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# EFFECTS OF DIFFERENTIAL THERMAL CONTRACTION BETWEEN THE MATRIX AND THE FILAMENTS IN MONO- AND MULTIFILAMENTARY $Nb_3Sn$ ON THE SUPERCONDUCTING CRITICAL TEMPERATURE

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# EFFECTS OF DIFFERENTIAL THERMAL CONTRACTION BETWEEN THE MATRIX AND THE FILAMENTS IN MONO- AND MULTIFILAMENTARY $Nb_3Sn$ ON THE SUPERCONDUCTING CRITICAL TEMPERATURE*

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## ABSTRACT

The strain on $Nb_3Sn$ due to the differential thermal contraction between the matrix (Cu, bronze) and the filaments (Nb, $Nb_3Sn$, Ta) of a superconducting wire is known to decrease the superconducting critical temperature $T_c$. In order to study the effects of heat treatment conditions and filament size on the degradation of $T_c$ by the strain, $T_c$ for monofilamentary wires and two types of multifilamentary wires [($Nb_3Sn$ and bronze in Ta) in Cu matrix, and (bronze in Nb tubings) in Cu matrix] were measured for heat-treating periods of 1 to 120 h at 725°C. Several observations were made regarding the effects on $T_c$ of thermal contraction strains from various components of the conductors. The influence of a Cu matrix on $T_c$ was small (~0.2 K). When the bronze matrix was inside Nb tubing the degradation of $T_c$ due to strains was substantially larger than when the Nb filaments were in a bronze. Wires with smaller filament diameters achieved a maximum $T_c$ in shorter heat treatment times than those with larger filaments. These results are discussed in terms of the critical currents of these wires under applied tensile strains.


## I. INTRODUCTION

As a result of increasing needs for the use of $Nb_3Sn$ and $V_3Ga$ multifilamentary superconductors in large technological applications such as for magnetic fusion systems, there has been an increase in the research activities investigating the responses of superconducting properties to mechanical strains [1]. It is now clearly established that the ratio of the bronze matrix to the core (Nb+$Nb_3Sn$+Ta) is the primary controlling factor in the behavior of these wires under tensile [2-4] and bending strains [5]. Neither tensile nor bending tests when used to determine conductor tolerance levels to mechanical strains are easy to perform. This is particularly true when the sizes of the conductors increase. The dependence of $T_c$ on the initial filament sizes of Nb and on the heat treating conditions for the "bronze processed" $Nb_3Sn$ wires are presented. Measurements made of the superconducting temperature $T_c$ of these wires with and without the matrix are quite easy to perform and are shown to be very informative regarding the state of strain in as-reacted wires. An attempt to predict the dependence of the superconducting critical current $J_c$ on strains in as-heat treated $Nb_3Sn$ wires is reported.

## II. EXPERIMENTAL PROCEDURE AND RESULTS

Three types of $Nb_3Sn$ wires were used for this study. 1) A series of monofilamentary wires for which the volume ratio of the matrix (a Cu-13 wt%Sn) to the core (Nb) $R_v$ varied from ~1.1 to ~58. (The details regarding fabrication of these wires are given in Ref. 2.) 2) A commercial multifilamentary wire in which fine Nb filaments were embedded in a bronze matrix which was itself surrounded by a Ta diffusion barrier and a Cu stabilizer. (This was supplied by Airco and the fabrication process is discussed in Ref. 6.) 3) A commercially manufactured multifilamentary wire consisting of a Cu layer and a Sn-Cu alloy inside Nb tubes which were in turn placed in a Cu matrix. (This wire was supplied by Showa Electric Co. and the fabrication method for similar wires is described in Ref. 7. It is similar in the final configuration after reaction to the wires which were made by Supercon and tested for their mechanical and superconducting properties by LLL [8].) The pertinent physical parameters and cross sectional views of the Airco (FM 101) and the Showa (FM 102) conductors are listed and shown in Table I and in Fig. 1, respectively.

TABLE I

Physical Parameters for the Multifilamentary Wires

| | FM 101 | | FM 102 | |
|---|---|---|---|---|
| o.d. | 0.54 mm | | 1.03 mm | |
| No. of Filament | 2869 | | 258 | |
| Filament Diameter | 2.95 µm | | 41.5 µm | |
| Sn in Bronze | 13 wt% | | 12 wt% | |
| Volume Fraction | Before H.T. | 120h/ 725°C | Before H.T. | 120h/ 725°C |
| Cu | 61.9% | 61.9 | 57.4% | 58.1 |
| Nb | 8.6 | 0 | 27.1 | 16.1 |
| $Nb_3Sn$ | 0 | 11.4 | 0 | 11.4 |
| Ta | 3.0 | 3.0 | 0 | 0 |
| Bronze | 26.5 | 23.7 | 15.5 | 14.4 |

For heat treatment to form $Nb_3Sn$ layers, all wires were cut to approximately 10 cm long pieces and vacuum encapsulated in quartz tubes. The heat treatment consisted of 1, 6, 24, 64, and 120 h at 725°C. After heat treatment, 2 to 4 pieces, depending on the size of the wire, of 0.5 cm long wires were cut for $T_c$ measurements. The inductive $T_c$ measurements [9] at ~220 Hz were first carried out on as-reacted specimens. Then, for the monofilamentary wires, $T_c$ was measured after the matrix was etched off and after the bare $Nb_3Sn$-Nb wires were annealed in vacuum for 0.5 h at 725°C. In the case of the multifilamentary wires, $T_c$ was measured in the as-reacted condition, with the Cu-etched off, and with the bronze etched off. The variations in $T_c$ after the above treatments for a monofilamentary wire ($R_v$=14) and two multifilamentary wires (FM 101 and FM 102) are shown in Figs. 2-4. For the monofilamentary wire and the wire FM 102, the onset and the midpoint of $T_c$ are indicated in Figs. 2 and 4. For the wire FM 101 the midpoint $T_c$ had to be corrected, see Fig. 3. This was necessary due to the effect of the temperature dependence of the penetration depth λ on the transition. This makes the inductively measured transition very broad even though the true (or intrinsic) transition is quite sharp [10]. The effect is only observable near $T_c$ when the filament size is compatible with the size of λ. The broadening in the transition for fine filaments (f·f) which is compared with a sharp inductive transition in large filaments (ℓ·f) is schematically illustrated in the insert of Fig. 3. Also the

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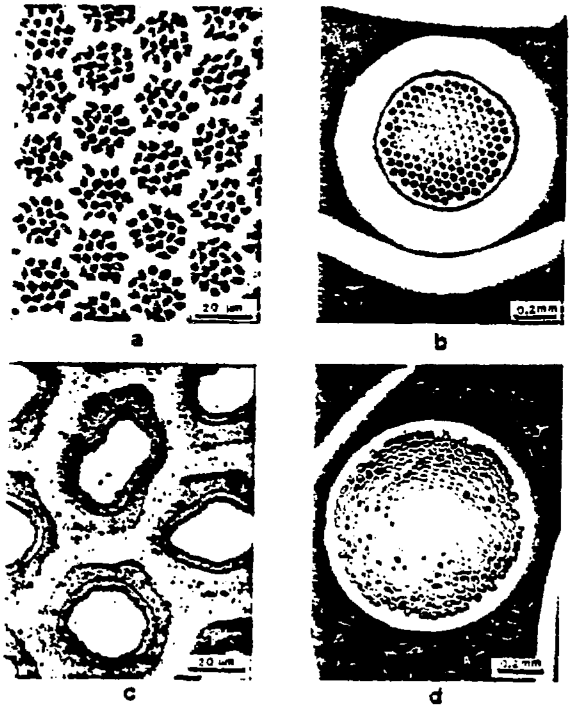


Figure 1. Cross sectional views of the multifilamentary wires (a,b) FM 101 and (c,d) FM 102.

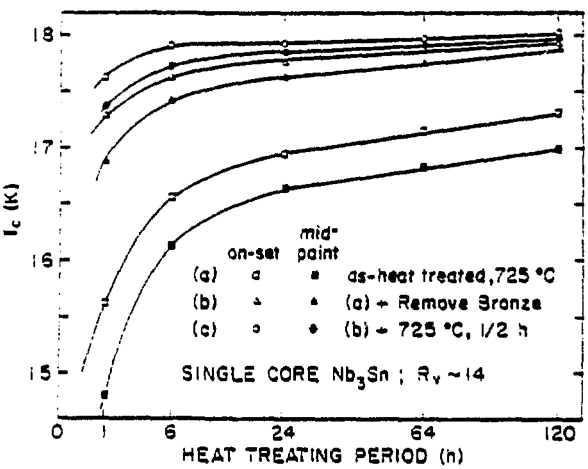


Figure 2. The variation in $T_c$ after removal of the bronze matrix and following the annealing treatment (0.5 h at 725°C) as a function of heat treatment periods is shown for the monofilamentary wire with a bronze to core ratio of 14.

method of the correction to determine the midpoint of the transition is shown on the insert. The $Nb_3Sn$ filament size (~30 µm) in FM 102 was large enough so that such correction was unnecessary. The result for monofilamentary wires heated at 725°C for 6 h are presented in Fig. 5 for $R_v$=1.1 to 58.

## III. DISCUSSION

### Effects of Heat Treatments on $T_c$

As shown in Figs. 2-4 $T_c$ in all cases, irrespective of the type of the wires, increased rapidly within

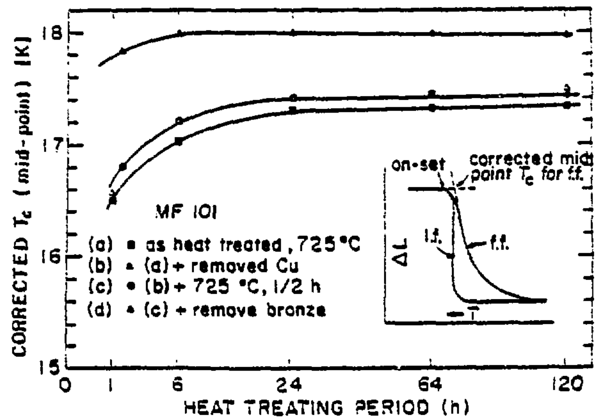


Figure 3. The variation in $T_c$ after removal of the copper and the bronze matrices is shown as a function of heat treatment periods for wire FM 101. The determination of the midpoint $T_c$ is defined in the insert.

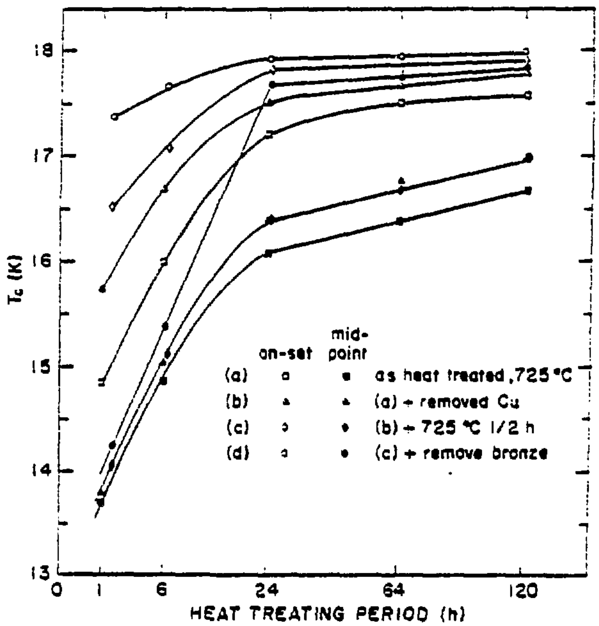


Figure 4. The variation in $T_c$ after removal of the copper and the bronze matrices is shown as a function of heat treatment periods for the wire FM 102.

1 to 24 h of heat treatment at 725°C. It then increased very slowly for longer treatment times. However, the values of $T_c$ for wire MF 101 for heat treating times less than 24 h were substantially higher than those for the monofilamentary wires and MF 102. MF101 achieved its maximum $T_c$ in a shorter time than the other two wires. These differences can be attributed to differences in three factors: filament sizes, the bronze to the core ratio $R_v$ and the geometric structures of these composites. When the Nb filaments in the bronze matrix become very small (~2-3 µm), as for MF 101, the time required to react the entire filament will be significantly shorter (~6 h) compared with that for larger filaments. If the filaments are totally reacted, it will not be necessary for composi-

tional gradients across the layer. Thus, the filament can reach the equilibrium (stoichiometric) composition and a high $T_c$ in a shorter time than conductors with larger filaments. The second factor is that $T_c$ of a bronze processed wire depends strongly on the ratio $R_v$ as was shown earlier [11] and is seen in Fig. 5. $R_v$ for the monofilamentary wire was ~14 while $R_v$ was ~1.6

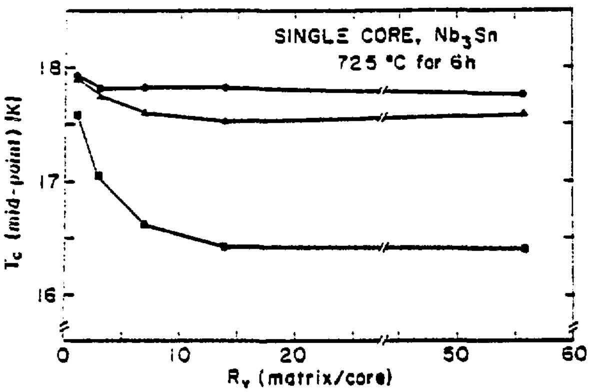


Figure 5. The effect of the variation in the matrix to the core ratio $R_v$ on $T_c$ after removal of the matrix and following annealing (0.5 h at 725°C) is illustrated for the monofilamentary wires heated for 16 h at 725°C.

for FM 101. When the bronze is placed in Nb tubing as in FM 102, the radial and tangential strains in the $Nb_3Sn$ layers resulting from the mismatch in the thermal expansion coefficients, are significantly larger than when Nb filaments were placed in the bronze matrix [4,8]. These strains are effective in lowering $T_c$ for MF 102 even though its $R_v$ is small (~0.57).

The effect of the Cu matrix in reducing $T_c$ through the difference in thermal contraction coefficients between Cu and the core is quite small (Figs. 3 and 4). Although the Cu matrix occupies ~60% of the conductor's volume in both wires (MF 101 and MF 102), the increases in $T_c$ after removing the Cu matrix are only ~0.1 and ~0.2 K for FM 101 and MF 102, respectively. This implies that the yield stress for pure Cu is sufficiently small so that it cannot apply significant axial strain to the $Nb_3Sn$ filaments.

When the bronze matrix was removed from the wires by etching with a $H_2O$-$HNO_3$ solution, very large increases in $T_c$ were observed, in addition to sharpening of the inductive transitions (see Figs. 2-4). This effect has been observed before [11]. The relative values of $T_c$ among the three types of wires were essentially the same before the bronze matrix was etched off. In this case, the differences in the values of $T_c$ among the wires can be attributed to two factors. The first is that there exists plastic strain in unreacted Nb cores of the monofilamentary and FM 102 wires. This strain is the result of plastic deformation of the Nb cores during cool-down of the wire from heat treatment temperatures [12], and can be eliminated by annealing for 0.5 h at 725°C. The increased $T_c$ after annealing the monofilamentary wire is shown in Fig. 2. The $T_c$ values for the monofilamentary wire are very close to those for FM 101 when the plastic strain in the core is removed by annealing. The remaining difference is probably due to the filament-size effect as discussed above. A similar annealing heat treatment was not performed on FM 102.

The effect of the residual plastic strain in the unreacted Nb core on $T_c$ of the monofilamentary wires can clearly be seen in Fig. 5. The increases in $T_c$ seen after removing the matrix and after annealing at 725°C for 0.5 h are presented for the wires with $R_v$ varying from ~1 to 58. As shown, when the compression on the core is small, due to small $R_v$, the increase in $T_c$ is small after the annealing treatment. But when $R_v$ is large, i.e. a large plastic strain exists in the core, the increase in $T_c$ becomes significantly larger. $T_c$ stays constant for the wires with values of $R_v$ larger than 14. Also, the values of $T_c$ after the annealing process are all nearly identical.

## Analysis of Strains from the Matrices

In an attempt to reduce values of compressive strains in $Nb_3Sn$ due to the Cu-matrix, the bronze matrix, and the unreacted Nb core from various $T_c$ measurements which are shown above, we will start with Eq. (1) knowing that the changes in $T_c$, $\Delta T_c$, due to nonhydrostatic (or tetragonal) strains are proportional to the square of the strain [2,4,13], i.e.

$$\Delta T_c = a\epsilon^2 \qquad (1)$$

here, a is the proportionality constant and its value may change from one compound to another among the A15-structure compounds. $\epsilon$ is the nonhydrostatic component of the strain on the compound. In order to separate out strains which are induced from thermal contraction of the matrix, the core, etc., we assume the following relationship:

$$\Delta T_c = T_{co} - T_{cas} = \Sigma \Delta T_{cj} = \sum_{\substack{j=o,1,2,\ldots \\ i=j+1}} (T_{cj} - T_{ci}) = a(\sum_j \epsilon_j)^2 \qquad (2)$$

where $T_{co}$ is an ideal $T_c$ or the maximum $T_c$ achievable for a given wire and $T_{cas}$ is $T_c$ for an as-reacted $Nb_3Sn$ wire. In the present case, $\Delta T_{co} = (T_{co} - T_{c1})$ is the difference in the value of $T_c$ between $T_{co}$ and that after an etched monofilamentary wire is annealed to remove the residual strain in the unreacted Nb core. The corresponding strain parameter is $\epsilon_0$. This strain could represent the amount of disorder in the compound and not necessarily tetragonal strain. $\Delta T_{c1}$ is the increased $T_c$ in a wire due to annealing the bare wire, and the corresponding strain parameter is $\epsilon_1$. This parameter represents the strain in $Nb_3Sn$ due to the residual plastic strain in the unreacted Nb core. $\Delta T_{c2}$ is the increase in $T_c$ after removal of the bronze matrix and the corresponding elastic strain in $Nb_3Sn$ is indicated by the parameter $\epsilon_2$. Finally, $\Delta T_{c3}$ is due to the removal of the Cu matrix and the corresponding strain parameter is $\epsilon_3$ in FM 101 and FM 102. From the present measurement, it is not possible to determine the constant a, thus the changes in the relative values of strain for various conditions are expressed as $a^{1/2}\epsilon_j$.

The calculated values for $a^{1/2}\epsilon_j$ for the monofilamentary wire are shown in Fig. 6 as a function of the ratio $R_v$. In this particular case, $T_{co}$ was chosen to be 18.0 K. The following observations can be made. Since $\epsilon_o$ is essentially constant for all $R_v$, the difference in $R_v$ does not influence the degree of the crystallographic order in the $Nb_3Sn$ layer. The strain induced by residual plastic deformation of unreacted Nb cores increased with ratio R as expected. An obvious explanation for the unexpected drop in $a^{1/2}\epsilon_1$ at R=58 is not available. The elastic compressive strain, $a^{1/2}\epsilon_2$, increases rapidly with $R_v$ and saturates beyond $R_v$=7, as expected from earlier results on $T_c$ and $J_c$ of similar wires [2,3].

The effects of heat treating time on $\epsilon_j$ for the monofilamentary wire was also studied. Here the largest change is observed in $a^{1/2}\epsilon_o$ indicating that the internal changes such as improvements in composition

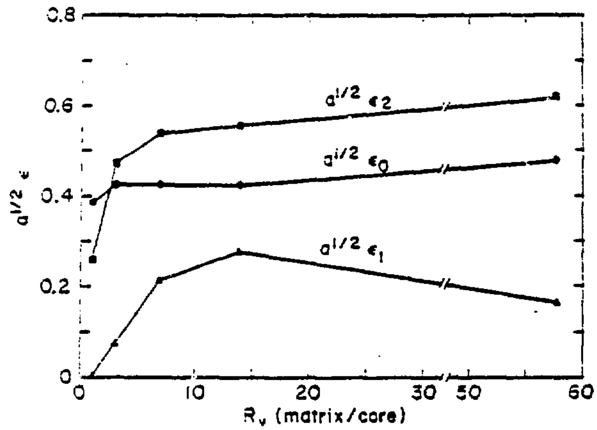


Figure 6. The calculated parameters, $a^{1/2}\varepsilon_0$, $a^{1/2}\varepsilon_1$, and $a^{1/2}\varepsilon_2$, which are proportional to the strains in $Nb_3Sn$ from disorder, the plastic strain in Nb, and the bronze matrix, are shown as a function of the volume ratio $R_v$ for the monofilamentary wires.

and order are taking place in $Nb_3Sn$ as the heat treatment time increased.

In order to compare the above results with tensile studies ($T_c$ and $J_c$) of $Nb_3Sn$ wires, we note that the axial strain ($\varepsilon_1+\varepsilon_2$) in $Nb_3Sn$ can be recovered by the application of tensile strain. The values of applied strain $\varepsilon_{max}$ for which $J_c$ or $T_c$ reach maximum values are normally considered to be the amount of prestrains in the compound [2,3,14,15]. In Fig. 7, the values of the prestrains ($\varepsilon_1+\varepsilon_2$) are calculated though the present $T_c$ measurements and are compared with $\varepsilon_{max}$ for $J_c$ [3] and $T_c$ [2] for the wires with $R\sim1$ to 58. For the calculation of ($\varepsilon_1+\varepsilon_2$) in percent, it was assumed that ($\varepsilon_1+\varepsilon_2$) is 1% for the wire with R=14. As shown in the figure, the agreement between the compressive prestrains calculated from the present data and those measured by the application of tensile strains during $T_c$ and $J_c$ measurements is extremely good. It is now possible to calculate the constant a. It was found to be $.69\times10^4$K. Thus it is shown here that in the case of a simple composite wire appropriate measurements of $T_c$ and the application of Eq. (2) can be used to separate out and to approximate the values of the various components of the prestrain.

The analysis technique discussed above was also applied to the multifilamentary wires FM 101 and FM 102, and the results are shown in Figs. 8 and 9. In Fig. 8 the effect on $T_c$ of residual plastic deformation in the unreacted cores is not observed since the filaments are so small that the cores are essentially all reacted after only a few hours of heat treatment. The affective strain by the Cu matrix on the $Nb_3Sn$ filaments is shown by $a^{1/2}\varepsilon_3$. Figure 8 suggests the following: 1) The parameter $\varepsilon_0$ dropped rapidly with time indicating that ordering of $Nb_3Sn$ takes place in a very short time when the filament dimension is small. 2) The compressive strain on $Nb_3Sn$ associated with the Cu matrix is very small in spite of its large volume fraction (~62%). This is likely to be the result of the low yield stress in pure Cu. 3) Since the bronze matrix is substantially softer when Sn in the matrix is depleted [16], it is expected that the strain ($\varepsilon_2$) on $Nb_3Sn$ will be smaller as the time of reaction increases. It is somewhat surprising that the strain ($\varepsilon_2$) from the bronze matrix did not decrease more than it is shown in Fig. 8. Rupp [14] has shown earlier that the effect of softening in the bronze matrix can be very large. On the other hand, Speckling et al. [16] have studied the effect of applied tensile strain on critical currents of a wire similar to that used in the present investigation

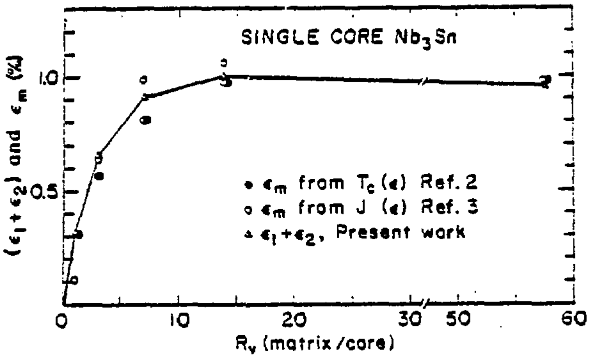


Figure 7. The axial strains, ($\varepsilon_1+\varepsilon_2$), in the monofilamentary wires ($R_v$=15), calculated from Eq. (2), are compared with those strains determined from the in-situ application of tensile strains for $T_c$ and $J_c$ measurements.

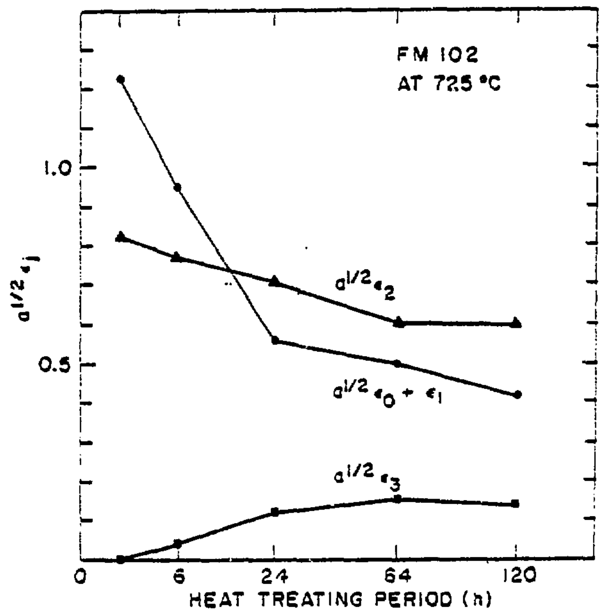


Figure 8. The strain parameters, $a^{1/2}\varepsilon_0^{1/2}$, $a^{1/2}\varepsilon_2$, and $a^{1/2}\varepsilon_3$, for FM 101 are shown as a function of heat treatment time.

and they found that the increase in $I_c$ with applied strain (~4%) and the strain (~0.2%) to reach the maximum in $I_c$ were indeed very small. This indicates a very small compressive strain in the as heat treated wire. These results do not agree with the large compressive strain indicated by the present $T_c$ measurements. 4) Finally, it should be possible to calculate the values for $\varepsilon_0$, $\varepsilon_2$, and $\varepsilon_3$ if one assumes that the value of the parameter a is the same for FM 101 as in the monofilamentary wire. However, in the present experiments the accuracy in determining $T_c$ in this case is not sufficient to enable meaningful values of the strains to be calculated.

As expected, the strain parameter $\varepsilon_3$ due to the Cu matrix is quite small in FM 102 in spite of a large portion of the wire consisting of a Cu matrix. In Fig. 4, a significant increase in $T_c$ was observed after removal of the bronze core from FM 102. This is refiected in a rather large value of $a^{1/2}\varepsilon_2$ although the matrix to the core ratio is small (∿0.5). This indicates a large strain is applied by the bronze core in

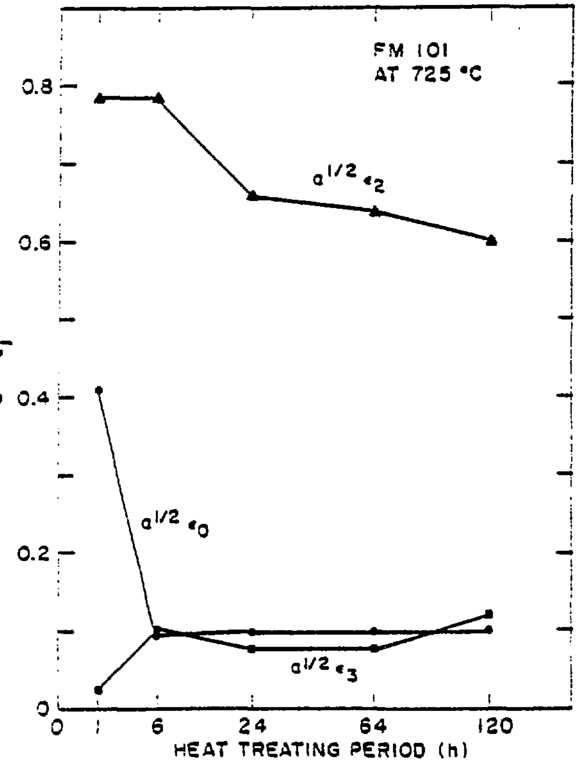


Figure 9. The strain parameters, $a^{1/2}(\varepsilon_0+\varepsilon_1)$, $a^{1/2}\varepsilon_2$, and $a^{1/2}\varepsilon_3$, for FM 102 are shown as a function of heat treatment time.

this configuration. In this case, the axial strain is very small but the tangential and the radial strains on the $Nb_3Sn$ layer, applied by the bronze, are very large (∿1.0%) [4,8]. As before, the value of $a^{1/2}\varepsilon_2$ decreased with the heat treating time. Interestingly, the strains $a^{1/2}\varepsilon_2$ from the matrix for all three types of the wires are essentially the same provided the value of a is taken as the same for the three wires. The strains, $\varepsilon_0$ and $\varepsilon_1$, for these wires were plotted in Fig. 9 as a sum of these two values. Since there is a high probability for oxidation in $Nb_3Sn$ during annealing after removal of the bronze, the heat treatment for annealing out the plastic deformation in Nb was not carried out. Hence the sum of $\varepsilon_0$ and $\varepsilon_1$ was shown for the FM 102 wires. Comparing this result with that for the monofilamentary wires, it is noted that the annealing time dependence $a^{1/2}(\varepsilon_0+\varepsilon_1)$ for all these wires are very similar. If it is assumed that $a^{1/2}\varepsilon_0$ for FM 102 is essentially identical with that for the monofilamentary wires, the values for $a^{1/2}\varepsilon_1$ for FM 102 are very similar to those in the monofilamentary wires indicating that the magnitude of the plastic strains in Nb in the monofilament (R∿15) and in FM 102 are very close. The above analysis indicates that the tetragonal strain in $Nb_3Sn$ in FM 102 is as large as that in the wires with a very large bronze to Nb core ratios. The tetragonal strain however cannot be as effectively reduced by application of tensile strain. That the strains in both cases are approximately 1% is consistent with the results of Hood et al. [8].

## IV. SUMMARY

It is shown that the measurements of $T_c$ for $Nb_3Sn$ composite wires after removal of the components provides qualitative information on the state of strain in as reacted conductors. In the case of the monofilamentary wires it was possible to quantitatively estimate the residual axial strain in $Nb_3Sn$ which arises from the differences in the thermal expansion coefficients. However, the variation of the penetration depth with temperature prohibited the quantitative analysis method from being applied to fine multifilamentary wires. The accuracy in the $T_c$ measurement was not high enough for this purpose. For wires made by the "internal bronze" method, the $T_c$ degradation, due to the axial residual strain in $Nb_3Sn$, was not possible to estimate since there are very large contributions by the radial and tangential strains. However, measurements of the relative changes in $T_c$ due to strains from the copper and the bronze, was shown to provide valuable insights in the accompanying metallurgical changes.


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REFERENCES


[1] Many publications on the effects of mechanical strains on critical properties of $Nb_3Sn$ wires are found in the Proc. of the 1976 and 1978 Appl. Supercon. Conf. (IEEE Trans. on Magn. MAG-13, 1977) and MAG-15 (1979) and of the 1977 and 1979 International Cryo. Mat. Conf., Adv. in Cryo. Engin., Vols. 24 and 26 (to be published).

[2] T. Luhman, M. Suenaga, and C.J. Klamut, Adv. in Cryo. Engin. 24, 325 (1978).

[3] M. Suenaga, T. Onishi, D.O. Welch, and T.S. Luhman, Bull. Am. Phys. Soc. 23, 229 (1978) and unpublished data.

[4] D.O. Welch, Adv. in Cryo. Engin., Vol. 26 (to be published.

[5] T. Kaiho, T. Luhman, M. Suenaga, and W.B. Sampson, submitted to Appl. Phys. Letters.

[6] C.R. Spencer, P.A. Sanger, and M. Young, IEEE Trans on Magn. MAG-15, 76 (1979); E.S. Easton, W. Speckling and P.A. Sanger (to be published in Adv. in Cryo. Engin., Vol. 26).

[7] S. Murase, Y. Koike, and H. Shiraki, J. Appl. Phys. 49, 6020 (1979); S. Murase, M. Koizumi, O. Horigami, H. Shiraki, Y. Koike, E. Suzuki, M. Ichihara, F. Nakane, and N. Aoki, IEEE Trans. on Magn. MAG-15, 83 (1979).

[8] D. Cornish, R. Hoard, R. Randall, R. Scanlan, J. Wong, and J. Zbasnik; R. Hoard, R. Scanlon, and D.G. Hirzel (to be published in Adv. in Cryo. Engin, Vol. 26).

[9] Unpublished.

[10] J.F. Bussiere, Private Communication.

[11] T. Luhman and M. Suenaga, Appl. Phys. Lett. 29, 61 (1976).

[12] J.F. Bussiere, D.O. Welch, and M. Suenaga (to be published in J. of Appl. Phys.; D.O. Welch, J.F. Bussiere, and M. Suenaga (to be published in Proc. of ICOMAT-79.

[13] L.R. Testardi, Physical Acoustics, W.P. Mason and R.N. Thurston, Eds., Vol. 10, p. 193, Academic Press (1973).

[14] G.Rupp, IEEE Trans. on Magn. MAG-13, 1565 (1977).

[15] J.Ekin, Adv. in Cryo. Engin. 24, 306 (1978).

[16] W.Speckling, D.S.Easton, D.M.Kroeger and P. Sanger (to be published in Adv. in Cryo. Engin., Vol. 26).