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Growth kinetics of monofilamentary Nb_3Sn and V_3Ga synthesized by solid-state diffusion

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Studies of growth kinetics of Nb_3Sn and V_3Ga formation have been carried for monofilamentary composites of niobium and vandium filaments embedded in bronze wires containing varying concentrations of tin and gallium, respectively. The samples are diffusion reacted at different temperatures and for different lengths of time and the thickness and the microstructure of the resulting A-15 layer are investigated using optical and scanning electron microscopy techniques. The results are discussed in the light of the analytical model previously proposed by the present authors and it is shown that while the rate controlling step for the formation of Nb_3Sn is diffusion of tin through the bronze matrix, for V_3Ga it is the diffusion of gallium through the grain boundaries of the compound layer. The data are used to calculate the activation energies for Nb_3Sn and V_3Ga formation.

1. Introduction

Multifilamentary Nb_3Sn and V_3Ga superconductors are now available commercially for a variety of applications. These are produced by the so-called bronze route. Here, niobium (or vanadium) rods (designated A) are inserted into holes drilled in Cu–B ingots (B stands for tin or gallium in the formula, A_3B) and then rolled or wire drawn to the final size. This composite is then heat treated in the temperature range of 550 to 850° C to form Nb_3Sn (or V_3Ga) around each niobium (or vanadium) filament by solid-state diffusion. Considerable work on the influence of various parameters on the superconducting properties has been reported [1–7]. These parameters include the reaction temperature and time, the initial concentration of B in the Cu–B matrix, the filament size and the presence of dopants in the matrix and/or in the filaments. However, no systematic data have been obtained to predict the mechanism of the formation and the kinetics of growth of these compound layers.

Reddi *et al.* [8] have developed a model for the growth kinetics of A_3B layers by the bronze process and have identified the underlying growth mechanisms of Nb_3Sn and V_3Ga compounds. They used the growth equation

$$R = k\,t^n \qquad (1)$$

where R is the layer thickness, t is time, k is the reaction rate constant, and n is the time exponent. This model identifies specific rate controlling steps in the overall growth process corresponding to a range of values of the time exponent n. The

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preliminary results of Reddi *et al.* [9] on Nb_3Sn indicated that the diffusion of tin in the bronze matrix is the rate controlling step in the formation of Nb_3Sn in a monofilamentary composite. The results of Tachikawa *et al.* [10] on V_3Ga show a fall of n with increasing reaction temperature. A comparison of these results with the model shows that the diffusion of gallium through the grain boundaries of the reacted compound layer (with simultaneous grain growth) is the rate controlling step in the formation of V_3Ga. However, paucity of experimental results on the growth kinetics of Nb_3Sn and V_3Ga compounds formed by the bronze route in monofilamentary composites motivated us to conduct further investigations on the growth kinetics in these systems. In this paper, we report our experimental results on the growth kinetics of Nb_3Sn and V_3Ga compounds formed at various temperatures for different initial concentrations of tin (or gallium) in the bronze matrix. The results obtained are interpreted in terms of the above model for the growth kinetics and are also compared with the more recent experimental results obtained by various workers in the field.

2. Experimental details

2.1. Processing the composites

The composites containing Cu–Sn/Nb and Cu–Ga/V are made as follows. Two sets of bronze ingots of 13 mm diameter containing different concentrations of tin ranging from 2.01 to 10.87 wt% in one set and of gallium from 1.5 to 5.65 wt% in the other set are induction melted and cast. The purity of the niobium and vanadium used is $>$ 99.95%. The bronzes do not contain more than 0.1% of total impurities such as zinc and aluminium. They are machined to 12 mm diameter, cold rolled to 10 mm rods and then annealed at 700° C to break up the cast structure. A central hole of approximately 1.5 mm diameter and 40 mm long is drilled into each rod to introduce the niobium or vanadium wires of the same diameter. These composites are first cold rolled and then wire drawn to the final size of 1.05 mm diameter with intermittent anneals at 450° C. The diameter of the final niobium (or vanadium) filament is 0.12 mm. For diffusion anneals, the composite wires are cut into 60 mm length, sealed in evacuated quartz tubes and annealed in the range of 650 to 850° C for periods ranging from 9 to 225 h.

2.2. Measurements on the reacted layer

X-ray diffraction patterns revealed the presence of Nb_3Sn and V_3Ga, respectively, in the reacted samples. For metallographic examination, composite wires are embedded in a brass mount, mechanically polished and etched. An etchant containing 87.0% lactic acid, 8.7% nitric acid and 4.3% hydrofluoric acid is used for Nb_3Sn [11] and a solution containing 60% glycerine, 20% nitric acid and 20% hydrofluoric acid for V_3Ga. The microstructures of the reacted layers are examined on a Stereoscan S4-10 scanning electron microscope. Thickness measurements of the reacted layer are made on four micrographs for each sample and the mean thickness is computed.

3. Results

The experimentally measured thickness values of Nb_3Sn and V_3Ga layers as a function of annealing time are analysed using the growth equation, $R = kt^n$. The time exponent n and the rate constant k are determined for different concentrations of tin or gallium in the bronze matrix. The values of k as a function of annealing temperature are used to calculate the experimental activation energy.

3.1. Time exponent n for the formation of the Nb_3Sn layer

The thickness of the annular Nb_3Sn layer around the niobium filament increases with increasing annealing time. To determine the value of n and k in Equation 1, a plot of log R against log t is made. The slope of this plot gives the time exponent n. The intercept on the y-axis yields log k.

Figs. 1 and 2 are plots of log R against log t for the reaction temperatures of 750 and 850° C with five different concentrations of tin in the matrix. The best fitting straight line in each case is found by a least squares fit. The values of n and k, so obtained for three reaction temperatures, are listed in Table I. At 750° C, the value of n decreases from 0.80 to 0.57, as the initial concentration of tin increases from 3.30 to 10.87 wt% in the bronze matrix. Similarly, for the composites reacted at 850° C, the decrease of n is from 0.90 to 0.65, as the initial tin concentration is varied from 2.01 to 8.36 wt%. The values of n earlier reported by Reddi *et al.* [8] for the reaction temperature of 700° C and for

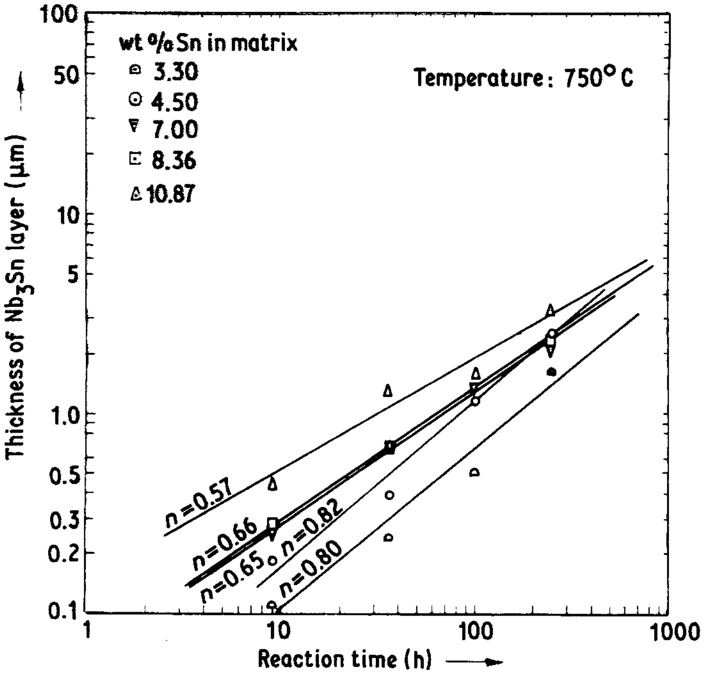

Figure 1 Log R–log t plots at 750° C for different concentrations of tin in bronze.

tin concentrations of 7.29, 9.45 and 15.87 wt% have been recalculated with corrected data. These new values of n for this temperature are also shown in Table I. In all these cases, n decreases with increasing tin concentrations.

The three n values obtained for 7.29, 9.45 and 15.87 wt% tin in the matrix reacted at 700° C are shown in Fig. 3 as a function of tin concentration. It is found that n decreases linearly with increasing concentration of tin. The n values for the monofilament composite reported by Dew-Hughes *et al.* [12] for 12 wt% Sn–bronze and Luhman and Suenaga [13] and Dew-Hughes and Suenaga [14] for 13 wt% Sn–bronze at the same reaction temperature are also shown in Fig. 3. The results appear to follow a consistent trend. Recently Takacs [15] also reported that n falls with increasing tin concentration. At the

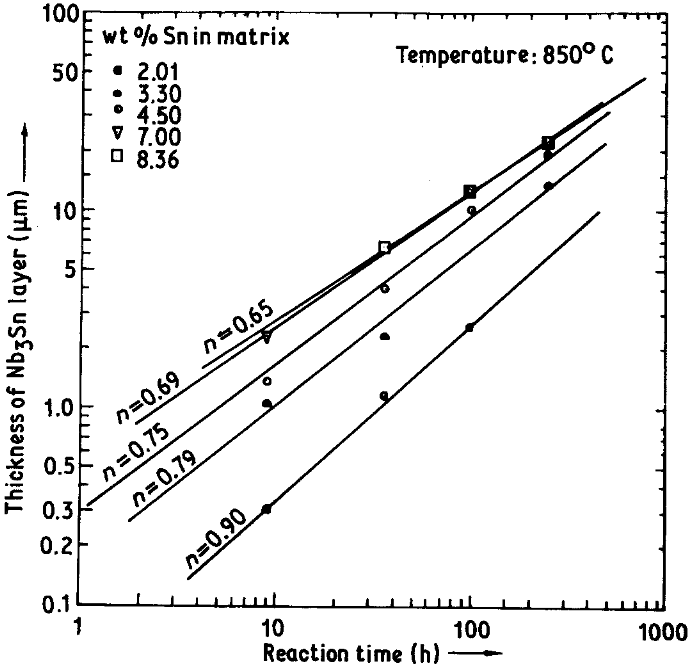

Figure 2 Log R–log t plots at 850° C for different concentrations of tin in bronze.

TABLE I Time exponent n and rate constant k for the Nb_3Sn layer obtained at the reaction temperatures 700, 750 and 850° C with different initial concentrations often in the bronze matrix

Reaction temperature (° C)	Tin in bronze matrix (wt%)	Time exponent, n	Rate constant, k
700	7.29	0.87	0.06
	9.45	0.78	0.12
	15.87	0.57	0.33
750	3.30	0.80	0.02
	4.50	0.82	0.03
	7.00	0.65	0.06
	8.36	0.66	0.06
	10.87	0.57	0.14
850	2.01	0.90	0.08
	3.30	0.79	0.17
	4.50	0.75	0.30
	7.00	0.69	0.52
	8.36	0.65	0.63

higher reaction temperature studied, namely 750 and 850° C, a similar decrease of n with increasing tin concentration occurs as shown in Fig. 4.

3.2. Time exponent n for the formation of the V_3Ga layer

The results obtained with Cu–Ga/V composite show that the thickness of the V_3Ga layer formed around the vanadium filaments also increases with annealing time, as shown in Fig. 5 for the reaction temperature of 650° C.

The n and k values obtained from similar plots for three different gallium concentrations, 1.50, 2.23 and 5.65 wt% at 650, 700 and 850° C are listed in Table II. Here, n is found to be unaffected by the variation in gallium concentration in the matrix or the reaction temperature. Unlike in the case of Cu–Sn/Nb composite, the value of n is constant at 0.5. The same n value has been obtained by Gubser *et al.* [16] and Dew-Hughes with the bronze matrix containing much higher concentrations of gallium ($>$ 15 wt %) than those used in this investigation.

3.3. The rate constant k for the formation of V_3Ga and Nb_3Sn

Even though the time exponent n is constant, the thickness of the reacted layer for a given annealing time and temperature increases with gallium concentration in the matrix, as seen in Fig. 5. This indicates that the rate constant k increases with increasing gallium concentration, as also seen in Table II. Fig. 6 shows the variation of the rate constant k as a function of gallium concentration for the three reaction temperatures.

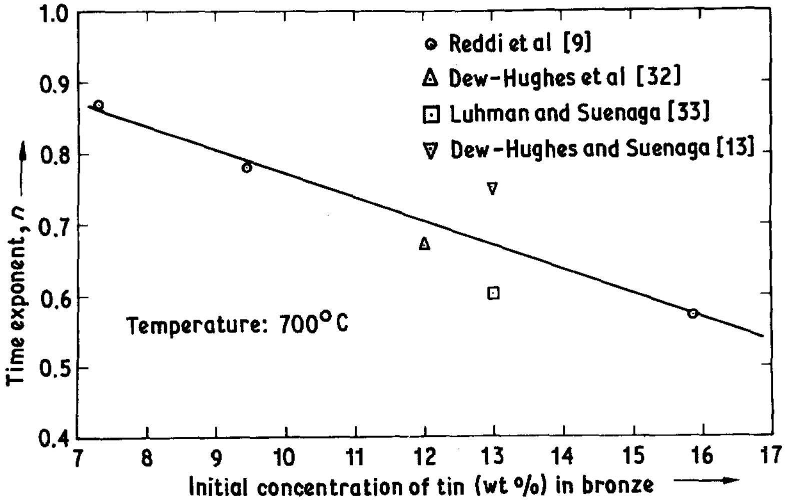

Figure 3 Variation of time exponent n with the initial concentration of tin in bronze at 700° C.

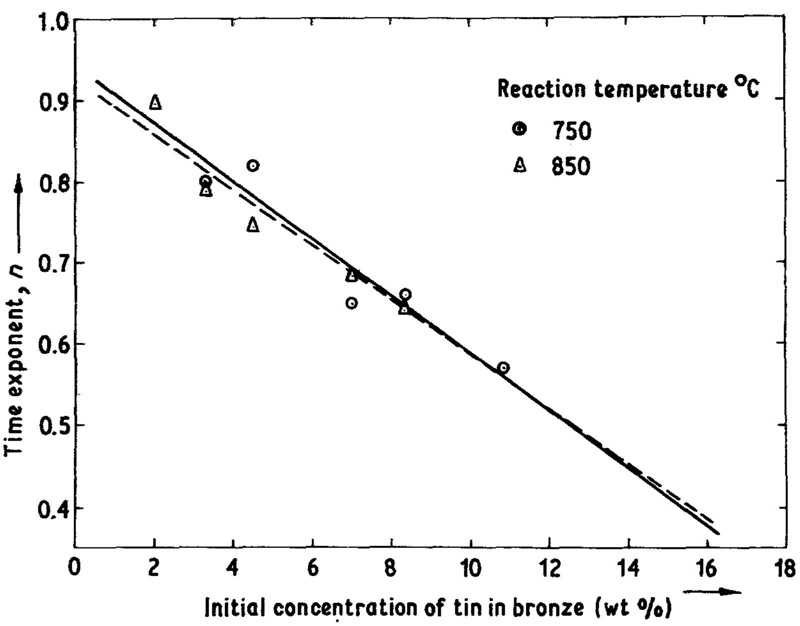

Figure 4 Variation of time exponent n with the initial tin in bronze at 750 and 850° C.

The variation is linear. The best fitting straight lines, when extrapolated backwards, show that k falls to zero at a finite gallium concentration. This may indicate that a minimum concentration of gallium in the matrix is necessary for growth of the V_3Ga layer, even though this minimum is small (<0.5 wt%) for all the three reaction temperatures.

Referring back to Figs. 1 and 2, for a given reaction time and temperature, the thickness of the reacted Nb_3Sn increases with increasing tin in the matrix. We have already seen that n decreases as tin concentration increases. This again indicates that the rate constant k increases with increasing tin concentration. The k values in Table I obtained from Figs. 1 and 2 indicate

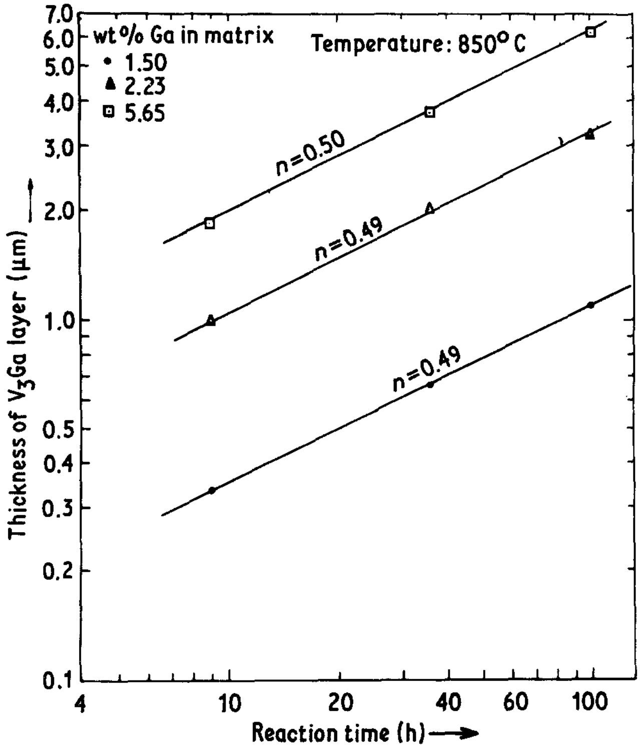

Figure 5 Log R–log t plots at 850° C for different concentrations of gallium in bronze.

TABLE II Time exponent n and rate constant k for the V_3Ga layer obtained at the reaction temperatures, 650, 700 and 850° C, with different initial concentrations of gallium in the bronze matrix

Reaction temperature (° C)	Gallium in bronze matrix (wt %)	Time exponent, n	Rate constant, k
650	1.50	0.49	0.04
	2.23	0.50	0.06
	5.65	0.50	0.15
700	1.50	0.50	0.09
	2.23	0.50	0.13
	5.65	0.49	0.38
850	1.50	0.49	0.12
	2.23	0.49	0.34
	5.65	0.50	0.64

this trend. Recent findings of Wada *et al.* [17] also indicate that k increases with increasing concentration of tin in the matrix.

As in the case of V_3Ga, the rate constant falls to zero at a finite tin concentration at all the three reaction temperatures. The minimum concentration of tin in the bronze that is necessary for growth of the Nb_3Sn layer is 5.5 wt % at 700° C, 2.8 wt % at 750° C and 1.0 wt % at 850° C.

For a given concentration of B in the matrix, the rate constant increases with increasing reaction temperature. This is evident from Fig. 6 as well as from the k values listed in Tables I and II. A similar increase of k with reaction temperature has also been reported by Dew-Hughes [18] in a composite of niobium filament in a matrix of Cu–6 wt % Sn–4 wt % Al reached at temperatures ranging from 650 to 800° C.

3.4. Determination of activation energy

It is possible from the results to determine the experimental activation energy for the growth of the compound layer. This will enable us to compare the experimental activation energy with the activation energy for the postulated diffusion processes either in the matrix or in the compound layer. Such a comparison helps in identifying further the rate limiting step in growth.

Let us define $k' = k^{1/n}$. Then k' becomes proportional to the diffusion coefficient of the solute, the diffusion of which is rate controlling. We can write:

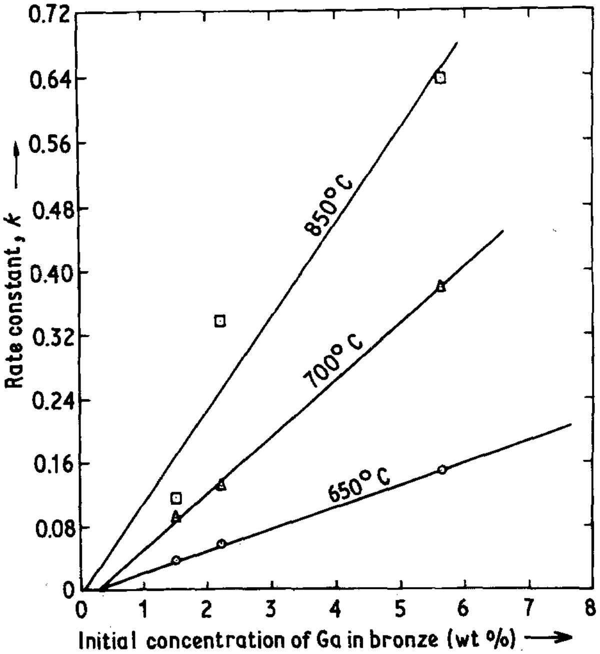

Figure 6 Variation of the rate constant k as a function of gallium concentration for three reaction temperatures.

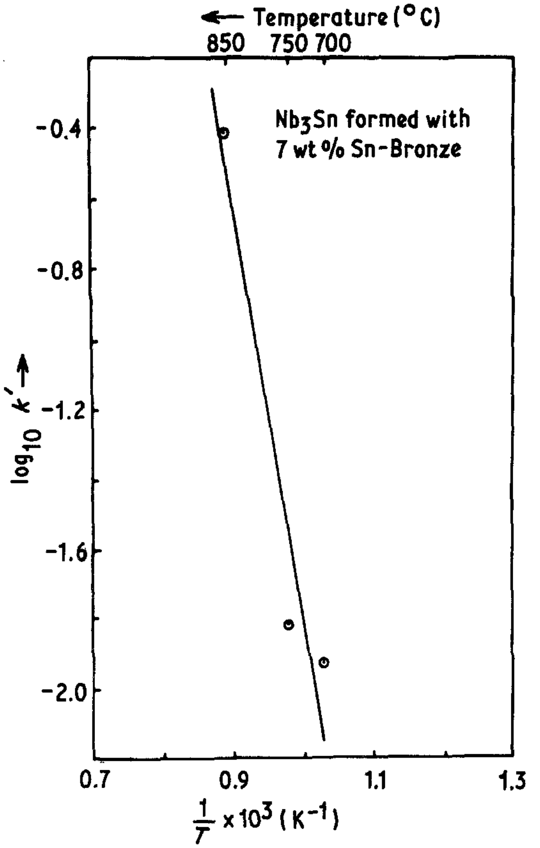

Figure 7 Variation of $\log k'$ with $1/T$.

$$k' = k^{1/n} = k_0 \exp(-Q/RT) \qquad (2)$$

where k_0 is a constant, Q is the activation energy for the diffusion process, T is the reaction temperature in Kelvin, and R is the gas constant. We can write from Equation 2,

$$\log k' = \frac{1}{n}\log k = -\frac{Q}{2.303RT} + \log k_0 \qquad (3)$$

For 7 wt % tin-bronze, taking $n = 2/3$ and plotting $\log k'$ against $1/T$, the activation energy can be computed from the slope of the best fitting straight line. The activation energy thus calculated from Fig. 7 is 230 kJ mol^{-1}.

The activation energy estimated in this investigation lies in the range of 206 to 293 kJ mol^{-1}, reported by others for the formation of Nb$_3$Sn compound through solid-state diffusion [14, 19–21]. The activation energies quoted in the literature for the diffusion in copper range from 138 to 230 kJ mol^{-1} [22–28]. Comparison of this range of values with that given above indicates that the diffusion of tin in the bronze matrix may be the rate controlling process, as already deduced in the context of the model developed by Reddi *et al.* [8].

Similarly, the activation energy calculated for the formation of V$_3$Ga from three different compositions of gallium in the matrix vary from 86 to 148 kJ mol^{-1}. The activation energy estimated here is considerably lower than the activation energy values, ranging from 275 to 325 kJ mol^{-1}, reported by others [16, 29–31]. The reason for this discrepancy is not clear.

4. Discussion

The above results can be understood on the basis of the growth kinetics model of Reddi *et al.* [8]. This model predicts distinct ranges of time exponent values depending on the rate controlling step in the overall growth of the A-15 compound by solid-state diffusion. The experiments conducted with varying concentrations of tin (2.01 to 10.87 wt %) in the matrix indicate that the time exponent decreases with increase in the initial tin concentration at all the three reaction temperatures: 700, 750 and 850° C. This is consistent with the prediction of the model. According to the model, if the effective diffusion distance y is small, the growth equation reduces to

$$R \approx k_1 (c_i - c_{\alpha\beta})t^{1/2} \qquad (4)$$

where k_1 is a constant equal to $D^{1/2}/\bar{c}_\beta$, D is the diffusion coefficient of B in the matrix, $\bar{c}_\beta$ is the average concentration in the reacted compound, c_i is the initial concentration of B in the matrix, and $c_{\alpha\beta}$ is the concentration of B in the matrix in local equilibrium with the reacted layer. Under such conditions, the time exponent $n = 0.5$. When y is large, the growth equation is given by

$$R = k_2 (c_i - c_{\alpha\beta})t^{2/3} \qquad (5)$$

where k_2 is a constant and is given by

$$k_2 = \frac{3D_\beta^{2/3}}{2\bar{c}_\beta (9r_F)^{1/3}} \qquad (6)$$

Here, r_F is the initial radius of the filament. The time exponent here is 2/3. When the initial concentration in the matrix is low, the rate of depletion is high and the effective diffusion distance is large. Under such circumstances, Equation 5 is valid. When the matrix tin concentration is high, the rate of depletion is low and the effective diffusion distance tends to be small, resulting in a time exponent of 0.5. Fig. 8 schematically illustrates

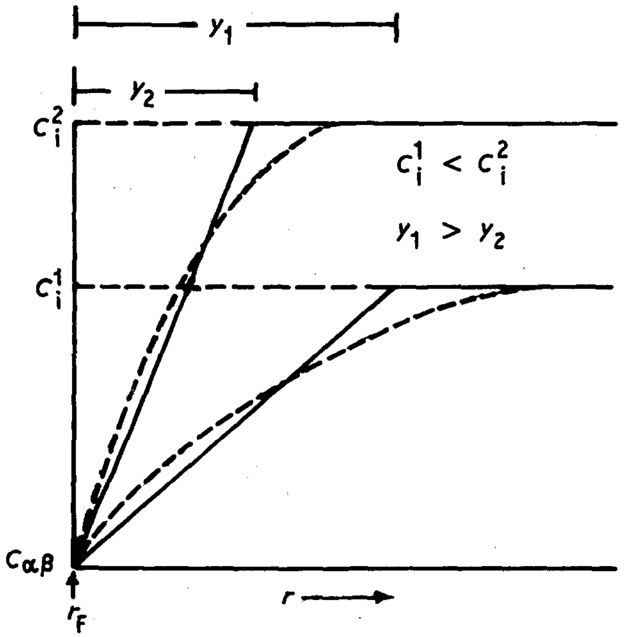

Figure 8 Schematic dependence of the effective diffusion distance with the initial concentration c_i.

the effect of the initial matrix concentration c_i on the effective diffusion distance y. Then, the gradual decrease of n with increasing concentration seen in Table I is as predicted by the model.

We have noted earlier that the time exponent decreases with increasing initial concentration of tin in the bronze matrix, whereas the thickness of the Nb_3Sn layer increases with tin concentration. The increase in the layer thickness is possible only when k increases with tin concentration. The n and k values given in Table I clearly indicate that n decreases and k increases with tin concentration. The results of Wada *et al.* [17] indicating the increase of k with the concentration of tin and of Dew-Hughes [18], indicating the increase of k with the reaction temperature are confirmed by our results.

A time exponent greater than 2/3 and approaching unity is expected, when the reaction is interface controlled. The exponents greater than 2/3 as sometimes observed by us and others [21, 32] can probably be attributed to a transition to the interface-controlled reaction.

The activation energy calculated for the formation of Nb_3Sn layer agrees with the values of activation energy for the diffusion of tin in the matrix. So, as printed out earlier by Reddi *et al.* [8], diffusion of tin through the matrix is the rate controlling step in the Nb–tin bronze composites.

In the case of V_3Ga, a time exponent equal to about 0.5 is observed, regardless of the concentration of gallium in the matrix or the reaction temperature. Either bulk or grain boundary diffusion through the reacted layer with a constant grain size can yield a time exponent of 1/2. But the results of Tachikawa *et al.* [10] indicate that n falls with increasing reaction temperature, as a result of grain growth during the diffusion anneal. When grain growth is superimposed on grain boundary diffusion, the model of Reddi *et al.* [8] predicts that n will range from 1/4 to 1/2. SEM studies of our diffusion-annealed samples indicate that the grain size of the V_3Ga layer is initially larger than the grain size observed by Livingston [33] and does not show an appreciable growth. Thus, we attribute n values of 0.5 to the rate controlling step being the diffusion of gallium atoms through the grain boundaries of the reacted compound layer (without superimposed grain growth).

5. Conclusions

The main conclusions of this study can be summarized as follows:

1. The time exponent n in the growth kinetics of Nb_3Sn increases from 1/2 to 2/3 and above with the fall of the initial concentration of tin in the matrix, as envisaged in the growth kinetics model.

2. The rate controlling step in the formation of Nb_3Sn is the diffusion of tin through the bronze matrix.

3. Grain boundary of gallium within the reacted V_3Ga layer appears to be the rate controlling step in the growth of V_3Ga.

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