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The microstructure and mechanical properties of Nb_3Sn filamentary superconducting composites

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The deformation processes in filamentary superconducting composites at both room temperature and 4.2 K have been studied using transmission and scanning electron microscopy. In all the composites, the filaments consisted of a central core of unreacted niobium surrounded by a reacted layer of Nb_3Sn. The Nb_3Sn failed in an intergranular manner without any prior dislocation activity and the radial cracks formed in the Nb_3Sn layer during deformation were stopped at the niobium core. The observed variations in ductility, fracture stress and secondary modulus between the different composites were accounted for quantitatively by the presence of the niobium cores.

1. Introduction

In common with other A15 compounds, and the intermetallic compounds in general, Nb_3Sn is extremely brittle and this raises many difficulties in its fabrication and use. One fabrication process currently employed is to produce filamentary Nb_3Sn composites by a solid-state reaction. Basically the procedure is to embed rods of niobium in a tin–bronze matrix, swage, cut and re-bundle and finally draw down to a wire. The composite wire is then reacted in the temperature range 600 to 800° C to allow diffusion of tin from the bronze into the niobium and hence form Nb_3Sn by solid-state reaction.

Care must be taken to minimize the stresses imposed on the reacted Nb_3Sn composite since it has been found that the current-carrying capacity is sensitive to mechanical damage [1–4]. Tensile tests have been carried out on Nb_3Sn filamentary composites by a number of workers (e.g. [2]) and in particular by the groups at A.E.R.E. and the Rutherford Laboratory [1, 5, 6]. Composites varying in filament size/density and reaction time/temperature have been tested at 4.2 K and room temperature and the stress–strain curves found to exhibit the following features:

(i) an initial linear region, extending up to about 0.1% strain, in which the composite behaves elastically;

(ii) this is followed by a second region with a linear relationship between stress and strain, but the constant of proportionality (secondary modulus) is less than the Young's modulus in the preceeding elastic region. This region extends up to 0.8 to 1.0% strain;

(iii) finally, deformation continues at a constant stress until failure occurs at a strain which in some cases may exceed 10%.

This paper reports the results of an electron microscopy investigation of the Nb_3Sn filamentary superconducting composites which were tested during the previously mentioned mechanical properties investigations carried out by the groups at A.E.R.E. and the Rutherford Laboratory. The mechanical properties data are re-analysed in the light of the information acquired from the metallographic study.

2. Experimental procedure

Foils for transmission electron microscopy were prepared from longitudinal sections of the composites using an ion-beam thinning technique.

TABLE I The mechanical properties of Nb_3Sn filamentary superconducting composites [1, 5, 6]

Code	Reaction time (h)/ temp. (° C)	Test temp. (K)	Young's modulus ($GN\,m^{-2}$)	Secondary modulus ($GN\,m^{-2}$)	Failure stress ($MN\,m^{-2}$)	Failure strain (%)
3780	144/665	4.2	138.1 ± 40.6	41.9 ± 2.9	559 ± 10	7.0 ± 1.8
343	16/750	295	113	20.9	325	11
37	100/800	295	102–110	38.8	350	0.5
1369	16/750	295	90–104	32.3	350	0.5–1.2
5143	16/750	295	103	29.2	335	10

TABLE II Characteristics of the reacted filaments

Code	Filament diameter (μm)	Nb_3Sn layer thickness (μm)		Nb_3Sn grain size (Å)	
		Measured	Calculated	Measured	Calculated
37	15	2.5	2.9	–	1200
343	3.0	1.3	1.6	950	800
1369	5.0	1.5	1.6	700	800
3780	6.0	1.8	1.55	800	750
5143	6.5	1.6	1.6	910	800

These foils were examined in a 100 kV electron microscope (Philips 301). Scanning electron microscopy (Cambridge 600) was also used to study the fracture surfaces of the composites.

The mechanical properties data for the specimens studied are given in Table I; the number of filaments in the composites is used as a code number. Samples of fractured and untested composites which had received the quoted heat-treatments were available for examination and, in addition, composites 3780 and 1369 were supplied after testing to various strains (3780, 0.8%; 1369, 0.52, 0.92 and 1.18%). A series of 1369 specimens, which had been reacted for times in the range 1 to 16 h at 700° C and tested at room temperature to strains in excess of 1.00%, were examined in order to study the effect of Nb_3Sn layer thickness on the deformation process.

3. Results and discussion

3.1. Nb_3Sn layer thickness and grain size

The layer thickness and grain size, as determined by transmission electron microscopy, are presented in Table II. Also given in this table are the average filament sizes; it can be seen that all the filaments contained a core of unreacted niobium. The layer thicknesses and grain sizes determined in this investigation are consistent with those calculated from previously reported data [7].

3.2. Fracture

Figs. 1 and 2 are scanning electron micrographs of filaments fractured at 4.2 K and room temperature, respectively. The Nb_3Sn layer and the niobium core of the filaments were easily distinguishable in the room temperature specimens. The fracture surface at 4.2 K was not so well defined, the main features being an increased number of voids or cracks at the Nb_3Sn–bronze interface and fragmented niobium cores. The latter feature is consistent with the reported ductile–brittle transition temperature for niobium of 43 K [8].

Transmission electron microscopy showed that at failure, and at smaller strains (e.g. 3780, 0.8%; 1369, 0.92%), many cracks had nucleated and propagated through the brittle Nb_3Sn layer but had been stopped at the niobium core (Figs. 3 and 4). This was observed even in the composites tested at 4.2 K in which the niobium would have been in the brittle state.

The stress situation at the crack tip in a filament can be analysed if it is assumed that the standard principles of fracture mechanics can be applied at this low temperature for a brittle material, regardless of the small specimen size. If a filament with a cracked Nb_3Sn layer is considered as a circumferentially cracked round bar, the stress intensity factor K, is given by [9],

$$K_1 = \frac{YP}{D^{3/2}} \quad (1)$$

where P is the load, D is the bar (in this case filament) diameter and Y is a constant which depends on the ratio of the bar diameter to the diameter of the uncracked core. For the cracked 3780 filaments this ratio was 2.3 and the corre-

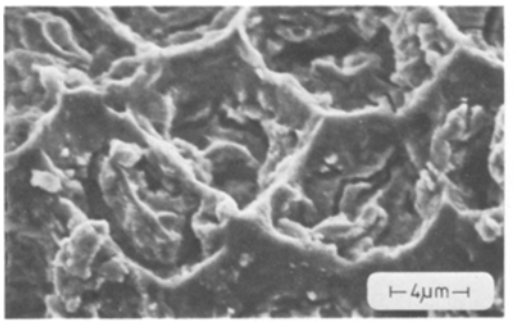

Figure 1 Scanning electron micrograph of the fracture surface of composite 3780 reacted 144 h at 665° C and tested at 4.2 K.

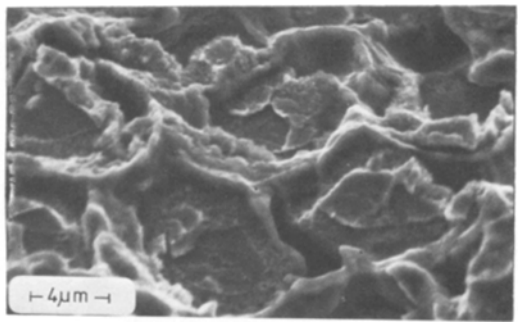

Figure 2 Scanning electron micrograph of the fracture surface of composite 1369 reacted 16 h at 700° C and tested at room temperature.

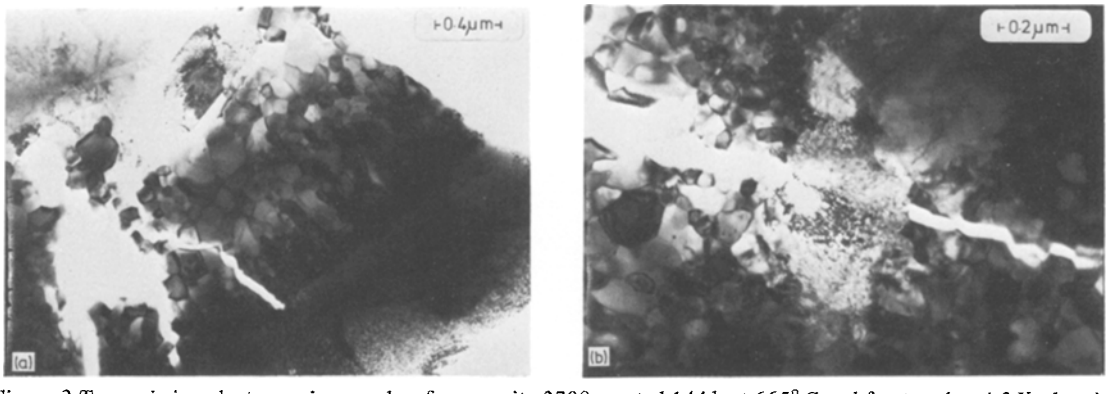

Figure 3 Transmission electron micrographs of composite 3780 reacted 144 h at 665° C and fractured at 4.2 K, showing intergranular cracks in the Nb_3Sn layer stopping at the niobium core. (a) The niobium core lies in the bottom right-hand corner of the micrograph with the Nb_3Sn layer running diagonally across from bottom left to top right. (b) The niobium core runs vertically down the centre of the micrograph. This longitudinal section is not through the centre of the wire, hence the apparent narrowness of the niobium core.

sponding Y value was 2.65. Two limits were taken for the strain at which the Nb_3Sn fails, namely:

(i) an upper limit of 0.8%, since electron microscopy results show that cracks are present at this strain (Table III) and further deformation of the composites to higher strains proceeds at nearly constant stress;

(ii) a lower limit of 0.5% as degradation of superconducting properties can take place at this strain and, since no dislocation activity has been observed, this degradation may be associated with cracking of the Nb_3Sn. Also, failure of some of the composites, even at room temperature, can occur at strains as low as this.

TABLE III Crack separation within the localized regions of damage

Code	Reaction time (h)/ temp. (° C)	Test temp. (K)	Strain (%)	Layer thickness (μm)	Crack separation (μm)
1369	1/700	295	>1	0.6	–*
1369	2/700	295	>1	1.2	3.13
1369	4/700	295	>1	1.0	1.44
1369	8/700	295	>1	1.5	3.69
1369	16/700	295	>1	1.5	3.68
1369	16/700	295	1.2	1.5	4.81
1369	16/700	295	0.9	1.5	3.46
1369	16/700	295	0.5	1.5	–*
3780	144/665	4.2	7	1.8	2.17
3780	144/665	4.2	0.8	1.8	–*

*Cracks present but data too limited to quantify a crack separation.

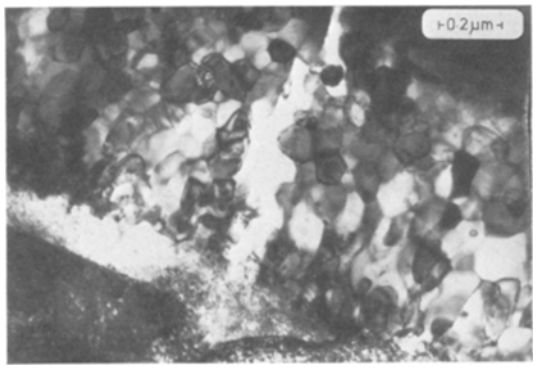

Figure 4 Transmission electron micrograph of composite 1369, reacted 16 h at 700° C and strained > 1%, showing an intergranular crack. The crack runs vertically downwards through the Nb_3Sn layer, stopping at the niobium core.

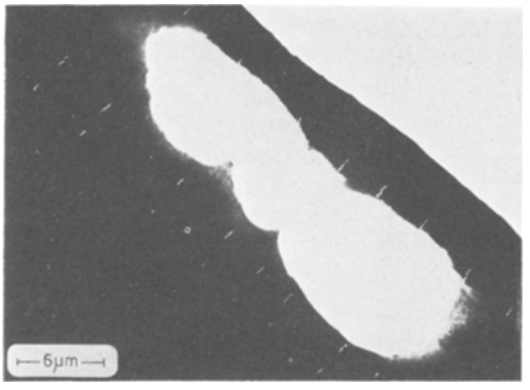

Figure 5 Transmission electron micrograph of composite 1369 reacted 8 h at 700° C and strained > 1%, showing regular arrays of cracks in the Nb_3Sn layers of two filaments. (The filaments lie either side of a section of the bronze matrix which has been removed during ion-beam thinning.)

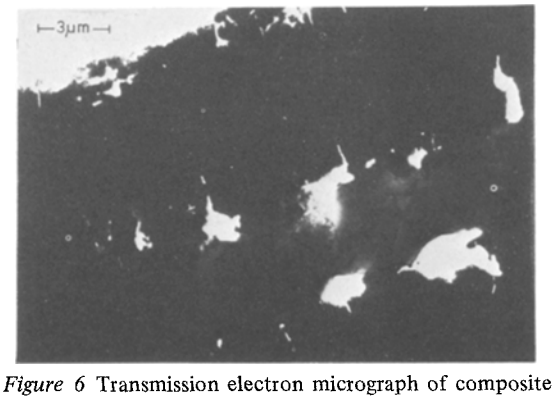

Figure 6 Transmission electron micrograph of composite 3780 reacted 144 h at 665° C and fractured at 4.2 K, showing cracks in the Nb_3Sn layer, several of which are associated with voids at the filament/matrix interface.

At these strains at 4.2 K, the cold-worked niobium core may be assumed to behave elastically. The load on the niobium core is, therefore, given by ϵEA where ϵ is the strain, E is the Young's modulus at 4.2 K and A is the cross-sectional area of the niobium. The room temperature modulus of niobium is 104.7 GN m^{-2} [10] and taking a typical temperature dependence of -5×10^{-4} per degree gives a value for E at 4.2 K of 120.5 GN m^{-2}. Substituting these values into Equation 1 for K_1 yields 0.58 to 0.92 MN m$^{-3/2}$.

The critical stress intensity factor, K_{IC}, is related to Young's modulus and the effective surface energy γ by

$$K_{IC} = (2\gamma E)^{1/2}.$$

The effective surface energy in b c c metals is greater by an order of magnitude, even at cryogenic temperatures, than the true surface energy, γ_s, due to localized plastic flow. The true surface energy of niobium is 2.55 J m^{-2} [11], hence the minimum value that K_{IC} could take for niobium is 0.78 MN m$^{-3/2}$ and a more realistic value, obtained by putting $\gamma = 10\gamma_s$, is 2.5 MN m$^{-3/2}$. Thus the niobium core acts as a crack stopper since K_1 for thin Nb_3Sn layer thicknesses is less than K_{IC}.

The cracking in the Nb_3Sn layer occurred in localized regions, the number of these regions increasing with strain. Within these regions the cracks were fairly evenly spaced (Fig. 5) and the crack separation was, within experimental error, independent of layer thickness and strain (Table III). McDougall [2] has suggested that cracking of the Nb_3Sn layer occurs as a consequence of splitting at the filament–matrix interface and predicts that such a filament–matrix split would have to be of the order of 3 μm in length to induce cracking in the Nb_3Sn at both ends. This value of 3 μm is not inconsistent with the crack separations given in Table III. However, thick Nb_3Sn layers would be more susceptible to cracking by this mechanism than thin layers and there is no indication from the present work that this is so. Furthermore, splitting at the filament–matrix interface was not frequently seen and was generally associated with voids produced during production. This was more noticeable for the 3780 composite (Fig. 6). Thus it is concluded that filament–matrix splitting can lead to failure of the Nb_3Sn but is not a prerequisite.

At both test temperatures, fracture in the Nb_3Sn layer area was intergranular in character (Figs. 3 and 4). Intergranular failure is not uncommon in intermetallic compounds and is

often attributed to a lack of slip systems and/or the restriction of cross-slip. Transmission electron microscopy revealed no signs of dislocation activity in the Nb_3Sn layer. The Griffith theory for fracture may be used to determine the effective surface energy of Nb_3Sn if it is assumed that the critical flow size was equal to the grain diameter. The Griffith equation for the fracture stress σ_F is

$$\sigma_F = \left(\frac{2E\gamma}{\pi c}\right)^{1/2}$$

where $2c$ is the crack length. The limits to σ_F were taken as the stress in the Nb_3Sn at 0.5 and 0.8% strain, and the values used for the Young's modulus of Nb_3Sn were 178.6 $GN\,m^{-2}$ at room temperature [5] and 167.9 $GN\,m^{-2}$ at 4.2 K (estimated assuming a temperature dependence of 2×10^{-4} per degree). The effective surface energies obtained from this analysis were 0.32 to 0.83 and 0.25 to 0.68 $J\,m^{-2}$ at 4.2 K and room temperature, respectively. These low values are in accordance with the brittle nature of Nb_3Sn.

Old and Charlesworth found that the room temperature fracture stress was approximately the same for a number of composites irrespective of volume fraction of filament, and concluded that a simple law of mixtures was not obeyed [5]. However, they considered the composites to consist solely of a bronze matrix with Nb_3Sn filaments, whereas it is clear from the metallographic evidence now available that the filaments have a niobium core and hence the volume fraction of Nb_3Sn is less than that used in their calculations. In view of this information, the fracture stresses of the composites, σ_c, have been re-calculated using the modified equation:

$$\sigma_c = \sigma_{Nb_3Sn} V_{Nb_3Sn} + \sigma_{Nb} V_{Nb} + \sigma_m V_m \quad (2)$$

where σ_{Nb_3Sn} is the ultimate tensile strength of the Nb_3Sn and σ_{Nb} and σ_m the stress on the niobium and bronze at the failure strain of the Nb_3Sn, V is the volume fraction of the particular component. The strains in the cold-worked niobium and the bronze were assumed to be plastic at failure. As neither of these materials work-hardens very rapidly, σ_{Nb} and σ_m are not strongly dependent on the strain selected for the calculation and values of 525 and 350 $MN\,m^{-2}$, respectively, were used. In contrast, the strain in the Nb_3Sn is elastic and hence σ_{Nb_3Sn} is directly proportional to strain. The value chosen for the strain is important as σ_c is dominated by the first term $\sigma_{Nb_3Sn} V_{Nb_3Sn}$. σ_c was evaluated using the two limits previously used for the strain, namely 0.5 and 0.8%. The results of this analysis and those previously obtained, assuming the filaments were fully reacted, are compared with the experimental data in Fig. 7. The calculated fracture stresses obtained after taking into account that the filaments were only partially reacted are lower than those determined assuming fully reacted filaments and do not vary so much from composite to

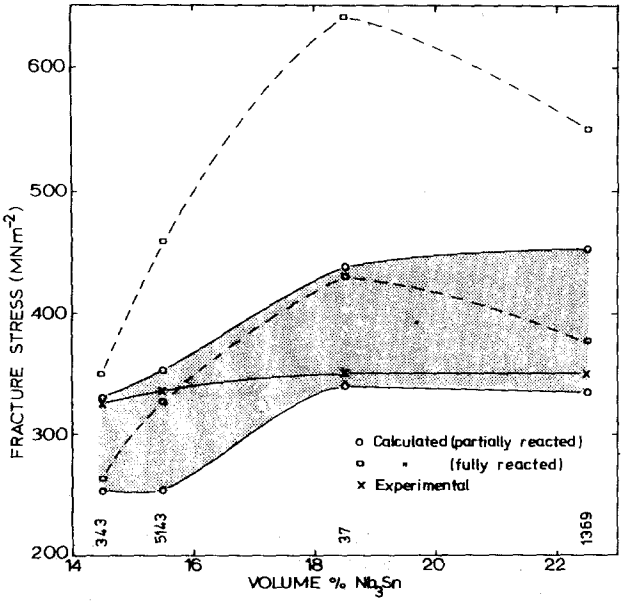

Figure 7 Comparison of experimental values of the fracture stress with those calculated from a simple law of mixtures (fully reacted) and Equation 2 (partially reacted).

composite. All the experimental results lie within the limits of the partially reacted σ_c.

The good room temperature ductilities of the 343 and 5143 composites are characteristic of composites containing volume fractions of fibres below a certain volume V_{min}, where V_{min} is given by:

$$V_{min} = \frac{\sigma_\mu - \sigma'_m}{\sigma_f + \sigma_\mu - \sigma'_m} \quad (3)$$

σ_μ is the U.T.S. of the matrix, σ'_m is the stress on the matrix at the failure strain of the filaments and σ_f is the failure stress of the filaments. Old and Charlesworth [5] put σ_f equal to the failure stress of Nb_3Sn, and calculated V_{min} to be 4.1% and compared this value with the volume percentage of fully reacted filaments. As the volume fraction of Nb_3Sn was, in all cases, greater than V_{min} they concluded that all the composites should have behaved in a brittle manner. This apparent inconsistency between experiment and theory can be accounted for by the crack-stopping capacity of the niobium cores. The presence of unreacted niobium means that the critical step in the failure of the composites is not the fracture of the Nb_3Sn but the failure of the niobium cores. It follows that V_{min} should be calculated using the U.T.S. of niobium for σ_f and then compared with the volume fraction of unreacted niobium. The U.T.S. of niobium will depend on the degree of cold-work and putting values obtained for heavily cold-rolled niobium into Equation 3 gives V_{min} in the range 7 to 10%. Thus this analysis successfully predicts that the 343 (2% unreacted niobium) and the 5143 (3.5% unreacted niobium) composites should be ductile and the 37 composite (16.5% unreacted niobium) brittle. The 1369 composite has a volume fraction of niobium of 7%, which is similar to V_{min}, and as a consequence its behaviour is borderline with ductilities varying from 0.5% (brittle) to above 1%. The 3780 composite was ductile at 4.2 K and had approximately 4% unreacted niobium. The mechanical properties data for bronze and niobium at 4.2 K are not available to calculate V_{min}; however, it is unlikely that V_{min} will change significantly with temperature so again there is agreement between experiment and theory.

3.3. Elastic and pseudo-elastic properties

Equation 2 may be written in terms of the Young's modulus of the components to yield a value for the Young's modulus of the composite (E_c). The values used for E_{Nb_3Sn} and E_{Nb} were as quoted previously and E_m was taken as $122\,GN\,m^{-2}$. It can be seen from Fig. 8 that the Young's modulus of the composites from this analysis, although lower than those calculated assuming fully reacted filaments, are still greater than the experimental modulus. The major contribution to E_c is from the bronze and the value used for the Young's modulus of the bronze matrix in the calculations was typical for a random polycrystalline material. This value would be inappropriately high if the matrix had a marked recrystallization texture with a "soft" elastic orientation parallel to the wire axis. However, X-ray diffraction studies revealed no signs of any texture in

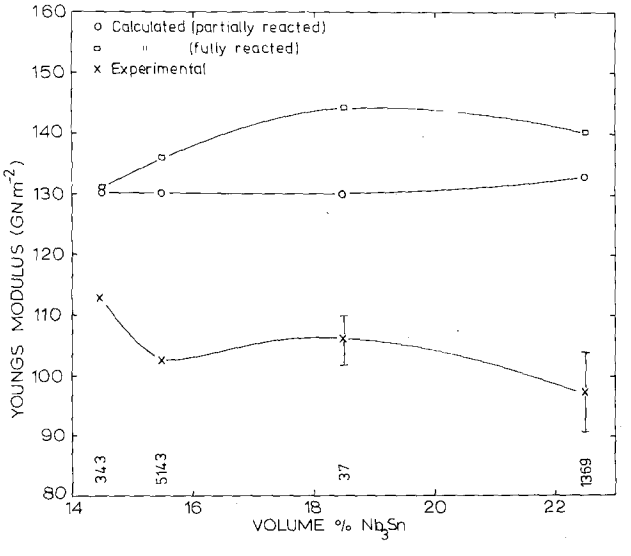

Figure 8 Comparison of experimental values of the Young's modulus with those calculated by the two methods discussed in the text.

the bronze and hence the anomaly cannot be attributed to an orientation effect in the matrix. A strong ⟨1 1 1⟩ deformation texture was found in the niobium cores but this is not significant as the contribution to E_c from the niobium is negligible. A large error in the value for E_{Nb_3Sn} could account for the discrepancy but there is no indication from the previous calculations, many of which involved E_{Nb_3Sn}, that the value used was unduly high. Furthermore when the elastic constants C_{44}, C_{11} and C_{12} [12] are substituted into Voigt's equation [13], the approximate value obtained for the Young's modulus of polycrystalline Nb_3Sn was similar to that used in the calculations. The reasons for the difference between theory and experiment remain unclear.

In the second linear stage of the stress–strain curve the composite behaves in a pseudo-elastic manner and the secondary modulus is given by

$$E_{sc} = E_{Nb_3Sn}V_{Nb_3Sn} + \left(\frac{\partial\sigma}{\partial\epsilon}V\right)_{Nb} + \left(\frac{\partial\sigma}{\partial\epsilon}V\right)_{m}$$

where $\partial\sigma/\partial\epsilon$ is the rate of work-hardening. The work-hardening rates of both the cold-worked niobium core and the recrystallized bronze matrix are relatively low, consequently the first term on the right-hand side of the equation predominates when determining the secondary modulus. Fig. 9 shows that there is good agreement between the calculated results and the experimental data when the fact that the filaments were only partially reacted is taken into account.

4. Conclusions

(1) In all the composites examined the filaments were only partially reacted and consisted of an outer Nb_3Sn layer surrounding a core of cold-worked niobium.

(2) Fracture of the Nb_3Sn was intergranular at room temperature and at 4.2 K. The effective surface energy was in the range 0.25 to 0.83 J m^{-2}. Cracking of the Nb_3Sn occurred in localized regions and within these regions the crack separation was found to be relatively independent of the Nb_3Sn layer thickness and the amount of strain.

(3) The unreacted niobium cores acted as crack stoppers and the variation in ductility between the different composites could be explained in terms of the volume fractions of unreacted niobium.

(4) When the presence of the unreacted niobium cores in the filaments was taken into account, there was agreement between the values of the fracture stress and the secondary modulus obtained experimentally and those values calculated using the law of mixtures. Such agreement was not found between the two sets of values for the Young's modulus.

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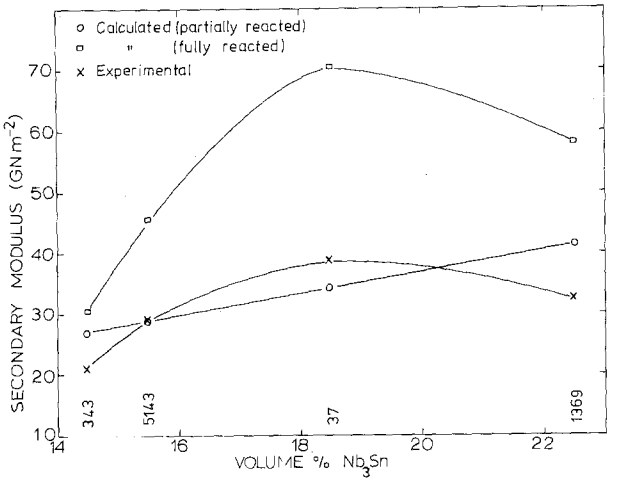

Figure 9 Comparison of experimental values of the secondary modulus with those calculated by the two methods discussed in the text.

References

1. D. C. LARBALESTIER, J. E. MAGRAW and M. N. WILSON, *IEEE Trans.* **MAG–13** (1977) 462.
2. I. L. MCDOUGALL, *ibid* **MAG–11** (1975) 1467.
3. D. C. LARBALESTIER and S. O. HONG, Proceedings of the 7th Symposium on Engineering Problems of Fusion Research, Knoxville, Tennessee, USA, (October 1977).
4. J. W. EKIN, *Appl. Phys. Letters* **29** (1976) 216.
5. C. F. OLD and J. P. CHARLESWORTH, AERE publication R7903 (1974).
6. J. A. LEE, C. F. OLD and D. LARBALESTIER, Colloques Internationaux C.N.R.S. No. 242 "Physique sous champ magnetique intenses" (1975) p. 87.
7. A. W. WEST and R. D. RAWLINGS, *J. Mater. Sci.* **12** (1977) 1862.
8. A. G. INGRAM, E. S. BARTLETT and H. R. OGDEN, *Trans. AIME* **227** (1963) 131.
9. W. F. BROWN and J. E. SRAWLEY, ASTM Special Technical Publication No. 410 (1969).
10. G. L. MILLER, "Metallurgy of Rarer Metals", Vol. 6, "Tantalum and Niobium" (Butterworths, London, 1959).
11. D. F. STEIN, "The Microstructure and Design of Alloys", 3rd International Conference on the Strength of Metals and Alloys, Vol. 2, Cambridge (1973) p. 58.
12. L. R. TESTARDI, *Rev. Mod. Phys.* **47** (1975) 637.
13. W. VOIGT, "Lehrbuch der Kristallphysik" (Leipzig, Teuber, 1928) p. 716.

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