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Growth of Nb_3Sn in multifilamentary bronze composites

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Growth of Nb_3Sn layers in multifilamentary composites has been investigated and their superconducting critical temperatures are measured using both resistive and inductive techniques. The growth parameters are discussed in the light of the analytical models of Reddi *et al.* Results show that for the composites studied, the rate controlling step for Nb_3Sn growth is diffusion of tin through grain boundaries of Nb_3Sn with the time exponent n determined by both the initial grain size and grain growth. T_c measurements show that for composites with a higher filament number, the width of superconducting transition is broader with no significant change in the onset T_c.

1. Introduction

During the last few years the bronze route [1, 2] has emerged as a commercially viable process for making superconducting A-15 compounds, namely, Nb_3Sn and V_3Ga in multifilamentary form. In this process niobium (or vanadium) strands, in the desired configuration, are embedded in a cylindrical bronze matrix containing tin (or gallium) and such a composite is subsequently drawn into a wire. The wire is then heat treated to form superconducting Nb_3Sn (or V_3Ga) at the bronze–niobium (or vanadium) interface by diffusion reaction of tin (or gallium) and niobium (or vanadium). It is now well established [3–6] that the growth of A-15 layer in the above process is governed by two sequential rate controlling steps, namely, (i) diffusion of tin from the bronze matrix to the bronze–Nb_3Sn interface, and (ii) diffusion of tin through the Nb_3Sn layer to the unreacted niobium interface for further growth. The slower of the two steps determines the growth rate of Nb_3Sn [3]. The growth kinetics models due to Reddi *et al.* [3] developed for monofilamentary composites have shown that depending on the experimental conditions, the time exponent n in the growth law $R = kt^n$, where R is the layer thickness and t is the reaction time, can vary over a wide range from 0.25 to 1. While these contentions have proven valid [3, 6] for monofilamentary Nb_3Sn and V_3Ga, the preliminary studies [4, 5] have indicated that the models could be stretched to explain the results of multifilametary composites as well.

In this paper we report growth kinetics studies carried out on multifilamentary Nb_3Sn composites containing 2601 and 10 000 filaments and compare the findings with the previously reported [4, 5] results on a Nb_3Sn composite with 1500 filaments. Superconducting critical temperatures at various stages of growth are also measured using both inductive and resistive techniques.

2. Experiments

The unreacted samples containing 2601 and 10 000 niobium filaments of 5 μm and 3 μm diameter, respectively, were obtained from the Vacuumschmelze, GmbH, Hanau. The distribution of niobium filaments in composites with 2601 (composite A) and 10 000 (composite B) filaments are depicted in Figs. 1a and b, respectively. These filament are embedded in a bronze matrix of 0.52 mm diameter in the case of composite A. The composite B of diameter 0.65 mm contains a central copper core with a tantalum barrier around it. The niobium filaments are distributed around this barrier in the bronze matrix. Both these composites differed from the previously studied [4, 5] one containing 1500 filaments in that while the latter contained an even distribution of individual filaments with uniform filament density over the

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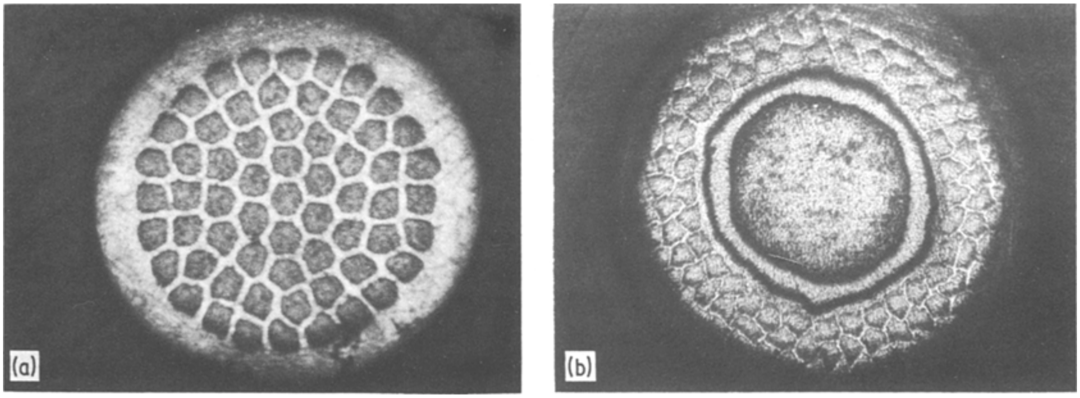

Figure 1 (a) Photomicrograph of the unreacted composite A with 2601 niobium filaments distributed in 51 bunches. Each bunch contains 51 filaments. (b) Photomicrograph of the unreacted composite B with 10 000 niobium filaments distributed in 114 bunches with an average of 87 filaments in each bunch.

entire conductor cross-section, the present composites as may be seen in Figs. 1a and b had a uniform distribution of rather closely packed bunches making the distribution of individual filaments uneven.

Short sections of the wires were heat treated in vacuum at different temperatures of 550, 650, 750 and 800° C for various durations of time ranging from 5 to 50 h. The diffusion reacted Nb_3Sn layers formed were studied for the growth kinetics using optical and scanning electron microscopy techniques. In the latter, the samples were first brittle fractured at liquid nitrogen temperature and after coating them with gold were examined using the scanning electron microscope Jeol JSM 35 CF operating at 25 kV. Typical SEM micrographs of composites A and B showing the Nb_3Sn layers formed after different heat treatments are shown in Figs. 2a and b, respectively. As may be seen in Fig. 2b the complete cross-section of the filament is transformed to Nb_3Sn and there is no unreacted niobium left over. In all the samples studied, the layer thickness measurements were confined to the outermost layers to keep uniformity in the analysis of the data.

Superconducting critical temperatures of the various specimens were measured using the standard four probe resistive as well as inductive techniques. The temperature measurements were accurate to within ± 0.05 K.

3. Results and discussion

Fig. 3 depicts $\ln R - \ln t$ plots for the composite A annealed at various temperatures mentioned above for different durations of time. The data for composite B annealed at 800° C are also plotted.

As may be seen, the time exponent n of the growth law varies for different annealing temperatures. The effect of increasing annealing temperatures for these samples is to raise n which is entirely consistent with the previously reported results of Upadhyay *et al.* [5] obtained for a composite containing an even distribution of 1500 filaments. Furthermore, n values observed in the present study are in accord with those reported in [5]. The composite B annealed at 800° C has yielded a higher value of 0.34 for the time exponent. It is interesting to note that in the case of the sample of composite A annealed at 800° C there is an abrupt increase in the value of n to 0.77 when the annealing time exceeds 35 h.

If we examine the above findings in the light of the analytical models of Reddi *et al.* [3], the following broad conclusions seem to emerge. The n values less than 0.5 imply that the observed growth of the Nb_3Sn layer is controlled by diffusion of tin atoms through the grain boundaries of the layer, i.e. diffusion of tin through the bronze matrix is faster than through the compound layer. The n values exceeding 0.5 simply means that the rate controlling step is diffusion of tin through the bronze matrix, i.e. the diffusion through the layer is faster than through bronze. All the values of n observed in the present study, except the composite A samples annealed at 800° C beyond 35 h, are less than 0.5 suggesting that the rate controlling step is via grain boundaries. It is worth pointing out that in the case of monofilamentary conductors having bronze to

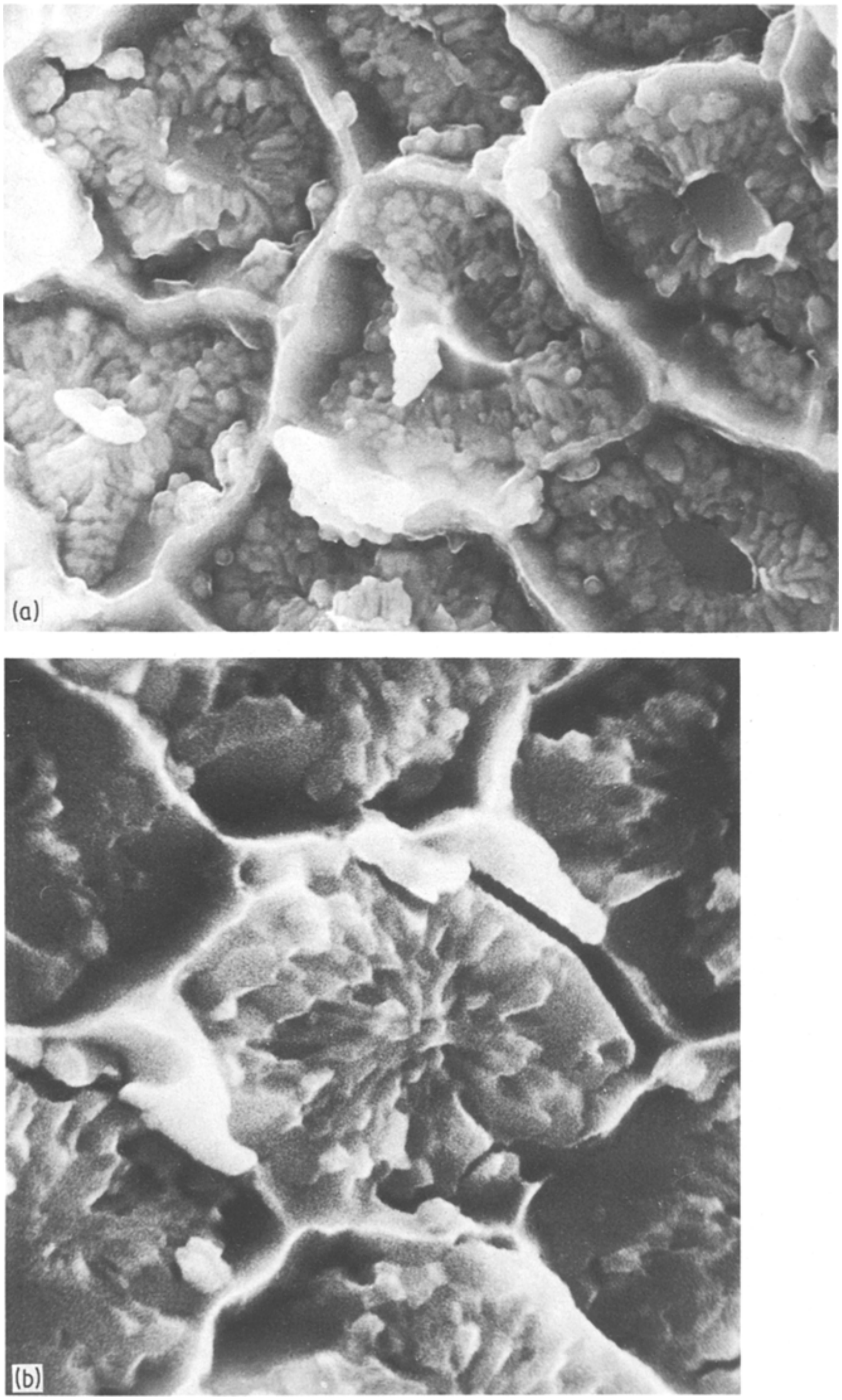

Figure 2 (a) Scanning electron micrograph of the composite A annealed at 550° C for 50 h (Magnification × 10 000). (b) Scanning electron micrograph of the composite A annealed at 800° C for 50 h (Magnification × 10 000).

niobium ratios of about 10 or more, the n values invariably exceed 0.5 [3, 6, 7, 8], while in multifilamentary situation having bronze to niobium ratio to be much smaller (around 2 or less), the reported n values [4, 5, 9, 10] are found to be less than 0.5. This is entirely justified as in multifilamentary conductors, because of considerable overlap of diffusion fields of neighbouring filaments and a larger volume fraction of niobium with greater surface area, the diffusion rate of tin atoms in bronze is considerably enhanced, thereby making the diffusion of tin through the compound

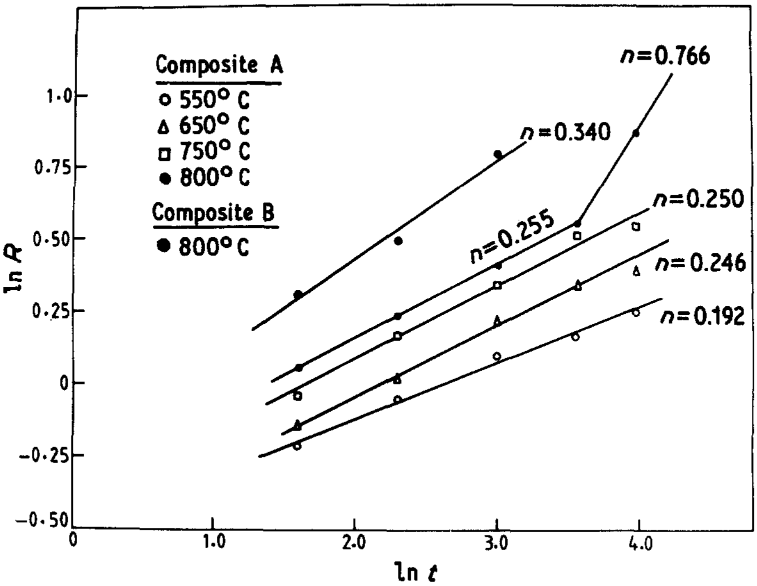

Figure 3 ln R–ln t plot for composite A and composite B for different reaction time and temperatures.

layer as the rate controlling step. The observed n values are consistent with the above contentions. The increase of n value from 0.26 to 0.77 after 35 h of annealing at 800° C (Fig. 3) suggests that the rate controlling step has changed from diffusion of tin through the grain boundaries to that through the bronze matrix. This is not entirely unexpected if the tin in bronze is depleted to such an extent that the flux rate of tin through the bronze matrix has now become smaller than through the grain boundaries of the compound layer. This increase in n resulting from depletion of tin atoms in the bronze matrix has been observed by Takacs [11].

The lowest value of the exponent n as observed for the composite A annealed at 550° C has been found to be 0.19 in contrast to 0.25 predicted by Reddi *et al.* [3] for the grain boundary diffusion process. It is worth stressing that the above prediction, $n = 0.25$, has emerged for the situation when the initial grain size d_i is small and the growth of Nb_3Sn grains of the layer is assumed to be governed by the parabolic relation $d_\mathrm{t}^2 - d_\mathrm{i}^2 = k_4 t$. In what follows we can briefly see how n is affected if the grain growth is described by a more general relation. The general diffusion equation is given by [3]

$$2\pi(r_\mathrm{F} - R) l \bar{C}_\beta \frac{\mathrm{d}R}{\mathrm{d}t} = L_\mathrm{gb} a D_\mathrm{gb} \left(\frac{C_{\beta\alpha} - C_{\beta\mathrm{F}}}{R}\right) \quad (1)$$

where L_gb is the total length of the network of grain boundaries that intersect the reaction interface, a is the thickness of the grain boundary perpendicular to the direction of flux and D_gb is the grain boundary diffusion coefficient of tin atoms in the compound layer. The other symbols carry the same meanings as in [3].

Substituting for L_gb and using a more general grain growth relation

$$d_\mathrm{t}^\mathrm{m} = d_\mathrm{i}^\mathrm{m} + k_4 t \quad (2)$$

or

$$d_\mathrm{t} = d_i \left[1 + \frac{k_4 t}{d_\mathrm{i}^m}\right]^{1/m}$$

Equation 1 takes the form

$$R \frac{\mathrm{d}R}{\mathrm{d}t} = \frac{2aD_\mathrm{gb}}{\bar{C}_\beta} \left(\frac{C_{\beta\alpha} - C_{\beta\mathrm{F}}}{d_\mathrm{i}}\right) d_\mathrm{i}(d_\mathrm{i}^m + k_4 t)^{-1/m} \quad (3)$$

(i) for the case when the initial grain size d_i is small,

$$R \frac{\mathrm{d}R}{\mathrm{d}t} = \frac{2aD_\mathrm{gb}}{\bar{C}_\beta} (C_{\beta\alpha} - C_{\beta\mathrm{F}})(k_4 t)^{-1/m}$$

which yields on integration

$$R^2 = \frac{4aD_\mathrm{gb}}{\bar{C}_\beta} (C_{\beta\alpha} - C_{\beta\mathrm{F}}) k_4 t^{(m-1)/m} \frac{m}{m-1}$$

or

$$R = \left[\frac{4aD_\mathrm{gb}}{\bar{C}_\beta} k_4 \frac{m}{m-1}\right]^{1/2} (C_{\beta\alpha} - C_{\beta\mathrm{F}})^{1/2} t^{(m-1)/2m}$$

or

$$R = k_5 (C_{\beta\alpha} - C_{\beta\mathrm{F}})^{1/2} t^{(m-1)/2m} \quad (4)$$

(ii) For the case when d_i is large Equation 2 takes the form

$$R\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{2aD_{\mathrm{gb}}}{\bar{C}_\beta}\left(\frac{C_{\beta\alpha}-C_{\beta\mathrm{F}}}{d_\mathrm{i}}\right)$$

or

$$R^2 = \frac{4aD_{\mathrm{gb}}}{\bar{C}_\beta}\left(\frac{C_{\beta\alpha}-C_{\alpha\mathrm{F}}}{d_\mathrm{i}}\right)t$$

or

$$R = \left(\frac{4aD_{\mathrm{gb}}}{\bar{C}_\beta}\right)^{1/2}(C_{\beta\alpha}-C_{\beta\mathrm{F}})^{1/2}t^{1/2} \qquad (5)$$

implying thereby a parabolic growth.

It follows from Equation 4 that the observed $n = 0.19$ would result when $m = 1.61$ implying the grain growth relation to be $d_\mathrm{t}^{1.61} - d_\mathrm{i}^{1.61} = k_4 t$ which represents a faster growth than parabolic as considered by Reddi *et al.* [3]. The higher values of n for higher annealing temperatures as observed in the present as well as in previous [5] findings would imply higher values of m in the above relation which results in a dilemma. If we assume the initial grain size d_i to be small and same for all annealing temperatures and assume the grain growth to be the sole factor in determining the time exponent n, we are led to an obvious contradiction that at higher anneal temperatures the grain growth is reduced! This discrepancy can, however, be resolved by the fact that the initial grain size d_i is not likely to remain constant but is expected to increase with increasing temperatures. Thus the observed n values after different temperatures of reaction anneal can be thought to be the consequence of two mutually competing processes, namely, a progressively rising rate of grain growth with temperature resulting in decrease in n and an increase in the initial grain size d_i causing an increase in n towards 0.5. The present investigation as well as the previously reported data [5] on 1500 filaments indicate the possible dominance of the latter of the two processes. In the light of the above one can interpret the unaccounted observation of Larbalestier *et al.* [12] that the time exponent n decreased from 0.20 to 0.17 when the reaction temperature was raised from 600 to 750° C. Equation 4 implies that the exponent m of the grain growth relation is reduced from 1.67 to 1.51 suggesting a faster grain growth at higher temperature to be the dominant factor in determining the layer growth of $\mathrm{Nb_3Sn}$. The observed difference between the above and the results of present studies and as well as those of Upadhyay *et al.* perhaps may be attributed to the purity of niobium filaments and of the bronze matrix in deciding both the initial grain size d_i and the exponent m of the grain growth relation. Due to rather small grain sizes observed reliable grain growth studies of $\mathrm{Nb_3Sn}$ layer are to-date lacking.

The onset T_c measured both resistively and inductively were found to be mutually consistent. The variation of the onset T_c with reaction time at different annealing temperatures for composite A is depicted in Fig. 4. As may be seen, the T_c values for samples annealed at 550, 650 and 800° C continually decrease with reaction time whereas for the 750° C annealed sample the variation is zigzag but tending to increase with reaction time. As already discussed by Upadhyay *et al.* [5], the observed variation in T_c may be linked to the two competing processes, namely,

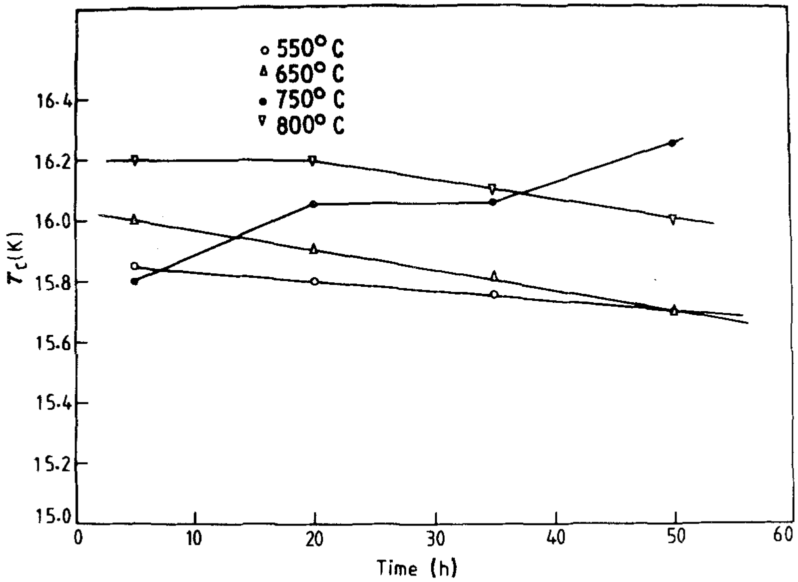

Figure 4 Variation of the onset T_c for composite A with different reaction time and temperature.

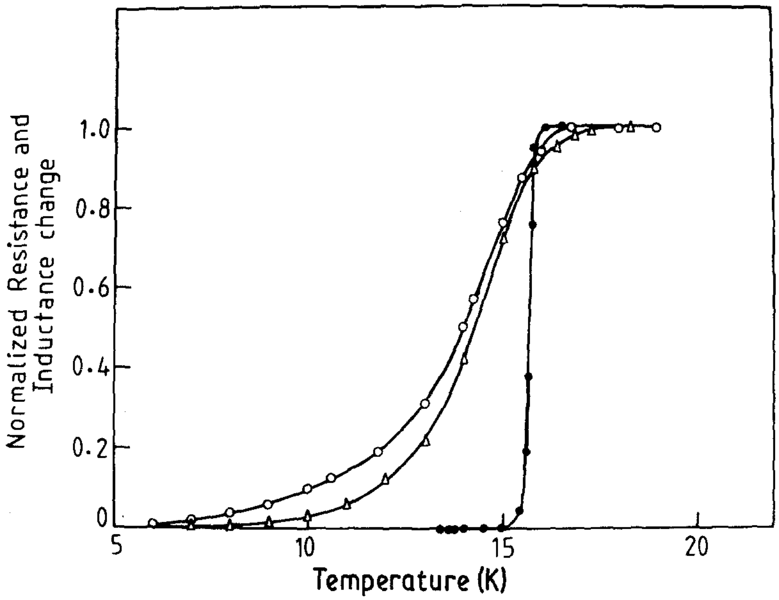

Figure 5 A comparison of the superconducting transitions of composite A and B measured by the resistive and inductive methods. ● and △ correspond to resistive and inductive transition for composite A annealed at 750° C (5 h) and ○ refers to inductive transition for composite B annealed at 800° C (5 h).

the volume expansion during the formation of Nb_3Sn layer causing building up to internal strains resulting in depression of T_c and simultaneous decrease of internal strains due to annealing treatment causing enhancement in T_c. The dominance of either of the above two processes dictates the net variation of T_c observed. In all the samples studied, the observed T_c values were less than the optimum T_c of 18.3 K of Nb_3Sn, in agreement with other workers [3, 4, 13, 14], which is attributed to compressive stresses caused by the bronze matrix during cool down. The denuded Nb_3Sn filaments have been found to exhibit enhanced T_c [13].

For samples studied it was consistently found that inductive measurements of T_c yielded a much broader transition width than resistive measurements (Fig. 5) in agreement with the observations of Suenaga *et al.* [15]. The reason for this being that the resistive measurements give only the highest T_c value of the layer while the inductive studies yield information about the T_c variation within the layer. In Fig. 5 the inductive transition curve for the composite B diffusion reacted for 5 h at 800° C, is also plotted. The present study showed that the samples of composite B containing a larger number density of filaments than composite A, in general showed a broader transition width. The maximum transition width recorded for composite B was about 7 K for the sample annealed at 800° C for 50 h in contrast to 4 K for the composite A annealed at 650° C for 50 h. For the composite containing still smaller number (1500) of filaments, uniformly distributed, Kwasnitza *et al.* [4] had earlier found maximum width to be about 1.2 K for a sample annealed for 50 h at 725° C. Moreover, for the same layer thickness the composite with 10 000 filaments exhibited a broader transition than for composites with 1500 and 2601 filaments. Thus, the larger T_c width observed for higher filament number composite does not seem to result from the stoichiometric variation within the layers. The close packing of several filaments in bunches in higher filament number composites is expected to result in enhanced internal strains which are perhaps responsible for larger transition width observed. Thus, the transition width seems to decrease as the number density of filaments in the composite goes down and is independent of the layer thickness.

4. Conclusions

The main conclusions of the study may be summarized as follows.

1. The rate controlling step for the growth of Nb_3Sn in multifilametary composites is the diffusion of tin atoms through the grain boundaries of the compound layer. After longer anneals at higher temperatures, with appreciable depletion of tin in the matrix, there are indications of the rate controlling step reverting to the diffusion of tin through the bronze matrix.

2. The time exponent n of the growth equation $R = kt^n$ increases with the reaction temperature in conformity with larger initial grain size at higher annealing temperature.

3. Whereas the onset T_c is affected little, the transition width does seem to be affected by the filament concentration; higher the filament concentration broader is the T_c.

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References

1. A. R. KAUFMANN and J. J. PICKETT, *Bull. Amer. Phys. Soc.* **15** (1970) 838.
2. K. TACHIKAWA, Proceedings of the IECE-3 (Illife Science and Technology Pub. Ltd., Surrey) p. 330.
3. B. V. REDDI, S. RAY, V. RAGHAVAN and A. V. NARLIKAR, *Phil. Mag.* **38A** (1978) 559.
4. K. KWASNITZA, A. V. NARLIKAR, H. U. NISSEN and D. SALATHE, *Cryogenics* **20** (1980) 715.
5. P. UPADHYAY, S. B. SAMANTA and A. V. NARLIKAR, *Mater. Res. Bull.* **16** (1981) 741.
6. B. V. REDDI, V. RAGHAVAN, S. RAY and A. V. NARLIKAR, *J. Mater. Sci.* **18** (1983) 1165.
7. D. DEW HUGHES, T. S. LUHMAN and M. SUENAGA, *Nucl. Technol.* **29** (1976) 268.
8. D. DEW HUGHES and M. SUENAGA, *J. Appl. Phys.* **49** (1978) 357.
9. T. S. LUHMAN and M. SUENAGA, *Adv. Cryog. Eng.* **22** (1977) 356.
10. D. S. EASTON and D. M. KROEGAR, *IEEE Trans. Mag.* **MAG-13** (1977) 800.
11. S. TAKACS, private communication (1979).
12. D. C. LARBALESTIER, P. E. MADSON, J. A. LEE, M. N. WILSON and J. P. CHARLESWORTH, *IEEE Trans. Mag.* **MAG-11** (1975) 247.
13. T. S. LUHMAN and M. SUENAGA, *ibid.* **MAG-13** (1977) 800.
14. D. DEW HUGHES, *Cryogenics* **15** (1975) 435.
15. M. SUENAGA, W. B. SAMPSON and C. J. KLAMUT, *IEEE Trans. Mag.* **MAG-11** (1975) 231.

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