Quantitative Explanation for Uphill Diffusion of Sn during Reactive Diffusion between Cu–Sn Alloys and Nb

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In a bronze method, uphill diffusion of Sn takes place from a binary Cu–Sn alloy to Nb₃Sn during reactive diffusion between the Cu–Sn alloy and Nb at temperatures around 1000 K. In order to account for the occurrence of the uphill diffusion quantitatively, the phase equilibria in the ternary Cu–Nb–Sn system were theoretically analyzed using a thermodynamic model for phases with different sublattices. In this ternary system, there is no ternary compound and the solubility of the third component is very small for all the phases. Consequently, the ternary interaction was assumed negligible, and thus the Gibbs energy of each phase was expressed with the thermodynamic parameters of the relevant binary systems. In an isothermal section calculated at 1053 K, the three-phase equilibrium of Cu + Nb + Nb₃Sn appears at an activity of Sn with 0.0047. If the activity a_{Sn}^{b} of Sn for the binary Cu–Sn alloy is greater than the activity a_{Sn}^{c} of Sn for the three-phase equilibrium of Cu + Nb + Nb₃Sn, Nb₃Sn is spontaneously produced owing to the reactive diffusion. As a result, the uphill diffusion of Sn occurs from the Cu–Sn alloy to Nb₃Sn. The chemical driving force ΔG_{Sn} for the uphill diffusion is evaluated by the equation $\Delta G_{\text{Sn}} = RT \ln(a_{\text{Sn}}^{\text{b}}/a_{\text{Sn}}^{\text{c}})$. This equation semi-quantitatively explains the growth behavior of Nb₃Sn.

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1. Introduction

A bronze method is widely used to manufacture multifilamentary superconductor materials with Nb₃Sn.^{1–9)} In this method, multifilamentary wires of Nb are embedded in a Cu–Sn alloy matrix and then annealed at an appropriate temperature. Owing to reactive diffusion during annealing, Nb₃Sn is formed as a layer at the interface between Nb and the Cu–Sn alloy. The growth behavior of the Nb₃Sn layer was studied by many investigators.^{1–9)} However, monofilamentary and multifilamentary diffusion couples were used in most of the studies. In such diffusion couples, the interdiffusion of the constituent components takes place in rather complicated manners, and hence the Nb₃Sn layer with a uniform thickness cannot be formed easily. Therefore, the filamentary diffusion couples are not adequate for examination of the kinetics for formation of the Nb₃Sn layer.

The growth behavior of the Nb₃Sn layer was experimentally studied by Osamura *et al.* using a different type of diffusion couple.¹⁰⁾ In their experiment, a Nb sheet was sandwiched between two plates of a binary Cu–7.4 at% Sn alloy. In this type of diffusion couple, the interdiffusion occurs along the direction perpendicular to the interface. The (Cu–7.4Sn)/Nb diffusion couple was annealed at temperatures of 973–1073 K, and then the Nb₃Sn layer with a rather uniform thickness was observed to form at the interface. According to their observation, the mean thickness of the Nb₃Sn layer is expressed as a power function of the annealing time. The exponent of the power function is 0.33 at 973 and 1023 K and 0.51 at 1073 K. If the growth of the Nb₃Sn layer is governed by the volume diffusion of the constituent components in each phase, the exponent is equal to 0.5. On the contrary, the grain boundary diffusion across the Nb₃Sn layer will control the growth at low temperatures where the volume diffusion is actually frozen out. When the growth is

purely governed by the grain boundary diffusion and grain growth takes place in the Nb₃Sn layer according to the parabolic law, the exponent becomes 0.25.¹¹⁾ Here, the parabolic law means that the grain size of a growing compound layer increases in proportion to the square root of the annealing time. For the growth of the Nb₃Sn layer, the exponent is 0.33 at 973 and 1023 K and increases with increasing annealing temperature. At 1073 K, it becomes 0.5. The exponent 0.33 shows that the grain boundary diffusion contributes to the rate-controlling process and the grain growth occurs at certain rates at 973 and 1023 K. However, at 1073 K, the volume diffusion becomes predominant, and thus the exponent coincides with 0.5. Such temperature dependence of the exponent was discerned also for the growth of binary Cu–Sn compound layers during reactive diffusion between Cu and Sn at 433–473 K.¹²⁾ Therefore, it may be expected that this type of rate-controlling process generally works in the bronze method.

A binary Cu–8.3 at% Sn alloy was used to examine experimentally the growth behavior of the Nb₃Sn layer in a previous study.¹³⁾ In that experiment, the diffusion couple was prepared by sandwiching a Nb sheet between two plates of the Cu–Sn alloy and then annealed at temperatures of 923–1053 K. Also for the (Cu–8.3Sn)/Nb diffusion couple, the mean thickness of the Nb₃Sn layer is described as a power function of the annealing time. Unlike the (Cu–7.4Sn)/Nb diffusion couple, however, the exponent of the power function is close to unity at 923 and 973 K and monotonically decreases from 0.96 to 0.77 with increasing annealing temperature from 973 to 1053 K. This means that the interface reaction is the rate-controlling process for the growth of the Nb₃Sn layer at 923–973 K and the interdiffusion contributes to the rate-controlling process at 973–1053 K. Considering the observation for the (Cu–7.4Sn)/Nb diffusion couple, we may expect that the volume diffusion governs the interdiffusion at 1053 K but the grain boundary diffusion contributes to the interdiffusion at 923–1023 K.

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However, the observation for the (Cu–8.3Sn)/Nb diffusion couple indicates that the temperature dependence of the rate-controlling process recognized for the Cu/Sn and (Cu–7.4Sn)/Nb diffusion couples does not work generally in the bronze method.

In the bronze method, Nb₃Sn is formed due to the reactive diffusion between Nb and a binary Cu–Sn alloy with a concentration of Sn even much smaller than 25 at%. This means that uphill diffusion of Sn occurs from the Cu–Sn alloy to Nb₃Sn. In order to account for the occurrence of the uphill diffusion quantitatively, the phase equilibria in the ternary Cu–Nb–Sn system have been theoretically analyzed in the present study. A thermodynamic model developed by Hillert and Staffansson¹⁴⁾ has been used for the analysis. In the (Cu–7.4Sn)/Nb diffusion couple,¹⁰⁾ the grain boundary diffusion contributes to the rate-controlling process at 973–1023 K, and the volume diffusion governs the rate-controlling process at 1073 K. In such a case, the local equilibrium is realized at each moving interface during the reactive diffusion at 973–1073 K. On the other hand, in the (Cu–8.3Sn)/Nb diffusion couple,¹³⁾ the interface reaction is the rate-controlling process at 923–973 K, and the interdiffusion mainly governs the rate-controlling process at 1053 K. In this case, the local equilibrium at the moving interface cannot be actualized at 923–973 K, and hence the phase equilibria have a less physical meaning.¹⁵⁾ Thus, the present analysis has been carried out at a temperature of 1053 K. On the basis of the phase equilibria, the driving force for the uphill diffusion will be estimated quantitatively.

2. Experimental Summary

As already mentioned in Section 1, the growth behavior of the Nb₃Sn layer was experimentally examined for the (Cu–7.4Sn)/Nb diffusion couple by Osamura *et al.*¹⁰⁾ and for the (Cu–8.3Sn)/Nb diffusion couple in a previous study.¹³⁾ The experimental results for these diffusion couples will be summarized briefly in this section. For simplicity, however, the type of diffusion couple is hereafter merely denoted by the composition of the Cu–Sn alloy in the diffusion couple.

In those experiments, the mean thickness l of the Nb₃Sn layer was determined as a function of the annealing time t . The results for the Cu–7.4Sn and Cu–8.3Sn diffusion couples are indicated as open squares and circles, respectively, in Fig. 1. In this figure, the ordinate and the abscissa show the logarithms of l and t , respectively. As can be seen in Fig. 1, the thickness l monotonically increases with increasing annealing time t . Furthermore, the plotted points for each diffusion couple lie well on a straight line. This indicates that l is mathematically described as a power function of t by the equation

$$l = k(t/t_0)^n, \quad (1)$$

where t_0 is unit time, 1 s. It is adopted to make the ratio t/t_0 dimensionless. The proportionality coefficient k has the same dimension as the thickness l , but the exponent n is dimensionless. From the plotted points in Fig. 1, we obtain $k = 7.3 \times 10^{-9}$ m and $n = 0.55$ for the Cu–7.4Sn diffusion couple and $k = 1.1 \times 10^{-9}$ m and $n = 0.77$ for the Cu–8.3Sn diffusion couple by the least-squares method. Using these

Fig. 1 The thickness l of the Nb₃Sn layer versus the annealing time t for the Cu–8.3Sn diffusion couple at 1053 K in a previous study¹³⁾ and for the Cu–7.4Sn diffusion couple at 1073 K by Osamura *et al.*¹⁰⁾ Straight lines indicate the calculations from eq. (1).

values of k and n , l was calculated as a function of t from eq. (1). The results for the Cu–7.4Sn and Cu–8.3Sn diffusion couples are shown as dashed and solid straight lines, respectively, in Fig. 1. As can be seen, the growth rate of the Nb₃Sn layer is greater for the Cu–8.3Sn diffusion couple than for the Cu–7.4Sn diffusion couple, even though the annealing temperature is lower by 20 K for the former diffusion couple than for the latter diffusion couple. Consequently, it is concluded that the addition of Sn with 1 at% into the Cu–7.4Sn alloy considerably accelerates the growth rate of the Nb₃Sn layer at annealing temperatures around 1000 K.

Typical concentration profiles of Cu, Nb and Sn across the Nb₃Sn layer in the Cu–8.3Sn diffusion couple are shown as open rhombuses, squares and circles, respectively, in Fig. 2. In this figure, the abscissa indicates the distance, and the ordinate shows the mol fraction x_i of component i ($i = \text{Cu, Nb, Sn}$). The annealing temperature and time of this diffusion couple are 1053 K and 156 h (5.62×10^5 s), respectively. As can be seen, the Nb₃Sn layer with $l = 30 \mu\text{m}$ is recognized between the Cu–Sn alloy and Nb. The concentration of Cu monotonically decreases from the Cu–Sn alloy to Nb, and that of Nb from Nb to the Cu–Sn alloy. However, the concentration of Sn is higher in the Nb₃Sn layer than in the Cu–Sn alloy. This means that the uphill diffusion of Sn occurs from the Cu–Sn alloy to the Nb₃Sn layer.

3. Analysis

A thermodynamic model for phases with different sublattices was recently developed by Hillert and Staffansson.¹⁴⁾ In this model, the fraction of sites in each sublattice occupied by a component is expressed by the site fraction. The sum of site fractions in each sublattice is equal to unity by definition. Their thermodynamic model was used to calculate the phase

Fig. 2 Concentration profiles of Cu, Nb and Sn across a Nb₃Sn layer in the Cu–8.3Sn diffusion couple annealed at 1053 K for 156 h (5.62×10^5 s).

equilibria in the ternary Cu–Nb–Sn system. The expression of the Gibbs energy for each phase will be explained below.

3.1 Liquid, Fcc and Bcc

The Gibbs energy G_m is described with a single-sublattice model for the liquid phase, the Cu-rich solid-solution phase with face-centered cubic (fcc), the Nb-rich solid-solution phase with body-centered cubic (bcc) and the bcc- β compound phase in the binary Cu–Sn system. It was assumed that Cu, Nb and Sn could substitute for one another on a single sublattice and there was no ternary interaction among these components. These assumptions result in the following equation for G_m per mol of atoms.

$$G_m = y_{\text{Cu}}^\circ G_{\text{Cu}} + y_{\text{Nb}}^\circ G_{\text{Nb}} + y_{\text{Sn}}^\circ G_{\text{Sn}} + RT(y_{\text{Cu}} \ln y_{\text{Cu}} + y_{\text{Nb}} \ln y_{\text{Nb}} + y_{\text{Sn}} \ln y_{\text{Sn}}) + {}^E G_m \quad (2)$$

Here, the excess Gibbs energy ${}^E G_m$ is represented by

$${}^E G_m = y_{\text{Cu}} y_{\text{Nb}} L_{\text{Cu,Nb}} + y_{\text{Cu}} y_{\text{Sn}} L_{\text{Cu,Sn}} + y_{\text{Nb}} y_{\text{Sn}} L_{\text{Nb,Sn}} \quad (3)$$

In these equations, y_i denotes the site fraction of component i on the sublattice. In the case of the single-sublattice model, however, the site fraction y_i coincides with the mol fraction x_i of component i . Furthermore, T is the absolute temperature, R is the gas constant, ${}^\circ G_i$ is the molar Gibbs energy of pure component i , and $L_{i,j}$ is the interaction parameter between components i and j described as a function of the composition according to a Redlich–Kister polynomial as follows.¹⁶⁾

$$L_{i,j} = {}^0 L_{i,j} + {}^1 L_{i,j}(y_i - y_j) + {}^2 L_{i,j}(y_i - y_j)^2 \quad (4)$$

$i, j = \text{Cu, Nb, Sn}$

The numerical value of ${}^\circ G_i$ is given relative to the molar enthalpy H_i^{SER} of a selected reference state for pure component or element i at 298.15 K. This state is denoted by SER (stable element reference).¹⁶⁾

3.2 Nb₃Sn

According to the concentration profiles in Fig. 2, the solubility of Cu in Nb₃Sn is very small. Thus, Nb₃Sn was assumed to be a binary Nb–Sn compound. The same assumption was applied to all the other Nb–Sn compounds. However, a different sublattice model was used for each compound. As to Nb₃Sn, a two-sublattice model was adopted according to a treatment by Toffolon *et al.*¹⁷⁾ In this model, Nb and Sn can substitute for each other on both sublattices. The chemical formula of Nb₃Sn is expressed as (Nb,Sn)₃(Nb,Sn). It yields the following expression of G_m for one formula unit.

$$G_m = y_{\text{Nb}}^s y_{\text{Nb}}^t {}^\circ G_{\text{Nb:Nb}} + y_{\text{Sn}}^s y_{\text{Nb}}^t {}^\circ G_{\text{Sn:Nb}} + y_{\text{Nb}}^s y_{\text{Sn}}^t {}^\circ G_{\text{Nb:Sn}} + y_{\text{Sn}}^s y_{\text{Sn}}^t {}^\circ G_{\text{Sn:Sn}} + RT[3(y_{\text{Nb}}^s \ln y_{\text{Nb}}^s + y_{\text{Sn}}^s \ln y_{\text{Sn}}^s) + y_{\text{Nb}}^t \ln y_{\text{Nb}}^t + y_{\text{Sn}}^t \ln y_{\text{Sn}}^t] + {}^E G_m \quad (5)$$

In this equation, y_i^s is the site fraction of component i on sublattice s , and y_i^t is that of component i on sublattice t . Here, the number of sites is three times greater for sublattice s than for sublattice t . Furthermore, ${}^\circ G_{\text{Nb:Nb}}$ and ${}^\circ G_{\text{Sn:Sn}}$ are the Gibbs energies for hypothetical states where all of the sublattices are filled with Nb and Sn, respectively. On the other hand, ${}^\circ G_{\text{Nb:Sn}}$ is the Gibbs energy for an ideal state where sublattices s and t are occupied by Nb and Sn, respectively, and ${}^\circ G_{\text{Sn:Nb}}$ is that for a hypothetical state where sublattices s and t are filled with Sn and Nb, respectively. The excess Gibbs energy ${}^E G_m$ in eq. (5) is described as

$${}^E G_m = y_{\text{Nb}}^s y_{\text{Sn}}^s (y_{\text{Nb}}^t L_{\text{Nb,Sn:Nb}} + y_{\text{Sn}}^t L_{\text{Nb,Sn:Sn}}) + y_{\text{Nb}}^t y_{\text{Sn}}^t (y_{\text{Nb}}^s L_{\text{Nb:Nb,Sn}} + y_{\text{Sn}}^s L_{\text{Sn:Nb,Sn}}) \quad (6)$$

Here, $L_{i,j;i}$ is the interaction parameter between components i and j on sublattice s with sublattice t occupied by only component i , and $L_{j,i;j}$ is that between components i and j on sublattice t with sublattice s filled with only component j . The colon distinguishes sublattices, and the comma separates components interacting in the same sublattice. The site fractions y_i^s and y_i^t are converted into the mol fraction x_i by the following equation.

$$x_i = (3y_i^s + y_i^t)/4 \quad (7)$$

3.3 Nb₆Sn₅

A three-sublattice model was used for Nb₆Sn₅ to express the chemical formula as Nb₂₄Sn₁₆(Nb,Sn)₄.¹⁷⁾ In this model, the following expression of G_m is obtained for one formula unit.

$$G_m = y_{\text{Nb}}^\circ G_{\text{Nb:Sn:Nb}} + y_{\text{Sn}}^\circ G_{\text{Nb:Sn:Sn}} + 4RT(y_{\text{Nb}} \ln y_{\text{Nb}} + y_{\text{Sn}} \ln y_{\text{Sn}}) + {}^E G_m \quad (8)$$

According to a treatment by Toffolon *et al.*,¹⁷⁾ ${}^E G_m$ in eq. (8) is omitted also in the present study.

3.4 NbSn₂

It is assumed by Toffolon *et al.*¹⁷⁾ that NbSn₂ is a binary line compound. Their assumption was adopted also in the present study. Thus, G_m for NbSn₂ becomes equal to the Gibbs energy ${}^\circ G_{\text{Nb:Sn}}$ for one formula unit.

Table 1 Summary of thermodynamic parameters. The numbers are in SI units with $R = 8.31451 \text{ J/molK}$.

Liquid (L)	
Constituents: Cu, Nb, Sn	
298.15 K < T < 1357.77 K:	
${}^{\circ}G_{\text{Cu}}^{\text{liq}} - H_{\text{Cu}}^{\text{SER}} = 5194.277 + 120.973331T - 24.112392T \ln T$	
$- 0.00265684T^2 + 1.29223 \times 10^{-7}T^3 + 52478T^{-1}$	
$- 5.849 \times 10^{-21}T^7$	
1357.77 K < T < 3200 K:	
${}^{\circ}G_{\text{Cu}}^{\text{liq}} - H_{\text{Cu}}^{\text{SER}} = -46.545 + 173.881484T - 31.38T \ln T$	
298.15 K < T < 2750 K:	
${}^{\circ}G_{\text{Nb}}^{\text{liq}} - H_{\text{Nb}}^{\text{SER}} = 21262.202 + 131.229057T - 26.4711T \ln T$	
$+ 2.03475 \times 10^{-4}T^2 - 3.50119 \times 10^{-7}T^3 + 93399T^{-1}$	
$- 3.06098 \times 10^{-23}T^7$	
2750 K < T < 6000 K:	
${}^{\circ}G_{\text{Nb}}^{\text{liq}} - H_{\text{Nb}}^{\text{SER}} = -7499.398 + 260.756148T - 41.77T \ln T$	
298.15 K < T < 505.08 K:	
${}^{\circ}G_{\text{Sn}}^{\text{liq}} - H_{\text{Sn}}^{\text{SER}} = 1247.957 + 51.355548T - 15.961T \ln T - 0.0188702T^2$	
$+ 3.121167 \times 10^{-6}T^3 - 61960T^{-1} + 1.47031 \times 10^{-18}T^7$	
505.08 K < T < 800 K:	
${}^{\circ}G_{\text{Sn}}^{\text{liq}} - H_{\text{Sn}}^{\text{SER}} = 9496.31 - 9.809114T - 8.2590486T \ln T$	
$- 0.016814429T^2 + 2.623131 \times 10^{-6}T^3 - 1081244T^{-1}$	
800 K < T < 3000 K:	
${}^{\circ}G_{\text{Sn}}^{\text{liq}} - H_{\text{Sn}}^{\text{SER}} = -1285.372 + 125.182498T - 28.4512T \ln T$	
${}^0L_{\text{Cu,Nb}}^{\text{liq}} = 204361.19 - 89.931411T$	
${}^1L_{\text{Cu,Nb}}^{\text{liq}} = -105148.17 + 57.81653T$	
${}^2L_{\text{Cu,Nb}}^{\text{liq}} = 0$	
${}^0L_{\text{Cu,Sn}}^{\text{liq}} = -9002.8 - 5.8381T$	
${}^1L_{\text{Cu,Sn}}^{\text{liq}} = -20100.4 + 3.6366T$	
${}^2L_{\text{Cu,Sn}}^{\text{liq}} = -10528.4$	
${}^0L_{\text{Nb,Sn}}^{\text{liq}} = 15640$	
${}^1L_{\text{Nb,Sn}}^{\text{liq}} = -3876 - 7.5T$	
${}^2L_{\text{Nb,Sn}}^{\text{liq}} = 0$	
Fcc (Cu)	
Constituents: Cu, Nb, Sn	
298.15 K < T < 1358 K:	
${}^{\circ}G_{\text{Cu}}^{\text{fcc}} - H_{\text{Cu}}^{\text{SER}} = -7770.458 + 130.485235T - 24.112392T \ln T$	
$- 0.00265684T^2 + 1.29223 \times 10^{-7}T^3 + 52478T^{-1}$	
1358 K < T < 3200 K:	
${}^{\circ}G_{\text{Cu}}^{\text{fcc}} - H_{\text{Cu}}^{\text{SER}} = -13542.026 + 183.803828T - 31.38T \ln T$	
$+ 3.642 \times 10^{29}T^{-9}$	
298.15 K < T < 2750 K:	
${}^{\circ}G_{\text{Nb}}^{\text{fcc}} - H_{\text{Nb}}^{\text{SER}} = 4980.647 + 143.745475T - 26.4711T \ln T$	
$+ 2.03475 \times 10^{-4}T^2 - 3.50119 \times 10^{-7}T^3 + 93398.8T^{-1}$	
2750 K < T < 6000 K:	
${}^{\circ}G_{\text{Nb}}^{\text{fcc}} - H_{\text{Nb}}^{\text{SER}} = -24169.3 + 273.420843T - 41.77T \ln T$	
$+ 1.52824 \times 10^{32}T^{-9}$	
298.15 K < T < 505.07 K:	
${}^{\circ}G_{\text{Sn}}^{\text{fcc}} - H_{\text{Sn}}^{\text{SER}} = -1705.135 + 60.243315T - 15.961T \ln T - 0.0188702T^2$	
$+ 3.121167 \times 10^{-6}T^3 - 61960T^{-1}$	
505.07 K < T < 800 K:	
${}^{\circ}G_{\text{Sn}}^{\text{fcc}} - H_{\text{Sn}}^{\text{SER}} = 6674.724 - 1.194731T - 8.2590486T \ln T$	
$- 0.016814429T^2 + 2.623131 \times 10^{-6}T^3 - 1081244T^{-1}$	
$- 1.2307 \times 10^{25}T^{-9}$	
800 K < T < 3000 K:	
${}^{\circ}G_{\text{Sn}}^{\text{fcc}} - H_{\text{Sn}}^{\text{SER}} = -4106.959 + 133.79688T - 28.4512T \ln T$	
$- 1.2307 \times 10^{25}T^{-9}$	

Continued

Table 1 (Continued)

$${}^0L_{\text{Cu,Nb}}^{\text{fcc}} = 88888.84 - 3.22785T$$

$${}^1L_{\text{Cu,Nb}}^{\text{fcc}} = {}^2L_{\text{Cu,Nb}}^{\text{fcc}} = 0$$

$${}^0L_{\text{Cu,Sn}}^{\text{fcc}} = -10672 - 1.4837T$$

$${}^1L_{\text{Cu,Sn}}^{\text{fcc}} = -15331.3 + 6.9539T$$

$${}^2L_{\text{Cu,Sn}}^{\text{fcc}} = 0$$

$${}^0L_{\text{Nb,Sn}}^{\text{fcc}} = {}^1L_{\text{Nb,Sn}}^{\text{fcc}} = {}^2L_{\text{Nb,Sn}}^{\text{fcc}} = 0$$

Bcc (Nb, β)

Constituents: Cu, Nb, Sn

298.15 K < T < 1357.77 K:

$${}^{\circ}G_{\text{Cu}}^{\text{bcc}} - H_{\text{Cu}}^{\text{SER}} = -3753.458 + 129.230235T - 24.112392T \ln T$$

$$- 0.00265684T^2 + 1.29223 \times 10^{-7}T^3 + 52478T^{-1}$$

1357.77 K < T < 3200 K:

$${}^{\circ}G_{\text{Cu}}^{\text{bcc}} - H_{\text{Cu}}^{\text{SER}} = -9525.026 + 182.548828T - 31.38T \ln T$$

$$+ 3.642 \times 10^{29}T^{-9}$$

298.15 K < T < 2750 K:

$${}^{\circ}G_{\text{Nb}}^{\text{bcc}} - H_{\text{Nb}}^{\text{SER}} = -8519.353 + 142.045475T - 26.4711T \ln T$$

$$+ 2.03475 \times 10^{-4}T^2 - 3.5012 \times 10^{-7}T^3 + 93399T^{-1}$$

2750 K < T < 6000 K:

$${}^{\circ}G_{\text{Nb}}^{\text{bcc}} - H_{\text{Nb}}^{\text{SER}} = -37669.3 + 271.720843T - 41.77T \ln T$$

$$+ 1.528238 \times 10^{32}T^{-9}$$

298.15 K < T < 505.07 K:

$${}^{\circ}G_{\text{Sn}}^{\text{bcc}} - H_{\text{Sn}}^{\text{SER}} = -1455.135 + 59.443315T - 15.961T \ln T$$

$$- 0.0188702T^2 + 3.121167 \times 10^{-6}T^3 - 61960T^{-1}$$

505.07 K < T < 800 K:

$${}^{\circ}G_{\text{Sn}}^{\text{bcc}} - H_{\text{Sn}}^{\text{SER}} = 6924.724 - 1.994731T - 8.2590486T \ln T$$

$$- 0.016814429T^2 + 2.623131 \times 10^{-6}T^3 - 1081244T^{-1}$$

$$- 1.2307 \times 10^{25}T^{-9}$$

800 K < T < 3000 K:

$${}^{\circ}G_{\text{Sn}}^{\text{bcc}} - H_{\text{Sn}}^{\text{SER}} = -3856.959 + 132.99688T - 28.4512T \ln T$$

$$- 1.2307 \times 10^{25}T^{-9}$$

$${}^0L_{\text{Cu,Nb}}^{\text{bcc}} = 49480.18$$

$${}^1L_{\text{Cu,Nb}}^{\text{bcc}} = {}^2L_{\text{Cu,Nb}}^{\text{bcc}} = 0$$

$${}^0L_{\text{Cu,Sn}}^{\text{bcc}} = -44821.6 + 51.2164T$$

$${}^1L_{\text{Cu,Sn}}^{\text{bcc}} = -6876.5 - 56.4271T$$

$${}^2L_{\text{Cu,Sn}}^{\text{bcc}} = 0$$

$${}^0L_{\text{Nb,Sn}}^{\text{bcc}} = 49831 - 10.3T$$

$${}^1L_{\text{Nb,Sn}}^{\text{bcc}} = -100203 + 28.40T$$

$${}^2L_{\text{Nb,Sn}}^{\text{bcc}} = 0$$

Bct (Sn)

Constituents: Sn

100 K < T < 250 K:

$${}^{\circ}G_{\text{Sn}}^{\text{bct}} - H_{\text{Sn}}^{\text{SER}} = -7958.517 + 122.750027T - 25.858T \ln T$$

$$+ 5.1185 \times 10^{-4}T^2 - 3.192767 \times 10^{-6}T^3 + 18440T^{-1}$$

250 K < T < 505.08 K:

$${}^{\circ}G_{\text{Sn}}^{\text{bct}} - H_{\text{Sn}}^{\text{SER}} = -5855.135 + 65.427891T - 15.961T \ln T - 0.0188702T^2$$

$$+ 3.121167 \times 10^{-6}T^3 - 61960T^{-1}$$

505.08 K < T < 800 K:

$${}^{\circ}G_{\text{Sn}}^{\text{bct}} - H_{\text{Sn}}^{\text{SER}} = 2524.724 + 3.989845T - 8.2590486T \ln T$$

$$- 0.016814429T^2 + 2.623131 \times 10^{-6}T^3 - 1081244T^{-1}$$

$$- 1.2307 \times 10^{25}T^{-9}$$

800 K < T < 6000 K:

$${}^{\circ}G_{\text{Sn}}^{\text{bct}} - H_{\text{Sn}}^{\text{SER}} = -8256.959 + 138.981456T - 28.4512T \ln T$$

$$- 1.2307 \times 10^{25}T^{-9}$$

Continued

Table 1 (Continued)

Nb ₃ Sn	
2 sublattices, sites 3:1	
Constituents: Nb, Sn: Nb, Sn	
$^{\circ}G_{\text{Nb}_3\text{Sn}}^{\text{bcc}} - 4^{\circ}G_{\text{Nb}}^{\text{bcc}} = 20000 + 37T$	
$^{\circ}G_{\text{Sn:Nb}}^{\text{bcc}} - 3^{\circ}G_{\text{Sn}}^{\text{bcc}} - ^{\circ}G_{\text{Nb}}^{\text{bcc}} = 86260 + 20000 + 37T + 27T$	
$^{\circ}G_{\text{Nb}_3\text{Sn}}^{\text{bcc}} - 3^{\circ}G_{\text{Nb}}^{\text{bcc}} - ^{\circ}G_{\text{Sn}}^{\text{bcc}} = -66260 + 37T - 27T$	
$^{\circ}G_{\text{Sn:Sn}}^{\text{bcc}} - 4^{\circ}G_{\text{Sn}}^{\text{bcc}} = 20000 + 37T$	
$L_{\text{Nb}_3\text{Sn}}^{\text{Nb}_3\text{Sn}} = 179808 - 142T$	
$L_{\text{Sn:Nb,Sn}}^{\text{Nb}_3\text{Sn}} = L_{\text{Nb,Sn:Nb}}^{\text{Nb}_3\text{Sn}} = L_{\text{Nb}_3\text{Sn:Sn}}^{\text{Nb}_3\text{Sn}} = 0$	
Nb ₆ Sn ₅	
3 sublattices, sites 24:16:4	
Constituents: Nb: Sn: Nb, Sn	
$^{\circ}G_{\text{Nb}_6\text{Sn}_5}^{\text{bcc}} - 28^{\circ}G_{\text{Nb}}^{\text{bcc}} - 16^{\circ}G_{\text{Sn}}^{\text{bcc}} = 200086.5$	
$^{\circ}G_{\text{Nb}_6\text{Sn}_5}^{\text{bcc}} - 24^{\circ}G_{\text{Nb}}^{\text{bcc}} - 20^{\circ}G_{\text{Sn}}^{\text{bcc}} = -651845.7 + 80.95T$	
NbSn ₂	
2 sublattices, sites 1:2	
Constituents: Nb: Sn	
$^{\circ}G_{\text{NbSn}_2}^{\text{bcc}} - ^{\circ}G_{\text{Nb}}^{\text{bcc}} - 2^{\circ}G_{\text{Sn}}^{\text{bcc}} = -46487 + 11.3T$

Fig. 3 Area at $x_{\text{Sn}} < 0.27$ of isothermal section calculated at 1053 K in the ternary Cu–Nb–Sn system.

4. Results and Discussion

4.1 Isothermal section

According to the sublattice models mentioned in the previous section, there is no ternary interaction among Cu, Nb and Sn in all the phases. Thus, the Gibbs energy G_m of each phase is described with the thermodynamic parameters of the relevant binary systems. The numerical values of the thermodynamic parameters in the binary Cu–Nb, Cu–Sn and Nb–Sn systems^{17–19} are listed in Table 1. In this table, however, the values are shown only for the phases stable at 1053 K. Using these values, an isothermal section at 1053 K of the phase diagram in the ternary Cu–Nb–Sn system was calculated by a technique reported in a previous study.²⁰ The result is shown in Fig. 3. In this figure, the ordinate indicates the mol fraction x_{Sn} of Sn, and the abscissa shows the mol fraction x_{Nb} of Nb. Furthermore, the Cu-rich and Nb-rich solid-solution phases are merely denoted by Cu and Nb, respectively, and the liquid phase is indicated as L. In the present study, however, attention is focused on the phase equilibria relevant to the Cu, Nb and Nb₃Sn phases. Therefore, only an area at $x_{\text{Sn}} < 0.27$ of the isothermal section is indicated in Fig. 3. As can be seen in this figure, Nb₃Sn is in equilibrium with the Cu, Nb, β and L phases. As a result, triangles for the three-phase equilibria of Cu + Nb + Nb₃Sn, Cu + β + Nb₃Sn and L + β + Nb₃Sn appear in the isothermal section. The calculation also indicates that the three-phase equilibria of L + Nb₃Sn + Nb₆Sn₅ and L + Nb₆Sn₅ + NbSn₂ emerge in an area at $x_{\text{Sn}} > 0.27$ of the isothermal section. Such three-phase equilibria are actually observed at an experimental phase diagram in the ternary Cu–Nb–Sn system.²¹

Since the solubility of Nb is very small for the Cu, β and L phases, the phase boundary of single-phase region is not clearly distinguishable for these phases in Fig. 3. Thus, an area at $x_{\text{Nb}} < 6.5 \times 10^{-4}$ of Fig. 3 is magnified in Fig. 4. As can be seen, the solubility of Nb is around $x_{\text{Nb}} = 1 \times 10^{-5}$ for

Fig. 4 Magnified area at $x_{\text{Nb}} < 6.5 \times 10^{-4}$ of the isothermal section in Fig. 3.

the Cu phase, $x_{\text{Nb}} = 5 \times 10^{-4}$ – 6×10^{-4} for the β phase and $x_{\text{Nb}} = 1.4 \times 10^{-5}$ – 1.8×10^{-5} for the L phase. According to the result in Fig. 3, the solubility of Cu in the Nb phase is also very small. As already mentioned in the previous section, the ternary interaction is omitted for all the phases. For phases with small solubility of the third component, the ternary interaction is actually considered negligible.

4.2 Activity Diagram

The kinetics of reactive diffusion is theoretically analyzed for a hypothetical binary A–B system consisting of two primary solid-solution phases and one compound phase in a previous study.²² In that analysis, the growth of the

Fig. 5 Activity a_{Sn} of Sn versus compositional parameter u_{Nb} corresponding to the result in Fig. 3.

compound layer formed at the interface between the two primary solid-solution phases with a semi-infinite thickness is mathematically described with diffusion equations. The analysis indicates that the growth rate of the compound layer is predominantly determined by the interdiffusion across the compound layer. The interdiffusion coefficient D is related with the intrinsic diffusion coefficients D_A and D_B of components A and B , respectively, by the following equation.²³⁾

$$D = x_B D_A + x_A D_B \quad (9)$$

Here, x_A and x_B are the mol fractions of components A and B , respectively. As already shown in Fig. 2, the solubility of Cu is very small for Nb_3Sn in the ternary Cu–Nb–Sn system. Thus, the growth rate of the Nb_3Sn layer is affected predominantly by the diffusional fluxes of Nb and Sn but scarcely by that of Cu. As a consequence, Nb_3Sn is approximately considered as a binary Nb–Sn compound. For the binary Nb_3Sn phase with $x_{\text{Nb}} = 0.75$ and $x_{\text{Sn}} = 0.25$, the interdiffusion coefficient D is related with the intrinsic diffusion coefficients D_{Nb} and D_{Sn} of Nb and Sn, respectively, as $D = x_{\text{Sn}} D_{\text{Nb}} + x_{\text{Nb}} D_{\text{Sn}} = 0.25 D_{\text{Nb}} + 0.75 D_{\text{Sn}}$ by eq. (9). The observation by Osamura *et al.*¹⁰⁾ implies that D_{Sn} is much greater than D_{Nb} and thus $D \approx 0.75 D_{\text{Sn}}$. This means that the intrinsic diffusion of Sn governs the interdiffusion across the Nb_3Sn layer and thus the growth rate of the Nb_3Sn layer. In quantitative explanation for the occurrence of the uphill diffusion, it is convenient to consider the activity instead of the composition. Consequently, the isothermal section in Fig. 3 is represented in a different manner in Fig. 5. In this figure, the ordinate indicates the activity a_{Sn} of Sn with a reference state of the L phase of pure Sn, and the abscissa shows the compositional parameter u_{Nb} between Nb and Cu defined as $u_{\text{Nb}} = x_{\text{Nb}} / (x_{\text{Nb}} + x_{\text{Cu}})$. In such an activity diagram, a three-phase equilibrium is shown as a horizontal straight line but not a triangle. As can be seen in Fig. 5, the activity of Sn is $a_{\text{Sn}} = 0.0047$, 0.030 and 0.044

Fig. 6 Single-phase region of the β phase in Fig. 5.

Fig. 7 Single-phase region of the Cu phase in Fig. 5.

for the three-phase equilibria of $\text{Cu} + \text{Nb} + \text{Nb}_3\text{Sn}$, $\text{Cu} + \beta + \text{Nb}_3\text{Sn}$ and $L + \beta + \text{Nb}_3\text{Sn}$, respectively. As mentioned earlier, however, the solubility is very small for Nb in the Cu, β and L phases and for Cu in the Nb phase. Thus, the single-phase regions of the β , Cu and Nb phases in Fig. 5 are magnified in Figs. 6, 7 and 8, respectively. As already shown in Fig. 4, the solubility of Nb is greater in the β phase than in the L and Cu phases. As a result, in Fig. 6, the β , L and Nb_3Sn phases construct a peritectic type of invariant reaction, whereas the β , Cu and Nb_3Sn phases compose a eutectoid type of invariant reaction. Therefore, the β phase is only stable between these two invariant reactions. On the contrary, in Fig. 7, the Cu phase is in equilibrium with the Nb and Nb_3Sn phases as well as the β phase. The activity of Sn for the three-phase equilibrium of $\text{Cu} + \text{Nb} + \text{Nb}_3\text{Sn}$ is greater than that for the $\text{Cu} + \text{Nb}$ two-phase region but smaller than that for the $\text{Cu} + \text{Nb}_3\text{Sn}$ two-phase region. At the Nb-rich

Fig. 8 Single-phase region of the Nb phase in Fig. 5.

Fig. 9 Schematic drawing of Fig. 5. A presumable diffusion path in the bronze method is shown as a dotted curve.

corner in Fig. 8, the solubility of Cu is very small in the Nb phase, but completely zero in Nb₃Sn according to the assumption. As a consequence, the Cu, Nb and Nb₃Sn phases construct a peritectoid type of invariant reaction. On the basis of the phase equilibria in Figs. 6–8, the characteristic feature of the activity diagram in Fig. 5 is schematically indicated in Fig. 9. In this figure, however, each single-phase region is exaggerated extremely. Furthermore, a capable diffusion path in the bronze method is sketchily depicted as a dotted curve. An open circle shows the activity of Sn for a binary Cu–Sn alloy, and an open triangle indicates that for pure Nb. Since the activity of Sn monotonically decreases from the open circle to the open triangle along the dotted curve in Fig. 9, the diffusion of Sn spontaneously occurs from the binary Cu–Sn alloy to pure Nb through Nb₃Sn. This is the

reason why the uphill diffusion of Sn takes place from the Cu–Sn alloy to Nb₃Sn.

4.3 Comparison with Observation

Since the activity of Sn is surely greater for the binary Cu–Sn alloy than for pure Nb, we may expect that Nb₃Sn is always produced in the bronze method. In order for Nb₃Sn to form spontaneously, however, the activity of Sn should be greater for the Cu–Sn alloy than for the three-phase equilibrium of Cu + Nb + Nb₃Sn. In Fig. 9, a_{Sn}^b is the activity of Sn for the Cu–Sn alloy, and a_{Sn}^c is that for the three-phase equilibrium of Cu + Nb + Nb₃Sn. Furthermore, open squares and rhombuses illustrate the local equilibria at the Cu/Nb₃Sn and Nb₃Sn/Nb interfaces, respectively. The difference between the activities of Sn for the open squares and rhombuses causes the driving force for the diffusion of Sn across the Nb₃Sn layer. However, the locations of the open squares and rhombuses cannot be determined only from the activity diagram in Fig. 5. For the determination, mobility of each component should be known for all the phases. On the other hand, the driving force for the spontaneous formation of Nb₃Sn is attributed to the difference between the values of a_{Sn}^b and a_{Sn}^c . In this case, both a_{Sn}^b and a_{Sn}^c are evaluated from the activity diagram.

The formation of Nb₃Sn was experimentally studied at 923–1123 K by Wada *et al.*⁵⁾ using various (Cu–Sn)/Nb diffusion couples with different compositions. In their experiment, binary Cu–Sn alloys with $x_{\text{Sn}} = 0.035, 0.05, 0.06$ and 0.07 were used to prepare the diffusion couples. After annealing for 100 h, Nb₃Sn was observed to form at 1023–1123 K for $x_{\text{Sn}} = 0.035$ and at 923–1123 K for $x_{\text{Sn}} = 0.05, 0.06$ and 0.07 . Thus, Nb₃Sn will be formed also at 1053 K for all the compositions. Using the thermodynamic parameters in Table 1, a_{Sn}^b is calculated by the equation²⁴⁾

$$a_{\text{Sn}}^b = y_{\text{Sn}} \exp(f/RT), \quad (10)$$

where f is defined as

$$f \equiv {}^\circ G_{\text{Sn}}^{\text{fcc}} - {}^\circ G_{\text{Sn}}^{\text{liq}} + y_{\text{Cu}}^2 [{}^0 L_{\text{Cu,Sn}}^{\text{fcc}} + {}^1 L_{\text{Cu,Sn}}^{\text{fcc}} (y_{\text{Cu}} - 3y_{\text{Sn}})]. \quad (11)$$

For the Cu phase with the single-sublattice, y_{Sn} and y_{Cu} are readily obtained from x_{Sn} by the equations $y_{\text{Sn}} = x_{\text{Sn}}$ and $y_{\text{Cu}} = 1 - x_{\text{Sn}}$, respectively. From eqs. (10) and (11), values of $a_{\text{Sn}}^b = 0.0093, 0.015, 0.019$ and 0.024 are evaluated for $x_{\text{Sn}} = 0.035, 0.05, 0.06$ and 0.07 , respectively, at 1053 K. Since these values of a_{Sn}^b are greater than $a_{\text{Sn}}^c = 0.0047$, Nb₃Sn can be produced spontaneously in all the diffusion couples.

A similar experiment was carried out at 973–1123 K by Reddi *et al.*⁸⁾ They used binary Cu–Sn alloys with compositions of $x_{\text{Sn}} = 0.0109$ – 0.0613 for preparation of various (Cu–Sn)/Nb diffusion couples. After annealing up to 226 h, Nb₃Sn was observed to form for $x_{\text{Sn}} = 0.0179, 0.0246, 0.0387, 0.0466$ and 0.0613 at 1023 K and for $x_{\text{Sn}} = 0.0109, 0.0179, 0.0246, 0.0387$ and 0.0466 at 1123 K. Hence, Nb₃Sn may be produced for $x_{\text{Sn}} = 0.0179$ – 0.0613 also at 1053 K. From eqs. (10) and (11), values of $a_{\text{Sn}}^b = 0.0042, 0.0061, 0.0106, 0.0136$ and 0.0199 are evaluated for $x_{\text{Sn}} = 0.0179, 0.0246, 0.0387, 0.0466$ and 0.0613 , respectively, at 1053 K.

Since most of the values except $a_{\text{Sn}}^b = 0.0042$ are greater than $a_{\text{Sn}}^c = 0.0047$, the evaluation rather quantitatively explains the observation by Reddi *et al.*⁸⁾

The value of a_{Sn}^c is predominantly determined by the phase stability of Nb_3Sn in the binary Nb–Sn system. The phase stability of Nb_3Sn was carefully considered in an assessment of the thermodynamic parameters in the binary Nb–Sn system by Toffolon *et al.*¹⁷⁾ In their assessment, the enthalpy of formation for Nb_3Sn was experimentally measured by themselves. Although experimental information was not available for the activities of Sn and Nb, their thermodynamic parameters deduced reliable phase equilibria relevant to Nb_3Sn in the binary Nb–Sn system. On the other hand, in the binary Cu–Sn system, the activity of Sn in the Cu phase was experimentally determined by Alcock and Jacob²⁵⁾ and by Sommer *et al.*²⁶⁾ Such experimental results were used by Shim *et al.*¹⁹⁾ for an assessment of the thermodynamic parameters in the binary Cu–Sn system. Their thermodynamic parameters provide values of a_{Sn}^b slightly smaller than the experimental results. This may be one of the reasons why $a_{\text{Sn}}^b = 0.0042$ for $x_{\text{Sn}} = 0.0179$ is slightly smaller than $a_{\text{Sn}}^c = 0.0047$. However, the difference between $a_{\text{Sn}}^b = 0.0042$ and $a_{\text{Sn}}^c = 0.0047$ is rather small. Therefore, it is concluded that the thermodynamic parameters in Table 1 result in satisfactorily reliable phase stability of Nb_3Sn in the ternary Cu–Nb–Sn system.

As mentioned earlier, the formation of Nb_3Sn was experimentally observed at 973–1073 K for the Cu–7.4Sn diffusion couple by Osamura *et al.*¹⁰⁾ and at 923–1053 K for the Cu–8.3Sn diffusion couple in a previous study.¹³⁾ From eqs. (10) and (11), a value of $a_{\text{Sn}}^b = 0.026$ is evaluated for $x_{\text{Sn}} = 0.074$ at 1053 K. According to the isothermal section in Fig. 4, however, the solubility of Sn in the Cu phase of the binary Cu–Sn system is $x_{\text{Sn}} = 0.081$ at 1053 K. Hence, the composition $x_{\text{Sn}} = 0.083$ is located in the Cu + β two-phase region. Actually, a small amount of the β phase was observed in the Cu–8.3Sn alloy at 1053 K.¹³⁾ From the activity diagram in Fig. 6, a value of $a_{\text{Sn}}^b = 0.030$ is obtained for the Cu + β two-phase region in the binary Cu–Sn system. Since both values of $a_{\text{Sn}}^b = 0.026$ and 0.030 are much greater than $a_{\text{Sn}}^c = 0.0047$, Nb_3Sn is spontaneously produced in the Cu–7.4Sn and Cu–8.3Sn diffusion couples at 1053 K. The chemical potentials G_{Sn}^b and G_{Sn}^c of Sn for the binary Cu–Sn alloy and the three-phase equilibrium of Cu + Nb + Nb_3Sn are related with a_{Sn}^b and a_{Sn}^c by the equations

$$G_{\text{Sn}}^b = {}^\circ G_{\text{Sn}}^{\text{fcc}} + RT \ln a_{\text{Sn}}^b \quad (12a)$$

and

$$G_{\text{Sn}}^c = {}^\circ G_{\text{Sn}}^{\text{fcc}} + RT \ln a_{\text{Sn}}^c, \quad (12b)$$

respectively. Thus, the chemical driving force ΔG_{Sn} for the uphill diffusion of Sn is evaluated by the following equation.

$$\Delta G_{\text{Sn}} = G_{\text{Sn}}^b - G_{\text{Sn}}^c = RT \ln(a_{\text{Sn}}^b/a_{\text{Sn}}^c) \quad (13)$$

When a_{Sn}^b is greater than a_{Sn}^c , ΔG_{Sn} takes a positive value. The positive value of ΔG_{Sn} also yields the spontaneous formation of Nb_3Sn . The greater the value of ΔG_{Sn} is, the faster the formation of Nb_3Sn occurs. Inserting $a_{\text{Sn}}^b = 0.026$ and 0.030 and $a_{\text{Sn}}^c = 0.0047$ into eq. (13), we obtain $\Delta G_{\text{Sn}} = 15$ and 16 kJ/mol for the Cu–7.4Sn and Cu–8.3Sn diffusion

couples, respectively, at 1053 K. Thus, ΔG_{Sn} is greater for the latter diffusion couple than for the former diffusion couple. This is the reason why the growth rate of the Nb_3Sn layer is greater in the Cu–8.3Sn diffusion couple than in the Cu–7.4Sn diffusion couple as shown in Fig. 1. In order to analyze the growth rate theoretically, the mobility should be known for each component in all the phases. Unfortunately, however, such information is very limited in the ternary Cu–Nb–Sn system.

5. Conclusions

The uphill diffusion of Sn occurs from the binary Cu–Sn alloy to Nb_3Sn during annealing at temperatures around 1000 K in the bronze method. In order to explain the occurrence of the uphill diffusion quantitatively, the phase equilibria in the ternary Cu–Nb–Sn system were theoretically analyzed using the thermodynamic model developed by Hillert and Staffansson.¹⁴⁾ Since the solubility of the third component is very small for all the phases, the ternary interaction was assumed negligible. Thus, the Gibbs energy G_m of each phase was described with the thermodynamic parameters of the relevant binary systems. An isothermal section at 1053 K of the phase diagram in the ternary Cu–Nb–Sn system was calculated by the technique reported in a previous study.²⁰⁾ In the isothermal section, the three-phase equilibrium of Cu + Nb + Nb_3Sn appears at an activity of Sn with 0.0047. When the activity a_{Sn}^b of Sn for the binary Cu–Sn alloy is greater than the activity a_{Sn}^c of Sn for the three-phase equilibrium of Cu + Nb + Nb_3Sn , Nb_3Sn is spontaneously formed due to the reactive diffusion between the Cu–Sn alloy and Nb. In such a case, the uphill diffusion of Sn takes place from the Cu–Sn alloy to Nb_3Sn . The chemical driving force ΔG_{Sn} for the uphill diffusion is evaluated by the equation $\Delta G_{\text{Sn}} = RT \ln(a_{\text{Sn}}^b/a_{\text{Sn}}^c)$. This equation also provides a semi-quantitative explanation for the growth behavior of Nb_3Sn .

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