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Intermetallics Disappearance Rates and Intrinsic Diffusivities Ratios Analysis in the Cu-Zn and the Cu-Sn Systems

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Intermetallics disappearance rates and intrinsic diffusivities ratios in the Cu-Zn system at temperature 400 °C and in the Cu-Sn system at temperatures from 190 °C to 250 °C are analyzed theoretically using literature experimental data. Diffusion activation energies and pre-exponential coefficients for the Cu-Sn system are calculated combining literature experimental results.

Keywords: diffusion, intermetallics, phases formation kinetics, copper, zinc, tin, Kirkendall-Frenkel porosity, Kirkendall shift.

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Introduction

A theoretical method to describe intermetallics disappearance rate in double multiphase systems was proposed in [1], and intermetallics disappearance rates in the Al-Cu system at temperatures from 175 °C to 225 °C were analyzed. Ref. 2 reported on another theoretical method of calculation the ratio of intrinsic diffusivities in double multiphase systems, and intrinsic diffusivities ratios of copper and aluminum in the Al-Cu system were calculated at temperatures from 400 °C to 535 °C and at temperatures less than 100°C. Both methods are confirmed experimentally during the investigation the Cu-Zn system at temperature 400 °C [5, 8].

The soldered copper/tin based contacts are the weakest part of the chip that can be related to intermetallics and the Kirkendall-Frenkel porosity formation in the contact zone [3, 4, 7]. One of the most common reasons for chip failure is the soldered. The typical range of packaging and operation of the integrated circuits is from room temperature up to 250 °C [32]. Therefore, it is very important to analyze the intermetallics disappearance rates and intrinsic diffusivities ratios in the Cu-Sn systems at temperatures from 190 °C to 250 °C .

I. Intermetallics disappearance rate analysis

I.1. The Zn-Cu system

We didn't analyze intermetallics disappearance rate in the Zn-Cu system [5, 8], so we can do it now. Three phases (ϵ -brass, Zn_5Cu , $C_1 \approx 0.83$; γ -brass, Zn_8Cu_5 , $C_2 \approx 0.62$; and β -brass, $ZnCu$, $C_3 \approx 0.5$, $C = C_{Zn}$) are formed during diffusion. Reaction rates of phases formation at temperature 400 °C were measured: $K_1 \approx 2025 \mu m^2/h$, $K_2 \approx 14400 \mu m^2/h$, $K_3 \approx 160 \mu m^2/h$, $K_2 \approx 7K_1$, $K_3 \approx 0,08K_1 \approx 0,011K_2$. Initial Zn covering thickness was $X_A \approx 115 \mu m$. Eqs.9 in [1] give:

$$K_{123} = \left(\sqrt{K_1} + \sqrt{K_2} + \sqrt{K_3} \right)^2 \approx 31500 \mu m^2/h,$$

$$K_{12} = \left(\sqrt{K_1} + \sqrt{K_2} \right)^2 \approx 27200 \mu m^2/h$$

($K_3 \ll K_1$ and $K_3 \ll K_2$). Zinc disappearance time, t_0 , at temperature 400°C can be estimated by Eq.11 [1]:

$$t_0 = \frac{X_{Zn}^2}{(C_1\sqrt{K_1} + C_2\sqrt{K_2} + C_3\sqrt{K_3})^2} \approx 0.94h \approx \frac{X_{Zn}^2}{C_1^2 K_{12}} \approx 0.7h. \quad (1)$$

The value $t_0=0.94h$ exactly corresponds with the experimentally obtained one [8] $t_0=0.92h$ in planar

samples. Phase 1 (ϵ -brass, Zn_5Cu) disappearance time, t_1 , can be estimated by Eq.13 [1]:

$$t_1 = \frac{X_{Zn}^2}{(C_2\sqrt{K_2^{(2\text{phases})}} + C_3\sqrt{K_3^{(2\text{phases})}})^2} \approx 2h \approx \frac{X_{Zn}^2}{C_2^2 K_{12}} \approx 1.3h. \quad (2)$$

Such values correspond to experimental result [8]: $t_1 = 1.64 h$ in cylindrical samples.

$$\tilde{D}_2^* = 1.55 \times 10^{-8} e^{-64.9 kJmol^{-1}/(RT)} m^2 / s, \quad (4)$$

and for phase 1 only (Cu/Cu₆Sn₅ sample) between 630 K and 677 K (357 °C and 404 °C):

$$\tilde{D}_1^{*(1\text{phase})} = 1.09 \times 10^{-6} e^{-78.2 kJmol^{-1}/(RT)} m^2 / s. \quad (5)$$

I.2. The Cu-Sn system

Two phases are formed in the Cu-Sn system during isothermal annealing of Cu/Sn samples at temperature $T = 200$ °C [3, 6, 9]: ϵ -phase Cu₃Sn (phase 1, $C_1 \approx 3/4 = 0.753$, $\Delta C_1 = 0.012$, $C = C_{Cu}$ [6]) and η -phase Cu₆Sn₅ (phase 2, $C_2 \approx 6/11 = 0.547$, $\Delta C_2 = 0.021$, $C = C_{Cu}$ [6]), at temperature $T = 210$ °C [10], and at temperature $T = 250$ °C (Sn is liquid) [11]. Parabolic growth constants for the layer thicknesses were measured in [6], also the range of homogeneity of each phase were measured, and the values of the mutual diffusion coefficients for the Cu₃Sn (phase 1) and Cu₆Sn₅ (phase 2) phases between 463 K and 493 K (190 °C and 220 °C) were calculated too:

$$\tilde{D}_1^* = 1.43 \times 10^{-8} e^{-70.7 kJmol^{-1}/(RT)} m^2 / s, \quad (3)$$

We can calculate the mutual diffusion penetrability (or Wagner diffusivity [26]) of each phase, D_i , taking into account that $D_i = D_i^* \Delta C_i$ and ΔC_i depends on temperature [6]:

$\Delta C_1 = 0.014$ (190 °C) = 0.018 (210 °C) = 0.010 (220 °C), $\Delta C_2 = 0.023$ (190 °C) = 0.022 (210 °C) = 0.017 (220 °C), $\Delta C_1^{(1\text{phase})} = 0.005$ (357 °C). Mutual diffusion penetrabilities of phase 1 can be calculated by Gibbs's method [12] or by "constant flux method" (Gurov's and Gusak's method) [13-23] or by other methods [26, 28-30] (data are from [6] as an example):

$$D_1 \approx \frac{1}{2} C_1 (1 - C_1) K_1 \approx \frac{3}{32} K_1 \approx 2.5 \times 10^{-18} m^2 / s \approx \left\{ 2.1 \times 10^{-18} m^2 / s [6], T = 190^\circ C \right\}. \quad (6)$$

Mutual diffusion penetrabilities of phase 1 and phase 2 can be calculated by "constant flux method" (data are

from [9] as an example):

$$D_1 \approx \frac{1}{2} (C_1 (1 - C_1) K_1 + C_2 (1 - C_1) \sqrt{K_1 K_2}) \approx \approx \frac{3}{32} K_1 + \frac{3}{44} \sqrt{K_1 K_2} \approx 29.4 \times 10^{-18} m^2 / s \approx \left\{ 19.4 \times 10^{-18} m^2 / s [9] \right\}; \quad (7)$$

$$D_2 \approx \frac{1}{2} (C_2 (1 - C_2) K_2 + C_2 (1 - C_1) \sqrt{K_1 K_2}) \approx \approx \frac{15}{121} K_2 + \frac{3}{44} \sqrt{K_1 K_2} \approx 53.6 \times 10^{-18} m^2 / s \approx \left\{ 56.4 \times 10^{-18} m^2 / s [9] \right\}, \quad (8)$$

so we can see a good agreement between applied methods (Table 1).

Initial Cu layer thickness [3] can be calculated using mass conservation law (Fig. 1):

$$X_{Cu}(t=0) \approx 5 \mu m + C_1 X_1(t) + C_2 X_2(t) \approx 12.4 \mu m.$$

Copper layer disappearance time can be calculated using Eq. 1 (Fig. 2):

Table 1

Comparison of diffusion penetrabilities calculated by different methods

Authors	$T, ^\circ C$	t, h	$K_1, \times 10^{-18} m^2/s$	$K_2, \times 10^{-18} m^2/s$	$\frac{K_2}{K_1}$	$D_1, \times 10^{-18} m^2/s$	$D_2, \times 10^{-18} m^2/s$	$\frac{D_2}{D_1}$	$K_1^{(1phase)}, \times 10^{-18} m^2/s$ Cu/Cu ₆ Sn ₅ couple	$K_2^{(1phase)}, \times 10^{-18} m^2/s$ Cu ₃ Sn/Sn couple
Onishi and Fujibuchi [6]	190	400	27.2	88.2	3.2	2.1	18	8.6	-	-
	200	400	38.4	112	2.9	2.6	23.5	9.0	-	-
	210	400	52.1	142	2.7	5.7	34.4	6	-	-
	220	400	74.1	204	2.75	4.5	37	8.2	-	-
	357	16	-	-	-	-	-	-	26900 $D_1^{(1phase)} =$ 1800	-
This work	190	-	-	-	-	6	14.3	2.4	-	-
	200	-	-	-	-	8.1	18.3	2.2	-	-
	210	-	-	-	-	10.7	23.5	2.2	-	-
	220	-	-	-	-	15.3	33.7	2.2	-	-
	357	-	-	-	-	-	-	-	$D_1^{(1phase)} =$ 1500	-
Paul <i>et al.</i> [9]	200	225	100	332	3.3	19.4	56.4	2.9	-	-
This work	-	-	-	-	-	29.4	53.6	1.8	-	-
Kumar <i>et al.</i> [3]	200	240	20	72	3.6	2.5	18.2	7.2	184	-
This work	-	-	-	-	-	4.5	11.5	2.6	$D_1^{(1phase)} =$ $10.3 \approx D_2$	-
Liashenko <i>et al.</i> [11]	250	8	820	6600	8.0	-	-	-	-	10270
This work	-	-	-	-	-	236	975	4.1	-	$D_2^{(1phase)} =$ $764 \approx D_2$

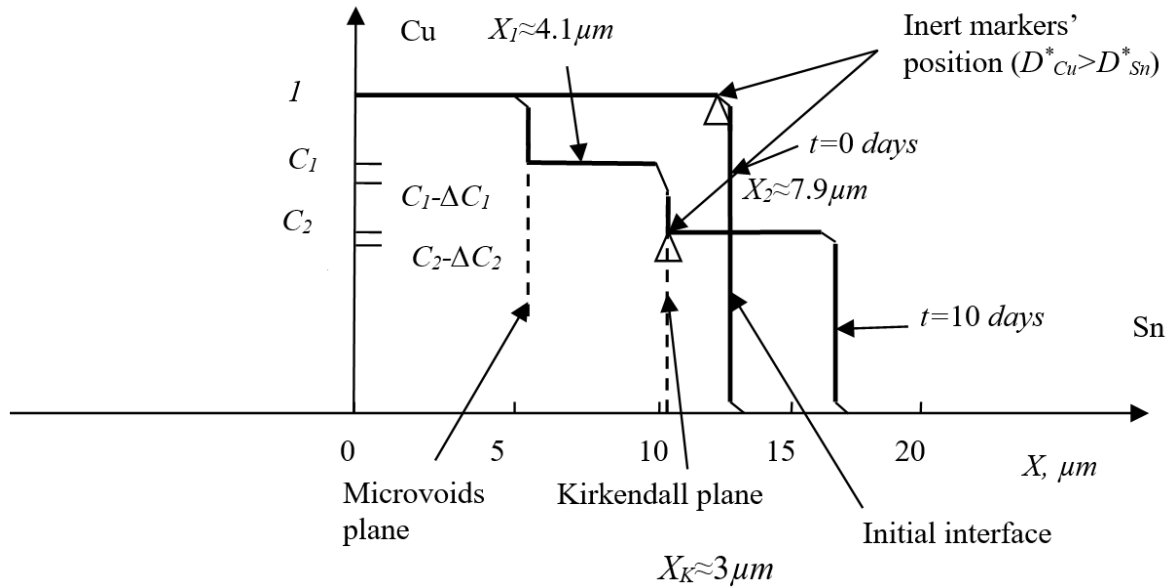


Fig. 1. Change of copper concentration profile during isothermal annealing of a Cu(99.9 %)/Sn couple at temperature $T = 200^\circ C$ within 10 days [3]: $D_{Cu}^* > D_{Sn}^*$, $D_{Sn}^* \approx 0.31 D_{Cu}^*$; $X_I < X_2$,

$$X_2 \approx 2X_I, X_K \approx 3\mu m; C_1 = 3/4; C_2 = 6/11, C = C_{Cu}.$$

$$t_0 = \frac{X_{Cu}^2}{(C_1 \sqrt{K_1} + C_2 \sqrt{K_2})^2} \approx \frac{154 \times 10^{-12} m^2}{6.4 \times 10^{-17} m^2/s} \approx 28 \text{ days}.$$

Phase 2 is formed between phase 1 and tin after disappearance of Cu, phase 1 homogenization occur after this time, concentration decreases from C_1 to $C_1 - \Delta C_1$, and

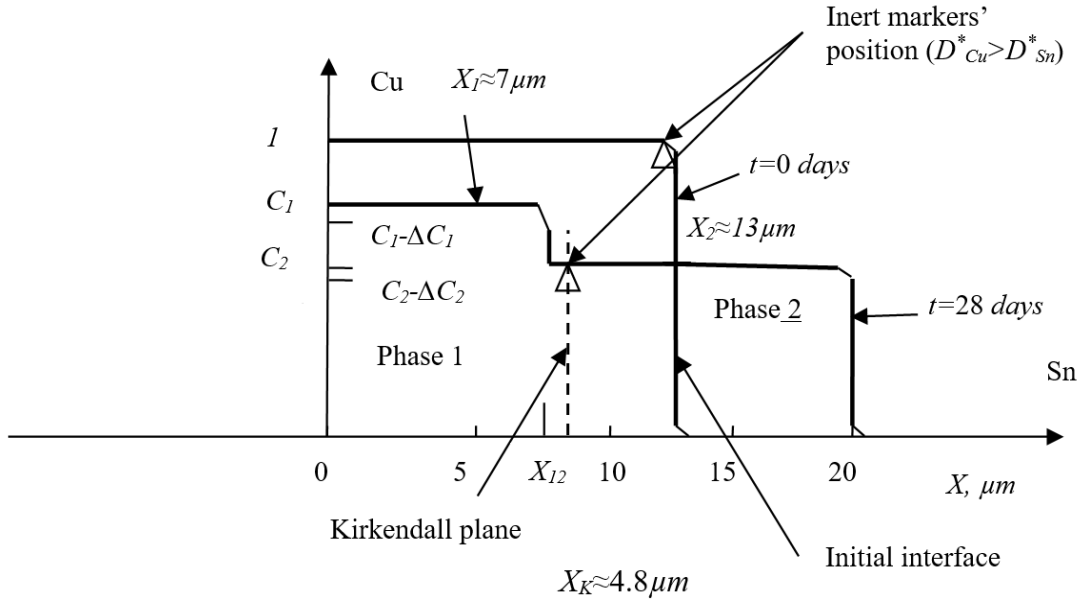


Fig. 2. Change of copper concentration profile during isothermal annealing at temperature $T = 200^\circ\text{C}$ within 28 days (calculation): $D_{Cu}^* > D_{Sn}^*$; $X_1 < X_2$; $X_2 \approx 2X_1$; $X_K \approx 4.8\mu\text{m}$; $C_1 = 3/4$; $C_2 = 6/11$, X_{12} is boundary between phase 1 and phase 2.

boundary between phase 1 and phase 2, X_{12} , moves to the left hand direction (see Fig. 2). The boundary moves to the left hand direction also after full homogenization

of phase 1. We can calculate assuming $C_1 = 3/4$ and $C_2 = 6/11$ and taking into account Eq. 6:

$$D_2^{(1\text{phase})} \approx \frac{C_2(C_1 - C_2)K_2^{(1\text{phase})}}{2C_1} \approx \frac{9}{121} K_2^{(1\text{phase})} \approx 764 \times 10^{-18} \text{ m}^2 / \text{s} \approx D_2^{(2\text{phases})}, \quad (9)$$

as should be expected. Phase 1 layer disappearance time can be calculated using Eq. 2 (Fig. 3):

$$t_1 = \frac{X_{Cu}^2}{C_2^2 K_2^{(1\text{phase})}} \approx 39 \text{ days}.$$

Phase 2 homogenization occur after this time, concentration decreases from C_2 to $C_2 - \Delta C_2$, and boundary between phase 2 and Sn moves to the left hand direction.

1.3. The Sn-Cu system

We can analyze experimental results in the Sn-Cu

system described in [11] (Fig. 4).

Two phases are formed in the Cu-Sn system during isothermal annealing of Cu/Sn samples at temperature $T = 250^\circ\text{C}$ during $t = 8 \text{ h}$ (Sn is liquid): $X_1 = 3.97 \mu\text{m}$, $X_2 = 12.75 \mu\text{m}$; $K_1 = 8.2 \times 10^{-16} \text{ m}^2/\text{s}$, $K_2 = 6.6 \times 10^{-15} \text{ m}^2/\text{s}$; $C_2 = 5/11$, $C_1 = 1/4$, $C = C_{Sn}$. The thickness of tin layer over the Cu and Cu_3Sn substrates varied from 20 to 200 μm . General phases formation rate can be calculated by Eqs. 9 in [1]:

$$K_{12} = \left(\sqrt{K_1^{(2\text{phases})}} + \sqrt{K_2^{(2\text{phases})}} \right)^2 = 12065 \times 10^{-18} \text{ m}^2 / \text{s} \approx K_2^{(1\text{phase})} = 10268 \times 10^{-18} \text{ m}^2 / \text{s}, \quad (10)$$

so phase 2 growth rate, $K_2^{(1\text{phase})}$, is approximately equal to initial general growth rate, K_{12} (Table 1). The disappeared Sn thickness can be estimated: $X_{Sn}(8h) = C_1 X_1(8h) + C_2 X_2(8h) \approx 6.8 \mu\text{m}$. Tin layer disappearance time can be calculated using Eq.1:

$$t_0(X_{Sn} = 20\mu\text{m}) = \frac{X_{Sn}^2}{(C_1 \sqrt{K_1} + C_2 \sqrt{K_2})^2} \approx 57h \approx 2.4 \text{ days};$$

$$t_0(X_{Sn} = 200\mu\text{m}) = \frac{X_{Sn}^2}{(C_1 \sqrt{K_1} + C_2 \sqrt{K_2})^2} \approx 240 \text{ days} \approx 8 \text{ months}.$$

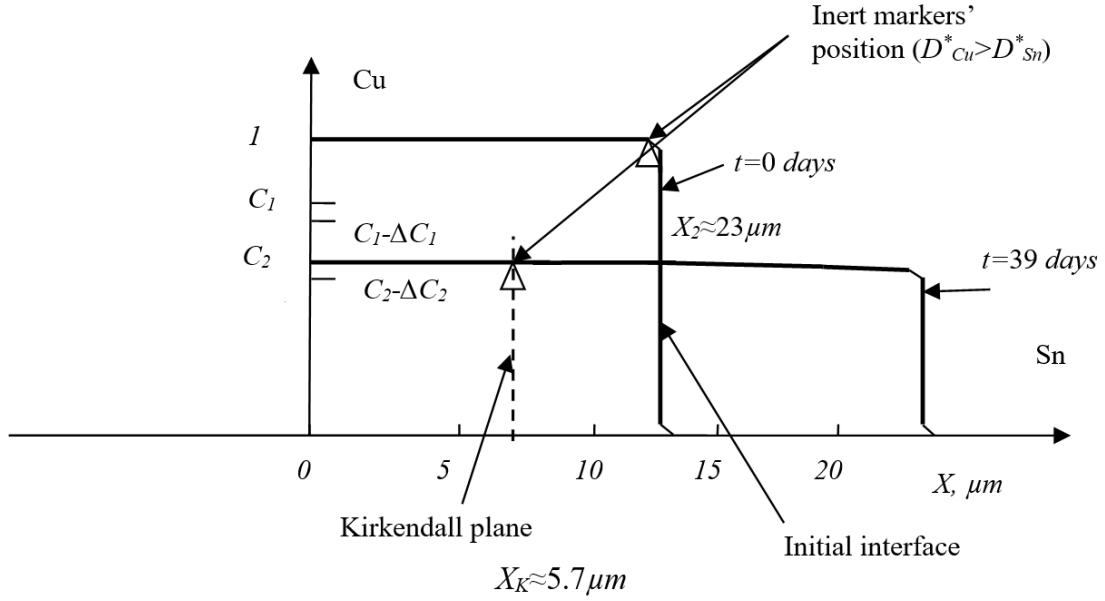


Fig. 3. Change of copper concentration profile during isothermal annealing at temperature $T = 200\text{ }^{\circ}\text{C}$ within 39 days (calculation): $D_{Cu}^* > D_{Sn}^*$; $X_2 \approx 23\mu\text{m}$; $X_K \approx 5.7\mu\text{m}$; $C_2 = 6/11 \approx 0.55$.

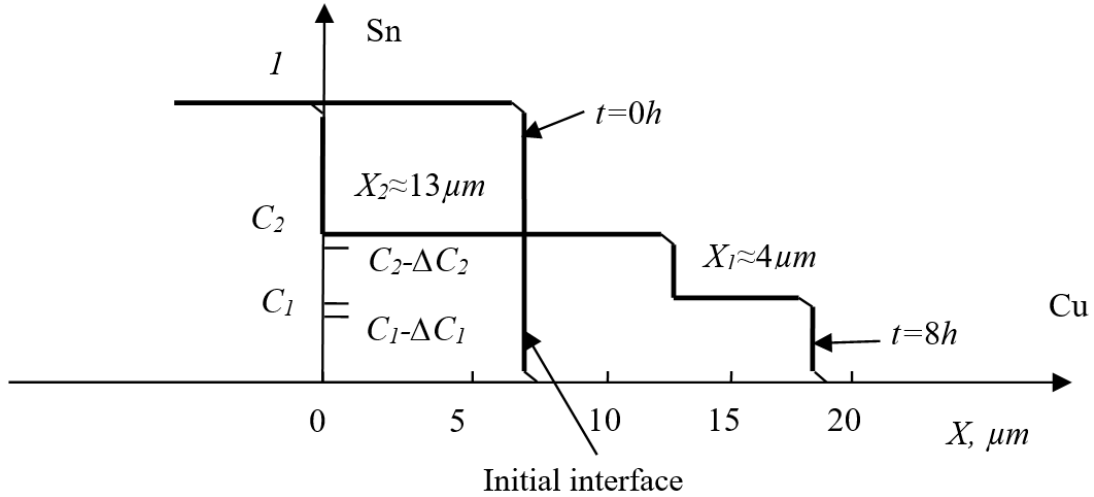


Fig. 4. Concentration profile of Sn change during isothermal annealing of a Cu (99.99 % purity)/Sn couple at temperature $T = 250^{\circ}\text{C}$ within 8h [11]: $X_2 = 12.75\mu\text{m}$, $X_1 = 3.97\mu\text{m}$, $X_2 \approx 3X_1$, $C_2 = 5/11$, $C_1 = 1/4$, $C = C_{Sn}$.

II. Intrinsic Diffusivities Ratio Analysis

II.1. The Zn-Cu system

We didn't analyze intrinsic diffusivities ratio in the Zn-Cu system [5], so we can do it now. Three phases can be formed: Zn_5Cu (phase 1, $C_1 \approx 0.83$), Zn_8Cu_5 (phase 2, $C_2 \approx 0.62$), and ZnCu (phase 3, $C_3 \approx 0.5$, $C = C_{Zn}$) (Fig. 5). Inert markers were in phase 2. Mutual diffusion coefficient in phase 2, D_2^* , and Kirkendall shift, X_K , were measured at $T = 400^{\circ}\text{C}$: $D_2^* = 9.1 \times 10^{-12}\text{ m}^2/\text{s}$, $t = 9\text{h}$, $X_K \approx 150\mu\text{m}$. Ratio of intrinsic diffusivities can be calculated in such a way (Eq.16 in [2]):

$$\frac{D_{Cu}^*}{D_{Zn}^*} \approx \frac{\sum_{j=1}^N X_j - X_K(1-C_i)\sqrt{\pi}}{\sum_{j=1}^N X_j + C_i X_K \sqrt{\pi}} \approx 0.56 < 1, \quad (11)$$

$$C_i = 8/13 = C_{Zn},$$

where $N = 3$ is formed phases quantity, X_j is phase j 's thickness, C_i is the average concentration of Zn in phase i , or (Eq.15 in [2]):

$$\frac{D_{Cu}^*}{D_{Zn}^*} = \frac{\sqrt{D_2^* t} - X_K(1-C_2)\sqrt{\pi}}{\sqrt{D_2^* t} + C_2 X_K \sqrt{\pi}} \approx 0.62. \quad (12)$$

Experimentally obtained ratio $D_{Cu}^*/D_{Zn}^* \approx 0.6$ in α -brass [24] and in γ -brass [25], so Eqs. 11 and 12 can be applied for other systems.

II.2. The Cu-Sn system

Another experiment was described in [3]. Phase 1 is formed between Cu and phase 2 during isothermal annealing at temperature $T = 200\text{ }^{\circ}\text{C}$ within 10 days: $X_1 \approx 12.6\mu\text{m}$, $X_K \approx 4.9\mu\text{m}$; $C_1 = 3/4$, $C_2 = 6/11$. The mutual diffusion penetrability of phase 1 can be calculated by

Eq. 6:

$$K_1^{(1\text{phase})} = \frac{X_1^2}{t} \approx 184 \times 10^{-18} \text{ m}^2/\text{s} \approx \frac{2(1-C_2)D_1^*\Delta C_1}{(1-C_1)(C_1-C_2)},$$

$$D_1 \approx \frac{(1-C_1)(C_1-C_2)}{2(1-C_2)} \frac{X_1^2}{t} \approx 10.3 \times 10^{-18} \text{ m}^2/\text{s}, \quad (13)$$

$D_1^* = D_1/\Delta C_1 \approx D_1/0.012$ [6] $\approx 860 \times 10^{-18} \text{ m}^2/\text{s}$. Ratio D_{Sn}^*/D_{Cu}^* in phase 1 can be calculated:

$$\frac{D_{Sn}^*}{D_{Cu}^*} \approx \frac{\sum_{j=1}^N X_j - X_K(1-C_1)\sqrt{\pi}}{\sum_{j=1}^N X_j + C_1 X_K \sqrt{\pi}} \approx 0.74 < 1,$$

$$C_1 = 3/4 = C_{Cu}, \quad N = 2. \quad (14)$$

Experimentally determined value in phase 1 according [3] is : $D_{Sn}^* \approx 0.4 \div 0.5 D_{Cu}^*$. Ref. [9] reported that Cu has a higher tracer diffusion coefficient than Sn in the Cu_3Sn phase (phase 1) at temperatures from 225 °C to 350 °C. Ratio D_{Sn}^*/D_{Cu}^* in phase 2 can also be calculated ($X_K \approx 3\mu\text{m}$):

$$D_2^* = D_2/\Delta C_2 \approx 18.2 \times 10^{-18} \text{ m}^2/\text{s} / 0.021$$
 [6] $\approx 870 \times 10^{-18} \text{ m}^2/\text{s}$,

$$\frac{D_{Sn}^*}{D_{Cu}^*} \approx \frac{\sum_{j=1}^N X_j - X_K(1-C_2)\sqrt{\pi}}{\sum_{j=1}^N X_j + C_2 X_K \sqrt{\pi}} \approx 0.8 < 1,$$

$$C_2 = 6/11 = C_{Cu}, \quad N = 2. \quad (15)$$

Experimentally determined value is as follows [3]: $D_{Sn}^* \approx 0.31 D_{Cu}^*$ in phase 2. Otherwise, according [6, 9] the diffusivity of Sn is higher than the diffusivity of Cu at temperatures 150 °C \div 220 °C, and markers moves toward Sn side in phase 2. More precise estimation of ratio D_{Sn}^*/D_{Cu}^* in phase 2 needs careful experiments under hydrostatic pressure of Argon gas (≈ 10 MPa) [5, 8] or under hot isostatic pressing ($p \approx 100$ MPa, Argon) to decrease Kirkendal-Frenkel porosity formation [33].

III. Diffusion activation energy calculation in the Cu-Sn system

We can calculate the diffusion activation energies and the pre-exponential factors combining experimental results at the temperature $T_2 = 357$ °C [6] and experimental results at the temperature $T_1 = 200$ °C [3] and combining experimental results at the temperature $T_2 = 250$ °C [11] and experimental results [3, 9, 6] at the temperature $T_1 = 200$ °C (Table 2):

$$Q_i = \frac{RT_1 T_2}{T_2 - T_1} \ln \left(\frac{D_i(T_2)}{D_i(T_1)} \right),$$

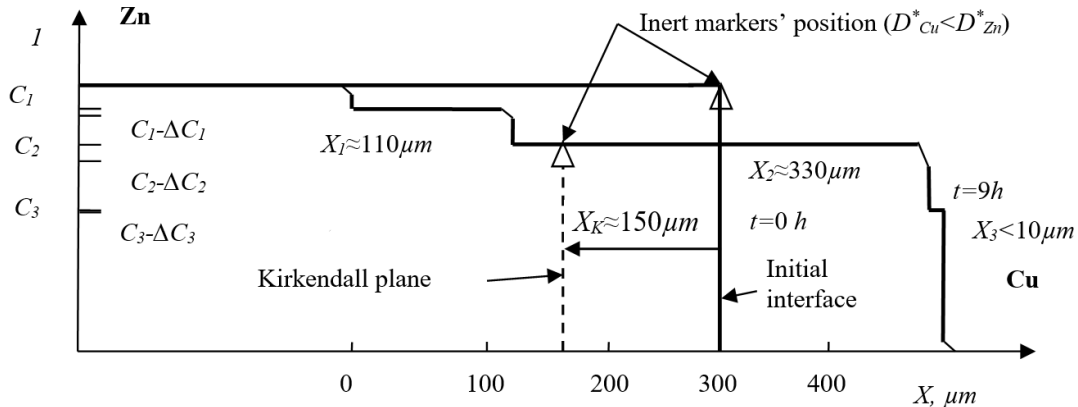


Fig. 5. Concentration profile of Zn change during isothermal annealing at temperature $T = 400$ °C within 9 h [5]: $D_{Zn}^* > D_{Cu}^*$; $X_1 < X_2$, $X_2 = 3X_1$, $X_3 \approx 0$; $C_1 = 5/6$, $C_2 = 8/13$, $C_3 = 1/2$, $C = C_{Zn}$.

Table 2

Comparison of the diffusion activation energies and the pre-exponential factors

		Onishi and Fujibuchi [6]	This work	Paul <i>et al.</i> [9]	This work	Kumar <i>et al.</i> [3]	This work
$Q_i, \text{kJ/mol}$	1=Cu ₃ Sn	70.7	124	73.8	85.7	38.7	39.0
	2=Cu ₆ Sn ₅	64.8	142	81	119.5	47.3	43.4
$D_{0i}, \text{m}^2/\text{s}$	1=Cu ₃ Sn	1.43×10^{-8}	3.77×10^{-4}	2.7×10^{-9}	8.7×10^{-8}	-	9×10^{-6}
	2=Cu ₆ Sn ₅	1.55×10^{-8}	4	5.6×10^{-8}	8.7×10^{-4}	-	7×10^{-5}
Q_2/Q_1	Cu/Sn couple	0.92	8.2×10^{-2}	1.1	1.4	1.22	1.11
			1.15				
$Q_1^{(1\text{phase})}, \text{kJ/mol}$ ($T_2 = 357$ °C)	1=Cu ₃ Sn (Cu/Cu ₆ Sn ₅ couple)	78.2	78.6	-	-	-	-
$D_{01}, \text{m}^2/\text{s}$		1.09×10^{-6}	5×10^{-9}	-	-	-	-

$$D_{0i} = D_i(T_1)e^{Q_i/(RT_1)} = D_i(T_2)e^{Q_i/(RT_2)}. \quad (16)$$

We can use five points ($T_1 = 190^\circ\text{C}$, $T_2 = 200^\circ\text{C}$, $T_3 = 210^\circ\text{C}$, $T_4 = 220^\circ\text{C}$ [6], and $T_5 = 250^\circ\text{C}$ [11]) for calculation by the least square method:

$$Q_i = -\frac{5 \sum_{j=1}^5 \left(\frac{1000}{RT_j} \ln D_i(T_j) \right) - \sum_{j=1}^5 \ln D_i(T_j) \sum_{j=1}^5 \frac{1000}{RT_j}}{5 \sum_{j=1}^5 \left(\frac{1000}{RT_j} \right)^2 - \left(\sum_{j=1}^5 \frac{1000}{RT_j} \right)^2} [kJ/mol] \quad (17)$$

$$D_{0i} = \exp \frac{\sum_{j=1}^5 \left(\frac{1000}{RT_j} \right)^2 \sum_{j=1}^5 \ln D_i(T_j) - \sum_{j=1}^5 \frac{1000}{RT_j} \sum_{j=1}^5 \left(\frac{1000}{RT_j} \ln D_i(T_j) \right)}{5 \sum_{j=1}^5 \left(\frac{1000}{RT_j} \right)^2 - \left(\sum_{j=1}^5 \frac{1000}{RT_j} \right)^2} [m^2/s] \quad (18)$$

Eqs.17 and 18 give Eqs.16 only for two points.

The data points from the Sn/Cu couple are in good agreement with the data from the incremental couples Cu/Cu₆Sn₅ and Cu₃Sn/Sn [9]. We can see a good agreement between calculations and results described in [3, 6] for one phase 1 (Cu/Cu₆Sn₅ couple). Really, the ratio Q_2/Q_1 should be less than 1 if $D_{01} \approx D_{02}$, as reported in [6].

The Sn diffusion coefficients in a concentrated solution (8 at. % Sn) are several times greater than Sn diffusion coefficients in dilute solution (2 at. % Sn) at temperatures from 500 °C to 650 °C [31], and diffusion activation energy of Sn vary from 89 kJ/mol to 187 kJ/mol (isotope data on Sn diffusion in a pure copper), therefore our calculated values should be correct.

Conclusions

The Zn atoms have higher intrinsic diffusivities than

the Cu atoms at temperature 400 °C in γ -brass Cu₅Zn₈, vacancies can disappear near dislocations at Zn side (sinks) and appear near dislocations at Cu side (sources), dislocations can climb, and the Kirkendall plane shifts toward Zn side. Calculated ratio $D_{Cu}^*/D_{Zn}^* \approx 0.6$ in γ -brass Cu₅Zn₈ is the same as experimentally obtained at temperature 400 °C.

The Cu atoms have higher intrinsic diffusivities than the Sn atoms at temperature 200 °C in ϵ -phase Cu₃Sn, vacancies can disappear near dislocations at Cu side (sinks) and appear near dislocations at Sn side (sources), dislocations can climb, and the Kirkendall plane shifts toward Cu side. Calculated ratio $D_{Sn}^*/D_{Cu}^* \approx 0.7$ in ϵ -phase Cu₃Sn is approximately equal to experimentally obtained at temperature 200 °C.

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Аналіз кінетики зникнення інтерметалідів та відношення внутрішніх коефіцієнтів дифузії у системах Cu-Zn та Cu-Sn

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Теоретично проаналізована кінетика зникнення інтерметалідів у системі Cu-Zn при температурі 400 °C та у системі Cu-Sn при температурах від 190 °C до 250 °C. Обчислено відношення внутрішніх коефіцієнтів дифузії у системі Cu-Zn при температурі 400 °C та у системі Cu-Sn при температурі 200 °C. Знайдено також енергію активації дифузії та передекспонентні множники для системи Cu-Sn. Для аналізу були використані літературні експериментальні дані.

Ключові слова: дифузія, інтерметаліди, кінетика утворення фаз, мідь, цинк, олово, пористість Кіркендалла-Френкеля, зсув Кіркендалла.