Kinetic Features of Reactive Diffusion between Sn–5Au Alloy and Ni at Solid-State Temperatures

Yu-ichi Yato^{*1} and Masanori Kajihara^{*2}

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

In order to examine microstructure evolution at the interconnection between the Sn-base solder and Au/Ni/Cu multilayer conductor alloys during energization heating, the kinetics of the reactive diffusion between a binary Sn–5 at% Au alloy and pure Ni was experimentally observed at solid-state temperatures. Sandwich (Sn–Au)/Ni/(Sn–Au) diffusion couples were prepared by a diffusion bonding technique, and then isothermally annealed at temperatures of $T = 433$, 453 and 473 K for various periods up to 1057 h. During annealing, AuNiSn_8 and Ni_3Sn_4 compound layers are formed along the (Sn–Au)/Ni interface in the diffusion couple. The total thickness of the compound layers is expressed as a power function of the annealing time. The exponent of the power function is close to 0.5 at $T = 453$ –473 K, and equal to 0.7 at $T = 433$ K. Therefore, volume diffusion is the rate-controlling process for the growth of the compound layers at $T = 453$ –473 K, but interface reaction contributes to the rate-controlling process at $T = 433$ K. The growth of the compound layers occurs slower for the reactive diffusion between the Sn–5Au alloy and Ni than for that between Sn and Au, but faster for that between the Sn–5Au alloy and Ni than for that between Sn and Ni. [doi:10.2320/matertrans.47.2277]

(Received April 10, 2006; Accepted July 4, 2006; Published September 15, 2006)

Keywords: diffusion bonding, reactive diffusion, intermetallic compounds, bulk diffusion, solder, conductor

1. Introduction

Owing to high electrical conductivity, Cu-base alloys are widely used as conductor materials in electronic industry. When the Cu-base conductor alloy is interconnected with a Sn-base solder alloy, Cu–Sn compounds are formed at the interconnection during soldering and then grow during heating under energization conditions.^{1–9)} Since the Cu–Sn compounds are brittle and possess high electrical resistivities, the growth of the compounds deteriorates the electrical and mechanical properties of the interconnection. The Cu-base alloy is usually plated with a Ni layer in order to inhibit the formation of the Cu–Sn compounds, and the Ni layer is plated with a Au layer for improvement of the corrosion resistance. If the Au layer of the Au/Ni/Cu multilayer conductor alloy is very thin, however, the Au layer completely dissolves into the molten solder during soldering.^{10–15)} As a consequence, the reactive diffusion between the Ni layer and the molten solder occurs immediately after the complete dissolution of the Au layer, and then a binary Ni–Sn compound is formed at the interface. Such a compound will grow under the energization heating conditions and may also deteriorate the electrical and mechanical properties at the interconnection.

Chen and Chen¹⁶⁾ experimentally observed the reactive diffusion in the binary Sn/Ni system. In their experiment, sandwich Sn/Ni/Sn diffusion couples were prepared by a soldering technique and then annealed at temperatures between $T = 433$ and 473 K. Their observation indicates that a layer of Ni_3Sn_4 is produced along the Sn/Ni interface in the diffusion couple during soldering and grows during annealing. The thickness of the Ni_3Sn_4 layer is nearly proportional to the square root of the annealing time. Such a relationship is called the parabolic relationship. The parabolic relationship implies that the growth of the Ni_3Sn_4 layer

is controlled by volume diffusion. However, in the soldering technique, the Ni_3Sn_4 layer with a certain thickness is formed during soldering before annealing. Therefore, it is not so easy to distinguish the growth rate during annealing from the formation rate during soldering. Consequently, the soldering technique is not appropriate to observe the growth behavior of the Ni_3Sn_4 layer during annealing at solid-state temperatures.

The reactive diffusion in various binary and ternary systems was experimentally observed at solid-state temperatures using sandwich diffusion couples prepared by a diffusion bonding technique in previous studies.^{17–30)} As to the binary Sn/Ni system,¹⁷⁾ Sn/Ni/Sn diffusion couples were isothermally annealed at $T = 433$, 453 and 473 K for various periods. Along the Sn/Ni interface in the diffusion couple, Ni_3Sn_4 is produced as a layer at $T = 453$ and 473 K but as fine particles at $T = 433$ K. On the other hand, AuSn_4 , AuSn_2 and AuSn layers are formed in Sn/Au/Sn diffusion couples at $T = 393$ –473 K,^{18–20)} and Cu_6Sn_5 and Cu_3Sn layers are produced in Sn/Cu/Sn diffusion couples at $T = 433$ –473 K.²¹⁾ In the binary Sn/Au, Sn/Cu and Sn/Ni systems, the total thickness of the compound layers is described as a power function of the annealing time. The exponent of the power function is mostly smaller than 0.5 at the experimental annealing temperatures. This indicates that grain boundary diffusion contributes to the rate-controlling process for the growth of the compound layers and grain growth takes place at certain rates in the compound layers. At each annealing temperature and time, the total thickness is about one order of magnitude smaller for the Cu–Sn compound layers than for the Au–Sn compound layers, but the thickness of the Ni_3Sn_4 layer is less than half of the total thickness of the Cu–Sn compound layers. As a result, the Ni layer acts as an effective inhibitor against the reactive diffusion between the Au/Ni/Cu multilayer conductor and Sn-base solder alloys during energization heating after the complete dissolution of the Au layer into the molten solder.

When the Au layer of the Au/Ni/Cu multilayer conductor

^{*1}Graduate Student, Tokyo Institute of Technology

^{*2}Corresponding author, E-mail: kajihara@materi.titech.ac.jp

alloy is sufficiently thick, however, the Au–Sn compounds are formed during soldering and then grow during energization heating.^{10–15} If the Au layer is uniformly depleted during growth of the Au–Sn compounds, the Ni layer will be reacted with the Au–Sn compounds after complete depletion of the Au layer. In order to examine characteristic features of such a reaction, the reactive diffusion in the ternary (Sn–Ni)/Au system was experimentally observed at solid-state temperatures using (Sn–Ni)/Au/(Sn–Ni) diffusion couples in a previous study.²² Here, the notation (A–B)/C indicates that reactive diffusion takes place between a binary A–B alloy and a pure C metal at appropriate annealing temperatures. In that experiment, binary Sn–Ni alloys with concentrations of 1, 3 and 5 mass% Ni were used to prepare the diffusion couples by the diffusion bonding technique. The diffusion couples were isothermally annealed at $T = 433$ – 473 K. Due to annealing, AuNiSn₈, AuSn₄, AuSn₂ and AuSn layers are produced along the (Sn–Ni)/Au interface in the diffusion couple. Also in this case, the total thickness of the compound layers is expressed as a power function of the annealing time, and the exponent of the power function takes values between 0.3 and 0.4. This deduces that the same rate-controlling process as the binary Sn/Au, Sn/Cu and Sn/Ni systems works for the ternary (Sn–Ni)/Au system. However, the overall growth rate of the compound layers is greater in the ternary (Sn–Ni)/Au system than in the binary Sn/Au system. This means that the reactive diffusion in the binary Sn/Au system is accelerated by the formation of AuNiSn₈ due to the reaction of Ni with AuSn₄ at $T = 433$ – 473 K.²²

If the Au layer of the Au/Ni/Cu multilayer conductor alloy is completely depleted during soldering and the Au–Sn compounds are non-uniformly produced in the molten solder, the Au–Sn compounds and the Sn-base solder will be simultaneously reacted with the Ni layer during energization heating. In order to examine kinetic features of such a complex reaction, the reactive diffusion in the ternary (Sn–Au)/Ni system was experimentally observed at solid-state temperatures in the present study. Sandwich (Sn–Au)/Ni/(Sn–Au) diffusion couples were prepared from pure Ni and a binary Sn–5 at% Au alloy by the diffusion bonding technique and then isothermally annealed at $T = 433$ – 473 K for various periods. The growth behavior of compound layers was observed in a metallographical manner. On the basis of the observation, the rate-controlling process was discussed for the growth of compound layers.

2. Experimental

A polycrystalline binary Sn–Au alloy containing 5 at% of Au was prepared as a 30 g button ingot by argon arc melting from pure Sn and Au with purity of 99.99%. The ingot was homogenized in an evacuated silica capsule at a temperature of $T = 473$ K for 284 h, followed by water quenching without breaking the capsule. Plate specimens with a dimension of $12\text{ mm} \times 5\text{ mm} \times 1\text{ mm}$ were cut from the ingot, and then the two surfaces with an area of $12\text{ mm} \times 5\text{ mm}$ of each plate specimen were mechanically polished on 1000 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 $1\text{ }\mu\text{m}$. The

mechanically polished plate specimen was chemically polished in an etchant consisting of 13 vol% of nitric acid, 37 vol% of hydrochloric acid and 50 vol% of ethanol.

A polycrystalline pure Ni specimen was prepared as a 25 g button ingot by argon arc melting from pure Ni with purity of 99.97%. Plate specimens with a size of $10\text{ mm} \times 4\text{ mm} \times 2\text{ mm}$ were cut from the button ingot and then cold rolled to a thickness of 0.1 mm . Sheet specimens with a dimension of $20\text{ mm} \times 7\text{ mm} \times 0.1\text{ mm}$ were cut from the cold rolled specimens and then separately annealed in evacuated silica capsules at 1223 K for 2 h, followed by air cooling without breaking the capsules. The annealed sheet specimens were chemically polished in an etchant composed of 9 vol% of nitric acid, 18 vol% of hydrochloric acid and 73 vol% of ethanol.

After chemical polishing, a Ni sheet specimen was immediately sandwiched between the finished surfaces of two freshly prepared Sn–Au plate specimens in ethanol by a technique used in previous studies.^{17–23} The (Sn–Au)/Ni/(Sn–Au) couples were completely dried and then heat treated for diffusion bonding in an oil bath with silicone oil at $T = 433$, 453 and 473 K for 192, 72 and 24 h, respectively. After the heat treatment, the diffusion couples were isothermally annealed at $T = 433$, 453 and 473 K for various times up to 985 h. The summation of the heat-treating and annealing times is hereafter merely denominated the annealing time t . Cross-sections of the annealed diffusion couples were mechanically polished using diamond with diameters of 15, 3 and $1\text{ }\mu\text{m}$ and then finished with an OP-S liquid by Struers Ltd. The microstructure of the cross-section was observed with a back-scattered electron image (BEI) by scanning electron microscopy (SEM) and with an optical microscope (OM). The composition of each phase was measured on the cross-section by electron probe microanalysis (EPMA).

3. Results and Discussion

3.1 Microstructure

Typical micrographs of OM for the cross-sections of the annealed diffusion couples are shown in Fig. 1. The (Sn–5Au)/Ni/(Sn–5Au) diffusion couple is hereafter merely called the Sn–5Au diffusion couple. Figure 1(a) indicates the micrograph for the Sn–5Au diffusion couple with $T = 433\text{ K}$ and $t = 12\text{ h}$ ($4.32 \times 10^5\text{ s}$). In this figure, the regions on the upper and lower sides are the Sn–5Au alloy, and the horizontal band with a thickness of about $100\text{ }\mu\text{m}$ is the Ni specimen. As can be seen, sound interconnection is realized at the interface between the Sn–5Au alloy and the Ni specimen. However, no compound layer is clearly observed at the interface. As a result, annealing was carried out for much longer periods at $T = 433\text{ K}$. On the other hand, Fig. 1(b) shows the micrograph for the Sn–5Au diffusion couple with $T = 473\text{ K}$ and $t = 48\text{ h}$ ($1.73 \times 10^5\text{ s}$). In this case, a layer composed of various compounds with different contrasts is formed along each interface. Such a layer grows mainly towards the Sn–5Au alloy but slightly towards the Ni specimen. The microstructure in Fig. 1(b) is magnified in Fig. 2(a). This figure indicates a micrograph of BEI. In Fig. 2(a), the regions on the upper and lower sides are the Sn–

Fig. 1 Optical micrographs of cross-sections for the Sn–5Au diffusion couples annealed (a) at $T = 433$ K for $t = 12$ h (4.32×10^4 s) and (b) at $T = 473$ K for $t = 48$ h (1.73×10^5 s).

5Au alloy and the Ni specimen, respectively. As to the Sn–5Au alloy, coarse bright grains are distributed in a dark matrix. The chemical composition of each phase was measured by EPMA. According to the EPMA measurement, the bright grain and the dark matrix are AuSn_4 and the primary solid-solution phase of Sn, respectively. A phase diagram in the binary Au–Sn system³¹⁾ indicates that the Sn phase is in equilibrium with AuSn_4 at $T < 490$ K. Furthermore, the solubility of Au in the Sn phase is less than 0.2 at%.³¹⁾ Thus, the Sn + AuSn_4 two-phase microstructure is stable for the Sn–5Au alloy at $T = 433$ – 473 K. In contrast, a layer consisting of bright and dark compounds is produced along the (Sn–Au)/Ni interface as mentioned earlier. The EPMA measurement shows that the bright and dark compounds are AuNiSn_8 and Ni_3Sn_4 , respectively. As can be seen in Fig. 2(a), Ni_3Sn_4 is formed as a slightly wavy thin layer along the interface between the AuNiSn_8 layer and the Ni specimen, and dispersed as fine particles in the AuNiSn_8 layer. The thickness is much smaller for the Ni_3Sn_4 layer than for the AuNiSn_8 layer. This means that interdiffusion takes place much faster across the AuNiSn_8 layer than across the Ni_3Sn_4 layer.³²⁾ The same type of microstructure as Fig. 2(a) was observed for most of the annealed diffusion couples. On the other hand, Fig. 2(b) indicates the BEI micrograph for the Sn–5Au diffusion couple with $T = 473$ K and $t = 722$ h

Fig. 2 Back-scattered electron images of cross-sections for the Sn–5Au diffusion couples annealed at $T = 473$ K for (a) $t = 48$ h (1.73×10^5 s) and (b) $t = 722$ h (2.60×10^6 s).

(2.60×10^6 s). As can be seen, the AuNiSn_8 and Ni_3Sn_4 layers are produced also in this diffusion couple. In Fig. 2(b), however, voids with a dark contrast are recognized along the interface between the AuNiSn_8 layer and the Sn–5Au alloy. Such voids are considered to form due to the Kirkendall effect. The occurrence of the Kirkendall effect indicates that the interdiffusion occurs according to a vacancy mechanism. The formation of voids was clearly observed only for the diffusion couples with $T = 473$ K and $t = 722$ and 840 h (2.60×10^6 and 3.02×10^6 s).

Recently, a phase diagram in the ternary Au–Ni–Sn system was experimentally determined by Liu *et al.*³³⁾ According to their result, a three-phase equilibrium of Sn + AuSn_4 + Ni_3Sn_4 as well as two-phase equilibria of Sn + AuSn_4 , Sn + Ni_3Sn_4 and AuSn_4 + Ni_3Sn_4 appears at the Sn-rich corner of the isothermal section with $T = 473$ K. The solubility of Ni in AuSn_4 is 11.5 at% at $T = 473$ K.³³⁾ This yields the composition $\text{Au}_{0.85}\text{Ni}_{1.15}\text{Sn}_8$. The composition AuNiSn_8 is close to $\text{Au}_{0.85}\text{Ni}_{1.15}\text{Sn}_8$. Consequently, the microstructure for the compound layers in the Sn–5Au diffusion couple is well explained by the phase equilibria in the ternary Au–Ni–Sn system.

3.2 Growth behavior of intermetallic layer

From the cross-sectional BEI micrographs like Fig. 2, the total thickness l of the compound layers was evaluated by the equation

Fig. 3 The total thickness l of the intermetallic layer versus the annealing time t for the Sn-5Au diffusion couple at $T = 433, 453$ and 473 K shown as open triangles, squares and circles, respectively. Straight lines indicate the calculations from eq. (2).

$$l = A/w, \quad (1)$$

where A and w are the total area and the total length of the compound layers, respectively, on the cross-section. Hereafter, the layer composed of various compounds is called the intermetallic layer. At each annealing time, l was calculated from eq. (1) using the total values of A and w for various cross-sections. The results of $T = 433, 453$ and 473 K are shown as open triangles, squares and circles, respectively, in Fig. 3. In this figure, the ordinate indicates the logarithm of the thickness l , and the abscissa shows the logarithm of the annealing time t . As can be seen, the thickness l monotonically increases with increasing annealing time t . The plotted points at each annealing temperature lie well on a straight line. This deduces that l is expressed as a power function of t by the following equation:

$$l = k(t/t_0)^n. \quad (2)$$

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 , but the exponent n is dimensionless. From the plotted points in Fig. 3, the values of k and n were evaluated by the least-squares method. The evaluated values are indicated in Fig. 3. Using these values of k and n , the thickness l was calculated as a function of the annealing time t from eq. (2). The results of $T = 433, 453$ and 473 K are shown as dotted, dashed and solid lines, respectively, in Fig. 3. At each annealing time, the thickness l increases with increasing annealing temperature T . Thus, the higher the annealing temperature is, the larger the overall growth rate of the intermetallic layer becomes. As mentioned in Section 3.1, the Kirkendall voids are formed along the interface between the AuNiSn₈ layer and the Sn-5Au alloy at $T = 473$ K for $t = 722$ and 840 h (2.60×10^6 and 3.02×10^6 s). However, the two open circles for these annealing times are located well on the solid line of

$T = 473$ K in Fig. 3. Thus, it is concluded that formation of the Kirkendall voids hardly affects the growth rate of the intermetallic layer.

The results of $T = 453$ and 473 K in Fig. 3 are plotted again as open circles with solid lines in Figs. 4(a) and (b), respectively. As mentioned in Section 1, the reactive diffusion was experimentally observed at solid-state temperatures for the binary Sn/Ni¹⁷⁾ and Sn/Au^{18–20)} systems using the Sn/Ni/Sn and Sn/Au/Sn diffusion couples, respectively, in previous studies. The Sn/Au/Sn and Sn/Ni/Sn diffusion couples are denoted by the Au and Ni diffusion couples, respectively. The intermetallic layer consisting of AuSn₄, AuSn₂ and AuSn is formed at $T = 393$ – 473 K in the Au diffusion couple, but that composed of only Ni₃Sn₄ is produced at $T = 453$ – 473 K in the Ni diffusion couple. The experimental values of l for the Au and Ni diffusion couples are represented as open squares and triangles, respectively, in Fig. 4. From these open symbols, k and n in eq. (2) were evaluated by the least-squares method. The evaluated values are shown in Fig. 4. Using these values of k and n , l was calculated as a function of t from eq. (2). The results for the Au and Ni diffusion couples are indicated as dashed and dotted lines, respectively, in Fig. 4. At each annealing temperature and time, the thickness l is about one order of magnitude greater for the Sn-5Au diffusion couple than for the Ni diffusion couple, but smaller for the Sn-5Au diffusion couple than for the Au diffusion couple. In the Sn-5Au diffusion couple, the intermetallic layer consisting of AuNiSn₈ and Ni₃Sn₄ is produced by the reactive diffusion between Ni and Sn + AuSn₄. The overall growth rate of the intermetallic layer is greater for the reactive diffusion between Ni and Sn + AuSn₄ than for that between Ni and Sn but smaller for that between Ni and Sn + AuSn₄ than for that between Au and Sn. Thus, the Ni layer still works as an inhibitor against the reactive diffusion between the Au/Ni/Cu multilayer conductor and Sn-base solder alloys during energization heating, even if AuSn₄ is non-uniformly formed in the molten solder and the Au layer of the Au/Ni/Cu multilayer conductor alloy is completely depleted during soldering.

3.3 Rate-controlling process

The values of the exponent n for the Sn-5Au, Au and Ni diffusion couples are plotted against the annealing temperature T as open circles, squares and triangles, respectively, in Fig. 5. Here, the ordinate and the abscissa indicate n and T , respectively. The reactive diffusion in the ternary Sn/(Au-Ni) system was experimentally observed using Sn/(Au-27Ni)/Sn and Sn/(Au-46Ni)/Sn diffusion couples in a previous study.²⁹⁾ The Sn/(Au-27Ni)/Sn and Sn/(Au-46Ni)/Sn diffusion couples are merely called the Au-27Ni and Au-46Ni diffusion couples, respectively. During isothermal annealing at $T = 433$ – 473 K, the intermetallic layer composed of Au_{1.5}Ni_{0.5}Sn₈ and AuNi₂Sn₄ is formed along the Sn/(Au-Ni) interface in the Au-46Ni diffusion couple, but that consisting of Au_{1.7}Ni_{0.3}Sn₈, AuSn₂ and Au₆Ni₄Sn₁₅ dispersed with fine particles of AuNi₂Sn₄ is produced along the interface in the Au-27Ni diffusion couple. Also for these diffusion couples, the total thickness l of the intermetallic layer is expressed as a power function of the annealing time t

Fig. 4 The results of $T = 453$ and 473 K in Fig. 3 are represented as open circles with solid lines in (a) and (b), respectively. The results for the Ni¹⁷⁾ and Au^{19,20)} diffusion couples are also shown as open triangles and squares, respectively.

by eq. (2). The values of the exponent n for the Au–27Ni and Au–46Ni diffusion couples²⁹⁾ are represented as open rhombuses and inverse-triangles, respectively, in Fig. 5.

As to the Au diffusion couple, n is equal to 0.36 at $T = 473$ K, and monotonically increases with decreasing annealing temperature.^{18–20)} At $T = 393$ K, n is close to 0.5. When the volume diffusion of the constituent elements in each phase is the rate-controlling process for the growth of the intermetallic layer, n is equal to 0.5. On the other hand, the growth will be governed by the grain boundary diffusion along grain boundaries with a finite thickness in the intermetallic layer at low annealing temperatures where the volume diffusion is practically frozen out. If grain growth takes place in the intermetallic layer, the volume fraction of the grain boundaries monotonically decreases with increasing annealing time. Such decrease in the volume fraction

Fig. 5 The exponent n versus the annealing temperature T for the Sn–5Au diffusion couple shown as open circles. The results for the Ni¹⁷⁾, Au^{19,20)}, Au–27Ni and Au–46Ni²⁹⁾ diffusion couples are also indicated as open triangles, squares, rhombuses and inverse-triangles, respectively.

results in the decrement of the effective cross-section, and decelerates the grain boundary diffusion. Thus, n becomes smaller than 0.5. When the grain size is proportional to the square root of the annealing time, n is equal to 0.25.³⁴⁾ If the grain growth occurs very sluggishly, the volume fraction of the grain boundaries remains almost constant during annealing. In such a case, the effective cross-section for the grain boundary diffusion hardly varies, and hence n is almost equal to 0.5. From the temperature dependence of n for the Au diffusion couple in Fig. 5, it is concluded that the grain boundary diffusion as well as the volume diffusion contributes to the rate-controlling process and the grain growth takes place at certain rates at higher annealing temperatures.^{19,20)} As the annealing temperature decreases, the contribution of the grain boundary diffusion becomes remarkable, but the grain growth slows down. Similar temperature dependence of the rate-controlling process was recognized also for the Ni¹⁷⁾ and Au–27Ni²⁹⁾ diffusion couples.

On the other hand, for the Sn–5Au diffusion couple, n is close to 0.5 at $T = 453$ – 473 K, but equal to 0.7 at $T = 433$ K. Like the Au, Ni and Au–27Ni diffusion couples, the grain growth in the intermetallic layer may occur at certain rates also for the Sn–5Au diffusion couple. Nevertheless, n is close to 0.5 at $T = 453$ – 473 K for the Sn–5Au diffusion couple. This means that the volume diffusion is the rate-controlling process.²⁵⁾ At $T = 433$ K, however, n is equal to 0.7 for the Sn–5Au diffusion couple. Thus, interface reaction contributes to the rate-controlling process.^{27,30)} According to the OM micrographs in Fig. 1, the intermetallic layer grows mainly towards the Sn–Au alloy but slightly towards the Ni specimen. Furthermore, the most predominant compound determining the overall growth rate of the intermetallic layer is AuNiSn₈. Therefore, the growth rate of the intermetallic layer is dominantly determined by the migration rate of the AuNiSn₈/(Sn–Au) interface. As a consequence, for the Sn–

5Au diffusion couple, the interface reaction at the migrating AuNiSn₈/(Sn–Au) interface becomes the bottleneck for the growth of the intermetallic layer at $T = 433$ K. The same temperature dependence of the rate-controlling process as the Sn–5Au diffusion couple was observed for the Au–46Ni diffusion couple.²⁹⁾

This type of rate-controlling process was experimentally examined for the reactive diffusion in the ternary (Cu–Sn)/Nb system in a previous study.²⁷⁾ In that experiment, (Cu–Sn)/Nb/(Cu–Sn) diffusion couples with a concentration of 8.3 at% Sn were isothermally annealed at temperatures of $T = 923$ – 1053 K. During annealing, a layer of Nb₃Sn is formed along the (Cu–Sn)/Nb interface in the diffusion couple, and the thickness l of the Nb₃Sn layer increases in proportion to a power function of the annealing time t . Thus, the growth of the Nb₃Sn layer is also described by eq. (2). Since the Nb₃Sn layer grows mainly towards the Nb specimen, the migration of the Nb₃Sn/Nb interface principally governs the growth of the Nb₃Sn layer. The exponent n in eq. (2) is nearly equal to unity at $T = 923$ – 973 K and monotonically decreases from 1 to 0.8 with increasing annealing temperature from $T = 973$ K to $T = 1053$ K. This indicates that the interface reaction at the Nb₃Sn/Nb interface is the rate-controlling process for the growth of the Nb₃Sn layer at $T = 923$ – 973 K and the volume diffusion across the Nb₃Sn layer contributes to the rate-controlling process at $T = 973$ – 1053 K. In the temperature range of $T = 923$ – 973 K, the temperature dependence of the proportionality coefficient k in eq. (2) was expressed as

$$k = k_0 \exp(-Q_k/RT), \quad (3)$$

and then the activation enthalpy Q_k was evaluated to be 150 kJ/mol.²⁷⁾ Here, k_0 and R are the pre-exponential factor and the gas constant, respectively. The value $Q_k = 150$ kJ/mol represents the activation enthalpy of the interface reaction at the Nb₃Sn/Nb interface. On the other hand, the corresponding value of Q_k for the rate-controlling process of the volume diffusion was estimated as 100 kJ/mol.²⁷⁾ The smaller the value of Q_k is, the less sensitive the temperature dependence of k becomes. As the annealing temperature increases, the rate of the interface reaction increases more remarkably than that of the volume diffusion. Therefore, the interface reaction is no longer the bottleneck for the migration of the Nb₃Sn/Nb interface at higher annealing temperatures. This is the reason why the interface reaction is the rate-controlling process at $T = 923$ – 973 K but the volume diffusion contributes to the rate-controlling process at $T = 973$ – 1053 K. Such an explanation may be possible also for the temperature dependence of the rate-controlling process for the Sn–5Au and Au–46Ni diffusion couples. Unfortunately, however, the value of Q_k is not known for the interface reaction in these diffusion couples. Consequently, the explanation is not available for the Sn–5Au and Au–46Ni diffusion couples, though the activation enthalpy of the volume diffusion has been estimated below.

When the reactive diffusion is controlled by the volume diffusion, the growth of the intermetallic layer is expressed by the following equation:³²⁾

$$l^2 = Kt. \quad (4)$$

Fig. 6 The parabolic coefficient K versus the reciprocal of the annealing temperature T for the Sn–5Au diffusion couple shown as open circles. The results for the Pd,²⁵⁾ Cu³⁹⁾ and Au–46Ni²⁹⁾ diffusion couples are also indicated as open triangles, rhombuses and squares, respectively. Straight lines show the calculations from eq. (5).

Equation (4) is a formula of the parabolic relationship, where K is the parabolic coefficient with a dimension of m^2/s . As mentioned above, the volume diffusion is the rate-controlling process for the Sn–5Au diffusion couple at $T = 453$ – 473 K. Thus, the values of K at $T = 453$ and 473 K for the Sn–5Au diffusion couple were evaluated from eq. (4) using the open squares and circles, respectively, in Fig. 3 by the least-squares method. The evaluation gives $K = 1.23 \times 10^{-14}$ and $4.03 \times 10^{-14} \text{ m}^2/\text{s}$ at $T = 453$ and 473 K, respectively. These values are plotted against the annealing temperature T as open circles in Fig. 6. In this figure, the ordinate shows the logarithm of K , and the abscissa indicates the reciprocal of T . The temperature dependence of K is described by the following equation with certain accuracy:^{35–38)}

$$K = K_0 \exp(-Q_K/RT). \quad (5)$$

Here, K_0 and Q_K are the pre-exponential factor and the activation enthalpy, respectively. Interconnecting the two open circles with a solid line in Fig. 6, we obtain $K_0 = 1.92 \times 10^{-3} \text{ m}^2/\text{s}$ and $Q_K = 106 \text{ kJ/mol}$ for the Sn–5Au diffusion couple. As mentioned earlier, the growth of the intermetallic layer is controlled by the volume diffusion also for the Au–46Ni diffusion couple at $T = 453$ – 473 K. The values of K for the Au–46Ni diffusion couple²⁹⁾ are represented as open squares in Fig. 6. Interconnection of the two open squares with a dashed line yields $K_0 = 2.26 \times 10^{-5} \text{ m}^2/\text{s}$ and $Q_K = 79.3 \text{ kJ/mol}$.²⁹⁾

The reactive diffusion in the binary Sn/Pd system was experimentally observed at $T = 433$ – 473 K using Sn/Pd/Sn diffusion couples in a previous study.²⁵⁾ The Sn/Pd/Sn diffusion couple is denominated the Pd diffusion couple. For the Pd diffusion couple, the intermetallic layer is composed of PdSn₄, PdSn₃ and PdSn₂ at $T = 433$ K but only PdSn₄ and PdSn₃ at $T = 453$ and 473 K. Although the grain growth surely occurs in the intermetallic layer, the thickness l is

almost proportional to the square root of the annealing time t at $T = 433\text{--}473\text{ K}$.²⁵⁾ This guarantees that the growth of the intermetallic layer is governed by the volume diffusion. The values of K for the Pd diffusion couple are represented as open triangles in Fig. 6. From the open triangles, $K_0 = 8.20 \times 10^{-2} \text{ m}^2/\text{s}$ and $Q_K = 106 \text{ kJ/mol}$ are obtained by the least-squares method. In contrast, Onishi and Fujibuchi experimentally observed the reactive diffusion in the binary Sn/Cu system at $T = 463\text{--}493\text{ K}$ using Sn/Cu diffusion couples.³⁹⁾ The Sn/Cu diffusion couple is denoted by the Cu diffusion couple. The values of K for the Cu diffusion couple are also represented as open rhombuses in Fig. 6. For the open rhombuses, $K_0 = 6.23 \times 10^{-10} \text{ m}^2/\text{s}$ and $Q_K = 57.7 \text{ kJ/mol}$ were reported by Onishi and Fujibuchi.³⁹⁾ Using these values of K_0 and Q_K , K was calculated as a function of T from eq. (5). The results for the Pd and Cu diffusion couples are indicated as dotted and dashed-and-dotted lines, respectively, in Fig. 6. As can be seen, K is smaller for the Sn–5Au diffusion couple than for the Au–46Ni and Pd diffusion couples, but greater for the Sn–5Au diffusion couple than for the Cu diffusion couple. The overall growth rate of the intermetallic layer is close to each other for the Pd and Au diffusion couples.^{19,20,25)} Thus, the reactive diffusion between Ni and Sn + AuSn₄ occurs more slowly than that between Au and Sn but more rapidly than that between Cu and Sn. Consequently, Ni layer still acts as an inhibitor against the reactive diffusion between the Au/Ni/Cu multilayer conductor and Sn-base solder alloys during energization heating, even if AuSn₄ is formed in the molten solder and the Au layer is completely depleted during soldering. However, the kinetics of this reactive diffusion is faster than that of the reactive diffusion between the Cu-base conductor and Sn-base solder alloys. The value $Q_K = 106 \text{ kJ/mol}$ for the Sn–5Au and Pd diffusion couples is rather close to that $Q_K = 79.3 \text{ kJ/mol}$ for the Au–46Ni diffusion couple, but greater than that $Q_K = 57.7 \text{ kJ/mol}$ for the Cu diffusion couple. When the intermetallic layer consists of compound layers with parallel interfaces and temperature dependencies of interdiffusion coefficients in relevant phases are known for reactive diffusion in a binary system, Q_K is quantitatively related with the activation enthalpies Q of the interdiffusion coefficients in an analytical manner.^{35–37)} Even in such a case, however, complex information of Q for the relevant phases is included in Q_K . Hence, it may not be valid to discuss the rate-controlling process of the reactive diffusion only from the value of Q_K .

4. Conclusions

The reactive diffusion in the ternary (Sn–Au)/Ni system was experimentally observed at solid-state temperatures using the sandwich (Sn–5Au)/Ni/(Sn–5Au) diffusion couple prepared by the diffusion bonding technique. The diffusion couple was isothermally annealed in the temperature range between $T = 433$ and 473 K for various times up to 1057 h in the oil bath with silicone oil. In this temperature range, the coarse grains of AuSn₄ are distributed in the primary solid-solution phase of Sn for the binary Sn–5Au alloy. During annealing, the AuNiSn₈ and Ni₃Sn₄ layers are formed along the (Sn–Au)/Ni interface in the diffusion couple. The total

thickness l of the compound layers is expressed as a power function of the annealing time t by the equation $l = k(t/t_0)^n$, where t_0 is unit time, 1 s . Here, n is close to 0.5 at $T = 453\text{--}473\text{ K}$, but equal to 0.7 at $T = 433\text{ K}$. This means that the growth of the compound layers is controlled by the volume diffusion of the constituent elements in each phase at $T = 453\text{--}473\text{ K}$ but the interface reaction at the migrating AuNiSn₈/(Sn–Au) interface contributes to the rate-controlling process at $T = 433\text{ K}$. The overall growth rate of the compound layers is smaller for the ternary (Sn–Au)/Ni system than for the binary Sn/Au system, but greater for the ternary (Sn–Au)/Ni system than for the binary Sn/Ni and Sn/Cu systems.

Acknowledgements

The authors are grateful to Messrs. K. Sakamoto and N. Kurokawa at Tyco Electronics AMP Co. Ltd., Japan for stimulating discussions. They also wish to thank Professor K. Ishida and Professor R. Kainuma at Tokohu University, Japan for their helpful information of the phase equilibria in the ternary Au–Ni–Sn system. The present study was supported by Tyco Electronics AMP Co. Ltd., Japan. The study was also partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

REFERENCES

- 1) L. Zakraysek: *Welding Res. Suppl.* Nov. (1972) 536–541.
- 2) K. N. Tu: *Acta Metall.* **21** (1973) 347–354.
- 3) H. N. Keller: *IEEE Trans. Components Hybrids Manuf. Tech.* CHMT-2 (1979) 180–195.
- 4) H. N. Keller and J. M. Morabito: *Surf. Interface Anal.* **3** (1981) 16–22.
- 5) J. O. G. Parent, D. D. L. Chung and I. M. Bernstein: *J. Mater. Sci.* **23** (1988) 2564–2572.
- 6) A. J. Sunwoo, J. W. Morris, Jr. and G. K. Lucey, Jr.: *Metall. Trans. A* **23** (1992) 1323–1332.
- 7) P. T. Vianco, P. F. Hlava and A. L. Kilgo: *J. Electron. Mater.* **23** (1994) 583–594.
- 8) D. R. Frear and P. T. Vianco: *Metall. Trans.* **25A** (1994) 1509–1523.
- 9) S. Choi, T. R. Bieler, J. P. Lucas and K. N. Subramanian: *J. Electron. Mater.* **28** (1999) 1209–1215.
- 10) P. G. Kim and K. N. Tu: *J. Appl. Phys.* **80** (1996) 3822–3827.
- 11) A. M. Minor and J. W. Morris, Jr.: *Metall. Mater. Trans.* **31A** (2000) 798–800.
- 12) J. H. Lee, J. H. Park, Y. H. Lee and Y. S. Kim: *J. Mater. Res.* **16** (2001) 1249–1251.
- 13) H. G. Song, J. P. Ahn, A. M. Minor and J. W. Morris, Jr.: *J. Electron. Mater.* **30** (2001) 409–414.
- 14) M. O. Alam and Y. C. Chan: *Chem. Mater.* **15** (2003) 4340–4342.
- 15) M. O. Alam and Y. C. Chan: *J. Mater. Res.* **19** (2004) 1303–1306.
- 16) C. M. Chen and S. W. Chen: *Acta Mater.* **50** (2002) 2461–2469.
- 17) M. Mita, M. Kajihara, N. Kurokawa and K. Sakamoto: *Mater. Sci. Eng. A* **403** (2005) 269–275.
- 18) M. Kajihara, T. Yamada, K. Miura, N. Kurokawa and K. Sakamoto: *Netsushori* **43** (2003) 297–298.
- 19) T. Yamada, K. Miura, M. Kajihara, N. Kurokawa and K. Sakamoto: *J. Mater. Sci.* **39** (2004) 2327–2334.
- 20) T. Yamada, K. Miura, M. Kajihara, N. Kurokawa and K. Sakamoto: *Mater. Sci. Eng. A* **390** (2005) 118–126.
- 21) T. Takenaka, S. Kano, M. Kajihara, N. Kurokawa and K. Sakamoto: *Mater. Sci. Eng. A* **396** (2005) 115–123.
- 22) M. Mita, K. Miura, T. Takenaka, M. Kajihara, N. Kurokawa and K. Sakamoto: *Mater. Sci. Eng. B* **126** (2006) 37–43.
- 23) T. Takenaka, S. Kano, M. Kajihara, N. Kurokawa and K. Sakamoto:

- Mater. Trans. **46** (2005) 1825–1832.
- 24) K. Suzuki, S. Kano, M. Kajihara, N. Kurokawa and K. Sakamoto: Mater. Trans. **46** (2005) 969–973.
- 25) T. Takenaka, M. Kajihara, N. Kurokawa and K. Sakamoto: Mater. Sci. Eng. A **406** (2005) 134–141.
- 26) T. Takenaka and M. Kajihara: Mater. Trans. **47** (2006) 822–828.
- 27) Y. Muranishi and M. Kajihara: Mater. Sci. Eng. A **404** (2005) 33–41.
- 28) T. Takenaka, M. Kajihara, N. Kurokawa and K. Sakamoto: Mater. Sci. Eng. A **427** (2006) 210–222.
- 29) Y. Yato and M. Kajihara: Mater. Sci. Eng. A **428** (2006) 276–283.
- 30) T. Hayase and M. Kajihara: Mater. Sci. Eng. A, in press.
- 31) T. B. Massalski, H. Okamoto, P. R. Subramanian and L. Kacprzak: *Binary Alloy Phase Diagrams* (ASM International, Materials Park, OH, 1990) vol. 1, p. 434.
- 32) M. Kajihara: Acta Mater. **52** (2004) 1193–1200.
- 33) X. J. Liu, M. Kinaka, Y. Takaku, I. Ohnuma, R. Kainuma and K. Ishida: J. Electron. Mater. **34** (2005) 670–679.
- 34) Y. L. Corcoran, A. H. King, N. de Lanerolle and B. Kim: J. Electron. Mater. **19** (1990) 1177–1183.
- 35) M. Kajihara: Mater. Sci. Eng. A **403** (2005) 234–240.
- 36) M. Kajihara: Mater. Trans. **46** (2005) 2142–2149.
- 37) M. Kajihara: Def. Diff. Forum **249** (2006) 91–96.
- 38) M. Kajihara: Mater. Trans. **47** (2006) 1480–1484.
- 39) M. Onishi and H. Fujibuchi: Trans. JIM **16** (1975) 539–547.