Ternary Diffusion and Thermodynamic Interactions in α Cu-Ni-Sn Solid Solutions*

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The interdiffusion experiment and thermodynamic study of Cu-rich α Cu-Ni-Sn solid solutions have been performed in a temperature range from 1023 to 1123 K. The concentration profiles indicate that the diffusion rate of Sn is greater than that of Ni in these solid solutions. The influence of the indirect flux becomes larger with increasing Ni concentration. The interdiffusion fluxes evaluated from the equations of Dayananda and Kim show that the zero-flux planes exist in the diffusion zone of Cu-Ni-Sn couples. The diffusion paths show S-shaped curves. The direct coefficients $\bar{D}_{\text{SnSn}}^{\text{Cu}}$ and $\bar{D}_{\text{NiNi}}^{\text{Cu}}$ are positive, and the indirect coefficients $\bar{D}_{\text{SnNi}}^{\text{Cu}}$ and $\bar{D}_{\text{NiSn}}^{\text{Cu}}$ are negative. The four interdiffusion coefficients are very sensitive to the Ni and Sn concentrations. The temperature dependence of $\bar{D}_{\text{SnSn}}^{\text{Cu}}$, $\bar{D}_{\text{SnNi}}^{\text{Cu}}$, $\bar{D}_{\text{NiNi}}^{\text{Cu}}$ and $\bar{D}_{\text{NiSn}}^{\text{Cu}}$ at the composition of Cu-6.0 at%Ni-3.7 at%Sn can be expressed by the following equations:

$$\begin{aligned}\bar{D}_{\text{SnSn}}^{\text{Cu}} &= 2.1 \times 10^{-5} \exp \left(-\frac{175000 \text{ J/mol}}{RT} \right) \text{ m}^2/\text{s}, \\ \bar{D}_{\text{SnNi}}^{\text{Cu}} &= -5.8 \times 10^{-7} \exp \left(-\frac{153000 \text{ J/mol}}{RT} \right) \text{ m}^2/\text{s}, \\ \bar{D}_{\text{NiNi}}^{\text{Cu}} &= 1.4 \times 10^{-5} \exp \left(-\frac{189000 \text{ J/mol}}{RT} \right) \text{ m}^2/\text{s}\end{aligned}$$

and

$$\bar{D}_{\text{NiSn}}^{\text{Cu}} = -3.1 \times 10^{-9} \exp \left(-\frac{120000 \text{ J/mol}}{RT} \right) \text{ m}^2/\text{s}.$$

The estimated values of interaction parameters indicate that the interaction energy of the Ni-Sn bond is much larger than those of the Cu-Sn and Cu-Ni bonds.

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I. Introduction

Many experimental studies of diffusion have been carried out on binary alloys⁽¹⁾⁽²⁾. However, the number of studies on ternary diffusion is very small in spite of its importance⁽²⁾⁻⁽⁴⁾. Interdiffusion in a ternary alloy 1-2-3 (solvent is indicated by 3) is expressed by

Fick's extended first law⁽⁵⁾⁽⁶⁾,

$$\bar{J}_i = - \sum_{j=1}^2 \bar{D}_{ij}^3 \partial C_j / \partial x, \quad (i=1, 2), \quad (1)$$

where $\bar{J}_i$ is the interdiffusion flux of i atom, C_i the concentration of i atom, x the distance and $\bar{D}_{ij}^3$ the interdiffusion coefficient. $\bar{D}_{ij}^3$ is referred to as 'direct coefficient' when $i=j$ and to as 'indirect coefficient' when $i \neq j$. Equation (1) indicates that four interdiffusion coefficients are necessary to describe the interdiffusion in a ternary alloy. On the other hand, interdiffusion in a binary alloy can be expressed by only one interdiffusion coefficient $\bar{D}$. The indirect coefficient cannot be ignored on describing interdiffusion in a non-ideal solid solution of three components, since the magnitude of the

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interdiffusion coefficient is not small. 'Up-hill' diffusion is often identified on the diffusion profile in a ternary alloy when the indirect coefficients are not equal to zero. These coefficients are closely related to the interaction, namely, attractive or repulsive force in the bond between constituent elements. Mehta and Axon⁽⁷⁾ have reported diffusion in Cu-Ni-Sn alloys. However, their studies have been focused on the areas of Cu-Ni and Cu-Sn binary diffusion, and direct and indirect coefficients of the Cu-Ni-Sn alloys have not been determined.

The purposes of the present work are (a) to determine the ternary diffusion coefficients in the α -phase region of the Cu-Ni-Sn system in a temperature range from 1023 to 1123 K by use of solid-solid couples, (b) to evaluate the interdiffusion fluxes of this system and (c) to estimate the interaction parameters in the Cu-Ni-Sn alloys from the interdiffusion coefficients.

II. Experimental Procedures

Sixteen diffusion couples were prepared in order to determine the interdiffusion coefficients in the α -phase field of this system. The terminal compositions of diffusion couples are listed in Table 1 and are in the α -phase solid solution⁽⁸⁾. The diffusion couples are designated by N1-N5, S1-S7 and C1-C4 on the basis of the combination of metals. The

diffusion couple N5 is a Darken type couple⁽⁹⁾ having a nearly constant concentration of Ni, and C1-C4 are diffusion couples for binary diffusion in the Cu-Sn system.

The Cu-Ni, Cu-Sn and α Cu-Ni-Sn alloys were prepared from 99.99 mass% Cu, 99.9 mass% Sn and a Cu-30.33 mass% Ni mother alloy in a high frequency induction furnace under an argon atmosphere. The alloy ingots were subsequently annealed at temperatures 50-70 K below their melting points for 604.8 ks, in order to establish homogenization and grain growth. The grain diameter of these alloys was more than about 1 mm. The Cu-Sn and α Cu-Ni-Sn alloys were turned to rods of $\phi 8$ mm $\times$ 80 mm by a lathe. A hole ($\phi 8$ mm $\times$ 80 mm) was drilled in blocks of the pure Cu and the Cu-Ni alloys (25 mm $\times$ 25 mm $\times$ 70 mm). Faces of the rod alloys and the hole of blocks were mechanically polished by 6/0 emery paper, and then washed with acetone. The rod of the alloys was inserted into the hole of the blocks. These composed metals were quickly rolled within about 180 s to 70% reduction in thickness after heating at 1048 K for 3.6 ks, and then quenched into ice water. The rolling has the advantage that any oxide film at the interface between metals is broken up and distributed over a much larger area⁽¹⁰⁾. The rolled metals were cut into 5 mm width as the diffusion couples. The interfaces of the diffusion couples were examined by a JEOL JXA-733 electron microanalyzer (EPMA). It was found that the diffusion during the bonding treatments was negligibly small.

Diffusion temperatures and times are listed in Table 2. All of the diffusion couples were annealed in a stream of purified argon gas at 1048 K for 318.1 ks. In addition, the couples N2 and S5 were annealed under the purified argon atmosphere in a temperature range from 1023 to 1123 K, in order to study the temperature dependence of diffusion coefficients. After the diffusion annealing, the couples were

Table 1 Terminal compositions of diffusion couples.

Couple designation	Composition (at%)
N1	Cu/Cu-3.5Ni-7.1Sn
N2	Cu/Cu-7.1Ni-5.4Sn
N3	Cu/Cu-9.8Ni-3.4Sn
N4	Cu/Cu-17.7Ni-2.4Sn
N5	Cu-7.1Ni/Cu-6.9Ni-5.4Sn
S1	Cu-7.1Ni/Cu-2.7Sn
S2	Cu-7.1Ni/Cu-4.1Sn
S3	Cu-8.1Ni/Cu-2.7Sn
S4	Cu-8.1Ni/Cu-4.1Sn
S5	Cu-8.1Ni/Cu-5.5Sn
S6	Cu-11.3Ni/Cu-5.5Sn
S7	Cu-14.1Ni/Cu-6.8Sn
C1	Cu/Cu-2.7Sn
C2	Cu/Cu-4.1Sn
C3	Cu/Cu-5.5Sn
C4	Cu/Cu-6.8Sn

Table 2 Diffusion temperatures and times for binary and ternary diffusion experiments.

Temp. (K)	1023	1048	1073	1098	1123
Time (ks)	488.5	318.1	181.0	107.1	63.81

quenched in ice water. The annealed couples were carefully ground to remove the oxidized regions. The diffusion couples were mounted on synthetic resin and polished along the plane parallel to the diffusion direction. Solute concentration profiles in these diffusion couples were measured by EPMA. The characteristic X-ray intensities of Ni and Sn were corrected for atomic number, absorption and fluorescence effects and were converted into concentration values of Ni and Sn using the bulk alloy compositions at the ends of the couples as standards⁽¹¹⁾⁽¹²⁾.

The binary Cu-Sn interdiffusion coefficients were determined by the Matano method⁽⁵⁾. The interdiffusion in a ternary alloy 1-2-3 is expressed by the extended Fick's second law on the basis of Matano coordinate⁽⁶⁾.

$$\partial C_1 / \partial t = \partial / \partial x (\bar{D}_{11}^3 \partial C_1 / \partial x) + \partial / \partial x (\bar{D}_{12}^3 \partial C_2 / \partial x) \quad (2)$$

and

$$\partial C_2 / \partial t = \partial / \partial x (\bar{D}_{21}^3 \partial C_1 / \partial x) + \partial / \partial x (\bar{D}_{22}^3 \partial C_2 / \partial x), \quad (3)$$

where x is the distance from Matano interface. In this study, the solvent 3 is Cu, and components 1 and 2 are Sn and Ni, respectively.

Kirkaldy *et al.*⁽¹³⁾ have shown that eqs. (2) and (3) can be solved by the extension of the Boltzmann-Matano method to ternary equation.

$$\int_{C_1^-}^{C_1^+} x dC_1 = -2t(\bar{D}_{11}^3 \cdot \partial C_1 / \partial x + \bar{D}_{12}^3 \cdot \partial C_2 / \partial x) \quad (4)$$

and

$$\int_{C_2^-}^{C_2^+} x dC_2 = -2t(\bar{D}_{21}^3 \cdot \partial C_1 / \partial x + \bar{D}_{22}^3 \cdot \partial C_2 / \partial x), \quad (5)$$

and the origin for x must be chosen in such a way that

$$\int_{C_1^-}^{C_1^+} x dC_1 = \int_{C_2^-}^{C_2^+} x dC_2 = 0, \quad (6)$$

where C_i^- and C_i^+ ($i=1, 2$) are the terminal compositions at the ends of the diffusion

couples. The four interdiffusion coefficients in eqs. (4) and (5) are evaluated at the common compositions (C_1 and C_2) of intersection of the diffusion paths. Furthermore, the values of $\bar{D}_{12}^3$ and $\bar{D}_{22}^3$ can be determined at the compositions corresponding to the maximum and minimum (i.e., $\partial C_i / \partial x = 0$) on the diffusion profiles.

III. Results and Discussion

1. Concentration profiles, interdiffusion fluxes and diffusion paths

Typical concentration profiles of the couples N4 and S5 annealed at 1048 K are shown in Figs. 1(a) and (b), respectively. The origin of each abscissa in Figs. 1(a) and (b) is the Matano interface. The concentration profiles indicate that the diffusion rate of Sn is greater than that of Ni in the Cu-Ni-Sn alloys. A pronounced 'up-hill' diffusion of Ni and Sn is observed in Figs. 1(a) and (b), respectively⁽³⁾. Such a maximum or a minimum in the concentration profiles can occur in an alloy of three or more components, as has been found in the Ni-Mn-Cu system⁽¹⁴⁾ and Cu-Ni-Zn system⁽¹⁵⁾⁽¹⁶⁾.

The interdiffusion flux $\bar{J}_i$ of component i at any composition in the diffusion zone of a solid-solid infinite diffusion couple is given by⁽¹⁷⁾

$$\bar{J}_i = 1/2t \int_{C_i^{(+\infty \text{ or } -\infty)}}^{C_i} x dC_i \quad (i=1, 2, \dots, n). \quad (7)$$

In Fig. 2(a) and (b), the concentration profiles and interdiffusion fluxes of Sn and Ni calculated from eq. (7) are presented for the diffusion couple N4. The values of $\bar{J}_{\text{Sn}}$ are negative in the diffusion zone, and Sn atoms flow in the direction from alloy side to Cu side. A zero flux plane (ZFP)⁽¹⁷⁾ for a component i in the diffusion couple is identified by the requirement that $\bar{J}_i = 0$. Hence, it follows from eq. (7) that

$$\int_{C_i^{(+\infty)}}^{C_i^{(\text{ZFP})}} x dC_i = \int_{C_i^{(-\infty)}}^{C_i^{(\text{ZFP})}} x dC_i = 0. \quad (8)$$

The application of eq. (8) to the Ni concentration profile in Fig. 2(a) requires

Fig. 1(a) Concentration profiles of Ni and Sn for diffusion couple N4 annealed at 1048 K for 318.1 ks.

Fig. 1(b) Concentration profiles of Ni and Sn for diffusion couple S5 annealed at 1048 K for 318.1 ks.

$$\int_{C_{\text{Ni}}^{(+\infty)}}^{C_{\text{Ni}}^{(\text{ZFP})}} x dC_{\text{Ni}} = \text{area } A + \text{area } B = 0, \quad (9)$$

where areas A and B are opposite in sign but are equal in magnitude. Similarly

$$\int_{C_{\text{Ni}}^{(-\infty)}}^{C_{\text{Ni}}^{(\text{ZFP})}} x dC_{\text{Ni}} = \text{area } C + \text{area } D = 0, \quad (10)$$

where areas C and D are equal in magnitude but are opposite in sign. $\bar{J}_{\text{Ni}}$ varies from negative values to positive values. ZFP is located in the region of high Ni concentration. Ni atoms flow in the direction from alloy side to Cu side on the left side of the ZFP, and do in the reverse direction on the right side of the ZFP.

Fig. 2 Concentration profiles (a) and interdiffusion fluxes calculated (b) for a diffusion couple N4 annealed at 1048 K for 318.1 ks; the couple develops a ZFP for Ni.

The interdiffusion flux $\tilde{J}_{\text{Sn}}$ is represented by

$$\tilde{J}_{\text{Sn}} = \tilde{J}_{\text{SnSn}} + \tilde{J}_{\text{SnNi}} \\ = -\tilde{D}_{\text{SnSn}}^{\text{Cu}} \partial C_{\text{Sn}} / \partial x - \tilde{D}_{\text{SnNi}}^{\text{Cu}} \partial C_{\text{Ni}} / \partial x. \quad (11)$$

The total flux of Sn, $\tilde{J}_{\text{Sn}}$, consists of the direct flux $\tilde{J}_{\text{SnSn}}$ and the indirect flux $\tilde{J}_{\text{SnNi}}$. A similar relation holds also for $\tilde{J}_{\text{Ni}}$. Figure 3 shows the relation between $\tilde{J}_{\text{SnNi}} / \tilde{J}_{\text{SnSn}}$ and the concentration of Ni in the couples N1-N4 at 1048 K (2 at% Sn). The direct and indirect fluxes can

be evaluated by substituting the values of $\tilde{D}_{ij}^k$ and $\partial C_i / \partial x$ ($i, j = 1, 2$) at the composition of intersection of the diffusion paths for eq. (11). As shown in Fig. 3, the influence of the indirect flux becomes larger with increasing Ni concentration. The relation between $\tilde{J}_{\text{SnNi}} / \tilde{J}_{\text{NiNi}}$ and Sn concentration has the same tendency as that between $\tilde{J}_{\text{SnNi}} / \tilde{J}_{\text{SnSn}}$ and Ni concentration. The values of $\tilde{D}_{\text{SnSn}}^{\text{Cu}}$ and $\tilde{D}_{\text{NiNi}}^{\text{Cu}}$ are positive, and those of $\tilde{D}_{\text{SnNi}}^{\text{Cu}}$ and $\tilde{D}_{\text{NiSn}}^{\text{Cu}}$ are negative (as shown later in Figs. 5(a) to (d)). When the concentration gradients of Sn and Ni have the same signs (see the profiles in Fig. 1(a)),

$$\tilde{J}_{\text{SnSn}} < 0, \quad \tilde{J}_{\text{SnNi}} > 0$$

and

$$\tilde{J}_{\text{NiSn}} > 0, \quad \tilde{J}_{\text{NiNi}} < 0. \quad (12)$$

On the other hand, when the concentration gradients of Ni has an opposite sign to that of Sn (see the profiles in Fig. 1(b)),

$$\tilde{J}_{\text{SnSn}} < 0, \quad \tilde{J}_{\text{SnNi}} < 0$$

and

$$\tilde{J}_{\text{NiSn}} > 0, \quad \tilde{J}_{\text{NiNi}} > 0. \quad (13)$$

In the couples N1 to N4 where the elements of Ni and Sn diffuse into Cu, it is probable that the total flux has ZFP in the high concentration ranges, since the indirect flux has the op-

Fig. 3 Relation between $\tilde{J}_{\text{SnNi}} / \tilde{J}_{\text{SnSn}}$ and Ni concentration for N1-N4 diffusion couples.

Fig. 4 Diffusion paths for diffusion couples annealed at 1048 K.

posite sign to the direct one (eq. (12)) and the magnitude of indirect flux approaches that of the direct flux. On the other hand, in the couples S1 to S7 where the elements of Ni and Sn diffuse into each other, the total flux may rarely has ZFP because of the same sign of the direct and indirect fluxes (eq. (13)).

The diffusion paths for the diffusion couples except N5 at 1048 K are shown in Fig. 4. The diffusion paths bend markedly and show S-shaped curves. The S-shaped diffusion paths have been observed in the Cu-Ni-Zn⁽¹⁶⁾⁽¹⁸⁾, Al-Ag-Zn⁽¹⁹⁾ and Cu-Mn-Zn⁽²⁰⁾ systems. The diffusion paths at the other temperatures are almost similar in shape to those in Fig. 4. The formation of S-shaped diffusion paths is attributed to the large difference between the diffusion rates of Ni and Sn (see in Figs. 1(a) and (b)) and to the presence of the marked interaction between diffusing elements.

2. Concentration and temperature dependence of diffusion coefficients

Reports of the lattice parameter in the Cu-Ni-Sn alloys indicate that the partial molar volumes of these alloys are constant in the concentration range of the present work⁽²¹⁾. Furthermore, since the molar volumes slightly vary with composition⁽²¹⁾⁻⁽²³⁾, the volume change in the diffusion zone is negligible. Therefore, eqs. (4) to (6) can be applied to the α Cu-Ni-Sn system to evaluate the interdiffusion coefficients $\bar{D}_{\text{SnSn}}^{\text{Cu}}$, $\bar{D}_{\text{SnNi}}^{\text{Cu}}$, $\bar{D}_{\text{NiNi}}^{\text{Cu}}$ and $\bar{D}_{\text{NiSn}}^{\text{Cu}}$.

The values of the four diffusion coefficients at 1048 K are listed in Table 3 and the concentration dependence of them are shown in Figs. 5(a) to (d). As mentioned with eqs. (4) and (5),

the two interdiffusion coefficients $\bar{D}_{\text{SnNi}}^{\text{Cu}}$ and $\bar{D}_{\text{NiNi}}^{\text{Cu}}$ can be calculated at the composition corresponding to the maximum or minimum on the concentration profiles in Fig. 1(b). Furthermore, the values of $\bar{D}_{\text{SnSn}}^{\text{Cu}}$ and $\bar{D}_{\text{NiSn}}^{\text{Cu}}$ evaluated from the Darken's couple N5 are also plotted in Figs. 5(a) and (d). Isodiffusion coefficient contours are shown by the broken lines in Figs. 5(a) and (d). The values of $\bar{D}_{\text{SnSn}}^{\text{Cu}}$ and $\bar{D}_{\text{NiNi}}^{\text{Cu}}$ are positive and those of $\bar{D}_{\text{SnNi}}^{\text{Cu}}$ and $\bar{D}_{\text{NiSn}}^{\text{Cu}}$ are negative. The values of $\bar{D}_{\text{SnSn}}^{\text{Cu}}$, $\bar{D}_{\text{SnNi}}^{\text{Cu}}$, $\bar{D}_{\text{NiNi}}^{\text{Cu}}$ and $\bar{D}_{\text{NiSn}}^{\text{Cu}}$ are very sensitive to the solute concentrations. The experimental values of the present work satisfy the thermodynamic conditions for the diffusion coefficients⁽²⁴⁾⁽²⁵⁾, that is,

$$\bar{D}_{11}^3 > 0, \quad \bar{D}_{22}^3 > 0, \quad \bar{D}_{12}^3 \cdot \bar{D}_{21}^3 \geq 0 \quad (14)$$

and

$$\bar{D}_{11}^3 \cdot \bar{D}_{22}^3 - \bar{D}_{12}^3 \cdot \bar{D}_{21}^3 \geq 0. \quad (15)$$

Almost all the direct and indirect coefficients reveal the relations of $\bar{D}_{\text{SnSn}}^{\text{Cu}} > \bar{D}_{\text{NiNi}}^{\text{Cu}} > 0$ and $\bar{D}_{\text{SnNi}}^{\text{Cu}} < \bar{D}_{\text{NiSn}}^{\text{Cu}} < 0$ in the α -phase region of the present system. As shown in eq. (14), the values of $\bar{D}_{12}^3$ and $\bar{D}_{21}^3$ should have the same sign, however, the positive values of $\bar{D}_{\text{NiSn}}^{\text{Cu}}$ are present in the neighborhood of the terminal composition mainly. As already reported⁽²⁶⁾⁽²⁷⁾, their positive values are liable to be induced in the vicinity of the terminal compositions, and in particular, such a tendency is pronounced in the indirect coefficients.

The limiting values of the interdiffusion coefficients on the sides of the ternary $i-j-k$ diagram have been established by Shuck and Tool⁽²⁸⁾. The limiting values of the direct coefficients $\bar{D}_{ii}^k$ are

$$\lim_{C_j \rightarrow 0} \bar{D}_{ii}^k = \bar{D}_{i-k} \quad (16)$$

on the $i-k$ side, where $\bar{D}_{i-k}$ is the diffusion coefficients of the binary $i-k$ system. The direct coefficients $\bar{D}_{\text{SnSn}}^{\text{Cu}}$ and $\bar{D}_{\text{NiNi}}^{\text{Cu}}$ approach the binary coefficients $\bar{D}_{\text{Cu-Sn}}$ and $\bar{D}_{\text{Cu-Ni}}$ ⁽²⁹⁾ on the Cu-Sn and Cu-Ni sides in Figs. 5(a) and (c), respectively.

The limiting values of $\bar{D}_{ii}^k$ are

$$\lim_{C_i \rightarrow 0} \bar{D}_{ii}^k = D_{i(j-k)}^* \quad (17)$$

on the $j-k$ side, where $D_{i(j-k)}^*$ is the impurity

Table 3 Interdiffusion coefficients in Cu-Ni-Sn alloys at 1048 K.

Diffusion couples	Composition (at%)		Interdiffusion coefficient ($10^{-15} \text{ m}^2/\text{s}$)			
	Ni	Sn	$\bar{D}_{\text{SnSn}}^{\text{Cu}}$	$\bar{D}_{\text{SnNi}}^{\text{Cu}}$	$\bar{D}_{\text{NiNi}}^{\text{Cu}}$	$\bar{D}_{\text{NiSn}}^{\text{Cu}}$
N1-S1	0.063	1.8	50	-45	6.7	0.18
N1-S2	0.50	2.7	52	-15	4.9	0.042
N1-S3	0.065	1.8	50	-47	5.6	0.34
N1-S4	0.41	2.6	56	-20	4.7	0.16
N1-S5	1.5	3.7	58	-22	6.6	0.36
N1-S6	1.4	3.6	58	-23	7.5	-0.69
N1-S7	2.6	4.9	71	-33	11	-3.6
N2-S1	0.82	1.5	43	-8.3	2.4	0.27
N2-S2	4.2	2.9	33	-8.5	3.1	-0.55
N2-S3	0.79	1.5	42	-8.2	2.3	0.51
N2-S4	3.4	2.5	45	-13	4.3	-3.0
N2-S5	6.2	3.9	38	-14	5.5	-3.6
N2-S6	6.5	4.1	37	-16	6.3	-3.5
N2-S7	7.1	5.4	39	-23	11	2.3
N3-S1	6.4	1.6	30	-4.7	1.4	2.0
N3-S2	7.1	1.7	16	-2.1	1.5	1.0
N3-S3	7.0	1.7	27	-4.7	1.5	1.0
N3-S4	7.7	1.9	24	-4.6	2.3	-2.3
N3-S5	7.9	1.9	19	-3.5	2.2	-1.8
N4-S1	7.2	0.69	16	-1.1	0.63	1.4
N4-S2	7.2	0.69	14	-0.92	0.62	1.5
N4-S3	8.1	0.77	4.0	-0.11	0.21	5.6
N4-S4	8.1	0.77	17	-1.3	0.61	1.2
N4-S5	8.0	0.76	14	-1.0	0.80	-0.92
N4-S6	11	1.1	13	-1.3	0.38	2.4
S1						
(maximum of Sn)	4.5	1.7	—	-5.9	2.2	—
(minimum of Sn)	1.2	1.5	—	-8.2	2.3	—
S2						
(maximum of Sn)	4.8	2.9	—	-8.0	2.9	—
(minimum of Sn)	1.2	2.7	—	-15	4.5	—
S3						
(maximum of Sn)	6.2	1.7	—	-5.3	1.8	—
(minimum of Sn)	1.3	1.5	—	-7.0	2.0	—
S4						
(maximum of Sn)	6.1	2.7	—	-12	4.2	—
(minimum of Sn)	1.8	2.5	—	-13	4.2	—
S5						
(maximum of Sn)	5.9	3.9	—	-17	6.0	—
(minimum of Sn)	2.1	3.7	—	-20	6.9	—
S6						
(maximum of Sn)	8.7	4.2	—	-14	5.1	—
(minimum of Sn)	1.7	3.6	—	-22	7.1	—
S7						
(maximum of Sn)	9.5	5.5	—	-18	9.0	—
(minimum of Sn)	1.7	4.8	—	-38	12	—

diffusion coefficient of component i in a binary $j-k$ alloy. The values of $D_{\text{Sn}(\text{Cu-Ni})}^*$ can be determined by Hall's method⁽³⁰⁾⁽³¹⁾ at the terminal compositions of the profiles obtained from the Cu-Ni sides of the diffusion couples S1-S7.

Results obtained at 1048 K are shown in Fig. 5(a). The direct coefficients $\bar{D}_{\text{SnSn}}^{\text{Cu}}$ on the Cu-Ni sides correspond to the impurity diffusion coefficients of Sn in the Cu-Ni alloys, $D_{\text{Sn}(\text{Cu-Ni})}^*$. The relations between $D_{\text{Sn}(\text{Cu-Ni})}^*$ and Ni concen-

Fig. 5 Direct and indirect interdiffusion coefficients (a) $\bar{D}_{\text{SnSn}}^{\text{Cu}}$, (b) $\bar{D}_{\text{SnNi}}^{\text{Cu}}$, (c) $\bar{D}_{\text{NiNi}}^{\text{Cu}}$ and (d) $\bar{D}_{\text{NiSn}}^{\text{Cu}}$ at 1048 K.

Fig. 6 Relation between $D_{\text{Sn(Cu-Ni)}}^*$ and Ni concentration.

tration at each temperature are shown in Fig. 6. The logarithm of $D_{\text{Sn(Cu-Ni)}}^*$ decreases linearly with increasing Ni concentration.

In addition, the limiting values of the cross coefficients $\bar{D}_{ij}^k$ are

$$\lim_{C_i \rightarrow 0} \bar{D}_{ij}^k = 0 \quad (18)$$

on the $j-k$ side. The indirect coefficients $\bar{D}_{\text{SnNi}}^{\text{Cu}}$ and $\bar{D}_{\text{NiSn}}^{\text{Cu}}$ approach zero on the Cu-Ni and Cu-Sn sides, respectively, as shown in Figs. 5(b) and (d).

Figure 7 shows the temperature dependence of the direct and indirect coefficients in the Cu-6.0 at%Ni-3.7 at%Sn alloys. A plot of the logarithms of $\bar{D}_{\text{SnSn}}^{\text{Cu}}$, $\bar{D}_{\text{SnNi}}^{\text{Cu}}$, $\bar{D}_{\text{NiNi}}^{\text{Cu}}$ and $\bar{D}_{\text{NiSn}}^{\text{Cu}}$ for the reciprocal of the absolute temperature shows a linear relationship and follows an Arrhenius-type equation.

Fig. 7 Temperature dependence of direct and indirect coefficients in Cu-6.0 at% Ni-3.7 at% Sn alloy.

$$\tilde{D}_{ij}^k = \tilde{D}_0 \exp(-\tilde{Q}_{ij}^k/RT), \quad (i, j = 1, 2) \quad (19)$$

where $\tilde{D}_0$ is the pre-exponential factor, $\tilde{Q}_{ij}^k$ is the activation energy and R is the gas constant. The four interdiffusion coefficients are expressed by

$$\tilde{D}_{SnSn}^{Cu} = 2.1 \times 10^{-5} \times \exp\left(-\frac{175000 \text{ J/mol}}{RT}\right) \text{ m}^2/\text{s}, \quad (20)$$

$$\tilde{D}_{SnNi}^{Cu} = -5.8 \times 10^{-7} \times \exp\left(-\frac{153000 \text{ J/mol}}{RT}\right) \text{ m}^2/\text{s}, \quad (21)$$

$$\tilde{D}_{NiNi}^{Cu} = 1.4 \times 10^{-5} \times \exp\left(-\frac{189000 \text{ J/mol}}{RT}\right) \text{ m}^2/\text{s} \quad (22)$$

and

$$\tilde{D}_{NiSn}^{Cu} = -3.1 \times 10^{-9} \times \exp\left(-\frac{120000 \text{ J/mol}}{RT}\right) \text{ m}^2/\text{s}. \quad (23)$$

The magnitude of the activation energy $\tilde{Q}_{SnSn}^{Cu}$ (175 kJ/mol) in the Cu-6.0 at% Ni-3.7 at% Sn alloys is slightly larger than that of the Cu-4.0

at% Sn alloys (169 kJ/mol⁽³²⁾). The values of $\tilde{Q}_{NiNi}^{Cu}$ (189 kJ/mol) is smaller than that of the Cu-6.0 at% Ni alloys (223 kJ/mol⁽²⁹⁾).

3. Thermodynamic interactions among the diffusing components

Kirkaldy *et al.*⁽³³⁾ have derived the relation between $\tilde{D}_{ij}^3/\tilde{D}_{ii}^3$ and Wagner's interaction parameters, $\epsilon_i^{(j)}$ and $\epsilon_i^{(j)}$.

$$\frac{\tilde{D}_{ij}^3}{\tilde{D}_{ii}^3} = \frac{\{N_i + N_i N_3 \epsilon_i^{(j)}\}}{\{1 - N_j + N_i N_3 \epsilon_i^{(j)}\}}, \quad (24)$$

where N_i , N_j and N_3 are the atom fractions of i , j and 3 components, respectively. For highly dilute solutions, eq. (24) reduces to the relation,

$$\frac{\tilde{D}_{ij}^3}{\tilde{D}_{ii}^3} = \{1 + \epsilon_i^{(j)}\} N_i. \quad (25)$$

The interdiffusion coefficients in the ternary system can be described in a different form by the choice of dependent component of 'solvent'. The dependent component can be changed from superscript 3(Cu) to 2(Ni) by using eq. (26) to (29)⁽³⁴⁾.

$$\tilde{D}_{11}^2 = \tilde{D}_{11}^3 - \bar{V}_1/\bar{V}_2 \tilde{D}_{12}^3, \quad (26)$$

$$\tilde{D}_{13}^2 = -\bar{V}_3/\bar{V}_2 \tilde{D}_{12}^3, \quad (27)$$

$$\tilde{D}_{31}^2 = \bar{V}_1/\bar{V}_3 (\tilde{D}_{22}^3 - \tilde{D}_{11}^3 + \bar{V}_1/\bar{V}_2 \tilde{D}_{12}^3 - \bar{V}_2/\bar{V}_1 \tilde{D}_{21}^3), \quad (28)$$

and

$$\tilde{D}_{33}^2 = \tilde{D}_{22}^3 + \bar{V}_1/\bar{V}_2 \tilde{D}_{12}^3, \quad (29)$$

where $\bar{V}_1$, $\bar{V}_2$ and $\bar{V}_3$ are the partial molar volumes of 1, 2 and 3, respectively.

In Fig. 8(a), the relation between $\tilde{D}_{SnNi}^{Cu}/\tilde{D}_{SnSn}^{Cu}$ and Sn concentration is shown. The values of $\tilde{D}_{SnSn}^{Ni}$ and $\tilde{D}_{SnCu}^{Ni}$ can be calculated by eqs. (26) and (27), and the relation between $\tilde{D}_{SnCu}^{Ni}/\tilde{D}_{SnSn}^{Ni}$ and Sn concentration is shown in Fig. 8(b). The values of $\bar{V}_1$, $\bar{V}_2$ and $\bar{V}_3$ calculated from the data of the lattice parameters are 10.6 , 6.60 and $7.11 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$, respectively⁽²¹⁾. The solid lines in Figs. 8(a) and (b) are drawn by eq. (25) with the values of $\epsilon_1^{(2)} = -11$ ($1=\text{Sn}$, $2=\text{Ni}$) and $\epsilon_1^{(3)} = 6.5$ ($1=\text{Sn}$, $3=\text{Cu}$). The experimental values fall on these straight lines, and they

Fig. 8(a) Relation between $\tilde{D}_{\text{SnNi}}^{\text{Cu}} / \tilde{D}_{\text{SnSn}}^{\text{Cu}}$ and Sn concentration at 1048 K.

Fig. 8(b) Relation between $\tilde{D}_{\text{SnCu}}^{\text{Ni}} / \tilde{D}_{\text{SnSn}}^{\text{Ni}}$ and Sn concentration at 1048 K.

satisfy eq. (25) in the dilute range from 0 to about 5 at% Sn. The values of $\epsilon_2^{(3)}$ have been determined in the same manner. In this way, the interaction parameters can be estimated from the ratios of the indirect coefficients to the direct ones. The negative values of $\tilde{D}_{\text{SnNi}}^{\text{Cu}}$ and $\tilde{D}_{\text{NiSn}}^{\text{Cu}}$ indicate that the activities of Sn and Ni decrease with Ni and Sn concentrations, respectively. The interaction parameters in the Cu-Ni-Sn system at 1048 K are listed in Table 4 with the values⁽¹⁶⁾⁽¹⁸⁾ in the Cu-Ni-Zn system. Since the interaction parameter $\epsilon_{\text{Sn}}^{(\text{Ni})}$ has a large negative value, and $\epsilon_{\text{Sn}}^{(\text{Cu})}$ and $\epsilon_{\text{Ni}}^{(\text{Cu})}$ have positive values, it is expected that the interaction energy of the Ni-Sn bond is much larger than the values for the Cu-Sn and Cu-Ni bonds. Table 4 indicates that the magnitude of the attractive force in the Ni-Sn bond is larger than

Table 4 Interaction parameters in Cu-Ni-Sn alloys at 1048 K, including results of Cu-Ni-Zn alloys at 1048 and 1133 K.

	$\epsilon_1^{(2)}$	$\epsilon_1^{(3)}$	$\epsilon_2^{(3)}$
Cu-Ni-Sn system	-11	6.5	4
Cu-Ni-Zn system	-3.5*	1**	3**

*1048 K⁽¹⁸⁾ **1133 K⁽¹⁶⁾

that of the Ni-Zn bond. These reasoning can be understood from the presence of relatively many intermetallic compounds, such as Ni_3Sn and so on in a constitution diagram⁽³⁵⁾ of Ni-Sn system. Since a mixing enthalpy ΔH in liquid Cu-Ni-Sn alloys has negative values at the compositions except the vicinity of the Cu-Ni side⁽³⁶⁾, the alloys have a tendency to form the equilibrium $(\text{Cu-Ni})_3\text{Sn}$ phase and so on⁽³⁷⁾. If we assume that this fact is applicable to the solid Cu-Ni-Sn alloys, it is expected that Ni atoms of Ni-Sn bonds are partly substituted by the Cu atoms in the proximity of the Ni-Sn bonds. Hence, it suggests that the probability of the Cu-Ni-Sn bonds may exist in the alloys.

IV. Summary

The interdiffusion experiment and the study of thermodynamic interactions among the diffusion elements in α Cu-Ni-Sn alloys have been performed in the temperature range from 1023 to 1123 K. The results are summarized as follows.

(1) The concentration profiles indicate that the diffusion rate of Sn is greater than that of Ni in the Cu-Ni-Sn alloy. The influence of the indirect flux becomes larger with increasing Ni concentration. The interdiffusion fluxes show that the zero flux planes are present in the diffusion zone of Cu-Ni-Sn couples. The diffusion paths bend markedly because of the difference between the diffusion rates of Ni and Sn.

(2) The direct coefficients $\tilde{D}_{\text{SnSn}}^{\text{Cu}}$ and $\tilde{D}_{\text{NiNi}}^{\text{Cu}}$ are positive, and the indirect coefficients $\tilde{D}_{\text{SnNi}}^{\text{Cu}}$ and $\tilde{D}_{\text{NiSn}}^{\text{Cu}}$ are negative. The four interdiffusion coefficients are very sensitive to the solute concentration. The temperature dependence of $\tilde{D}_{\text{SnSn}}^{\text{Cu}}$, $\tilde{D}_{\text{SnNi}}^{\text{Cu}}$, $\tilde{D}_{\text{NiNi}}^{\text{Cu}}$ and $\tilde{D}_{\text{NiSn}}^{\text{Cu}}$ at the composition of Cu-6.0 at% Ni-3.7 at% Sn can be expressed by the following equations.

$$\begin{aligned}\tilde{D}_{\text{SnSn}}^{\text{Cu}} &= 2.1 \times 10^{-5} \\ &\times \exp \left(-\frac{175000 \text{ J/mol}}{RT} \right) \text{ m}^2/\text{s},\end{aligned}$$

$$\begin{aligned}\tilde{D}_{\text{SnNi}}^{\text{Cu}} &= -5.8 \times 10^{-7} \\ &\times \exp \left(-\frac{153000 \text{ J/mol}}{RT} \right) \text{ m}^2/\text{s},\end{aligned}$$

$$\begin{aligned}\tilde{D}_{\text{NiNi}}^{\text{Cu}} &= 1.4 \times 10^{-5} \\ &\times \exp \left(-\frac{189000 \text{ J/mol}}{RT} \right) \text{ m}^2/\text{s}\end{aligned}$$

and

$$\begin{aligned}\tilde{D}_{\text{NiSn}}^{\text{Cu}} &= -3.1 \times 10^{-9} \\ &\times \exp \left(-\frac{120000 \text{ J/mol}}{RT} \right) \text{ m}^2/\text{s}.\end{aligned}$$

(3) From the estimated values of interaction parameters, it is concluded that the interaction energy of the Ni-Sn bond is much larger than those of the Cu-Sn and Cu-Ni bonds.

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REFERENCES

- (1) K. Hirano: Bulletin Japan Inst. Metals, **6** (1967), 856 (in Japanese).
- (2) D. B. Butrymowicz, J. R. Manning and M. E. Read: Incra Monograph V The Metallurgy of Copper, Diffusion Rate Data and Mass Transport Phenomena for Copper Systems, Diffusion in Metals Data Center, Metallurgy Division, Institute for Materials Research, National Bureau of Standards, Washington, D.C., USA, (1977), p. 18.
- (3) K. Hirano: Bulletin Japan Inst. Metals, **7** (1968) 34 (in Japanese).
- (4) K. Hirano: Foudamentals and Application of Diffusion, Seminar Text of the Japan Inst. Metals, Japan, (1984), p. 1, (in Japanese).
- (5) C. Matano: Japan J. Phys., **8** (1933), 109.
- (6) J. S. Kirkaldy: Can. J. Phys., **35** (1957), 435.
- (7) M. L. Mehta and H. J. Axon: Acta Met., **3** (1955), 538.
- (8) J. Eash and C. Upthegrove: Trans. AIME, **104** (1933), 221.
- (9) L. S. Darken: Trans. AIME, **180** (1949), 430.
- (10) J. B. Murphy: Acta Meta., **9** (1961), 563.
- (11) I. Uchiyama, A. Watanabe and S. Kimoto: X-ray Micro Analyser, Nikkan Kogyo Newspaper Co., Tokyo, Japan, (1974) p. 127.
- (12) Y. Tezuka and A. Kimoto; J. Japan Inst. Light Met., **34** (1984), 301 (in Japanese).
- (13) J. S. Kirkaldy, J. E. Lane and G. R. Masson: Can. J. Phys., **41** (1963), 2174.
- (14) M. Yokota, R. Harada and H. Mitani: J. Japan Inst. Metals, **43** (1979), 799 (in Japanese).
- (15) R. D. Sisson, Jr. and M. A. Dayananda: Met. Trans., **8A** (1977), 1849.
- (16) T. Takahashi, M. Kato, Y. Minamino and T. Yamane: Met. Sci., **18** (1984), 580.
- (17) M. A. Dayananda and C. W. Kim: Met. Trans., **10A** (1979), 1333.
- (18) T. Takahashi, M. Kato, Y. Minamino and T. Yamane: Z. Metallk., **74** (1983), 727.
- (19) Y. Minamino, T. Yamane, K. Tsukamoto, J. Takahashi and H. Kimura: Trans. Japan Inst. Metals, **25** (1984), 142.
- (20) T. Takahashi, M. Kato, Y. Minamino and T. Yamane: J. Japan Inst. Metals, **50** (1986), 243 (in Japanese).
- (21) W. B. Pearson: A Handbook of Lattice Spacings and Structures of Metals and Alloys, Pergamon Press, New York, (1958), p. 597.
- (22) T. Sogabe, T. Takahashi and T. Ouchi: Memoirs of Niihama Technical College, **17** (1981), 63 (in Japanese).
- (23) M. Miki, T. Sogabe and S. Hori: J. Japan Inst. Metals, **46** (1982), 307 (in Japanese).
- (24) J. S. Kirkaldy, D. Weichert and Zia-Ul-Haq: Can. J. Phys., **41** (1963), 2166.
- (25) J. S. Kirkaldy: Isothermal Diffusion in Multicomponent Systems, Advances in Materials Research, (Ed. H. Hermam), Interscience, New York, (1970), p. 60.
- (26) T. R. Heyward and J. I. Goldstein: Met. Trans., **4** (1973), 2335.
- (27) G. W. Roper and D. P. Whittle: Met. Sci., **14** (1980), 21.
- (28) F. O. Shuck and H. L. Tool: J. Phys. Chem., **67** (1963), 540.
- (29) G. Brunel, G. Cizeron and P. Lacombe: CR Acad. Sci., **C269** (1969), 895.
- (30) L. D. Hall: J. Chem. Phys., **21** (1953), 87.
- (31) A. Vignes and J. P. Sabatier: Trans. AIME, **245** (1969), 1795.
- (32) K. Hoshino, Y. Iijima and K. Hirano: Trans. Japan Inst. Metals, **21** (1980), 674.
- (33) J. S. Kirkaldy, Zia-Ul-Haq and L. C. Brown: ASM Trans. Q., **56** (1963), 834.
- (34) A. Brunsch and S. Steeb: Z. Metallk., **65** (1974), 765.
- (35) M. Hansen and K. Anderko: Constitution of Binary Alloys, (2nd Ed.), McGraw-Hill Book Co., New York, (1958), p. 1042.
- (36) M. J. Pool, I. Arpshofen, B. Predel and E. Schultheiß: Z. Metallk., **70** (1979), 1042.
- (37) R. Watanabe: Precipitation in Alloys, Maruzen, Japan, (1972), p. 223 (in Japanese).