 T) being reduced to half its value (1450 vs. 2900 A/mm²), following four 550°C, rather than 450°C anneals. The separation between the J_c values of the 450°C and 550°C series *diverges strongly for M68. A very much smaller effect* is however seen for CF136. Decreasing the wire and filament size diminishes the J_c of both series, the 550 C series having a slightly lower J_c.

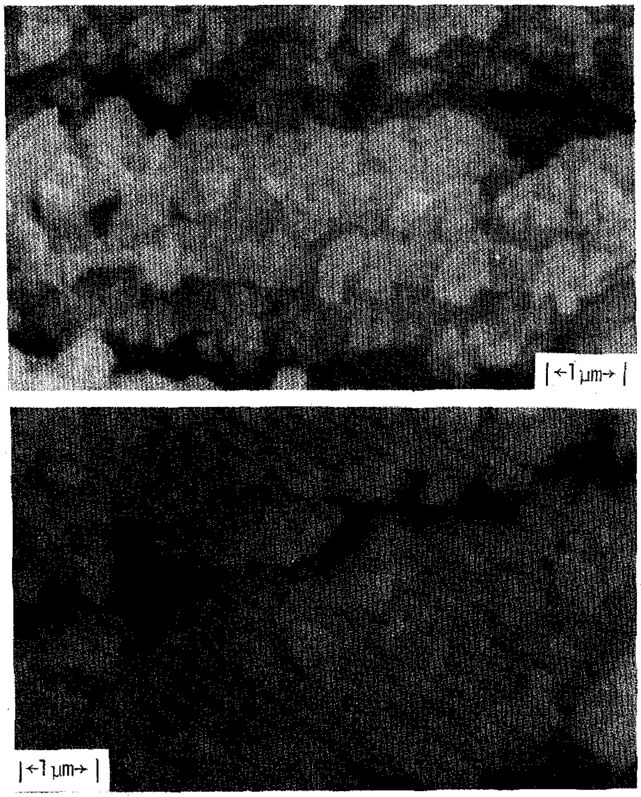

Fig. 6. M68 filaments at 0.27 mm wire diameter after annealing at 550°C. Upper: unreacted; Lower: reacted.

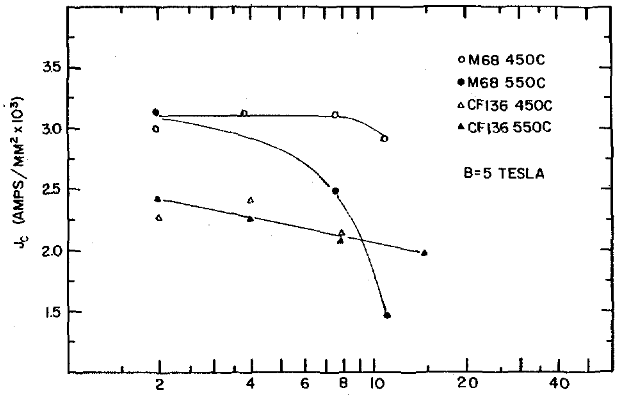

Fig. 7. J_c (5 T, 10^{-14} Ωm) normalized to the bronze + Nb cross-section as a function of inverse area reduc*tion. Ai is the area at initial size (CF136: 1.02 mm;* M68: 0.91 mm).

V. Discussion

The preceeding metallographic observations show that 3 or 4 anneals at 550 rather than 450°C are quite sufficient to produce a significant change in the morphology of the Nb_3Sn formed both by the anneal itself and any subsequent reaction process. The layers produced by the lower temperature anneal are less nodular and more uniform and this characteristic is retained on subsequent reaction.

The layer of Nb_3Sn formed during annealing is progressively fractured on subsequent drawing, the debris being presumably embedded in the bronze and Nb at the filament-matrix interface. During subsequent bronze anneals, further Nb_3Sn growth occurs and it may be assumed that some of this occurs preferentially at the existing Nb_3Sn particles. This is likely to occur particularly rapidly for the particles embedded in the bronze and this may be the origin of the nodules which appear to be scattered on the filaments in Figs. 3 and 4. Although the controlled experiments described in Part III only permitted the effect of four anneals to be studied, the rather larger irregularities seen in Figs. 1 and 2 suggest that the effects of pre-reaction are cumulative over many annealing cycles.

The present results emphasize that a high current density conductor requires not only that the appropriate <u>micro</u>structural conditions be satisfied (e.g. fine grain size and correct chemical composition) on a scale of λ to ξ but that the <u>macro</u> structural aspects of the filament be correctly arranged too. These involve such parameters as the selection of the correct grain size for the Nb, the avoidance of filament sausaging and the minimization of pre-reaction so as to produce regular layers of Nb_3Sn of uniform cross-section. Judged by this latter criterion, it is not at all surprising that low J_c values were found for the composites in Figs. 2 and 6. However, the very different behavior of M68 and CF136 requires some discussion. There are two factors which could be responsible for the greater degradation in M68. The first is that the normal anneals given to M68 before delivery to us were for 1/2 hr at 475°C whereas the CF136 had a higher temperature two-step anneal (4 hrs/280°C + 2 hrs/475°C). The M68 composite was, thus, cleaner and less reacted to start with, a point confirmed by the SEM pictures and the T_c measurements. Although both composites started with very high J_c values, that of M68 was particularly high (3100 A/mm^2 at 5 T). The high value for M68 is noteworthy since we know that the filaments are unevenly reacted in this composite, due to the preferential placement of bronze towards the center of the composite. The CF136 composite may already have been partially degraded by its higher temperature anneals. The second point is that the filaments of M68 started at $\sim 8 \times 2$ µm at 0.91 mm composite diameter, reducing to $\sim 2.5 \times 0.6$ µm at final size. Nodular Nb_3Sn growth on a scale of $\sim 0.5 - 1$ µm would, thus, be a much more significant perturbation to these filaments than to the approximately round ones found in CF136 (~ 8 µm at starting size and ~ 2 µm diameter at final size).

There are a number of questions raised by the present work which we are not yet able to answer. One relates to the composite or filament size at which it becomes important to limit Nb_3Sn growth. Nb_3Sn growth is likely to be of less importance at large filament sizes but as the filaments are reduced to smaller diameters, it would certainly be important to limit Nb_3Sn pre-reaction. A second question relates to the final reaction. A significant expense of time and resources is still needed to determine the optimum reaction conditions for individual Nb_3Sn composites. If a significant quantity of Nb_3Sn particle debris is present at the matrix-filament interface, this must first be "glued" back together before diffusion can occur. The debris also provides a very heterogeneous nucleation environment for subsequent Nb_3Sn growth. Pre-reaction may, thus, be a major contributor to the variability of reaction conditions found in industrial composites. We have already commented on the possibility of particularly rapid growth for the Nb_3Sn particles embedded in the bronze, some of which may never be incorporated into the bulk of the growing layer and will, thus, make no contribution to the transport current density.

The very clean filaments seen in Fig. 3 for a composite given on the order of ten 1/2 hr at 475 C anneals suggests that the problem of pre-reaction is controllable under production conditions. It is relatively easy to monitor the pre-reaction by inductive T_c measurements or by SEM metallography as was done here or by magnetization measurements.[10] At present, we cannot be quantitative about how large a role pre-reaction plays in limiting the J_c available from a given composite. Nevertheless, the observations of this paper suggest that a strong prima facie case can be made that the existence of variable pre-reaction is a major contributor to the degraded and variable properties of bronze Nb_3Sn conductors. Since the problem can both be controlled and monitored, we may hope for an early decision on this issue.

Acknowledgements

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