Influence of Ag on Kinetics of Solid-State Reactive Diffusion between Pd and Sn

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The influence of Ag on the kinetics of the solid-state reactive diffusion between Pd and Sn was experimentally examined using Sn/(Pd–Ag)/Sn diffusion couples with a Ag concentration of 75 at% in the present study. The diffusion couples were isothermally annealed at temperatures of 433, 453 and 473 K for various periods up to 1365 h. During annealing, a compound layer dominantly consisting of polycrystalline Pd$_3$Sn$_4$ and Ag$_3$Sn lamellae is formed at the (Pd–Ag)/Sn interface in the diffusion couple. The square of the thickness of the compound layer increases in proportion to the annealing time. This relationship is called the parabolic relationship. On the other hand, the interlamellar spacing in the compound layer is proportional to a power function of the annealing time, and thus grain growth occurs in the compound layer. The exponent of the power function is close to 1/3. The parabolic relationship of the layer growth and the occurrence of the grain growth guarantee that the growth of the compound layer is controlled by volume diffusion. The addition of Ag with 75 at% into Pd decreases the parabolic coefficient by 93, 88 and 78% at 433, 453 and 473 K, respectively. Hence, Ag works as an effective suppressant against the growth of the compound during the solid-state reactive diffusion between Pd and Sn.

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1. Introduction

Due to high electrical conductivity, Cu-base alloys are widely used as conductor materials in the electronics industry. If the Cu-base alloy is interconnected using a Sn-base solder, binary Cu–Sn compounds are formed at the interconnection owing to the reactive diffusion between the Cu-base alloy and the molten Sn-base solder during soldering and then gradually grow under usual energization heating conditions at solid-state temperatures. Since the Cu–Sn compounds are brittle and possess high electrical resistivities, their formation deteriorates the electrical and mechanical properties of the interconnection. The formation behavior of the Cu–Sn compounds has been experimentally studied by many investigators.\textsuperscript{1–17} To suppress the formation of the Cu–Sn compounds, the Cu-base alloy is generally plated with a Ni layer. Such a Ni layer actually acts as an effective barrier against the reactive diffusion between the Sn-base solder and the Cu-base alloy.\textsuperscript{18–39} Unfortunately, however, Ni is not completely corrosion resistant. Thus, the Ni layer on the Cu-base alloy is usually plated with a Au or Pd layer to improve corrosion resistance. In such a multilayer Au/Ni/Cu or Pd/Ni/Cu conductor, reactive diffusion occurs at the interconnection between the Sn-base solder and the Au or Pd layer during solid-state energization heating unless the Au or Pd layer completely dissolves into the molten solder during soldering.

The solid-state reactive diffusion in the Cu/Sn system was experimentally examined using Sn/Au/Sn diffusion couples in previous studies.\textsuperscript{40–43} In these experiments, the diffusion couples were isothermally annealed at temperatures of $T = 393–473$ K. Due to annealing, compound layers of AuSn$_4$, AuSn$_3$ and AuSn are produced at the Au/Sn interface in the diffusion couple. The total thickness of the compound layers is proportional to a power function of the annealing time. The exponent of the power function is 0.48, 0.42, 0.39 and 0.36 at $T = 393, 433, 453$ and 473 K, respectively. The exponent smaller than 0.5 means that both boundary and volume diffusion contributes to the growth of the compound layers and grain growth occurs in the compound layers.

As to the Pd/Sn system, the solid-state reactive diffusion was experimentally observed using Sn/Pd/Sn diffusion couples in a previous study.\textsuperscript{44} The diffusion couples were isothermally annealed at $T = 433–473$ K in this experiment. At the Pd/Sn interface in the diffusion couple, Pd$_3$Sn$_4$, Pd$_3$Sn and PdSn$_3$ layers are formed at $T = 433$ K, but only PdSn$_4$ and PdSn$_3$ layers are produced at $T = 453$ and 473 K. In this case, however, the square of the total thickness of the compound layers is proportional to the annealing time, though grain growth takes place in the compound layers. This relationship between the thickness and the annealing time is called the parabolic relationship. Consequently, the growth of the compound layers is controlled by volume diffusion. Thus, the rate-controlling process of reactive diffusion varies depending on the alloy system. Nevertheless, the overall growth rate of the compound layers is similar in the Pd/Sn and Au/Sn systems.

The effect of Ag on the solid-state reactive diffusion in the Au/Sn system was experimentally examined in previous studies.\textsuperscript{45–47} In these experiments, Sn/(Au–Ag)/Sn diffusion couples with different Ag concentrations were isothermally annealed at $T = 393–473$ K. For Ag concentrations of 25–63 at%, AuSn$_4$ and AuSn$_2$ layers dispersed with small Ag$_3$Sn particles are produced at the (Au–Ag)/Sn interface in the diffusion couple due to annealing. On the other hand, AuSn$_4$ and Ag$_3$Sn layers are formed for Ag concentrations of 75–87 at%. The overall growth rate of the compound layers is almost independent of the Ag concentration for 0–63 at%, but gradually decreases with increasing Ag concentration for 63–100 at%. Consequently, addition of Ag into Au up to 63 at% cannot suppress the growth of the compounds at the interconnection between the Sn-base solder and the multilayer Au/Ni/Cu conductor during solid-state energization heating.

In contrast, the solid-state reactive diffusion in the (Pd–Ag)/Sn system was experimentally observed using Sn/
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2. Experimental

A binary Pd–Ag alloy containing 75 at% of Ag was prepared as a 25 g button ingot by argon arc melting from pure Pd and Ag with purities of 99.9 and 99.99%, respectively, in a manner similar to a previous study. Plate specimens with a size of 10 mm × 5 mm × 2 mm were cut from the ingot and cold rolled to a thickness of 0.1 mm. Sheet specimens with a dimension of 20 mm × 7 mm × 0.1 mm were cut from the plate specimen and then chemically polished in an etchant consisting of 10 vol% of nitric acid, 20 vol% of hydrochloric acid and 70 vol% of distilled water. The chemically polished sheet specimens were separately annealed in evacuated silica capsules at 1173 K for 200 h, followed by air cooling without breaking the capsules. The annealed sheet specimens were again chemically polished in the etchant mentioned above.

Polycrystalline plate specimens of Sn with a size of 12 mm × 5 mm × 2 mm were prepared by cold rolling and spark erosion from a commercial 1 kg rectangular ingot of pure Sn with 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 mm × 5 mm of each Sn plate specimen were mechanically polished on 800 emery paper. One of the two polished surfaces was again mechanically polished on 1000–4000 emery papers until a depth of 100 μm and then finished using diamond with a diameter of 1 μm.

After chemical polishing, a Pd–Ag sheet specimen was immediately sandwiched between the finished surfaces of two freshly prepared Sn plate specimens in ethanol by the technique used in previous studies. The Sn/(Pd–Ag)/Sn couples were completely dried and then heat treated for diffusion bonding in an oil bath with silicone oil for 24, 18 and 12 h at 433, 453 and 473 K, respectively. After the heat treatment, the diffusion couples were isothermally annealed at temperatures of 433, 453 and 473 K for various times up to 1341 h. The summation of the heat-treating and annealing times is hereafter called the annealing time $t$, and the annealing temperature is denoted by $T$. 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 by Struers Ltd. The microstructure of the cross-section was observed by optical microscopy (OM) and scanning electron microscopy (SEM). Concentrations of Pd, Ag and Sn in each phase on the cross-section were measured by electron probe microanalysis (EPMA).

3. Results and Discussion

3.1 Microstructure

A typical micrograph of OM for the cross-section of the annealed diffusion couple is shown in Fig. 1. This figure indicates the micrograph for the diffusion couple annealed at $T = 473$ K for $t = 89$ h (320 ks). In Fig. 1, the upper and lower regions are the Sn specimen and the Pd–Ag alloy, respectively. As can be seen, a compound layer with a thickness of about 75 μm is formed at the interface between the Pd–Ag and Sn. A magnified SEM micrograph of the compound layer in the diffusion couple with $T = 473$ K and $t = 92$ h (331 ks) is shown in Fig. 2. As can be seen, the compound layer mainly consists of two polycrystalline lamellar phases with slightly dark and bright contrasts. The overall longitudinal direction of the lamellae is parallel to the initial (Pd–Ag)/Sn interface. According to the EPMA measurement, the dark and bright phases are Ag$_3$Sn and Pd$_2$Sn$_4$, respectively. The solubility of Pd in Ag$_3$Sn and that of Ag in Pd$_2$Sn$_4$ are negligible. Rather small particles of Ag$_3$Sn
are also distributed in the matrix of PdSn$_3$. Hereafter, the compound layer with the Ag$_5$Sn + PdSn$_2$ two-phase microstructure is merely called the intermetallic layer. This type of intermetallic layer was recognized in all the diffusion couples annealed at $T = 433–473$ K. The intermetallic layer grows mainly towards the Sn.

The solid-state reactive diffusion in the Ag/Sn system was experimentally observed using Sn/Ag/Sn diffusion couples in a previous study.\textsuperscript{35} In this experiment, the diffusion couples were isothermally annealed at $T = 433–473$ K. Owing to annealing, Ag$_5$Sn and $\xi$ layers are formed at the Ag/Sn interface in the diffusion couple. In the case of the solid-state reactive diffusion in the Pd/Sn system,\textsuperscript{44} however, PdSn$_4$, PdSn$_3$ and PdSn$_2$ layers are produced at $T = 433$ K, but only PdSn$_4$ and PdSn$_3$ layers are formed at $T = 453–473$ K. On the other hand, during the solid-state reactive diffusion in the (Pd–Ag)/Sn system with Ag concentrations of 25–50 at%,\textsuperscript{48} a PdSn$_4$ layer dispersed with fine Ag$_5$Sn particles is dominantly formed at $T = 433–473$ K. For a Ag concentration of 75 at%, however, Ag$_5$Sn is mostly lamellar and partially granular as shown in Fig. 2. Thus, in the (Pd–Ag)/Sn system, the morphology of the Ag$_5$Sn + PdSn$_4$ two-phase microstructure in the intermetallic layer varies depending on the Ag concentration. In contrast, PdSn$_3$, PdSn$_2$ and $\xi$ were not clearly recognized in the (Pd–Ag)/Sn system with Ag concentrations of 25–75 at%.

### 3.2 Growth behavior of intermetallic layer

From cross-sectional OM micrographs like Fig. 1, the mean thickness $l$ of the intermetallic layer was evaluated by the equation

$$l = A/w,$$

where $A$ and $w$ are the area and the length of the intermetallic layer, respectively, on the cross-section. 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 rhombuses, squares and circles, respectively, in Fig. 3. In this figure, the ordinate and the abscissa indicate the logarithms of the thickness $l$ and the annealing time $t$, respectively. As can be seen, the thickness $l$ monotonically increases with increasing annealing time $t$, and the plotted points at each annealing temperature are located well on a straight line. This means that $l$ is mathematically expressed as a power function of $t$ as follows.

$$l = k(t/t_0)^n$$

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 $k$ possesses the same dimension as $l$, and the exponent $n$ is dimensionless. From the plotted points in Fig. 3, $k$ and $n$ were estimated by the least-squares method. The estimated values are shown in Fig. 3. Using these values of $k$ and $n$, $l$ was calculated as a function of $t$ from eq. (2). The results of $T = 433, 453$ and 473 K are indicated as dotted, dashed and solid lines, respectively, in Fig. 3. At each annealing time, the thickness $l$ monotonically increases with increasing annealing temperature $T$.

### 3.3 Rate-controlling process

As mentioned earlier, the solid-state reactive diffusion in the (Pd–Ag)/Sn system was experimentally examined using Sn/(Pd–Ag)/Sn diffusion couples with Ag concentrations of $0, 25, 50$ and 100 at% in previous studies. Hereafter, the concentration of Ag in the Pd–Ag alloy of the diffusion couple is described with the mol fraction $y$ of Ag. The experimental values of $n$ for $T = 433, 453$ and 473 K are plotted against $y$ as open circles with error bars in Fig. 4(a), (b) and (c), respectively. As can be seen, $n$ is close to 0.5 for $y = 0–0.75$ but slightly smaller than 0.5 for $y = 1$. If the growth of the intermetallic layer is controlled by volume diffusion, $n$ is equal to 0.5,\textsuperscript{49–56} In contrast, boundary diffusion may govern the layer growth at low temperatures where volume diffusion is frozen out. When the layer growth is purely controlled by boundary diffusion across the intermetallic layer and grain growth occurs in the intermetallic layer according to a parabolic law, $n$ becomes equal to
Here, the parabolic law means that the grain size is proportional to the square root of the annealing time. However, $n$ is also equal to 0.5 even for the layer growth controlled by boundary diffusion unless grain growth occurs. Experimental results of many alloy systems in previous studies indicate that the reactive diffusion is not necessarily controlled by volume diffusion. 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 $n$.

3.4 Grain growth in intermetallic layer

To estimate the rate-controlling process for the layer growth, the occurrence of grain growth in the intermetallic layer should be confirmed experimentally. As shown in Fig. 2, PdSn$_4$ and Ag$_3$Sn mostly construct the lamellar two-phase microstructure, and Ag$_3$Sn is partially distributed as small particles in the matrix of PdSn$_4$. For the Ag$_3$Sn lamellae, the mean interlamellar spacing $d$ was measured from cross-sectional SEM micrographs like Fig. 2. Since the overall longitudinal direction of the lamellae is almost parallel to the initial (Pd–Ag)/Sn interface and thus normal to the cross-section, $d$ almost corresponds to the mean of the three-dimensional interlamellar spacing. Furthermore, the mean grain sizes of the polycrystalline PdSn$_4$ and Ag$_3$Sn lamellae may be proportional to $d$. The results of $y = 0.75$ for $T = 433$, 453 and 473 K are shown as open rhombuses, squares and circles, respectively, in Fig. 5. In this figure, the

![Fig. 4](image_url)
Grain growth and hence the interfacial energy between PdSn that a mechanism similar to Ostwald ripening governs the diffusion. However, it is concluded that the solid-state reactive diffusion in the (Pd–Ag)/Sn system with is expressed as a power function of \( t \) by the following equation of the same formula as eq. (2).

\[
d = k_{d}(t/t_{0})^{p}
\]  

(3)

From the plotted points in Fig. 5, the proportionality coefficient \( k_{d} \) and the exponent \( p \) were estimated by the least-squares method. In this figure, dotted, dashed and solid lines show the results of \( T = 433, \ 453 \) and \( 473 \) K, respectively. As can be seen, these lines are nearly parallel to one another. At each annealing time, \( d \) is smaller for \( T = 433 \) K than for \( T = 453-473 \) K but similar in \( T = 453-473 \) K.

The values of \( p \) for \( y = 0.75 \) are plotted against the annealing temperature \( T \) as open circles in Fig. 6. In this figure, the corresponding results of \( y = 0.25, \ 0.5, \ 0.75 \) are also represented as open rhombuses, squares and triangles, respectively. For \( y = 1 \), however, each grain in the intermetallic layer was not distinguished in a metallographical manner, and thus grain growth could not be confirmed experimentally. As can be seen in Fig. 6, \( p \) is greater than 0 for \( y = 0-0.75 \). This means that grain growth occurs in the intermetallic layer. Nevertheless, as shown in Fig. 4, \( n \) is close to 0.5 for \( y = 0-0.75 \) at \( T = 433-473 \) K. Consequently, it is concluded that the solid-state reactive diffusion in the (Pd–Ag)/Sn system with \( y = 0-0.75 \) is controlled by volume diffusion. However, \( p \) is smaller than 0.5, and thus the grain growth does not obey the parabolic law. In the case of \( y = 0.75 \), \( p \) is close to 1/3 at \( T = 433-473 \) K. This implies that a mechanism similar to Ostwald ripening governs the grain growth and the interfacial energy between PdSn and Ag_{2}Sn is the most important driving force of the grain growth. On the other hand, for \( y = 0-0.5 \), \( p \) is smaller than 1/3 and gradually increases with increasing value of \( T \).

Therefore, a different mechanism of grain growth works for \( y = 0-0.5 \).

3.5 Composition dependence of kinetics

For the reactive diffusion controlled by volume diffusion, the parabolic relationship holds between the thickness \( l \) of the intermetallic layer and the annealing time \( t \). The parabolic relationship is expressed by the following equation:

\[
I^{2} = Kt.
\]  

(4)

Here, \( K \) is the parabolic coefficient. The open symbols in Fig. 3 are plotted again in Fig. 7. In this figure, however, the ordinate shows \( l \), and the abscissa indicates the square root of \( t \). From the plotted points in Fig. 7, \( K \) was estimated by the least-squares method. Using the estimated values of \( K, l \) was calculated as a function of \( t \) from eq. (4). The results of \( T = 433, \ 453 \) and \( 473 \) K are shown as dotted, dashed and solid lines, respectively, in Fig. 7. Since \( n \) is almost equal to 0.5 for \( y = 0.75 \) at \( T = 433-473 \) K as indicated in Fig. 4, the open rhombuses, squares and circles are located well on the dotted, dashed and solid lines, respectively, in Fig. 7.

The mean and the standard error of \( K \) for \( y = 0.75 \) at \( T = 433-473 \) K are listed in Table 1. In this table, the corresponding results for \( y = 0.25, \ 0.5, \ 0.75 \) at \( T = 433-473 \) K determined in previous studies are also represented. As shown in Fig. 4, however, \( n \) is slightly smaller than 0.5 for \( y = 1 \). This means that both boundary and volume diffusion contributes to the growth of the intermetallic layer. Thus, eq. (4) may not be valid for \( y = 1 \). Nevertheless, to find the composition dependence of the overall growth rate of the intermetallic layer, eq. (4) is still convenient. The values of \( K \) for \( T = 433, \ 453 \) and \( 473 \) K in Table 1 are plotted against \( y \) as open rhombuses, squares and circles, respectively, with error bars in Fig. 8. As can be seen, \( K \) monotonically decreases with increasing value of \( y \). The dependence of \( K \) on \( y \) is more remarkable for \( y > 0.5 \) than for \( y < 0.5 \). Thus, addition of Ag with \( y > 0.5 \) into Pd consid-
respectively. For $y$ of 0.75 loses excellent corrosion resistance with increasing value of Ag)/Ni/Cu conductor. Using the values of $K$ and $Q_K$ in Table 1, for $T$ = 433, 453 and 473 K, respectively, with error bars. The calculations by eqs. (15) and (16) are indicated as bold and thin curves, respectively.

Eventually, the deceleration effect of Ag is remarkably decelerates the growth of the intermetallic layer. According to Table 1, $K$ is smaller by 93, 88 and 78% for $y$ = 0.75 than for $y$ = 0 at $T$ = 433, 453 and 473 K, respectively. For $y$ > 0.6, however, the Pd–Ag alloy gradually loses excellent corrosion resistance with increasing value of $y$. Hence, $y$ = 0.6 is the upper limit of Ag concentration for the corrosion resistant Pd–Ag layer in the multilayer (Pd–Ag)/Ni/Cu conductor. Using the values of $K$ for $y$ = 0.5 and 0.75, we obtain interpolated values of $K = 3.66 \times 10^{-15}$, $1.37 \times 10^{-14}$ and $6.08 \times 10^{-14}$ m$^2$/s for $y = 0.6$ at $T$ = 433, 453 and 473 K, respectively. Thus, $K$ is smaller by 72, 75 and 44% for $y = 0.6$ than for $y = 0$ at $T$ = 433, 453 and 473 K, respectively. Consequently, the deceleration effect of Ag is notable at $T = 433$–453 K but less remarkable at $T = 473$ K.

The logarithm of $K$ is plotted against the reciprocal of $T$ as various open symbols for different values of $y$ in Fig. 9. As can be seen, the open symbols lie well on the corresponding straight lines. Hence, the dependence of $K$ on $T$ is expressed by an Arrhenius equation as follows:

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

(5)

The pre-exponential factor $K_0$ and the activation enthalpy $Q_K$ were estimated from the plotted points in Fig. 9 by the least-squares method. The estimated values of $Q_K$ are plotted against $y$ as open circles in Fig. 10. As can be seen, $Q_K$ monotonically increases from 90.4 to 142 kJ/mol with increasing Ag concentration from $y = 0$ to $y = 0.75$, but decreases to 64.6 kJ/mol for $y = 1$.

In the reactive diffusion controlled by volume diffusion was theoretically analyzed using a mathematical model in a previous study.\(^{29}\) In this analysis, a hypothetical binary alloy system composed of one intermetallic compound and two primary solid-solution phases was treated, and then the growth rate of the compound layer was evaluated for various semi-infinite diffusion couples initially consisting of the two primary solid-solution phases. The analysis indicates that the most predominant parameters determining the growth rate are the diffusion coefficient and the solubility range of the growing compound phase. However, the diffusion coefficients and the solubility ranges of the primary solid solution phases also possess certain effects on the growth rate. Hence, the mathematical model was also used to analyze numerically the relationship between the temperature dependence of the interdiffusion in each phase and the kinetics of the reactive
In the numerical analysis, the temperature dependence of the interdiffusion coefficient $D$ was expressed by an Arrhenius equation of

$$D = D_0 \exp \left( -\frac{Q}{RT} \right),$$

and the following assumptions were adopted: (A) the molar volume, the solubility range and the pre-exponential factor $D_0$ are constant and equivalent for all the phases; and (B) the activation enthalpy $Q$ is equivalent for the solution phases but different between the compound and the solution phase. According to the numerical analysis, eq. (5) is reliable enough to express the temperature dependence of experimental values of $K$ but not completely exact. If $Q$ is smaller for the compound than for the solution phases, $Q_K$ is close to $Q$ of the compound. In this case, the temperature dependence of $K$ corresponds well with that of $D$ of the compound. Such a relationship no longer holds unless $Q$ is smaller for the compound than for the solution phases. To examine whether these conclusions are universally valid, assumption (B) was eliminated in previous numerical analyses. Nevertheless, attention was focused on the relationship between the temperature dependency of the kinetics and those of the interdiffusion coefficients of the constituent phases. As a consequence, assumption (A) still remained in these numerical analyses. Under such conditions, the validity of the relationship between $Q_K$ and $Q$ could be confirmed conclusively.

### 3.6 Diffusion models

As shown in Figs. 8 and 9, $K$ decreases by more than two orders of magnitude with increasing value of $y$ from 0 to 1. In this section, simple diffusion models were used to explain quantitatively the dependence of $K$ on $y$.

Cross-sectional microstructures of a hypothetical intermetallic layer composed of the $\alpha$ and $\beta$ phases are schematically drawn in Fig. 11. Here, the $\alpha$ and $\beta$ phases are the compounds in the binary A–C and B–C systems, respectively, and the intermetallic layer possesses a uniform thickness of $l$. For simplification, the following assumptions were adopted: (a) the solubility range $\Delta c$ of component C is equivalent between the $\alpha$ and $\beta$ phases; (b) the solubility is negligible for components B and A in the $\alpha$ and $\beta$ phases, respectively; and (c) the diffusion coefficient is independent of the composition for the $\alpha$ and $\beta$ phases. In Fig. 11, the interface between the $\alpha$ and $\beta$ phases is perpendicular to the cross-section. On the other hand, the $\alpha/\beta$ interface is perpendicular to the intermetallic layer in Fig. 11(a), but parallel to that in Fig. 11(b). The models in Fig. 11(a) and (b) are hereafter
called models I and II, respectively. In both models, the overall diffusional flux \( J \) of component C across the intermetallic layer is expressed by the equation \(^{49} \)

\[
J = -D \frac{\Delta c}{l},
\]

where \( D \) is the effective interdiffusion coefficient of the intermetallic layer. In contrast, the following relationships hold for model I in Fig. 11(a):

\[
J_1 = -D_1 \frac{\Delta c}{l_1},
\]

\[
J_2 = -D_2 \frac{\Delta c}{l_2},
\]

and

\[
J = f_1 J_1 + f_2 J_2.
\]

Here, \( J_1 \) and \( J_2 \) are the diffusional fluxes of component C across the \( \alpha \) and \( \beta \) phases, respectively, \( D_1 \) and \( D_2 \) are the interdiffusion coefficients of the \( \alpha \) and \( \beta \) phases, respectively, and \( f_1 \) and \( f_2 \) are the volume fractions of the \( \alpha \) and \( \beta \) phases, respectively. The volume fraction \( f_i \) is calculated by the following equation.

\[
f_i = \frac{w_i}{w_1 + w_2} \quad (i = 1, 2)
\]

Here, \( w_1 \) and \( w_2 \) are the lengths of the \( \alpha \) and \( \beta \) phases, respectively, along the intermetallic layer. From eqs. (7) and (8), we obtain the relationship

\[
D = f_1 D_1 + f_2 D_2.
\]

On the other hand, the following relationships are valid for model II in Fig. 11(b):

\[
J_1 = -D_1 \frac{\Delta c_1}{l_1},
\]

\[
J_2 = -D_2 \frac{\Delta c_2}{l_2},
\]

and

\[
J = J_1 = J_2.
\]

Here, \( l_1 \) and \( l_2 \) are the thicknesses of the \( \alpha \) and \( \beta \) phases, respectively, and \( \Delta c_1 \) and \( \Delta c_2 \) are the concentration differences of component C in the \( \alpha \) and \( \beta \) phases along the distances \( l_1 \) and \( l_2 \), respectively. The following relationships hold for these parameters:

\[
l = l_1 + l_2
\]

and

\[
\Delta c = \Delta c_1 + \Delta c_2.
\]

In model II, the volume fraction \( f_i \) is calculated from the thickness \( l_i \) by the following equation.

\[
f_i = \frac{l_i}{l_1 + l_2} = \frac{l_i}{l} \quad (i = 1, 2)
\]

Consequently, eqs. (7) and (11)–(13) yield the relationship

\[
D = \frac{D_1 D_2}{f_1 D_2 + f_2 D_1}.
\]

According to the mathematical analysis in a previous study, \(^{49} \) we may expect that \( K \) and \( K_i \) \((i = 1, 2)\) are proportional to \( D \) and \( D_i \), respectively, and the proportionality coefficient is equivalent between \( K \) and \( K_i \). Here, \( K_1 \) and \( K_2 \) are the values of \( K \) for the \( \alpha \) and \( \beta \) phases, respectively. Assuming that the molar volume of the \( \alpha \) phase is equal to that of the \( \beta \) phase, we finally obtain the relationships

\[
K = (1 - y)K_1 + yK_2
\]

and

\[
K = \frac{K_1 K_2}{(1 - y)K_2 + yK_1}
\]

for models I and II, respectively. Here, \( y \) is the overall mol fraction of component B in the intermetallic layer. The dependence of \( K \) on \( y \) was calculated from eqs. (15) and (16) using the values of \( K \) for \( y = 0 \) and 1 in Fig. 8. In this calculation, \( y \) stands for the relative mol fraction of Ag between Ag and Pd in the intermetallic layer, and \( K_1 \) and \( K_2 \) correspond to the values of \( K \) for the binary Pd–Sn and Ag–Sn systems, respectively. Since the volume diffusion of Sn in the Pd–Ag alloy is frozen out and the solubilities of Ag and Pd in Sn are negligible at \( T = 433–473 \) K, the mol fraction \( y \) of Ag in the Pd–Ag alloy is equal to the relative mol fraction owing to mass conservation. The calculations by eqs. (15) and (16) are shown as bold and thin curves, respectively, in Fig. 8. As can be seen, \( K \) is much smaller for model II than for model I at intermediate values of \( y \). This means that the growth rate of the intermetallic layer is sensitive to the morphology of microstructure for the intermetallic layer even at the same value of \( y \). At \( y = 0.75 \), like model II, the overall direction of the lamellar microstructure is rather parallel to the intermetallic layer as shown in Figs. 1 and 2. Nevertheless, most of the open symbols lie well on the bold curves at \( y = 0–1 \). Thus, the dependence of \( K \) on \( y \) is satisfactorily explained by model I. On the other hand, the open rhombus with \( T = 433 \) K and \( y = 0.75 \) is located on the lower side of the bold dotted curve. The lamellar microstructure of the intermetallic layer is rather granularly coarse at \( T = 453–473 \) K as shown in Fig. 2, but lamellarily fine at \( T = 433 \) K. Therefore, at \( T = 433 \) K, the diffusion process of model II considerably contributes to the growth of the intermetallic layer with \( y = 0.75 \).

4. Conclusions

The solid-state reactive diffusion in the ternary (Pd–Ag)/Sn system was experimentally observed using the sandwich Sn/(Pd–Ag)/Sn diffusion couples containing 75 at% of Ag. The diffusion couples were prepared by the diffusion bonding technique, and then isothermally annealed in the temperature range between 433 and 473 K for various times up to 1365 h in the oil bath with silicone oil. Under such conditions, the compound layer with the PdSn

\[4 \] Sn interface in the diffusion couple. The overall longitudinal direction of the PdSn and AgSn lamellae is almost parallel to the (Pd–Ag)/Sn interface, and each lamella is a polycrystalline material. The square of the thickness of the compound layer is proportional to the annealing time. Such
a relationship is denominated the parabolic relationship. Furthermore, the interlamellar spacing increases in proportion to a power function of the annealing time, and hence grain growth takes place in the compound layer. Consequently, the growth of the compound layer is governed by volume diffusion. Since the exponent of the power function is close to 1/3, a mechanism similar to Ostwald ripening may control the grain growth. The parabolic coefficient for the ternary (Pd–Ag)/Sn system with a Ag concentration of 75 at% is 6.7, 11.8 and 22.4% of that for the binary Pd/Sn system at 433, 453 and 473 K, respectively. Thus, the growth of the compound during the solid-state reactive diffusion in the Pd/Sn system is considerably decelerated by the addition of Ag with 75 at% into Pd.

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