Kinetics of Solid-State Reactive Diffusion in the (Sn–Ni)/Cu System

Misako Nakayama¹ and Masanori Kajihara^{2,*}

¹Graduate School, Tokyo Institute of Technology, Yokohama 226-8502, Japan

²Department of Materials Science and Engineering, Tokyo Institute of Technology, Yokohama 226-8502, Japan

The kinetics of the solid-state reactive diffusion between Sn–Ni alloys and pure Cu was experimentally observed to examine effects of addition of Ni into Sn on the growth behavior of compounds at the interconnection between the Sn-base solder and the multilayer Au/Ni/Cu conductor during energization heating. In this experiment, sandwich (Sn–Ni)/Cu/(Sn–Ni) diffusion couples with Ni concentrations of $y = 0.01$ and 0.03 were isothermally annealed in the temperature range of $433\text{--}473\text{ K}$ for various periods up to 1152 h , where y is the mol fraction of Ni. After annealing, a compound layer consisting of Cu_6Sn_5 and Cu_3Sn was recognized between the Sn–Ni alloy and the Cu specimen in the diffusion couple. Here, the thickness of the Cu_3Sn layer is smaller than that of the Cu_6Sn_5 layer. The $(\text{Cu},\text{Ni})_6\text{Sn}_5$ grains were transformed from the Ni_3Sn_4 grains in the Sn–Ni alloy in the neighborhood of the Cu_6Sn_5 layer, and then adhered to the Cu_6Sn_5 layer. The overall growth of the compound layer including the $(\text{Cu},\text{Ni})_6\text{Sn}_5$ grains is remarkably accelerated by the adhesion, but that of the compound layer excluding the $(\text{Cu},\text{Ni})_6\text{Sn}_5$ grains is slightly decelerated by the adhesion. The mean thickness of each layer increases in proportion to a power function of the annealing time. For annealing at $433\text{--}473\text{ K}$, the ratio between the thicknesses of the Cu_6Sn_5 and Cu_3Sn layers is hardly affected by the addition of Ni into Sn up to $y = 0.03$. [doi:10.2320/matertrans.M2014038]

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1. Introduction

Owing to high electrical conductivity, Cu-base alloys are widely used as conductor materials in the electronics industry. If the Cu-base conductor is interconnected with a Sn-base solder, Cu_6Sn_5 and Cu_3Sn are formed at the interconnection between the conductor and the solder during soldering and then gradually grow during energization heating at solid-state temperatures.^{1–11} Since the Cu–Sn compounds are brittle and possess high electrical resistivities, their growth deteriorates the mechanical and electrical properties of the interconnection. To inhibit the formation of the compounds, the Cu-base conductor is usually plated with a Ni layer. However, Ni is not sufficiently corrosion resistant. Thus, the Ni layer is plated with a Au or Pd layer to improve corrosion resistance.^{12–15}

For the multilayer Au/Ni/Cu conductor with a thin Au layer, the Au layer quickly dissolves into a molten Sn-base solder during soldering, and then the Ni layer is contacted with the solder. Consequently, the Ni layer is directly reacted with the solder during solid-state energization heating. The solid-state reactive diffusion in the Ni/Sn system was experimentally examined using sandwich Sn/Ni/Sn diffusion couples prepared by a diffusion bonding technique in a previous study.¹⁶ In this experiment, the diffusion couples were isothermally annealed at temperatures of $T = 433\text{--}473\text{ K}$. At the interface in the annealed diffusion couple, a layer of Ni_3Sn_4 was observed at $T = 453\text{--}473\text{ K}$, but granular particles of Ni_3Sn_4 were recognized at $T = 433\text{ K}$. The mean thickness of the Ni_3Sn_4 layer increases in proportion to a power function of the annealing time. The exponent of the power function is 0.46 and 0.41 at $T = 453$ and 473 K , respectively. The exponent smaller than 0.5 indicates that the growth of Ni_3Sn_4 is controlled by boundary and volume diffusion and grain growth occurs in Ni_3Sn_4 . Although the growth of Ni_3Sn_4 may be accelerated by boundary diffusion,

the overall growth rate is smaller for Ni_3Sn_4 ¹⁶ than for Cu_6Sn_5 and Cu_3Sn .^{3,11} As a consequence, the Ni layer works as a barrier against the reactive diffusion at the interconnection between the Sn-base solder and the multilayer Au/Ni/Cu conductor with a thin Au layer during solid-state energization heating.

After prolonged energization heating, however, the Ni layer will be completely depleted by the growth of Ni_3Sn_4 . Due to the depletion of the Ni layer, the Cu-base conductor is directly contacted with the solder. In such a case, the reactive diffusion between the conductor and the solder occurs at the interconnection. The solid-state reactive diffusion in the Cu/Sn system was experimentally observed in a previous study.¹¹ In this experiment, like the Ni/Sn system,¹⁶ Sn/Cu/Sn diffusion couples were prepared by a diffusion bonding technique and then isothermally annealed at $T = 433\text{--}473\text{ K}$. At all the annealing temperatures, an intermetallic layer composed of Cu_6Sn_5 and Cu_3Sn is formed at the original Cu/Sn interface in the diffusion couple. Also in this case, the intermetallic layer grows according to the power relationship. The exponent of the power function is close to 0.5 at $T = 473\text{ K}$ but becomes 0.37 and 0.43 at $T = 433$ and 453 K , respectively. Thus, in the Cu/Sn system,¹¹ the growth of the intermetallic layer is controlled by volume diffusion at $T = 473\text{ K}$ but by volume and boundary diffusion at $T = 433$ and 453 K . Therefore, the rate-controlling process of reactive diffusion varies depending on the annealing temperature and the metal system.

As previously mentioned, during prolonged energization heating, the Ni layer of the multilayer Au/Ni/Cu conductor is entirely consumed by the growth of Ni_3Sn_4 , and then the Cu-base conductor is reacted with the Sn-base solder dispersed with Ni_3Sn_4 . The dispersion of Ni_3Sn_4 in the solder may influence the kinetics of the reactive diffusion between the conductor and the solder at the interconnection. Unfortunately, however, reliable information on such influence is rather limited. To examine this influence, the kinetics of the solid-state reactive diffusion in the (Sn–Ni)/Cu system

*Corresponding author, E-mail: kajihara@materia.titech.ac.jp

was experimentally observed at temperatures of $T = 433$ – 473 K using sandwich (Sn–Ni)/Cu/(Sn–Ni) diffusion couples with Ni mol fractions of 0.01–0.03 in the present study.

2. Experimental

Binary Sn–Ni alloys with Ni concentrations of $y = 0.01$ and 0.03 were made as 25 g button ingots by argon arc melting from pure Sn and Ni with purities of 99.99 and 99.97%, respectively, where y is the mol fraction of Ni. Plate specimens with a size of $12\text{ mm} \times 5\text{ mm} \times 2\text{ mm}$ were prepared by cold rolling and spark erosion from the button ingots. The plate specimens were isothermally heated in an oil bath with silicone oil at 473 K for 2 h, followed by water quenching. The two surfaces with an area of $12\text{ mm} \times 5\text{ mm}$ of each heated Sn–Ni plate specimen were mechanically polished on # 800 emery paper. One of the two polished surfaces was again mechanically polished on # 1500–4000 emery papers until a depth of $100\text{ }\mu\text{m}$ and then finished using diamond with a diameter of $1\text{ }\mu\text{m}$.

Sheet specimens with a size of $20\text{ mm} \times 7\text{ mm} \times 0.2\text{ mm}$ were cut from a pure Cu commercial sheet with dimensions of $300\text{ mm} \times 100\text{ mm} \times 0.2\text{ mm}$ and purity of 99.96% and then separately annealed in evacuated silica capsules at 1173 K for 2 h, followed by air cooling without breaking the capsules. The annealed sheet specimens were chemically polished in nitrohydrochloric acid for 60 s.

After chemical polishing, a Cu sheet specimen was immediately sandwiched between the finished surfaces of two freshly prepared Sn–Ni plate specimens in ethanol by the technique used in a previous study.¹¹⁾ The sandwich (Sn–Ni)/Cu/(Sn–Ni) couples were completely dried and then heat treated for diffusion bonding in the oil bath at 433 K , 453 K and 473 K for 12.5 h. After the heat treatment, the diffusion couples were isothermally annealed at 433 K , 453 K and 473 K for various times up to 1139.5 h. The summation of the heat-treating and annealing times is hereafter merely called the annealing time t , and the annealing temperature is denoted by T . The chemical composition of the Sn–Ni alloy is described as Sn– y Ni. The Sn–0.01Ni and Sn–0.03Ni alloys are designated alloys N1 and N2, respectively, and the diffusion couples with alloys N1 and N2 are called diffusion couples N1 and N2, respectively. Cross-sections of the annealed diffusion couple were mechanically polished using diamond with diameters of 15, 3 and $1\text{ }\mu\text{m}$, and then finished with an OP-S liquid manufactured by Struers Ltd. The microstructure of the cross-section was observed by differential interference contrast optical microscopy (DICOM). Concentrations of Sn, Ni and Cu in each phase on the cross-section were measured by electron probe microanalysis (EPMA).

3. Results and Discussion

3.1 Microstructure

Typical DICOM images for the cross-section of diffusion couple N1 with $T = 473\text{ K}$ and $t = 144\text{ h}$ ($5.18 \times 10^5\text{ s}$) are shown in Fig. 1. For each DICOM image in Fig. 1, the top and bottom regions are the Sn–Ni alloy and the Cu specimen,

Fig. 1 DICOM images of diffusion couple N1 annealed at $T = 473\text{ K}$ for $t = 144\text{ h}$ ($5.18 \times 10^5\text{ s}$): (a) $(\text{Cu,Ni})_6\text{Sn}_5$, Cu_6Sn_5 and Cu_3Sn layers; and (b) Cu_6Sn_5 and Cu_3Sn layers.

respectively. As can be seen, layers with different contrasts are formed at the original (Sn–Ni)/Cu interface. To identify each layer, concentration profiles of Sn, Ni and Cu were measured by EPMA along the direction normal to the original interface. Results of the layers in Fig. 1(a) and 1(b) are indicated in Fig. 2(a) and 2(b), respectively. In Fig. 2, the ordinate and the abscissa show the mol fraction y_i of component i and the distance x measured from an arbitrary origin, respectively, and open circles, rhombuses and squares represent the mol fractions y_{Sn} , y_{Ni} and y_{Cu} , respectively. In Fig. 2(b), the layers on the Sn–Ni and Cu sides are Cu_6Sn_5 and Cu_3Sn , respectively. The thickness is much smaller for Cu_3Sn than for Cu_6Sn_5 . On the other hand, in Fig. 2(a), $(\text{Cu,Ni})_6\text{Sn}_5$ is recognized on the Sn–Ni side of the Cu_6Sn_5 layer. Here, the Cu/ Cu_3Sn , $\text{Cu}_3\text{Sn}/\text{Cu}_6\text{Sn}_5$, $\text{Cu}_6\text{Sn}_5/(\text{Cu,Ni})_6\text{Sn}_5$ and $(\text{Cu,Ni})_6\text{Sn}_5/\text{Sn}$ interfaces are denoted by interfaces A, B, C and D, respectively. The thickness of the Cu_6Sn_5 layer is smaller in Figs. 1(a) and 2(a) with $(\text{Cu,Ni})_6\text{Sn}_5$ than in Figs. 1(b) and 2(b) without $(\text{Cu,Ni})_6\text{Sn}_5$. The EPMA measurement was conducted also for compound grains dispersed in the Sn–Ni alloy of the diffusion couple shown in Fig. 1. Figure 2(c) indicates the result of a compound grain near by the $\text{Cu}_6\text{Sn}_5 + \text{Cu}_3\text{Sn}$ two-phase layer, and Figure 2(d) represents that of a compound grain far from the two-phase layer. The compound grain in the Sn–Ni alloy is originally Ni_3Sn_4 as shown in Fig. 2(d). In Fig. 2(c), however, Ni_3Sn_4 transforms into $(\text{Cu,Ni})_6\text{Sn}_5$ by diffusion of Cu from the Cu specimen to the Sn–Ni alloy across the compound layers. The $(\text{Cu,Ni})_6\text{Sn}_5$ grains remain separately in Fig. 1(b) but adhere to the Cu_6Sn_5 layer in Fig. 1(a). In diffusion couples N1 and N2 annealed at $T = 433$ – 473 K , the microstructure type of Fig. 1(a) was observed predominantly, and that of Fig. 1(b) was recognized partially.

Recently, the phase equilibria at the Sn-rich corner in the ternary Sn–Cu–Ni system were experimentally determined at

Fig. 2 Concentration profiles of Sn, Ni and Cu across compound layers and compound grains for the diffusion couple shown in Fig. 1: (a) $(\text{Cu,Ni})_6\text{Sn}_5$, Cu_6Sn_5 and Cu_3Sn layers; (b) Cu_6Sn_5 and Cu_3Sn layers; (c) $(\text{Cu,Ni})_6\text{Sn}_5$ grain; and (d) Ni_3Sn_4 grain.

solid-state temperatures in a previous study.¹⁷⁾ The isothermal section at $T = 473 \text{ K}$ of the phase diagram in this ternary system is shown in Fig. 3. As can be seen, a three-phase equilibrium of $\text{Sn} + (\text{Cu,Ni})_6\text{Sn}_5 + \text{Ni}_3\text{Sn}_4$ appears at this temperature. According to the tie-triangle of this three-phase equilibrium, the solubility $y_{\text{Ni}}^{\text{Cu}_6\text{Sn}_5}$ of Ni in Cu_6Sn_5 is 0.224, and that $y_{\text{Cu}}^{\text{Ni}_3\text{Sn}_4}$ of Cu in Ni_3Sn_4 is 0.046.¹⁷⁾ Thus, $y_{\text{Cu}}^{\text{Ni}_3\text{Sn}_4}$ is much smaller than $y_{\text{Ni}}^{\text{Cu}_6\text{Sn}_5}$. Therefore, in Fig. 3, Cu_6Sn_5 is described as $(\text{Cu,Ni})_6\text{Sn}_5$, but Ni_3Sn_4 is merely expressed as Ni_3Sn_4 . In Fig. 3, the concentration profiles for the two-phase layer and the $(\text{Cu,Ni})_6\text{Sn}_5$ grain in Fig. 2 are plotted as diffusion paths with open circles and squares, respectively. For the two-phase layer, the open circles are located in the neighborhood of the binary Sn–Cu side. In contrast, for the $(\text{Cu,Ni})_6\text{Sn}_5$ grain, the open squares lie almost on the $(\text{Cu,Ni})_6\text{Sn}_5$ corner of the three-phase tie-triangle. Thus, the concentration of Ni in the $(\text{Cu,Ni})_6\text{Sn}_5$ grain reaches the solubility limit.

3.2 Growth behavior of intermetallic layer

As shown in Fig. 1(a), a multi-phase layer consisting of $(\text{Cu,Ni})_6\text{Sn}_5$, Cu_6Sn_5 and Cu_3Sn formed at the original (Sn–Ni)/Cu interface in diffusion couples N1 and N2 due to isothermal annealing at $T = 433\text{--}473 \text{ K}$. Hereafter, the multi-phase layer is merely called the intermetallic layer. From DICOM images, such as that indicated in Fig. 1(a), the area A_j of the intermetallic layer corresponding to the partial length w_i of the original (Sn–Ni)/Cu interface were measured for cross-section j . The sums A and w were obtained by the equations¹¹⁾

$$A = \sum_{j=1}^m A_j \quad (1a)$$

and

$$w = \sum_{j=1}^m w_j \quad (1b)$$

Fig. 3 Diffusion paths for the concentration profiles of the Cu_6Sn_5 and Cu_3Sn layers and the $(\text{Cu,Ni})_6\text{Sn}_5$ grain in Fig. 2 shown as open circles and squares, respectively.

from A_i and w_i , respectively, where $w_j = 422 \mu\text{m}$ and $m \geq 5$. Using the values of A and w , the total thickness l of the intermetallic layer was evaluated at each annealing time t as follows:¹¹⁾

$$l = \frac{A}{w}. \quad (2)$$

The results of diffusion couples N0,¹¹⁾ N1 and N2 are shown as open circles, squares and rhombuses, respectively, in Fig. 4. Here, diffusion couple N0 stands for the Sn/Cu/Sn diffusion couple from a previous study.¹¹⁾ Figure 4(a), 4(b) and 4(c) shows the results for $T = 433$, 453 and 473 K, respectively. In this figure, the ordinate and the abscissa indicate the logarithms of l and t , respectively. As can be seen, the thickness l monotonically increases with increasing annealing time t . Furthermore, at $T = 433$ –473 K, the experimental points for each diffusion couple lie well on a straight line. Consequently, l is expressed as a power function of t as follows

$$l = k \left(\frac{t}{t_0} \right)^n, \quad (3)$$

where t_0 is unit time, 1 s, which is adopted to make the argument t/t_0 of the power function dimensionless. The proportionality coefficient k has the same dimension as the thickness l , and the exponent n is dimensionless. From the experimental points in Fig. 4, k and n were evaluated by the least-squares method as indicated with various straight lines. The evaluated values of k and n are also shown in Fig. 4. According to the evaluation at $T = 433$ –473 K, the overall growth rate of the intermetallic layer considerably increases with increasing Ni concentration y within the experimental annealing times.

3.3 Growth behavior of two-phase layer

According to Fig. 1(a), each compound is clearly distinguished in the intermetallic layer. From DICOM images, such as that shown in Fig. 1(a), the mean thickness l_i of compound

Fig. 4 The thickness l in eq. (2) versus the annealing time t for diffusion couples N0,¹¹⁾ N1 and N2 shown as open circles, squares and rhombuses, respectively: (a) 433 K, (b) 453 K and (c) 473 K.

layer i in the intermetallic layer was evaluated using the relationships similar to eqs. (1a), (1b) and (2), where $i = 3$ and 6 for the Cu_3Sn and Cu_6Sn_5 layers, respectively. The total thickness l_s of the Cu_3Sn and Cu_6Sn_5 layers was calculated by the equation

$$l_s = l_3 + l_6. \quad (4)$$

The $\text{Cu}_3\text{Sn} + \text{Cu}_6\text{Sn}_5$ two-phase layer excluding the $(\text{Cu},\text{Ni})_6\text{Sn}_5$ grains from the intermetallic layer is hereafter denominated the two-phase layer. The results of l_s , l_6 and l_3 are shown as open circles, triangles and squares, respectively, in Figs. 5 and 6. In these figures, like Fig. 4, the ordinate and the abscissa indicate the logarithms of l_i and t , respectively. Figure 5(a), 5(b) and 5(c) shows the results for diffusion couple N1 at $T = 433$, 453 and 473 K, respectively, and Fig. 6(a), 6(b) and 6(c) represents those for diffusion couple N2 at $T = 433$, 453 and 473 K, respectively. Although the open squares are slightly scattered due to small values of l_3 , most of the open symbols are located well on the corresponding straight line. Therefore, we consider that l_i is expressed as a power function of t by the following equation of the same formula as eq. (3).

$$l_i = k_i \left(\frac{t}{t_0} \right)^n \quad (5)$$

From the experimental points in Figs. 5 and 6, k_s and n for l_s in eq. (5) were evaluated by the least-squares method as shown with solid lines. Since l_3 and l_6 are smaller than l_s , the values of k_3 , k_6 and n for l_3 and l_6 cannot be estimated with the same reliability as those of k_s and n for l_s . Consequently, using the same value of n as l_s , k_3 and k_6 for l_3 and l_6 in eq. (5) were estimated from the open squares and triangles by the least-squares method as indicated with dashed and dotted lines, respectively. The values of n , k_s , k_3 and k_6 are shown in Figs. 5 and 6. Since l_3 is very small for diffusion couple N2 at $T = 433$ K, l_3 and thus l_6 could not be reliably determined for most of the annealing times except the longest time of $t = 1152$ h (4.15×10^6 s) in Fig. 6(a). Therefore, k_3 and k_6 were not evaluated for diffusion couple N2 at $T = 433$ K. As can be seen, l_3 is smaller than l_6 for diffusion couples N1 and N2 at $T = 433$ –473 K. Although the identical value of n was adopted for each diffusion couple at each annealing temperature, k_3 , k_6 and k_s were independently evaluated from the corresponding experimental points in Figs. 5 and 6 as mentioned earlier. As a result, the relationship $k_s = k_3 + k_6$ does not necessarily hold, even though equation (4) holds at each experimental annealing time.

The values of l_s in Figs. 5 and 6 are again plotted against the annealing time t in Fig. 7. In this figure, the corresponding result of diffusion couple N0⁽¹¹⁾ in Fig. 4 is also shown. Figure 7(a), 7(b) and 7(c) indicates the results for $T = 433$, 453 and 473 K, respectively, and open circles, squares and rhombuses represent the results of diffusion couples N0⁽¹¹⁾, N1 and N2, respectively. Unlike l in Fig. 4, l_s rather gradually decreases with increasing Ni concentration y within the experimental annealing times at each annealing temperature in Fig. 7. As mentioned in Section 3.1, Ni_3Sn_4 in the Sn–Ni alloy transforms into $(\text{Cu},\text{Ni})_6\text{Sn}_5$ owing to diffusion of Cu from the Cu specimen to the Sn–Ni alloy across the two-phase layer. After transformation, $(\text{Cu},\text{Ni})_6\text{Sn}_5$ grains mainly

Fig. 5 The thicknesses l_s , l_6 and l_3 in eq. (4) versus the annealing time t for diffusion couple N1 shown as open circles, triangles and squares, respectively: (a) 433 K, (b) 453 K and (c) 473 K.

Fig. 6 The thicknesses l_s , l_6 and l_3 in eq. (4) versus the annealing time t for diffusion couple N2 shown as open circles, triangles and squares, respectively: (a) 433 K, (b) 453 K and (c) 473 K.

Fig. 7 The thickness l_s in eq. (4) versus the annealing time t for diffusion couples N0,⁽¹⁾ N1 and N2 shown as open circles, squares and rhombuses, respectively: (a) 433 K, (b) 453 K and (c) 473 K.

Fig. 8 The ratios r_3 and r_6 in eq. (6) versus the annealing time t at $T = 473$ K shown as open circles and squares, respectively, with error bars: (a) diffusion couple N1, and (b) diffusion couple N2.

adhere to the Cu_6Sn_5 layer as shown in Fig. 1(a). The grain size is greater for the $(\text{Cu},\text{Ni})_6\text{Sn}_5$ grains adhered to the Cu_6Sn_5 layer than for those isolated in the Sn–Ni alloy. According to the same mechanism as Ostwald ripening,¹⁸⁾ the coarse $(\text{Cu},\text{Ni})_6\text{Sn}_5$ grains grow, but the fine $(\text{Cu},\text{Ni})_6\text{Sn}_5$ grains shrink. As a consequence, the adhesion of $(\text{Cu},\text{Ni})_6\text{Sn}_5$ spontaneously proceeds during isothermal annealing. Although the adhesion directly contributes to the increase in the thickness l of the intermetallic layer, it consumes the Cu atoms transported from the Cu specimen across the two-phase layer as indicated in Fig. 2(a). The growth of the two-phase layer will be decelerated by the consumption of the Cu atoms. This is the reason why the increase in the Ni concentration y accelerates the overall growth of the intermetallic layer as shown in Fig. 4 but decelerates that of the two-phase layer as indicated in Fig. 7.

Fig. 9 The ratios r_3 and r_6 in eq. (6) versus the Ni mol fraction y at $T = 473$ K shown as open circles and squares, respectively, with error bars. Horizontal solid lines indicate the mean values of r_3 and r_6 for $y = 0$.

At each experimental annealing time, the ratio r_i of the thickness l_i to the total thickness l_s was evaluated by the equation

$$r_i = \frac{l_i}{l_s}. \quad (6)$$

The values of r_3 and r_6 at $T = 473$ K are plotted against the annealing time t as open circles and squares, respectively, in Fig. 8. Figure 8(a) and 8(b) shows the results of diffusion couples N1 and N2, respectively. As indicated in Figs. 5 and 6, l_3 is smaller than l_6 . Consequently, r_3 is smaller than 0.5, but r_6 is greater than 0.5. Although the open symbols are slightly scattered in Fig. 8, there exists no systematic dependence of r_i on t . Thus, we may consider that r_i is constant independent of t for each diffusion couple. The mean values of r_3 and r_6 were estimated from the open circles and squares, respectively, as shown as horizontal solid lines with error bars in Fig. 8. Here, the error bar indicates the standard error. The mean values of r_3 and r_6 are plotted against the Ni concentration y as open circles and squares, respectively, with error bars in Fig. 9. In this figure, the corresponding results of r_3 and r_6 for $y = 0$ ¹¹⁾ are also shown as open circles and squares, respectively, with error bars. Furthermore, their mean values for $y = 0$ are emphasized with horizontal solid lines. As can be seen, the values of r_3 and r_6 at $y = 0.03$ are almost equal to those of r_3 and r_6 at $y = 0$, respectively, and there are no systematic dependencies of r_3 and r_6 on y . Thus, we may consider that r_3 and r_6 are constant independent of y . As a consequence, it is concluded that the addition of Ni into Sn up to 3 at% slightly decelerates the overall growth of the Cu_6Sn_5 and Cu_3Sn layers but hardly influences the ratio of their thicknesses.

4. Conclusions

The solid-state reactive diffusion in the (Sn–Ni)/Cu system was experimentally observed using the (Sn–Ni)/

Cu/(Sn–Ni) diffusion couples with Ni mol fractions of $y = 0.01$ and 0.03 . The diffusion couples were isothermally annealed at temperatures of $T = 433$, 453 and 473 K for various times up to $t = 1152$ h. During annealing, the $\text{Cu}_6\text{Sn}_5 + \text{Cu}_3\text{Sn}$ two-phase layer forms at the original (Sn–Ni)/Cu interface in the diffusion couple, where the thickness is smaller for the Cu_3Sn layer than for the Cu_6Sn_5 layer. The Ni_3Sn_4 grains in the Sn–Ni alloy near by the two-phase layer transform into $(\text{Cu},\text{Ni})_6\text{Sn}_5$ and adhere to the Cu_6Sn_5 layer. Although the adhesion of $(\text{Cu},\text{Ni})_6\text{Sn}_5$ considerably accelerates the overall growth of the $(\text{Cu},\text{Ni})_6\text{Sn}_5 + \text{Cu}_6\text{Sn}_5 + \text{Cu}_3\text{Sn}$ layer, it slightly decelerates that of the $\text{Cu}_6\text{Sn}_5 + \text{Cu}_3\text{Sn}$ layer. The mean thickness of each compound layer is proportional to a power function of the annealing time. The addition of Ni into Sn within $y = 0\text{--}0.03$ hardly influences the ratio between the thicknesses of the Cu_6Sn_5 and Cu_3Sn layers at $T = 433\text{--}473$ K.

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