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

Misako Nakayama^{1,*1} and Masanori Kajihara^{2,*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 in the (Sn–Cu)/Ni system was experimentally observed to examine effects of addition of Cu 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–Cu)/Ni/(Sn–Cu) diffusion couples with Cu concentrations of $y = 0.01$ – 0.03 were isothermally annealed at solid-state temperatures of $T = 453$ – 473 K for various periods up to 1972 h, where y is the mol fraction of Cu. After annealing, an intermetallic layer consisting of $(\text{Cu,Ni})_6\text{Sn}_5$ and Ni_3Sn_4 was recognized between the Sn–Cu and Ni specimens in the diffusion couple. The total thickness of the intermetallic layer is proportional to a power function of the annealing time, and the exponent of the power function takes values of 0.37–0.44 at $T = 453$ K and those of 0.63–0.69 at $T = 473$ K. Thus, the growth of the intermetallic layer is controlled by boundary and volume diffusion at $T = 453$ K. On the other hand, at $T = 473$ K, interface reaction and interdiffusion contribute to the rate-controlling process of the intermetallic growth. The addition of Cu into Sn accelerates the intermetallic growth within the experimental annealing times. [doi:10.2320/matertrans.M2015059]

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1. Introduction

Due to high electrical conductivity, Cu-base alloys are widely used as conductor materials in the electronics industry. When 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. Hence, 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. As a consequence, 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 $T = 433$ – 473 K. At the interface in the annealed diffusion couple, a layer of Ni_3Sn_4 was observed at $T = 453$ – 473 K, but granular particles of Ni_3Sn_4 were recognized at $T = 433$ K. The mean thickness of the Ni_3Sn_4 layer is proportional 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)} Consequently, 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.

Since the price is much lower for Cu than for Ag, Sn–Cu alloys are more preferentially used as a low-cost Pb-free solder than Sn–Ag alloys. In the Sn–Cu solder, small particles of Cu_6Sn_5 are dispersed in the Sn matrix. The dispersion of Cu_6Sn_5 in the solder may influence the kinetics of the reactive diffusion between the Sn matrix and the Ni layer at the interconnection. Unfortunately, however, reliable information on such influence is rather limited. To examine this influence, the kinetics of the reactive diffusion in the (Sn–Cu)/Ni system was experimentally observed at solid-state temperatures of $T = 453$ – 473 K using sandwich (Sn–Cu)/Ni/(Sn–Cu) diffusion couples with Cu mol fractions of 0.01–0.03 in the present study.

2. Experimental

Binary Sn–Cu alloys with Cu concentrations of $y = 0.01$, 0.02 and 0.03 were made as 25 g button ingots by argon arc melting from pure Sn and Cu with purities of 99.99 and 99.96%, respectively, where y is the mol fraction of Cu. Plate specimens with a size of 12 mm $\times$ 5 mm $\times$ 2 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 mm $\times$ 5 mm of each heated Sn–Cu 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 μm and then finished using diamond with a diameter of 1 μm .

Sheet specimens with a size of 20 mm $\times$ 7 mm $\times$ 0.2 mm were cut from a pure Ni commercial sheet with dimensions of 300 mm $\times$ 100 mm $\times$ 0.2 mm and purity of 99.97% and then

*1Graduate Student, Tokyo Institute of Technology

*2Corresponding author, E-mail: kajihara@materia.titech.ac.jp

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 Ni sheet specimen was immediately sandwiched between the finished surfaces of two freshly prepared Sn–Cu plate specimens in ethanol by the technique used in a previous study.¹¹⁾ The sandwich (Sn–Cu)/Ni/(Sn–Cu) couples were completely dried and then heat treated for diffusion bonding in the oil bath for 69 and 44.5 h at 453 and 473 K, respectively. After the heat treatment, the diffusion couples were isothermally annealed at 453–473 K for various times up to 1903 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–Cu alloy is described as Sn– y Cu. The Sn–0.01Cu, Sn–0.02Cu and Sn–0.03Cu alloys are designated alloys C1, C2 and C3, respectively, and the diffusion couples with alloys C1, C2 and C3 are called diffusion couples C1, C2 and C3, respectively. Cross-sections of the annealed diffusion couple were mechanically polished using diamond with diameters of 15, 3 and 1 μm , 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, Cu and Ni in each phase on the cross-section were measured by electron probe microanalysis (EPMA) using pure Sn, Cu and Ni with purity of 99.99% as standard specimens under the following conditions: the accelerating voltage was 20 kV; the probe current was 5 nA; the analyzing crystal was polyethylene terephthalate (PET) for Sn– L_α and lithium fluoride (LiF) for Cu– K_α and Ni– K_α ; and the chemical composition was evaluated by a standard ZAF correction technique.

3. Results and Discussion

3.1 Microstructure

A typical DICOM image for the cross-section of diffusion couple C1 with $T = 473$ K and $t = 787.5$ h (2.84×10^6 s) is shown in Fig. 1. In this figure, the top and bottom regions are the Sn–Cu and Ni specimens, respectively. As can be seen, a layer with rather uniform thickness is formed at the original interface between the Sn–Cu and Ni specimens. To identify each phase, concentration profiles of Sn, Cu and Ni were determined by EPMA along the direction normal to the original interface. A result for diffusion couple C2 with $T = 473$ K and $t = 1264.5$ h (4.55×10^6 s) is indicated in Fig. 2. 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, squares and rhombuses represent the mol fractions y_{Sn} , y_{Cu} and y_{Ni} , respectively. As can be seen, the layer consists of two compounds. They are Ni_3Sn_4 and $(\text{Cu},\text{Ni})_6\text{Sn}_5$ on the Ni and Sn–Cu sides, respectively. The thickness is much smaller for Ni_3Sn_4 than for $(\text{Cu},\text{Ni})_6\text{Sn}_5$. Furthermore, the concentration of Cu in Ni_3Sn_4 is smaller than that of Ni in $(\text{Cu},\text{Ni})_6\text{Sn}_5$. Hereafter, the $(\text{Cu},\text{Ni})_6\text{Sn}_5 + \text{Ni}_3\text{Sn}_4$ two-phase layer is merely called the intermetallic layer. If we observe the edge of diffusion couple on the cross-section, we can find the

Fig. 1 Cross-sectional DICOM image of diffusion couple C1 annealed at $T = 473$ K for $t = 787.5$ h (2.84×10^6 s).

Fig. 2 Concentration profiles of Sn, Cu and Ni across the intermetallic layer for diffusion couple C2 annealed at $T = 473$ K for $t = 1264.5$ h (4.55×10^6 s).

location of the original (Sn–Cu)/Ni interface. This observation indicates that the intermetallic layer grows mainly into the Sn–Cu specimen but slightly towards the Ni specimen. The EPMA measurement was conducted also for diffusion couples C1 and C3. Since the volume fraction of Ni_3Sn_4 in the intermetallic layer gradually decreases with increasing Cu concentration of the Sn–Cu specimen, however, Ni_3Sn_4 is rather invisible at shorter annealing times for diffusion couple C3.

Recently, the phase equilibria at the Sn-rich corner in the ternary Sn–Cu–Ni system were experimentally determined at solid-state temperatures in a previous study.¹⁷⁾ The isothermal section at $T = 473$ K of the phase diagram in this ternary system is shown in Fig. 3. As can be seen, a three-phase equilibrium of $\text{Sn} + (\text{Cu},\text{Ni})_6\text{Sn}_5 + \text{Ni}_3\text{Sn}_4$ appears at this temperature. According to the tie-triangle of this three-phase equilibrium, the solubility $s_{\text{Ni}}^{\text{Cu}_6\text{Sn}_5}$ of Ni in Cu_6Sn_5 is 0.224, and that $s_{\text{Cu}}^{\text{Ni}_3\text{Sn}_4}$ of Cu in Ni_3Sn_4 is 0.046.¹⁷⁾ Hence, $s_{\text{Cu}}^{\text{Ni}_3\text{Sn}_4}$ is

Fig. 3 Diffusion path for the concentration profiles shown in Fig. 2. The three-phase equilibrium of Sn + (Cu,Ni)₆Sn₅ + Ni₃Sn₄ in the ternary Sn-Cu-Ni system¹⁷⁾ is also indicated as a tie-triangle.

much smaller than $s_{y_{\text{Ni}}^{\text{Cu}_6\text{Sn}_5}}$. Therefore, in Fig. 3, Cu₆Sn₅ is described as (Cu,Ni)₆Sn₅, but Ni₃Sn₄ is merely expressed as Ni₃Sn₄. The concentration profiles across the intermetallic layer for diffusion couple C2 in Fig. 2 are plotted as open circles in Fig. 3. On the other hand, in Fig. 3, open rhombuses represent the chemical compositions of the Sn-Cu and Ni specimens for diffusion couple C2. As can be seen, the open circles for (Cu,Ni)₆Sn₅ and Ni₃Sn₄ are located in the neighborhood of the (Cu,Ni)₆Sn₅ and Ni₃Sn₄ corners, respectively, of the Sn + (Cu,Ni)₆Sn₅ + Ni₃Sn₄ tie-triangle. Thus, the mol fraction $y_{\text{Ni}}^{\text{Cu}_6\text{Sn}_5}$ of Ni in (Cu,Ni)₆Sn₅ and that $y_{\text{Cu}}^{\text{Ni}_3\text{Sn}_4}$ of Cu in Ni₃Sn₄ in Fig. 2 are close to the solubilities $s_{y_{\text{Ni}}^{\text{Cu}_6\text{Sn}_5}}$ and $s_{y_{\text{Cu}}^{\text{Ni}_3\text{Sn}_4}}$, respectively.

As indicated in Fig. 1, small particles of Cu₆Sn₅ are thinly dispersed in the Sn matrix of the Sn-Cu specimen. Furthermore, the solubilities of Cu and Ni in the Sn matrix are negligible as shown in Fig. 3. Therefore, in the early stages of the reactive diffusion, a very thin Ni₃Sn₄ layer is formed at the interface between the Sn matrix and the Ni specimen. As the annealing time increases, Cu atoms are transported from the Cu₆Sn₅ particles to the Ni₃Sn₄ layer through the Sn matrix. The mol fraction $y_{\text{Cu}}^{\text{Ni}_3\text{Sn}_4}$ of Cu in Ni₃Sn₄ is increased by the Cu-atoms transportation and then reaches the solubility $s_{y_{\text{Cu}}^{\text{Ni}_3\text{Sn}_4}}$. If $y_{\text{Cu}}^{\text{Ni}_3\text{Sn}_4}$ slightly exceeds $s_{y_{\text{Cu}}^{\text{Ni}_3\text{Sn}_4}}$, Ni₃Sn₄ is transformed into (Cu,Ni)₆Sn₅. When local equilibrium is realized at the interface between (Cu,Ni)₆Sn₅ and Ni₃Sn₄, $y_{\text{Ni}}^{\text{Cu}_6\text{Sn}_5}$ and $y_{\text{Cu}}^{\text{Ni}_3\text{Sn}_4}$ coincide with $s_{y_{\text{Ni}}^{\text{Cu}_6\text{Sn}_5}}$ and $s_{y_{\text{Cu}}^{\text{Ni}_3\text{Sn}_4}}$, respectively, at the interface. Since the (Cu,Ni)₆Sn₅/Ni₃Sn₄ interface is produced by the transformation, it is not so clearly distinguishable in cross-sectional DICOM images as shown in Fig. 1.

3.2 Growth behavior of intermetallic layer

From the cross-sectional DICOM images like Fig. 1, the area A_j of the intermetallic layer corresponding to the partial length w_j of the original (Sn-Cu)/Ni interface were measured for cross-section j . The sums A and w were obtained by the equations¹¹⁾

Fig. 4 The total thickness l of the intermetallic layer versus the annealing time t shown as open rhombuses, squares and circles for $y = 0.01$, 0.02 and 0.03 , respectively: (a) $T = 453$ K and (b) $T = 473$ K. The corresponding results of $y = 0$ ¹⁶⁾ are also indicated as open triangles.

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

and

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

from A_j and w_j , 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 C1, C2 and C3 are plotted as open rhombuses, squares and circles, respectively, in Fig. 4, where the ordinate and the abscissa show the logarithms of l and t , respectively. In this figure, open triangles indicate the corresponding results of diffusion couple C0 reported in a

Fig. 5 The thickness l_6 at $t = 10^6$ s versus the mol fraction y of Cu in the Sn–Cu alloy shown as open squares and circles for $T = 453$ and 473 K, respectively, with error bars. The corresponding results of $y = 0^{(16)}$ are also represented.

previous study.¹⁶⁾ Here, diffusion couple C0 stands for the Sn/Ni/Sn diffusion couple with $y = 0$.¹⁶⁾ Figure 4(a) and 4(b) indicates the results for $T = 453$ and 473 K, respectively. As can be seen, the thickness l monotonically increases with increasing annealing time t . Furthermore, the plotted points for each diffusion couple lie well on a straight line. Consequently, l is expressed as a power function of t as follows.

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

Here, t_0 is unit time, 1 s. It 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 open symbols plotted in Fig. 4, k and n in eq. (3) were determined by the least-squares method as shown with various straight lines. The determined values are shown in Fig. 4. Since n varies depending on y , it is rather difficult to find a systematic relationship between k and y . Therefore, to estimate the compositional dependence of the overall growth rate of the intermetallic layer, the thickness l_6 at $t = 10^6$ s is plotted against y as open squares and circles for $T = 453$ and 473 K, respectively, with error bars in Fig. 5. Hereafter, the error bar represents the standard error. For $T = 453$ – 473 K, l_6 monotonically increases with increasing value of y at $y < 0.1$ but becomes rather insensitive to y at $y > 0.1$. As previously mentioned, the intermetallic layer consists of Ni_3Sn_4 and $(\text{Cu},\text{Ni})_6\text{Sn}_5$. As the value of y increases, the volume fraction of $(\text{Cu},\text{Ni})_6\text{Sn}_5$ increases, but that of Ni_3Sn_4 decreases. According to the observations in previous studies,^{11,16,17)} the layer growth is much faster for $(\text{Cu},\text{Ni})_6\text{Sn}_5$ than for Ni_3Sn_4 . Consequently, the overall growth rate of the intermetallic layer monotonically increases with increasing value of y . At larger values of y , however, the volume fraction f is much greater for $(\text{Cu},\text{Ni})_6\text{Sn}_5$ than for Ni_3Sn_4 , and hence the dependence of f on y becomes less

Fig. 6 The exponent n versus the mol fraction y of Cu in the Sn–Cu alloy shown as open circles with error bars: (a) $T = 453$ K and (b) $T = 473$ K. The corresponding results of $y = 0^{(16)}$ are also represented.

remarkable. This is the reason why l_6 monotonically increases with increasing value of y at $y < 0.1$ but becomes rather insensitive to y at $y > 0.1$.

3.3 Rate-controlling process of intermetallic growth

The values of n at $T = 453$ and 473 K are plotted against y as open circles with error bars in Fig. 6(a) and 6(b), respectively. If the layer growth of the intermetallic layer is controlled by volume diffusion, n is equal to 0.5.^{18–27)} On the other hand, boundary diffusion may govern the layer growth at low temperatures where volume diffusion is frozen out. When the layer growth is controlled by boundary diffusion across the intermetallic layer and grain growth occurs in the intermetallic layer, n becomes smaller than 0.5.²⁸⁾ For $y = 0$ – 0.03 at $T = 453$ K, n takes values of 0.37–0.46, and thus boundary diffusion mainly governs the layer growth. Such a rate-controlling process works also for $y = 0$ at $T = 473$ K. On the other hand, n takes values of 0.63–0.69 for $y = 0.01$ – 0.03 at $T = 473$ K. If the interface reaction at the moving

interface controls the layer growth, n is equivalent to unity.^{29–37} As mentioned in Section 3.1, the intermetallic layer grows predominantly into the Sn–Cu specimen. Furthermore, $(\text{Cu,Ni})_6\text{Sn}_5$ and Ni_3Sn_4 are located on the Sn–Cu and Ni sides, respectively. Thus, the values $n = 0.63$ – 0.69 indicate that the layer growth is governed by the interface reaction at the migrating $(\text{Sn–Cu})/(\text{Cu,Ni})_6\text{Sn}_5$ interface as well as the interdiffusion across the intermetallic layer. Such a mixed rate-controlling process of reactive diffusion has been observed for various metal systems. For instance, the reactive diffusion in the $(\text{Cu–Sn})/\text{Nb}$ system was experimentally examined using diffusion couples consisting of Cu–Sn alloys and Nb in previous studies.^{29–31} In these experiments, the diffusion couple was isothermally annealed at $T = 923$ – 1053 K. During annealing, a single-phase Nb_3Sn layer is formed at the original $(\text{Cu–Sn})/\text{Nb}$ interface in the diffusion couple and grows mainly towards the Nb. Here, Nb_3Sn is one of the most important superconducting materials. According to the results in Fig. 5, the overall growth rate of the intermetallic layer and thus the migration rate of the $(\text{Sn–Cu})/(\text{Cu,Ni})_6\text{Sn}_5$ interface is greater for $y = 0.01$ – 0.03 than for $y = 0$. For the fast interface migration, the interface reaction is a bottleneck for the overall layer growth, and hence n becomes greater than 0.5.^{36,37} Therefore, at $T = 473$ K, n is greater than 0.5 for $y = 0.01$ – 0.03 , though n is smaller than 0.5 for $y = 0$. As the annealing temperature T decreases, the interdiffusion across the intermetallic layer becomes sluggish, and thus the interface reaction is no longer a bottleneck. Consequently, at $T = 453$ K, n is smaller than 0.5 not only for $y = 0$ but also for $y = 0.01$ – 0.03 .

4. Conclusions

The solid-state reactive diffusion in the $(\text{Sn–Cu})/\text{Ni}$ system was experimentally observed using the $(\text{Sn–Cu})/\text{Ni}/(\text{Sn–Cu})$ diffusion couples with Cu mol fractions of $y = 0.01$ – 0.03 . The diffusion couples were isothermally annealed in the temperature range of $T = 453$ – 473 K for various times up to $t = 1972$ h. During annealing, the $(\text{Cu,Ni})_6\text{Sn}_5 + \text{Ni}_3\text{Sn}_4$ two-phase layer is formed at the original $(\text{Sn–Cu})/\text{Ni}$ interface in the diffusion couple. The total thickness of the two-phase layer is proportional to a power function of the annealing time. The exponent of the power function takes values of 0.37–0.44 at $T = 453$ K and those of 0.63–0.69 at $T = 473$ K. Therefore, at $T = 453$ K, the growth of the two-phase layer is controlled by boundary and volume diffusion. In contrast, at $T = 473$ K, interface reaction as well as interdiffusion contributes to the rate-controlling process of the layer growth. The overall growth of the two-phase layer is accelerated by the addition of Cu into Sn.

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