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Influence of third elements on growth of Nb_3Sn compounds and on global pinning force

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The crystal growth of Nb_3Sn by the bronze method has been investigated by using diffusion couples consisting of niobium and bronze with the addition of third elements. When the specimens were annealed at temperatures between 973 and 1073 K, the time-dependence of layer thickness was represented approximately by the function of $d = kt^m$. The time exponent changed from 1/3 to unity depending on the annealing condition as well as on the nature of the third element. By the addition of titanium, hafnium, zirconium, indium and galium to the bronze, the growth rate of the compound layer increases. Faster layer growth corresponds to a larger time exponent. The following three processes are suggested to be important for controlling layer growth: diffusivity of tin atoms through grain boundaries in the compound layer, diffusivity of tin atoms through the matrix of the compound, and the rate of the chemical reaction to form the compound. Essentially these combined processes control the overall rate of layer growth. The grain size is found to be the most effective structural parameter to affect directly the maximum global pinning force. The critical current at a magnetic field of 5 T can be scaled by both the layer thickness and the inverse grain size.

1. Introduction

The development of a large-scale superconducting magnet is one of the most important engineering requisites for the realization of a nuclear fusion reactor. As A–15 compounds reveal excellent superconducting properties, many studies [1] have been focussed on developing a magnet using A–15 superconductors. For their practical usage, it is still necessary to investigate the method and/or the technique of improving the properties and of manufacturing reliable and highly-controlled materials. From the viewpoint of materials science, a quantitative understanding of the interrelation between the microstructure and superconducting properties is urgently needed. The growth kinetics of an A_3B layer by the bronze method has been discussed by many authors [2–4]. However, no unified model explaining the overall growth process has been yet developed. To solve the diffusion equations, the geometry of the system concerned should first be defined because both cylindrical and plane types of specimen are often used in experiments. A plane specimen is favourable for investigating the mechanism of growth kinetics. Recently, it was found that the critical current density of Nb_3Sn wires can be significantly increased by alloying the niobium filaments and/or the Cu–Sn matrix with third elements such as tantalum [5] and titanium [6–8]. It has been suggested that the addition of a third element can effectively influence the growth kinetics of the compound layer, or directly influence the superconductivity properties.

The purpose of the present study is to clarify the fundamental process of crystal growth of Nb_3Sn by the bronze method as well as the influence of microstructure on the superconducting properties. Using the two-phase diffusion couples Cu–Sn–M/Nb, where M is the third element, the growth rate and microstructure of the Nb_3Sn compound layer have been investigated in detail. The effect of the third element on crystal growth has been examined. The superconducting critical current of those diffusion couples was measured after the metallographical investigation. The microstructure dependence of the global pinning force has been evaluated and the origin of the pinning force discussed.

2. Experimental procedure

The diffusion couples used here had a sandwich structure of a niobium sheet between two bronze layers. The bronze was prepared in an induction furnace under vacuum, where the third element was added to the melt. The chemical composition of materials is listed in Table I. After homogenization, a sheet of bronze with a thickness of about 2 mm was made by repeated solution-treating and cold-rolling. After the three sheets were put together in a stainless steel tube, they were hot-pressed under vacuum at 1023 K for about 600 sec. For some specimens, alumina filaments with a diameter of about 15 μm were inserted between the sheets in order to examine the mass flow through the interface. Its pre-preg was annealed at temperatures of 973, 1023 and 1073 K for various periods. After annealing, the thickness of the Nb_3Sn compound layer and the grain size were measured by a scanning electron microscope (SEM).

The superconducting critical current was measured on the same diffusion couples used for the metallographical investigations. The external magnetic field was applied perpendicular to the surface of the compound layer. The range of applied magnetic field was from 5 to 8 T and the critical current I_c was determined

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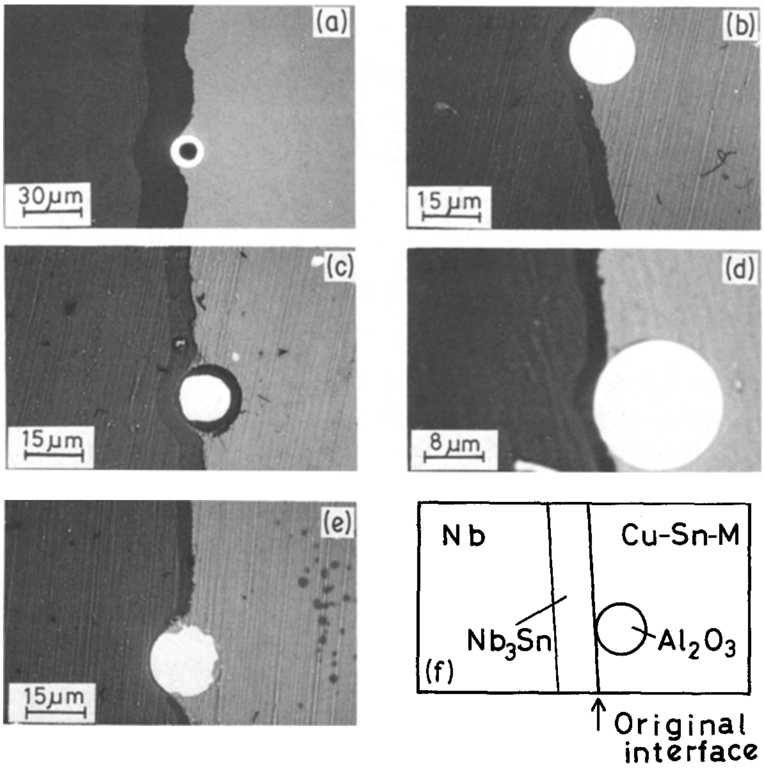


Figure 1 SEM photos of Nb_3Sn compound layer formed in Cu–Sn–M/Nb diffusion couples annealed at 1023 K for 100 ksec, where the third element, M, is (a) titanium, (b) gallium, (c) hafnium, (d) indium, (e) zirconium, (f) shematic of couple.

under the condition of $1 \times 10^{-6}\,\mathrm{V\,cm^{-1}}$. The critical current density was defined as $J_c^0 = I_c/s$ where s is the cross-section of the Nb_3Sn compound layer formed at the interface of the diffusion couple.

3. Experimental results

Fig. 1 shows typical microstructures including the Nb_3Sn layer formed by annealing, where the white circle is the alumina filament. As the marker locates the position of the original interface, the photos show that a growth interface is present between the niobium phase and the compound, and the compound grows towards the niobium phase. It is found that the thickness of the compound layer formed under a given annealing condition is different depending on the nature of the third element.

Fig. 2 shows the change of layer thickness of Nb_3Sn as a function of annealing time in the Cu–Sn/Nb system. The annealing-time dependence was found to be similar for specimens annealed at 1023 and 973 K, whereas in the case of 1073 K, a higher time-dependence was observed. The layer thickness can be approximately expressed as a function of annealing time by

$$d = kt^m \tag{1}$$

TABLE I Chemical composition and thickness of starting materials for the diffusion experiments

Material	Chemical Composition (at %)	Thickness (mm)
Nb	99Nb	0.22
Cu–Sn	Cu–7.4Sn	1.9
Cu–Sn–Ti	Cu–7.5Sn–1.0Ti	1.6
Cu–Sn–Zr	Cu–7.0Sn–1.0Zr	1.6
Cu–Sn–In	Cu–7.0Sn–1.0In	1.6
Cu–Sn–Ga	Cu–7.0Sn–1.0Ga	1.6
Cu–Sn–Hf	Cu–7.0Sn–1.0Hf	1.6

The time exponent obtained from the solid lines in the figure was 0.33, 0.33 and 0.51 for temperatures of 973, 1023 and 1073 K, respectively. The result for the Cu–Sn–Ti system is shown in Fig. 3. At a fixed annealing condition, the layer thickness became thicker by about 10 times compared with the former Cu–Sn/Nb system. As listed in Table II, it is remarkable that the time exponent exceeds 0.5 at every annealing temperature. Similar experiments were performed for the other systems with different third elements. The results are summarized in Fig. 4. Here the original data points are not displayed, but the accuracy of each linear line is the same as those shown in Figs. 2 and 3. It is clear that the layer thickness becomes thicker by adding those third elements investigated here. Fitting Equation 1 with these lines, the time exponent and the proportional constant are evaluated as summarized in Table II. The time exponent changes from 0.3 up to

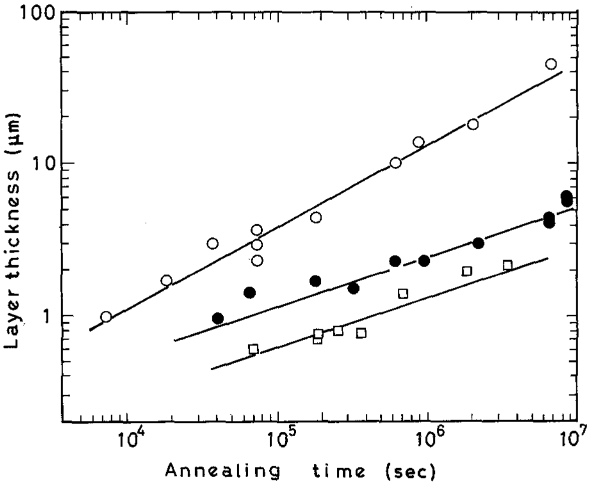


Figure 2 Change of layer thickness of Nb_3Sn as a function of annealing time for Cu–Sn/Nb diffusion couples. (□) 973 K, (●) 1023 K, (○) 1073 K.

TABLE II Constants appeared in the function $d = k\,t^m$, where k is given in unit of $10^{-3}\,\mu\text{m}\,\text{sec}^{-m}$

System	T_A = 1073 K		T_A = 1023 K		T_A = 973 K	
	m	k	m	k	m	k
Cu–Sn–Ti/Nb	0.98	1.1	0.91	0.33	0.78	0.49
Cu–Sn–Hf/Nb	0.85	1.8	0.86	0.27	0.48	4.5
Cu–Sn–Zr/Nb	0.83	1.9	0.82	0.30	0.52	2.7
Cu–Sn–In/Nb	0.73	2.1	0.73	0.62	0.64	1.1
Cu–Sn–Ga/Nb	0.66	4.2	0.62	3.3	0.50	5.5
Cu–Sn/Nb	0.51	11	0.33	26	0.33	14

unity depending on both the annealing temperature and the nature of the third element. The most important observation is that faster layer growth corresponds to a larger time exponent. Titanium, hafnium and zirconium seem to be effective elements for layer growth. When a comparison is made of the data for different temperatures, there is a change in their order of effectiveness, suggesting that the temperature dependence differs for each different third element. An experimental examination of the time exponent has been performed by many authors [2, 4, 9–11]. The time exponents and the absolute values of layer thickness reported by them are in the same ranges as those obtained in the present study. Several mechanisms for layer growth have been proposed based on the experimental data. However, they still seem to be insufficient to explain all the data. The problems will be made clear as mentioned later.

Typical fracture surfaces of the compound layer are shown in Fig. 5. The grain size L of the compound layer was determined by measuring the number of grains along several straight lines perpendicular and parallel to the layer and averaging these numbers together with both directions. The results are listed in Table III. The average grain size became smaller when the specimen was annealed at a lower temperature and when a third element was added. The shape of grain tends to become rather equiaxial by high-temperature annealing, but the grains are columnar and fine when the compound is grown at a low temperature.

The superconducting critical current was measured for the specimens listed in Table III. Fig. 6 shows the change of critical current density as a function of external magnetic field for specimens with different third elements. In the present range of magnetic field, J_c^0 is highest at 5 T and decreases with increasing magnetic field. Here the data indicated by crosses refer to values for the reference sample [12], which was a multifilamentary composite wire. It is found that the present specimens reveal the same magnitude of J_c^0 in comparison with that for the reference sample, but the rate of decrease with increasing magnetic field becomes larger for the present data. As shown here, there seems to be no remarkable difference among the specimens, but for the specimens with titanium or hafnium additives, the rate of decrease of J_c^0 becomes relatively smaller.

In the present study, the global pinning force is defined as $F_p^0 = J_c^0 B$, where B is the external magnetic field. The change of F_p^0 as a function of magnetic field is typically shown in Fig. 7. The values of F_p at 5 and 8 T for the other specimens are listed in Table III.

As the present range of magnetic field was from 5 to 8 T no maximum of F_p could be observed, but from preliminary experiments it was determined that $F_{p,\max}^0$ occurs at about 4 T and the difference $(F_{p,\max}^0 - F_{p,5T}^0)/F_{p,\max}^0$ is less than 10%.

TABLE III Layer thickness, grain size and global pinning force of Nb_3Sn compound made by the bronze method

Sample	Heat treatment				F_p^0 ($10^9\,\text{N}\,\text{m}^{-3}$)	
	T_A (K)	t_A (ksec)	d (μm)	L (μm)	at 5 T	at 8 T
Cu–Sn–Ti/Nb	1073	3	6.5	0.27	10.5	7.5
	1023	20	3.2	0.20	19.7	14.2
	1023	150	19.9	0.23	14.2	12.4
Cu–Sn–Zr/Nb	1073	8	4.6	0.31	18.8	9.8
	1023	32	1.3	0.19	20.4	8.2
	973	820	2.0	0.12	16.9	7.1
Cu–Sn–In/Nb	1073	10	3.4	0.18	14.7	8.2
	1023	32	1.2	0.13	36.0	12.2
	973	71	1.1	0.12	35.1	12.6
Cu–Sn–Ga/Nb	1073	10	3.1	0.32	12.7	4.6
	1023	25	1.1	0.12	31.4	10.6
	973	100	2.8	0.19	27.7	11.5
Cu–Sn–Hf/Nb	1073	20	13.2	0.26	15.5	12.5
	1023	100	8.9	0.19	29.1	17.1
	973	820	11.8	0.15	31.3	15.7
Cu–Sn/Nb	1073	20	1.2	0.19	24.7	7.5
	1073	200	2.7	0.54	11.3	2.8
	1023	820	2.7	0.54	13.9	5.4

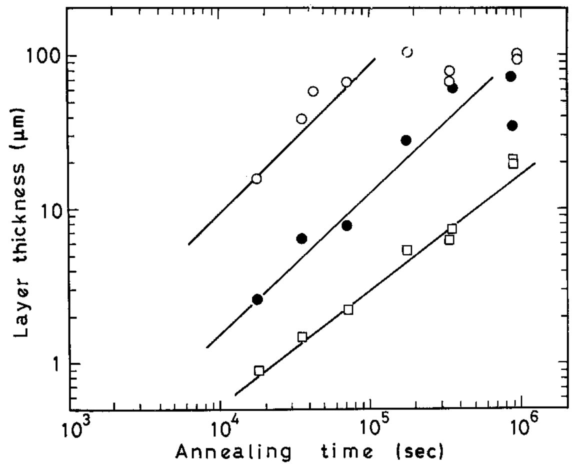


Figure 3 Change of layer thickness of Nb_3Sn as a function of annealing time for Cu–Sn–Ti/Nb diffusion couples. (□) 973 K, (●) 1023 K, (○) 1073 K.

4. Discussion

Here the mechanism of the rate-controlling process of layer growth is discussed as follows. As shown schematically in Fig. 8, the experiments made clear that tin atoms from the bronze matrix diffuse through the compound layer and reach the interface between the compound and the niobium phase, and there react with niobium to form the compound Nb_3Sn. The present diffusion couples have a sandwich structure of niobium sheet surrounded by bronze layers. The thickness and solute concentration of the bronze layer were about 1.6 mm and 7 at % Sn, respectively. For instance, when the Nb_3Sn compound is formed with thickness of 40 μm, the reduction of tin concentration in the bronze matrix is estimated to be 8% and is relatively small. Therefore the change of solute concentration in the bronze matrix has not been taken into consideration in the following discussion. Several processes are suggested to control the overall rate of layer growth: (i) diffusivity of tin atoms in the bronze matrix, (ii) diffusivity of tin atoms through the grain boundary in the compound layer, (iii) diffusivity of tin atoms through the matrix of the compound layer, and (iv) the rate of chemical reaction to form the compound at the interface. When one of the above proposed processes is a unique rate-limiting process, the time dependence of layer thickness is proportional to $t^{0.5}$, $t^{0.35}$, $t^{0.5}$ and t for the respective process as mentioned below.

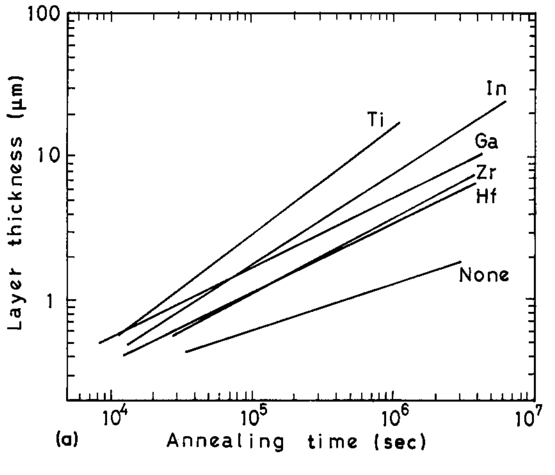
When the unique rate-limiting process is the diffusion of tin atoms in the bronze matrix, Fick's second law [13] is solved under the semi-infinite boundary condition of $c = c_0$ at the interface between the bronze and the compound layer and $c = c_b$ at the opposite side of bronze layer, where c_b is the average solute concentration in the original bronze matrix. Let us suppose that all the solute diffusing out from the bronze produces the compound by reacting with niobium. The time dependence of layer thickness is then given by the equation

$$d = \frac{c_b v_c}{c_c v_b} S\,(4Dt)^{1/2} \qquad (2)$$

where c_c is the atomic fraction of tin in the compound, v_b and v_c are the atomic volume of the bronze and the compound, respectively, and S is a numerical constant given as a function of c_0/c_b. Substituting the parameters in the above equation with numerical values $c_c = 0.25$, $c_b = 0.074$, $v_b = 0.0125\,\mathrm{nm}^3$, $v_c = 0.0185\,\mathrm{nm}^3$ and $S = 0.284$ for $c_0/c_b = 0.5$ and adopting the reported value [14] of the diffusion constant, the following expression is obtained (in units of μm):

$$d = 0.249\,(Dt)^{1/2} \qquad (3)$$

Fig. 9 shows the estimated thickness due to this process in the range of present experimental conditions.



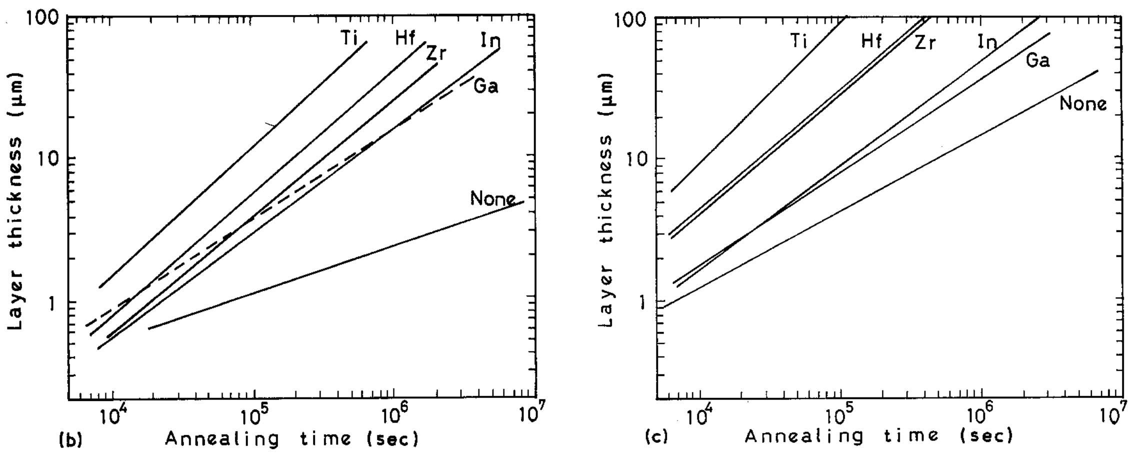


Figure 4 Time-dependence of layer thickness for diffusion couples with added third element annealed at (a) 973 K, (b) 1023 K and (c) 1073 K.

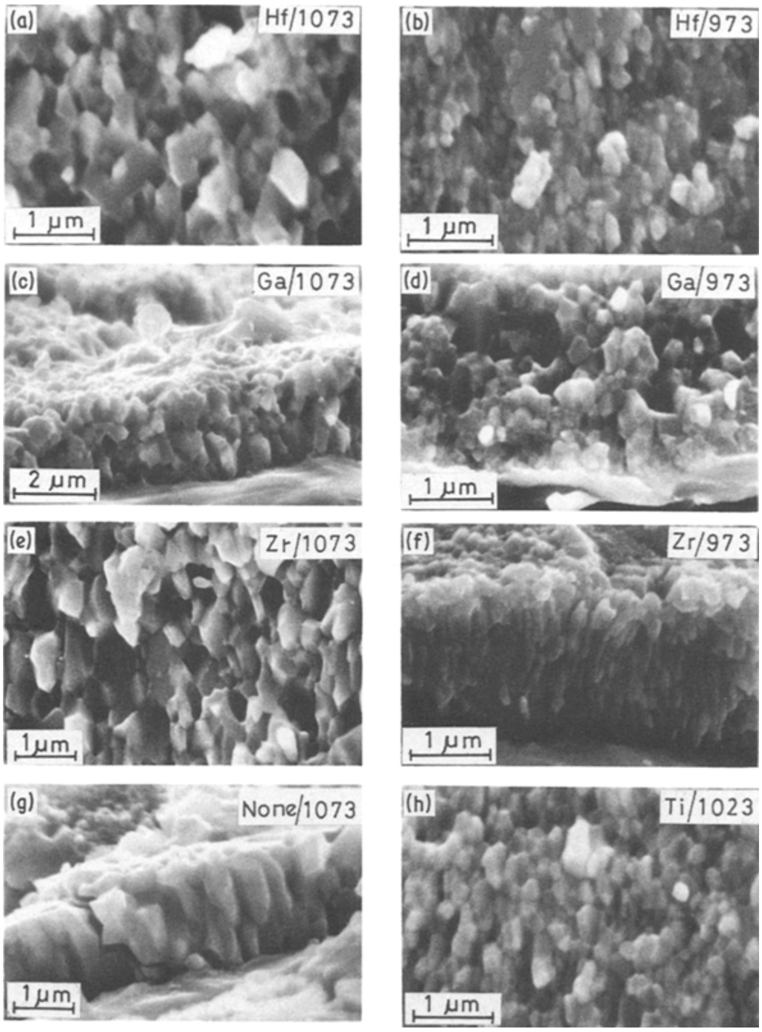


Figure 5 Fracture surfaces of Nb_3Sn compound layer. Each photo corresponds to a specimen listed in Table III.

Farrell *et al.* [2] have discussed in detail the grain-boundary diffusion in the compound layer. Their essential point is that the time dependence of layer growth does not obey the parabolic law attributed to the growth of grain size during annealing. When we recalculate the rate of layer growth by using their experimental data, the time dependence of layer thickness can be expressed by the equation (in unit of μm)

$$d = 1.28 \times 10^{-3}\, t^{0.35} \exp\left(-Q_G/RT\right) \qquad (4)$$

where Q_G is the effective activation energy and is 12.4 kcal mol^{-1} (51.9 kJ mol^{-1}). Here the time exponent should be noted as being 0.35, that is, nearly 1/3. Its absolute value depends on the grain size, its dispersion and other structure parameters. A direct comparison

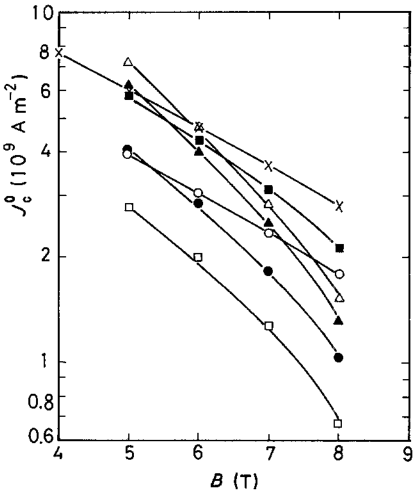


Figure 6 Critical current density as a function of magnetic field for Cu–Sn–M/Nb diffusion couples annealed at 1023 K, where the respective annealing time is listed in Table III, and (X) indicates the multifilamentary wire specimen [12] used as a reference sample. Third element (○) titanium, (●) zirconium, (△) indium, (▲) gallium, (■) hafnium, (□) none.

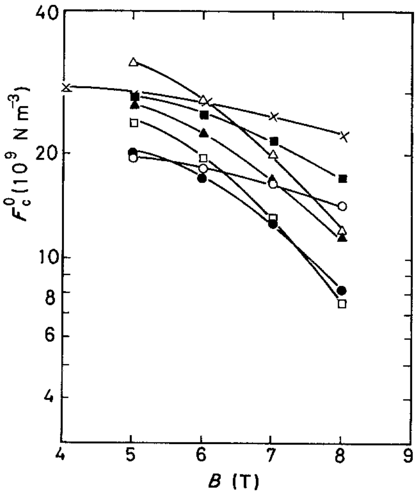


Figure 7 Global pinning force as a function of magnetic field for Cu–Sn–M/Nb diffusion couples annealed at various conditions, of which details are listed in Table III. Values of M/T_A/t_A as follows: (○) Ti 1023 20, (●) Zr 1023 32, (△) In 1023 32, (▲) Ga 973 100, (■) Hf 1023 100, (□) none 1073 20, (X) ref. [12] 973 432.

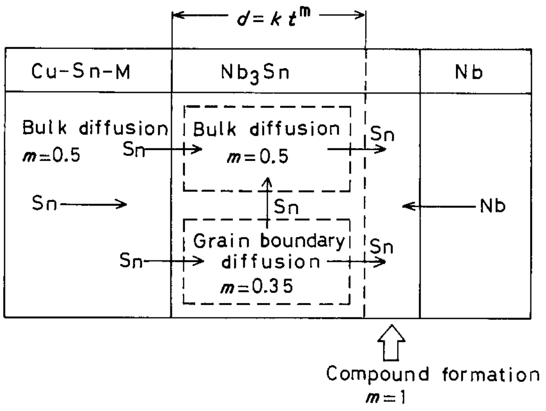


Figure 8 Schematic illustration explaining several processes controlling the rate of compound formation by the bronze method.

of the present data with the result by Farrell *et al.* [2] is reasonable because the microstructures of both compound layers resemble each other. The change of layer thickness with annealing time is displayed in Fig. 9. Equation 4 can explain quantitatively the present experimental data at 973 and 1023 K for the non-additive Cu–Sn/Nb system as shown in Fig. 2. Up to here, it has been emphasized that grain-boundary diffusion is one of the rate-limiting processes, but the diffusion of tin atoms through the bronze matrix is too fast for this to be so in the case shown in Fig. 9.

On the other hand, for Cu–Sn–M/Nb systems with an added third element, the time exponent is larger always than 1/3 and the absolute value of layer thickness is in the range between two sets of thickness given by Equations 3 and 4 as shown in Fig. 9. As noted by Farrell *et al.* [2], bulk diffusion in the compound layer may occur at high temperatures and/or under the conditions in which bulk diffusion is enhanced. When the bulk (b) and grain-boundary (g) diffusions operate equally in magnitude, the total flux of tin atoms through the compound layer to the growth interface can be expressed by the equations (in units of mol sec^{-1})

$$J = J_b + J_g - \Delta J_{g\rightarrow b} \tag{5}$$

$$J_b = \gamma L^2 D_c \varrho_c (c_0 - c_e)/d \tag{6}$$

$$J_g = aLD'_c \varrho_c (c_0 - c_e)/d \tag{7}$$

where $\Delta J_{g\rightarrow b}$ is the by-passed flux from the grain boundary to the matrix within the layer compound. ϱ_c is the molar density of the compound. D_c and D'_c are the diffusion constants of tin atoms in the Nb_3Sn bulk and in the grain boundary. c_0 is the tin concentration at the interface between the bronze and the compound, and c_e is that at the growth interface. $(c_0 - c_e)/d$ is the steady–state concentration gradient. $2a$ is the width of grain boundary. γ is a geometrical factor and L is the grain size. The layer thickness d is then controlled by a rate obtained from the conservation equation

$$J = \gamma L^2 c_e \varrho_c \frac{\mathrm{d}d}{\mathrm{d}t} \tag{8}$$

During layer growth, the grain size has been recognized to increase. The time dependence of the fraction of cross-section which is covered by grain boundaries is

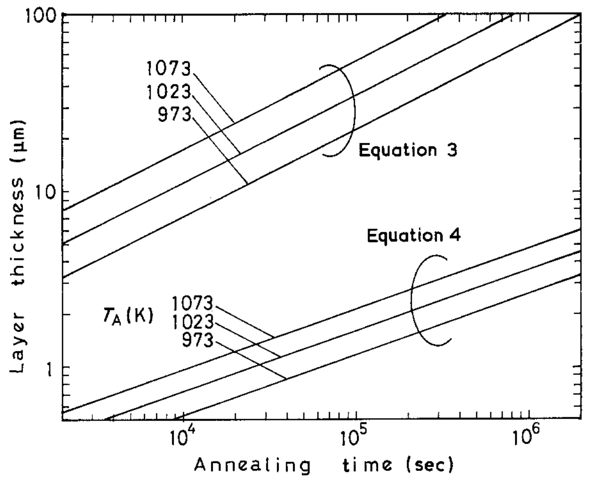


Figure 9 Theoretical estimations of the time-dependence of layer thickness as mentioned in the text.

given according to Farrell *et al.* [2] by

$$f_g = \frac{aL}{\gamma L^2} = f_g^0 t^{2m-1} \tag{9}$$

where m is the constant of 0.31 found experimentally [2]. Here we simply assume that the by-passing flux to the matrix is neglected. Then the differential equation (Equation 8) is solved using the initial condition of $d = 0$ at $t = 0$ to give

$$d^2 = \frac{D_c(c_0 - c_e)t}{c_e} + \frac{D'_c(c_0 - c_e)f_g^0 t^{2m}}{2mc_e} \tag{10}$$

When the condition of $D_c \ll D'_c$ holds, that is the case of the above mentioned non-additive Cu–Sn/Nb system, Equation 10 is reduced to the same form as Equation 4,

$$d = \left[\frac{D'_c(c_0 - c_e)f_g^0}{2mc_e}\right]^{1/2} t^m \tag{11}$$

In the case of $D_c \gg D'_c$, which means that bulk diffusion maintains the whole rate, Equation 10 becomes

$$d = \left[\frac{D_c(c_0 - c_e)}{c_e}\right]^{1/2} t^{1/2} \tag{12}$$

In the framework of the dual process due to two diffusion paths, the time exponent of layer growth can be expected qualitatively to change from 0.31 to 0.5. Therefore it is still insufficient to explain all the data from the present experiments.

When the diffusion of tin atoms through the compound layer becomes extremely high, the reaction to form the compound may operate as a rate-limiting process. The rate of consuming the tin species by the surface chemical reaction can be expressed [15, 16] by

$$R_s = K(c_0 - c_e) \tag{13}$$

assuming a first-order reaction, where K is the heterogeneous rate constant, c_e the equilibrium concentration at the reaction interface and $(c_0 - c_e)$ the excess concentration driving the reaction. The rate of reaction of tin is equated to the rate of consuming the niobium species to give

$$vR_s = \varrho_{Nb} \frac{\mathrm{d}x_{Nb}}{\mathrm{d}t} \tag{14}$$

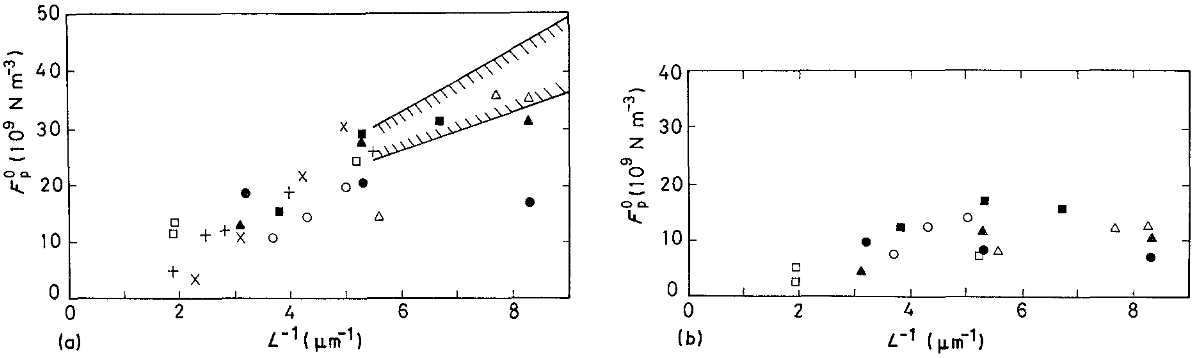


Figure 10 Correlation of global pinning force with inverse grain size at a constant magnetic field, where (a) $B = 5\,T$ and (b) $B = 8\,T$. Third element (○) titanium, (●) zirconium, (△) indium, (▲) gallium, (■) hafnium, (□) none. Values of $F^0_{p,\,max}$ from (X) reference sample [12], (+) Scanlan *et al.* [19], shaded area between lines Schauer and Schelb [18].

where v is 3 for Nb_3Sn and ϱ_{Nb} is the molar density of the niobium phase. Combining the two equations and integrating with an initial condition of $x_{Nb} = 0$ at $t = 0$, we obtain the expression (converted for the thickness of compound layer)

$$d = \frac{(1 + v)\,K}{\varrho_c}(c_0 - c_e)\,t \qquad (15)$$

Obviously the change of layer thickness can be expressed as a linear function of time. In the present case it is difficult to evaluate Equation 15 numerically because the estimation of the heterogeneous rate constant K is impossible.

If neither chemical reaction nor diffusion controls the overall process completely, both steps should be taken into consideration simultaneously in obtaining the expression for the overall rate. The dual rate control is expressed [16] by the equation

$$d + \frac{K(1 + v)\,c_e}{D_c\varrho_c}d^2 = \frac{K(1 + v)}{\varrho_c}(c_0 - c_e)\,t \qquad (16)$$

In the extreme case of the ratio $K/D_c \ll 1$ the above equation reduces to Equation 15, that is the overall rate is controlled by the chemical reaction. If $K/D_c \gg 1$, Equation 16 reduces to Equation 12 and bulk diffusion maintains the overall rate. Thus the time exponent changes continuously from 0.5 to 1 depending on the ratio K/D_c.

As discussed above, it is made clear that an operation of multiple processes is needed to explain the experimental observation in which the time exponent takes the value from 1/3 to unity. When the time exponent is not fixed at a constant value like 0.5 or 1, multiple processes operate in the system. The relation $d = kt^m$ then becomes an inadequate fitting function for the experimental data. Therefore it should be recognized that Equation 1 is only an approximate function for expressing the time-dependence of layer growth by the bronze method.

Bulk diffusion in the Nb_3Sn compound without any artificial additives has been reported to be fairly slow at the temperatures concerned here [17]. All data for specimens including third elements show that the time exponent is larger than 0.35 and the layer thickness becomes relatively thicker. Therefore it is suggested that bulk diffusion is enhanced by the addition of a third element, although there is no evidence at present.

There is a question as to which is the process giving the maximum rate of layer growth. The experimental values together with published data [2, 4, 9–11] locate in the range surrounded by the two sets of theoretical lines shown in Fig. 9. This suggests that the upper rate will be limited finally by the diffusivity of tin atoms in the bronze matrix after removal of other impediments.

The geometric factor seriously influences the rate of layer growth. When a niobium wire with radius R is embedded in the bronze matrix and the diffusivity of tin atoms in the bronze matrix controls the overall rate, as treated by Reddi *et al.* [4], the rate of layer thickness increases excessively by reducing the area of the growth interface, and the left-hand side of Equation 2 is then replaced by $d - d^2/2R$. Thus Equation 1 is not guaranteed for a cylindrical geometry.

Fig. 10 shows the change of global pinning force as a function of the inverse of grain size, L, where the published data for $F^0_{p,max}$ are included [18, 19]. At $B = 5\,T$, all the data along with the reported values are found to exist in the same range and F^0_p seems to correlate with the inverse grain size. There may exist several imperfections pinning the magnetic fluxes. However, the result shown in Fig. 10a suggests that the grain boundary is the most effective centre for the maximum global pinning [19–22]. At present, however, we could not observe any evidence within the present experimental accuracy that any specific third element influences the pinning force preferentially and directly. Thus, it is suggested that third elements directly influence the growth rate of compound formation and the microstructure. Through the change of microstructure, they affect the superconducting properties. Accordingly, the critical current I_c at $B = 5\,T$ may be scaled by both structural parameters, the layer thickness d and the grain size L, as follows:

$$I_c = \text{constant}\,(d/L) \qquad (17)$$

Therefore it is important in further studies to find a specific third element which has the effect of enhancing the growth rate of compound formation and making a finer grain size.

On the other hand, in the case of $B = 8\,T$ (Fig. 10b) a linear relation of F^0_p with inverse grain size seems to disappear. In a recent paper Suenaga *et al.* [22] have commented that the size of Nb_3Sn grains appear to be a dominant factor in determining J_c, as similarly reported here, but at very high magnetic fields exceeding 20 T the importance of the grain size diminishes. Instead, the value of H_{c2} becomes important in determining J_c at these high fields. Comparing the data for $B = 5$ and 8 T at a constant inverse grain size of about 5.3 m^{-1} in Figs. 10a and b, a plausible tendency distinguishing the effect of the third element is becoming clear. Hafnium and titanium are suggested to be effective third elements. However, a quantitative metallographical investigation as well as I_c measurements at high magnetic fields will be further needed to make clear the interrelation between the microstructure and the pinning force.

5. Conclusions

During the growth of the compound, the marker experiments made clear that tin atoms of the bronze matrix diffuse through the compound layer and reach the growth interface with the niobium phase, and there react with niobium to form the compound Nb_3Sn. When the specimens were annealed at temperatures between 973 and 1073 K, the time-dependence of layer thickness was represented approximately by the function $d = kt^m$. The time exponent changed from 1/3 to unity depending on the annealing condition as well as on the species of third element. By addition of titanium, hafnium, zirconium, indium and gallium to the bronze, the growth rate of the compound layer increases in comparison with that for the non-additive specimen. The fact that faster layer growth corresponds to a larger time exponent can be essentially explained by multiple-rate limiting processes. The grain size is found to be the most effective structural parameter to directly affect the maximum global pinning force. The critical current at a magnetic field of 5 T can be scaled by both the layer thickness and the inverse grain size.

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References

1. M. SUENEGA, in "Superconducting Materials Science, Metallurgy, Fabrication and Applications", edited by S. Foner and B. B. Schwartz (Plenum, New York, 1981) p. 201.
2. H. H. FARRELL, G. H. GILMER and M. SUENAGA, *J. Appl. Phys.* **45** (1974) 4025.
3. D. DEW-HUGHES, T. S. LUHMAN and M. SUENAGA, *Nucl. Technol.* **29** (1976) 268.
4. B. V. REDDI, S. RAY, V. RAGHAVAN and A. V. MARLIKAR, *Phil. Mag.* **38A** (1978) 559.
5. J. D. LIVINGSTON, *IEEE Trans. Magn.* **14** (1978) 611.
6. M. SUENAGA, W. B. SAMPSON and T. S. LUHMAN, *ibid.* **17** (1981) 646.
7. K. TACHIKAWA, T. ASANO and T. TAKEUCHI, *Appl. Phys. Lett.* **39** (1981) 766.
8. K. TACHIKAWA, H. SEKINE and Y. IIJIMA, *J. Appl. Phys.* **53** (1982) 5534.
9. T. LUHMAN, in "Metallurgy of Superconducting Materials", edited by T. Luhman and D. Dew-Hughes (Academic Press, New York, 1979) p. 221.
10. S. K. AGARWAL, S. B. SAMANTA, V. K. BATRA and A. V. NARLIKAR, *J. Mater. Sci.* **19** (1984) 2057.
11. H. WADA, M. KIMURA and K. TACHIKAWA, *ibid.* **13** (1978) 1943.
12. S. OCHIAI, K. OSAMURA and T. UEHARA, *J. Mater. Sci.* **21** (1986) 1020.
13. J. CRANK, in "Mathematics of Diffusion" (Oxford University Press, 1957) p. 26.
14. H. OIKAWA and A. HOSOI, *Scripta Metall.* **9** (1975) 823.
15. J. SZEKELY, J. W. EVANS and H. Y. SOHN, in "Gas–Solid Reactions" (Academic Press, New York, 1976) p. 65.
16. E. T. TURKDOGAN, in "Physical Chemistry of High Temperature Technology" (Academic Press, New York, 1980) p. 258.
17. G. N. RONAMI, V. I. GRYZUNOV, I. A. BARANOV, N. T. KONOVALOV, V. I. SOKOLOV and N. S. VOROBEVA, *Izv. Akad. Nauk SSSR Neorg. Mater.* **7** (1971) 1490.
18. W. SCHAUER and W. SCHELB, *IEEE Trans. Magn.* **MAG-17** (1981) 374.
19. R. M. SCANLAN, W. A. FIETZ and E. F. KOCH, *J. Appl. Phys.* **46** (1975) 2244.
20. B. J. SHAW, *ibid.* **47** (1976) 2146.
21. J. D. LIVINGSTON, *Phys. Stat. Solids* (a) **44** (1977) 295.
22. M. SUENAGA, K. TSUCHIYA, N. HIGUCHI and K. TACHIKAWA, *Cryogenics* **25** (1985) 123.

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