Kinetics of Solid-State Reactive Diffusion in the (Pd–Cr)/Sn System

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The growth of compounds during energization heating at the interconnection between a Sn-based solder and a multilayer Pd/Ni/Cu conductor may be inhibited by alloying of Pd with Cr. To examine such influence of Cr on the compound growth, the kinetics of solid-state reactive diffusion in the (Pd–Cr)/Sn system was experimentally determined in the present study. Experiments were conducted using Sn/(Pd–Cr)/Sn diffusion couples with Cr mol fractions of $y = 0.110, 0.215$ and 0.323 which were prepared by a diffusion bonding technique. The diffusion couples were isothermally annealed in the temperature range of $T = 433\text{--}473$ K for various times up to $t = 360$ h. During annealing, a compound layer consisting of different matrices and lamellar phases is formed at the original (Pd–Cr)/Sn interface in the diffusion couple. From the Pd–Cr side to the Sn side in the compound layer, the matrices are PdSn_2 , PdSn_3 and PdSn_4 , and the lamellar phases are $(\text{Cr}_{0.9}\text{Pd}_{0.1})_3\text{Sn}$, $(\text{Cr}_{0.95}\text{Pd}_{0.05})_2\text{Sn}$, $(\text{Cr}_{0.9}\text{Pd}_{0.1})\text{Sn}$ and CrSn_2 . The total thickness of the compound layer is proportional to a power function of the annealing time. The exponent n of the power function is rather close to 0.5 independent of y at $T = 453\text{--}473$ K. At $T = 433$ K, however, $n \cong 0.5$ for $y = 0\text{--}0.110$, but $n = 0.7\text{--}0.8$ for $y = 0.215\text{--}0.323$. Thus, the overall compound growth is controlled by volume diffusion for $y = 0\text{--}0.323$ at $T = 453\text{--}473$ K and for $y = 0\text{--}0.110$ at $T = 433$ K. On the other hand, for $y = 0.215\text{--}0.323$ at $T = 433$ K, the interface reaction at the moving interface contributes to the rate-controlling process. The overall growth rate of the compound layer is insensitive to y at $y < y_c$ but monotonically decreases with increasing value of y at $y > y_c$, where $y_c = 0.1$ and 0.2 at $T = 433\text{--}453$ K and 473 K, respectively. Consequently, the compound growth is actually decelerated by the addition of Cr with $y > 0.2$ into Pd in the multilayer Pd/Ni/Cu conductor.

[doi:10.2320/matertrans.M2014202]

(Received May 30, 2014; Accepted October 14, 2014; Published December 5, 2014)

Keywords: metallization, solder, conductor, intermetallics

1. Introduction

Copper-based alloys are widely used as conductor materials in the electronics industry due to high electrical conductivity. If the Cu-based conductor is interconnected using a Sn-based 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 suppress Cu–Sn compound formation, the Cu-based conductor is generally 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)}

The reactive diffusion in the Pd/Sn system was experimentally examined at solid-state temperatures using Sn/Pd/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 $T = 433\text{--}473$ K. At the Pd/Sn interface in the diffusion couple, PdSn_4 , PdSn_3 and PdSn_2 layers are formed at $T = 433$ K, but only PdSn_4 and PdSn_3 layers are produced at $T = 453$ K and 473 K. In this case, the total thickness of the compound layers is proportional to the square root of the annealing time. Such a relationship is called the parabolic relationship. Furthermore, grain growth occurs in the compound layers. As a consequence, the layer growth is controlled by volume diffusion.¹⁷⁾ At $T = 433\text{--}473$ K, however, the overall growth rate of the compound layers is one order of magnitude greater for the reactive diffusion in the Pd/Sn system¹⁶⁾ than for that in the Cu/Sn system.¹¹⁾

Hence, the Pd layer of the multilayer Pd/Ni/Cu conductor accelerates the deterioration of the interconnection during solid-state energization heating.

The effect of Ag on the solid-state reactive diffusion in the Pd/Sn system was experimentally examined in previous studies.^{18,19)} In these experiments, Sn/(Pd–Ag)/Sn diffusion couples with Ag concentrations of $y = 0.25\text{--}0.75$ were isothermally annealed at $T = 433\text{--}473$ K, where y stands for the mol fraction of Ag. As to $y = 0.25\text{--}0.50$,¹⁸⁾ a PdSn_4 layer dispersed with fine Ag_3Sn particles is predominantly formed at the (Pd–Ag)/Sn interface in the diffusion couple during annealing. On the other hand, for $y = 0.75$,¹⁹⁾ a compound layer composed of PdSn_4 and Ag_3Sn lamellae is produced at the interface. Like the Pd/Sn system, the parabolic relationship holds between the thickness of the compound layer and the annealing time also in the (Pd–Ag)/Sn system. Here, the notation (A–B)/C means that reactive diffusion occurs between a binary A–B alloy and a pure C metal. As the Ag concentration y increases, the parabolic coefficient decreases slightly at $y < 0.5$ but remarkably at $y > 0.5$. Therefore, the growth of compounds at the interconnection between the Sn-based solder and the multilayer Pd/Ni/Cu conductor is effectively inhibited by addition of Ag with $y > 0.5$ into Pd.

According to a recent phase diagram in the binary Pd–Cr system,²⁰⁾ the solubility of Cr in Pd reaches to $y = 0.5$ at 1588 K. Here, y represents the mol fraction of Cr. The melting temperature T_m is 2136 K and 1828 K for Cr and Pd, respectively, and hence T_m is much higher for Cr than for Pd. Therefore, we may intuitively expect that alloying of Pd with Cr decelerates the interdiffusion between Pd and Sn and thus inhibits the formation of the Pd–Sn compounds at solid-state temperatures. Unfortunately, however, no reliable information is available for effects of Cr on the compound formation. In the present study, the influence of Cr on the solid-state reactive diffusion between Pd and Sn was experimentally examined using Sn/(Pd–Cr)/Sn diffusion couples with Cr

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concentrations of $y = 0.1$ – 0.3 in the temperature range of 433–473 K. The rate-controlling process of the reactive diffusion was discussed on the basis of the experimental result.

2. Experimental

Plate specimens of pure Sn with a size of $12\text{ mm} \times 5\text{ mm} \times 2\text{ mm}$ were prepared by cold rolling and spark erosion from a commercial 1 kg rectangular ingot of pure Sn with a purity of 99.99%. The cold-rolled plate specimens were separately annealed in evacuated silica capsules at 473 K for 2 h, followed by air cooling without breaking the capsules. The annealed Sn plate specimens were chemically polished in an etchant consisting of 20 vol% of nitric acid, 20 vol% of hydrochloric acid and 60 vol% of distilled water. The two surfaces with an area of $12\text{ mm} \times 5\text{ mm}$ of each Sn 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 $1\text{ }\mu\text{m}$.

Binary Pd–Cr alloys with Cr mol fractions of $y = 0.110$, 0.215 , 0.323 and 0.336 were made as 20 g button ingots by argon arc melting from pure Pd and Cr with purities of 99.9 and 99.99%, respectively. Plate specimens with dimensions of $15\text{ mm} \times 7\text{ mm} \times 3\text{ mm}$ were cut from the button ingot, and then separately homogenized in evacuated silica capsules at 1173 K for 336 h, followed by air cooling without breaking the capsules. Sheet specimens with a size of $12\text{ mm} \times 5\text{ mm} \times 0.2\text{ mm}$ were prepared by cold rolling and spark erosion from the homogenized plate specimen. Each sheet specimen was annealed in an evacuated silica capsule at 1173 K for 2 h, followed by water quenching without breaking the capsule. The annealed sheet specimen was chemically polished in nitrohydrochloric acid for 60 s.

After chemical polishing, a Pd–Cr sheet specimen was immediately sandwiched between the finished surfaces of two freshly prepared Sn plate specimens in ethanol by the technique used in a previous study.¹⁸⁾ Sandwich Sn/(Pd–Cr)/Sn couples were entirely dried, and then heat treated for diffusion bonding in an oil bath with silicone oil at temperatures of 433 K, 453 K and 473 K for 3 h, 0.75 h and 0.5 h, respectively. After the heat treatment, the diffusion couples were isothermally annealed in this temperature range for various times up to 357 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 Pd–Cr alloy is described as Pd– y Cr, where y is the mol fraction of Cr as mentioned earlier. The Pd–0.110Cr, Pd–0.215Cr, Pd–0.323Cr and Pd–0.336Cr alloys are designated alloys C1, C2, C3 and C4, respectively, and the diffusion couples with alloys C1, C2, C3 and C4 are denominated diffusion couples C1, C2, C3 and C4, respectively. As to diffusion couple C4, isothermal annealing was extended to $t = 2100\text{ h}$ at $T = 433$ – 473 K . 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-

Fig. 1 Cross-sectional DICOM photographs of the compound layer in diffusion couple C2 annealed at $T = 473\text{ K}$ for (a) $t = 9\text{ h}$ ($3.24 \times 10^4\text{ s}$) and (b) $t = 18\text{ h}$ ($6.48 \times 10^4\text{ s}$).

section was observed by differential interference contrast optical microscopy (DICOM) and scanning electron microscopy (SEM). A backscattered electron image (BEI) technique was preferably used in the SEM observation. Concentrations of Sn, Pd and Cr in each phase on the cross-section were measured by electron probe microanalysis (EPMA). Diffusion couples C1–C3 were used mainly for the kinetic observation, and diffusion couple C4 was utilized only for the EPMA measurement.

3. Results and Discussion

3.1 Microstructure

Typical cross-sectional DICOM photographs of diffusion couple C2 annealed at $T = 473\text{ K}$ are shown in Fig. 1. Figure 1(a) and 1(b) indicates the DICOM photographs of $t = 9\text{ h}$ ($3.24 \times 10^4\text{ s}$) and $t = 18\text{ h}$ ($6.48 \times 10^4\text{ s}$), respectively. In these photographs, the top region is the Sn specimen, and the bottom region is the Pd–Cr alloy. Here, alloys C1–C4 possess the single-phase microstructure with the face-centered cubic (fcc) crystal structure. As can be seen in Fig. 1, a compound layer composed of matrices with different grain sizes and lamellar phases is produced between the Sn and the Pd–Cr alloy. If we observe the edge of diffusion couple on the cross-section, we can find the location of the original (Pd–Cr)/Sn interface. This observation indicates that the compound layer grows mainly into the Sn but slightly towards the Pd–Cr alloy. To identify each phase, concentration profiles of Sn, Pd and Cr across the compound layer were determined by EPMA along the direction normal to the original (Pd–Cr)/Sn interface. A result of the diffusion couple in Fig. 1(b) is indicated in Fig. 2. In this figure, 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_{Pd} and y_{Cr} , respectively. As can be seen, the matrices are PdSn_2 , PdSn_3 and PdSn_4 from the Pd–Cr side to the Sn side, and the thickness is much smaller for PdSn_2 and PdSn_3 than for PdSn_4 . Comparing Fig. 1(b) with Fig. 2, the fine-grained contrast may be

Fig. 2 Concentration profiles of Sn, Pd and Cr across the compound layer in diffusion couple C2 shown in Fig. 1(b).

recognized for PdSn₂ but not for PdSn₃ and PdSn₄. Thus, in Fig. 1(b), the interface is distinguishable between PdSn₂ and PdSn₃ but not between PdSn₃ and PdSn₄. Since the thickness of the compound layer is smaller for Fig. 1(a) than for Fig. 1(b), however, PdSn₂ is invisible in Fig. 1(a). Although the concentration of Cr is much larger for the lamellar phases than for the matrices, the thicknesses of the lamellar phases in diffusion couples C1–C3 were not sufficiently large com-

pared with the spatial resolution of EPMA. Consequently, unlike the matrices, the chemical compositions of the lamellar phases could not be reliably determined by EPMA.

Cross-sectional BEI photographs of diffusion couple C4 with $T = 473$ K and $t = 2100$ h (7.56×10^6 s) are shown in Fig. 3. In Fig. 3(a), the top and bottom regions are the Sn and the Pd–Cr alloy, respectively. As can be seen, the compound layer with a thickness of about $500 \mu\text{m}$ is produced between the Sn and the Pd–Cr alloy. The lower, middle and upper parts of the compound layer are magnified in Fig. 3(b), 3(c) and 3(d), respectively. At each part, concentration profiles of Sn, Pd and Cr across each second phase were determined by EPMA along the direction normal to the original (Pd–Cr)/Sn interface. Results are shown in Fig. 4. As indicated in Fig. 3(a), a dark layer with a rather uniform thickness is formed between the Pd–Cr alloy and PdSn₂. The concentration profiles across this dark layer are shown in Fig. 4(a). According to Fig. 4(a), the dark layer is $(\text{Cr}_{0.9}\text{Pd}_{0.1})_3\text{Sn}$. On the other hand, the result in Fig. 4(b) corresponds to the region in Fig. 3(b), and those in Fig. 4(c) and 4(d) correlate to the medium and upper regions in Fig. 3(c), respectively. Figures 3(b) and 4(b) show that $(\text{Cr}_{0.9}\text{Pd}_{0.1})_3\text{Sn}$ is also distributed as coarse flakes in PdSn₃. Since the fine-grained contrast is rather discerned for PdSn₂ but not for PdSn₃ and PdSn₄ in Fig. 3(b), the PdSn₂/PdSn₃ interface is slightly distinguishable in this figure. In contrast, thin flakes composed of darker and brighter phases are recognized in Fig. 3(c). Furthermore, the darker phase is surrounded by the brighter phase. Figure 4(c) indicates that the darker and brighter phases are $(\text{Cr}_{0.95}\text{Pd}_{0.05})_2\text{Sn}$ and $(\text{Cr}_{0.9}\text{Pd}_{0.1})\text{Sn}$,

Fig. 3 Cross-sectional BEI photographs of the compound layer in diffusion couple C4 with $T = 473$ K and $t = 2100$ h (7.56×10^6 s): (a) whole region, (b) lower part, (c) middle part and (d) upper part.

Fig. 4 Concentration profiles of Sn, Pd and Cr across various phases of the compound layer for diffusion couple C4 shown in Fig. 3: (a) the dark layer between the Pd–Cr alloy and the compound layer in Fig. 3(a), (b) a coarse flake in Fig. 3(b), (c) a thin flake composed of darker and brighter phases, and (d) the lamellar microstructure in Fig. 3(d).

respectively, and the matrix is PdSn₄. For the medium region in Fig. 3(c), however, the thickness of (Cr_{0.9}Pd_{0.1})Sn is not large enough to conduct the EPMA measurement reliably. Thus, the result in Fig. 4(c) actually corresponds to a different region of the diffusion couple in Fig. 3. On the other hand, a rather fine lamellar microstructure is observed in Fig. 3(d). Figure 4(d) represents that the matrix and the second phase in the fine lamellar microstructure are PdSn₄ and CrSn₂, respectively.

The experimental points in Fig. 4 are plotted as a diffusion path with open circles in a composition triangle of the ternary Sn–Pd–Cr system in Fig. 5. According to Fig. 4(a) and 4(b), (Cr_{0.9}Pd_{0.1})₃Sn is directly contacted with both PdSn₂ and PdSn₃. This implies that the three-phase equilibrium of PdSn₂ + PdSn₃ + (Cr_{0.9}Pd_{0.1})₃Sn exists in this ternary system. On the other hand, as indicated in Fig. 4(c) and 4(d), (Cr_{0.95}Pd_{0.05})₂Sn, (Cr_{0.9}Pd_{0.1})Sn and CrSn₂ are distributed in PdSn₄. This means that there appear the three-phase equilibrium of PdSn₄ + (Cr_{0.95}Pd_{0.05})₂Sn + (Cr_{0.9}Pd_{0.1})Sn

and that of PdSn₄ + (Cr_{0.9}Pd_{0.1})Sn + CrSn₂. As reported in previous studies, at $T = 433\text{--}473\text{ K}$, the three-phase equilibrium of Sn⁺ + PdSn₄ + CrSn₂ exists in the ternary Sn–Pd–Cr system,²¹⁾ and the two-phase equilibrium of Sn + CrSn₂ appears in the binary Sn–Cr system.²²⁾ The experimental compositions of these two-phase and three-phase equilibria are shown as open triangles and squares, respectively, in Fig. 5. Although the solubility of Pd in CrSn₂ is small, the solubility range of CrSn₂ is slightly extended to the Sn-rich side by addition of Pd into CrSn₂. The same phase relationships as Fig. 5 were observed also at $T = 433\text{ K}$ and 453 K . Since the volume fraction of each Cr-rich compound on the cross-section is very small even for diffusion couple C4 with $t = 2100\text{ h}$ ($7.56 \times 10^6\text{ s}$), however, the crystal structures of the Cr-rich compounds could not be determined by an X-ray diffraction technique.

As shown in Fig. 3, the compound layer with periodic lamellar microstructure is formed owing to the reactive diffusion in the (Pd–Cr)/Sn system at $T = 433\text{--}473\text{ K}$. This

Fig. 5 Diffusion path for the concentration profiles shown in Fig. 4. The experimental compositions for the three-phase equilibrium of Sn + PdSn₄ + CrSn₂ in the ternary Sn-Pd-Cr system²¹⁾ and the two-phase equilibrium of Sn + CrSn₂ in the binary Sn-Cr system²²⁾ are also indicated as open squares and triangles, respectively.

type of compound formation is usually called a Liesegang phenomenon. Originally, Liesegang found periodic precipitation of a compound in a solvent.²³⁾ On the other hand, a solid-state Liesegang phenomenon was observed by Osinski *et al.* for the reactive diffusion in the (Fe-Si)/Zn system at $T = 668$ K.²⁴⁾ In a previous study,²²⁾ a solid-state Liesegang phenomenon was recognized also for the reactive diffusion in the (Ni-Cr)/Sn system at $T = 453$ – 473 K. The compound formation due to a solid-state Liesegang phenomenon can be explained by a geometrical model reported in a previous study.²²⁾

As mentioned in Section 1, the solid-state reactive diffusion in the Pd/Sn system was experimentally observed using the Sn/Pd/Sn diffusion couple in a previous study.¹⁶⁾ Hereafter, the Sn/Pd/Sn diffusion couple is called diffusion couple C0. In diffusion couple C0,¹⁶⁾ PdSn₄, PdSn₃ and PdSn₂ were observed at $T = 433$ K, but only PdSn₄ and PdSn₃ were discerned at $T = 453$ – 473 K. On the other hand, in diffusion couples C1–C4, PdSn₂ as well as PdSn₄ and PdSn₃ was clearly recognized at $T = 433$ – 473 K. Hence, the phase stability and the relative growth rate among PdSn₄, PdSn₃ and PdSn₂ vary depending on the chemical composition of the Pd-Cr alloy in the Sn/(Pd-Cr)/Sn diffusion couple, though the solubilities of Cr in PdSn₄, PdSn₃ and PdSn₂ are negligible as mentioned earlier. In the binary Pd-Sn system,²⁰⁾ ten Pd-Sn compounds with different stoichiometries appear as stable phases at $T = 433$ – 473 K. Of the ten compounds, however, only PdSn₄, PdSn₃ and PdSn₂ were clearly recognized in diffusion couples C1–C4. Therefore, the phase equilibria among the other seven Pd-Sn compounds and the Cr-rich compounds were not determined in the present study.

3.2 Growth behavior of intermetallic layer

As previously mentioned, various compounds are produced in diffusion couples C1–C4. The chemical composi-

Fig. 6 Schematic of the morphology of the intermetallic layer for cross-section i .

tion of each compound was reliably determined by EPMA for diffusion couple C4 but not for diffusion couples C1–C3. Although the PdSn₂/PdSn₃ interface is distinguishable in DICOM photographs, PdSn₂ is invisible due to small thicknesses at short annealing times. Hence, for the kinetic observation using diffusion couples C1–C3, only the overall layer growth was examined experimentally. However, the thickness is much greater for PdSn₄ than for PdSn₂ and PdSn₃, and the volume fraction is much smaller for the second phases than for PdSn₄. As a consequence, the layer growth of PdSn₄ predominantly governs the overall layer growth. Hereafter, the layer consisting of various compounds is merely called the intermetallic layer. The schematic morphology of the intermetallic layer on cross-section i is shown in Fig. 6. From DICOM photographs such as that shown in Fig. 1, the area A_i of the intermetallic layer corresponding to the partial length w_i of the original (Pd-Cr)/Sn interface in Fig. 6 was measured on each cross-section, and then the sums A and w were obtained as¹⁸⁾

$$A = \sum_{i=1}^m A_i \quad (1a)$$

and

$$w = \sum_{i=1}^m w_i \quad (1b)$$

from A_i and w_i , respectively, where $m \geq 5$. Using the values of A and w , the total thickness l of the intermetallic layer was evaluated at each annealing time t by the equation¹⁸⁾

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

Here, w and A are the total length parallel to the original (Pd-Cr)/Sn interface and the total area of the intermetallic layer, respectively, on the cross-section. The results of diffusion couples C0,¹⁶⁾ C1, C2 and C3 at $T = 433$ – 473 K are plotted as open circles, triangles, rhombuses and squares, respectively, in Fig. 7(a)–(c). According to Fig. 3(a), a very thin crack is observed along the PdSn₄/Sn interface in diffusion couple C4. This thin crack may be formed by aggregation of Kirkendall voids during extended annealing. On the other

Fig. 7 The total thickness l of the intermetallic layer versus the annealing time t for diffusion couples C0,¹⁶ C1, C2 and C3 shown as open circles, triangles, rhombuses and squares, respectively, at (a) $T = 433$ K, (b) $T = 453$ K and (c) $T = 473$ K.

hand, as indicated in Fig. 1, such a crack was not recognized for diffusion couples C0–C3 within the experimental annealing times. Since the values of l measured for diffusion

Fig. 8 The thickness l_5 at $t = 10^5$ s versus the mol fraction y of Cr in the Pd–Cr alloy at $T = 433$ K, 453 K and 473 K shown as open rhombuses, squares and circles, respectively, with error bars. The corresponding results of $y = 0$ ¹⁶ are also represented.

couple C4 are considerably scattered due to the crack formation, only the results of diffusion couples C0–C3 are included in Fig. 7. In this figure, the ordinate and the abscissa show the logarithms of l and t , respectively. As can be seen, the thickness l monotonically increases with increasing annealing time t . Furthermore, the plotted points of each diffusion couple are located 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 points plotted in Fig. 7, k and n were determined by the least-squares method as indicated with various straight lines. The determined values are shown in Fig. 7. Since n varies depending on y , it is rather difficult to find a systematic relationship between k and y . Therefore, to estimate the composition dependence of the overall growth rate of the intermetallic layer, the thickness l_5 at $t = 10^5$ s is plotted against y as open rhombuses, squares and circles for $T = 433$ K, 453 K and 473 K, respectively, in Fig. 8. At $T = 433$ –453 K, l_5 is rather insensitive to y at $y < 0.1$ but monotonically decreases with increasing value of y at $y > 0.1$. On the other hand, at $T = 473$ K, l_5 remains almost constant independent of y at $y < 0.2$ but gradually decreases with increasing value of y at $y > 0.2$. As previously mentioned, the intermetallic layer consists of the Pd–Sn compounds dispersed with the lamellar Cr-rich compounds. In order for the intermetallic layer to grow during annealing, the interdiffusion among the constituent components should occur across the Cr-rich compounds as well as the Pd–Sn compounds. The volume fraction f of the Cr-rich compounds in the intermetallic layer increases with increasing value of y . Hence, the increase in f causes the decrease in l_5 . This implies

that the interdiffusion is more sluggish for the Cr-rich compounds than for the Pd–Sn compounds. Furthermore, the dependencies of l_5 on y and T in Fig. 8 indicate that the difference of the interdiffusion between the Cr-rich compounds and the Pd–Sn compounds increases with decreasing annealing temperature. Consequently, it is concluded that the Cr-rich compounds work as effective diffusion barriers against the growth of the intermetallic layer at $y > 0.2$.

3.3 Rate-controlling process of intermetallic growth

The values of n at $T = 433$ K, 453 K and 473 K are plotted against y as open circles with error bars in Fig. 9(a), 9(b) and 9(c), respectively. The result in Fig. 9 is represented in a different manner in Fig. 10. In this figure, the ordinate and the abscissa show n and T , respectively, and open circles, triangles, rhombuses and squares indicate the results of $y = 0$,¹⁶⁾ 0.110, 0.215 and 0.323, respectively. If the layer growth of the intermetallic layer is controlled by volume diffusion, n is equal to 0.5.^{25–32)} 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 0.5.¹⁷⁾ However, n is equal to 0.5 even for the layer growth controlled by boundary diffusion unless grain growth takes place.¹⁷⁾ Consequently, in the case of $n = 0.5$, there are two possibilities for the rate-controlling process. In such a case, the rate-controlling process cannot be conclusively determined only from the value of n . To estimate the rate-controlling process for the layer growth, the grain growth in the intermetallic layer was experimentally examined for $y = 0$ in a previous study.¹⁶⁾ This experiment indicates that the grain growth actually occurs at $T = 433$ –473 K. On the other hand, grain growth in the (Pd–Ni)/Sn system was experimentally observed in a previous study.³³⁾ Also in the (Pd–Ni)/Sn system, like the (Pd–Cr)/Sn system, PdSn₄, PdSn₃ and PdSn₂ are formed at $T = 433$ –473 K due to reactive diffusion. In the Pd–Sn compounds, however, the solubility is much greater for Ni than for Cr.³³⁾ The grain growth of the intermetallic layer may be decelerated by addition of a solute. Nevertheless, the dissolution of Ni in the Pd–Sn compounds hardly affects the kinetics of grain growth.³³⁾ As a result, we may consider that grain growth takes place also in the (Pd–Cr)/Sn system. Thus, the value $n = 0.5$ guarantees that the layer growth is controlled by volume diffusion. According to Fig. 9, n is close to 0.5 independent of y at $T = 453$ –473 K and for $y = 0$ –0.110 at $T = 433$ K. Consequently, it is concluded that the layer growth is mostly controlled by volume diffusion under these experimental conditions.

On the other hand, n takes values of 0.790–0.722 for $y = 0.215$ –0.323, respectively, at $T = 433$ K. If the interface reaction at the moving interface governs the layer growth, n is equivalent to unity.^{34–41)} As mentioned in Section 3.1, the intermetallic layer grows mainly into the Sn. Thus, the values $n = 0.790$ –0.722 indicate that the layer growth is controlled by the interface reaction at the PdSn₄/Sn interface as well as the volume diffusion across the intermetallic layer. Such a mixed rate-controlling process of reactive diffusion has been observed for various alloy systems. For instance, the reactive

Fig. 9 The exponent n versus the mol fraction y of Cr in the Pd–Cr alloy shown as open circles with error bars at (a) $T = 433$ K, (b) $T = 453$ K, and (c) $T = 473$ K. The corresponding results of $y = 0$ ¹⁶⁾ are also represented.

diffusion in the (Cu–Sn)/Nb system was experimentally examined using diffusion couples consisting of Cu–Sn alloys and Nb in previous studies.^{34–36)} In these experiments, the

Fig. 10 The exponent n versus the annealing temperature T for $y = 0$,¹⁶⁾ 0.110, 0.215 and 0.323 shown as open circles, triangles, rhombuses and squares, respectively.

diffusion couple was isothermally annealed at $T = 923$ – 1053 K. During annealing, a single-phase Nb_3Sn layer is formed at the original (Cu–Sn)/Nb interface in the diffusion couple, and grows mainly towards the Nb. Here, Nb_3Sn is one of the most important superconducting materials. Like the (Pd–Cr)/Sn and (Pd–Ni)/Sn systems, eq. (3) holds between the thickness l of the Nb_3Sn layer and the annealing time t . The exponent n in eq. (3) is plotted against the annealing temperature T in Fig. 11. In this figure, open triangles, squares and circles show the results of the Cu–8.3Sn,³⁴⁾ Cu–8.1Sn–0.3Ti³⁵⁾ and Cu–9.3Sn–0.3Ti³⁶⁾ diffusion couples, respectively, where the concentrations of Sn and Ti are measured in atomic percent. Since the superconducting properties of Nb_3Sn are improved by addition of Ti into the Cu–Sn alloy, the Cu–Sn alloy contains 0.3 at% of Ti for the latter two diffusion couples. As can be seen in Fig. 11, n is rather close to unity at $T = 923$ K. As T increases, however, n gradually decreases, and then reaches to intermediate values of 0.7–0.8 at $T = 1053$ K. This means that the interface reaction at the $\text{Nb}_3\text{Sn}/\text{Nb}$ interface predominantly controls the growth of the Nb_3Sn layer at the lower annealing temperatures and the volume-diffusion across the Nb_3Sn layer contributes to the rate-controlling process at the higher annealing temperatures. Hence, the contribution of volume diffusion increases with increasing annealing temperature. As shown in Fig. 10, such temperature dependence of the rate-controlling process is realized also for $y = 0.215$ – 0.323 in the (Pd–Cr)/Sn system.

For the volume-diffusion rate-controlling process, n is equal to 0.5 as mentioned earlier. In this case, eq. (3) may be rewritten by the following formula.

$$l^2 = Kt = \frac{k^2}{t_0} t \quad (4)$$

Equation (4) is another expression of the parabolic relationship. Here, the parabolic coefficient K has a dimension of area per unit time. As previously mentioned, n is close to 0.5 except $y = 0.215$ – 0.323 at $T = 433$ K. Thus, excluding this

Fig. 11 The exponent n versus the annealing temperature T for the reactive diffusion in the (Cu–Sn)/Nb system. The results of the Cu–8.3Sn,³⁴⁾ Cu–8.1Sn–0.3Ti³⁵⁾ and Cu–9.3Sn–0.3Ti³⁶⁾ diffusion couples are shown as open triangles, squares and circles, respectively.

Fig. 12 The logarithm of the parabolic coefficient K versus the reciprocal of the annealing temperature T for $y = 0$,¹⁶⁾ 0.110, 0.215 and 0.323 shown as open circles, triangles, rhombuses and squares, respectively, with error bars.

exception, K was evaluated from the open symbols in Fig. 7 by the least-squares method. The evaluated values of K are plotted against the annealing temperature T as various open symbols with error bars in Fig. 12. In this figure, the ordinate shows the logarithm of K , and the abscissa indicates the reciprocal of T . Open circles, triangles, rhombuses and squares represent the results of $y = 0$,¹⁶⁾ 0.110, 0.215 and 0.323, respectively. For $y = 0$ –0.110, the plotted points are located well on each straight line. Thus, the temperature dependence of K is expressed by the equation

$$K = K_0 \exp\left(-\frac{Q_K}{RT}\right), \quad (5)$$

where K_0 is the pre-exponential factor, Q_K is the activation enthalpy, and R is the gas constant. From the open circles and triangles in Fig. 12, K_0 and Q_K were evaluated by the least-squares method for $y = 0$ and 0.110 as shown with solid and dashed lines, respectively. The evaluation gives $Q_K = 213$ – 255 kJ/mol for $y = 0$ – 0.110 , respectively. Although the value $Q_K = 255$ kJ/mol for $y = 0.110$ is slightly greater than that $Q_K = 213$ kJ/mol for $y = 0$, K takes similar values for $y = 0$ – 0.110 at $T = 433$ – 473 K. As a consequence, it is concluded that K hardly varies depending on y within $y = 0$ – 0.110 at $T = 433$ – 473 K. Since the exception was excluded as mentioned above, there are merely two plotted points for $y = 0.215$ – 0.323 in Fig. 12. If the two plotted points are interconnected with each other, $Q_K = 490$ – 418 kJ/mol are obtained for $y = 0.215$ – 0.323 , respectively. Although the evaluation of Q_K is less reliable for $y = 0.215$ – 0.323 than for $y = 0$ – 0.110 , Q_K is almost twice greater for $y = 0.215$ – 0.323 than for $y = 0$ – 0.110 . If the interdiffusion coefficients of all the phases in the diffusion couple are known, K is estimated by an appropriate mathematical model.^{25–32} In such a case, Q_K is related to the activation enthalpies of the interdiffusion coefficients. Unfortunately, however, reliable information is not available even for the self-diffusion coefficient of each component in the Cr-rich compounds and the Pd–Sn compounds. Nevertheless, the volume fraction of each Cr-rich compound should monotonically increase with increasing value of y . Therefore, the large values of Q_K for $y = 0.215$ – 0.323 imply that the activation enthalpy of the interdiffusion coefficient is much greater for the Cr-rich compounds than for the Pd–Sn compounds.

4. Conclusions

The kinetics of the solid-state reactive diffusion in the (Pd–Cr)/Sn system was experimentally examined using the Sn/(Pd–Cr)/Sn diffusion couples with Cr mol fractions of $y = 0.110$, 0.215 and 0.323 . The diffusion couples were isothermally annealed at temperatures of $T = 433$ – 473 K for various periods up to $t = 360$ h. At the original (Pd–Cr)/Sn interface in the diffusion couple, a compound layer composed of different matrices and lamellar phases is produced due to annealing. The chemical composition of each phase in the compound layer was measured by electron probe micro-analysis (EPMA) using the diffusion couples with $y = 0.336$ annealed for $t = 2100$ h at $T = 433$ – 473 K. The EPMA measurement indicates that the matrices are PdSn_2 , PdSn_3 and PdSn_4 from the Pd–Cr side to the Sn side. The $(\text{Cr}_{0.9}\text{Pd}_{0.1})_3\text{Sn}$ phase is formed as a rather uniform layer at the (Pd–Cr)/ PdSn_2 interface and as coarse flakes in PdSn_3 . On the other hand, PdSn_4 is directly contacted with the $(\text{Cr}_{0.95}\text{Pd}_{0.05})_2\text{Sn}$, $(\text{Cr}_{0.9}\text{Pd}_{0.1})\text{Sn}$, CrSn_2 and Sn phases. Thus, the following three-phase equilibria appear at $T = 433$ – 473 K in the ternary Sn–Pd–Cr system: $\text{PdSn}_2 + \text{PdSn}_3 + (\text{Cr}_{0.9}\text{Pd}_{0.1})_3\text{Sn}$, $\text{PdSn}_4 + (\text{Cr}_{0.95}\text{Pd}_{0.05})_2\text{Sn} + (\text{Cr}_{0.9}\text{Pd}_{0.1})\text{Sn}$, $\text{PdSn}_4 + (\text{Cr}_{0.9}\text{Pd}_{0.1})\text{Sn} + \text{CrSn}_2$, and $\text{Sn} + \text{PdSn}_4 + \text{CrSn}_2$. The total thickness of the compound layer is proportional to a power function of the annealing time. The exponent of the power function is nearly equal to 0.5 independent of y at $T = 453$ – 473 K and for $y = 0$ – 0.110 at $T = 433$ K, but becomes 0.7–0.8 for $y = 0.215$ – 0.323 at $T = 433$ K. Since

grain growth should occur in the compound layer, the exponent close to 0.5 means that the overall compound growth is mostly controlled by volume diffusion. If the exponent is larger than 0.5, however, the interface reaction at the moving interface contributes to the rate-controlling process. The overall growth rate of the compound layer is not sensitive to y at $y < y_c$, but decreases with increasing value of y at $y > y_c$. Here, the critical composition y_c is 0.1 and 0.2 at $T = 433$ – 453 K and 473 K, respectively. The volume fraction f of the Cr-rich compounds in the compound layer monotonically increases with increasing value of y , and the interdiffusion may be slower for the Cr-rich compounds than for the Pd–Sn compounds. Thus, the influence of Cr on the kinetics is attributed to the dependence of f on y . Consequently, the addition of Cr with $y > 0.2$ into Pd effectively inhibits the compound growth during energization heating at the interconnection between a Sn-based solder and a multilayer Pd/Ni/Cu conductor.

Acknowledgements

The authors are grateful to Mr. K. Sakamoto and Mr. N. Kurokawa at Tyco Electronics AMP Co. Ltd., Japan for stimulating discussions. Thanks are also due to Mr. W. Shinmei with Graduate School at Tokyo Institute of Technology, Japan for assistance in the early stages of the present study. 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.

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