Compound Growth due to Reactive Diffusion between Solid-Ni and Liquid-Zn

Shuhei Murakami¹, Minho O² and Masanori Kajihara²,*

¹Graduate School, Tokyo Institute of Technology, Yokohama 226-8502, Japan
²Department of Materials Science and Engineering, Tokyo Institute of Technology, Yokohama 226-8502, Japan

To examine the kinetics of the reactive diffusion in the solid-Ni/liquid-Zn system, an isothermal bonding technique was used to prepare semi-infinite Ni/Zn diffusion couples. The diffusion couples were isothermally annealed in the temperature range of \( T = 773–923 \) K for various periods up to \( t = 10.8 \) ks (3 h). In this temperature range, the \( \beta_1 \) and \( \gamma \) phases are the stable intermetallic compounds in the binary Ni-Zn system. During isothermal annealing, however, only the \( \gamma \) phase forms as a visible compound layer at the original Ni/Zn interface in the diffusion couple. The \( \gamma \) layer grows mainly towards the liquid-Zn and slightly into the solid-Ni. The mean thickness \( l \) of the \( \gamma \) layer is described as a power function of the annealing time \( t \). According to the observation, the exponent of the power function is rather close to 0.5 independently of \( T \). Thus, we may consider that the square of \( l \) is proportional to \( t \) at \( T = 773–923 \) K: \( l^2 = Kt \). This relationship is called a parabolic relationship. The temperature dependence of \( K \) was evaluated from the experimental results. The evaluation provides the activation enthalpy of 40 kJ/mol for the layer growth. [doi:10.2320/matertrans.M2018199]

(Received June 18, 2018; Accepted September 18, 2018; Published November 2, 2018)

Keywords: reactive diffusion, intermetallic compounds, soldering, bulk diffusion, Ni–Zn system

1. Introduction

In the binary Sn–Zn system,¹ the melting temperature \( T_m \) reaches the minimum of 472 K at the Zn concentration of 15 at% (9 mass%) due to the eutectic reaction, where \( T_m^{\text{Sn}} = 505 \) K for pure Sn and \( T_m^{\text{Zn}} = 693 \) K for pure Zn. At the eutectic temperature \( T_e = 472 \) K, the solubility is smaller than 1 at% for Zn in the Sn phase and negligible for Sn in the Zn phase. Since \( T_e = 472 \) K is 33 K lower than \( T_m^{\text{Sn}} = 505 \) K, the eutectic Sn–15 at% Zn alloy is one of the most useful low-melting Pb-free Sn-base solders.²⁻⁷ In contrast, Cu-base alloys with high electrical conductivity are largely utilized as conductor materials for electronic equipments. When the Cu-base conductor is connected to a Sn-base solder, the intermetallic compounds Cu₆Sn₅ and Cu₃Sn form at the conductor/solder connection during soldering process. Their thicknesses increase gradually, if the connection is subsequently heated at solid-state temperatures.⁸⁻¹⁰ These Cu–Sn compounds are mechanically brittle and have electrically high resistivity; consequently, their growth results in deterioration of the mechanical and electrical properties of the connection. To inhibit the compound formation, the Cu-base conductor is usually coated with a Ni layer, where the Ni layer works as diffusion barrier. Since corrosion resistance is not sufficient for Ni, however, the Ni layer is gilt with a thin Au layer to improve the corrosion resistance.²⁰⁻²³

For such a multilayered Au/Ni/Cu conductor, the Au layer speedily solves into a molten Sn-base solder due to soldering, and then the Ni layer is contacted with the solder. Consequently, during soldering, the Ni layer is immediately interacted with the solder. The reactive diffusion between solid-Ni and liquid Sn–Zn alloys was experimentally examined by Gandova.²⁴ In his experiment, Ni/(Sn–Zn) diffusion couples were made from pure Ni and binary Sn–Zn alloys with Zn mol fractions of 0.25, 0.5 and 0.75, and then isothermally annealed at 673 K and 723 K for 120 h and 192 h, respectively. However, he focused attention on phase relationships among the solid Ni phase, the liquid Sn–Zn phase and intermetallic compounds at these temperatures in the ternary Ni–Sn–Zn system. Thus, the growth behavior of each compound was not observed by Gandova.²⁴

Attention was focused on the compound growth in a previous study.²⁵ In that study,²⁵ the reactive diffusion between solid Ni and liquid Sn was experimentally examined at temperatures of \( T = 533–623 \) K using an isothermal bonding (IB) technique.²⁵ In the IB technique, preheating and subsequent isothermal bonding-and-annealing are conducted at an equivalent temperature in a vacuum. Thus, unlike a usual immersion technique, the compound growth during really isothermal reactive diffusion is reliably observed in the experiment using the IB technique. At the original interface in the Ni/Sn diffusion couple prepared by the IB technique, a Ni₃Sn₄ layer formed in this temperature range. Although Ni₃Sn, Ni₃Sn₂ and Ni₃Sn₄ are stable at \( T = 533–623 \) K in the binary Ni–Sn system,²⁶ only Ni₃Sn₄ was detected in all the annealed diffusion couples. The layer growth of Ni₃Sn₄ occurs according to a power relationship, where the mean layer thickness is proportional to a power function of the annealing time. In this case, the exponent \( n \) of the power function takes values between 0.31 and 0.43. If volume diffusion controls the layer growth, \( n = 0.5 \).²⁷⁻³⁷ This relationship is called a parabolic relationship. When boundary diffusion conduces to the layer growth and grain growth takes place in the compound layer, however, \( n < 0.5 \).³⁸ Since grain growth actually occurs in the compound layer, boundary diffusion mainly governs the layer growth of Ni₃Sn₄ under the present experimental conditions.

In contrast, the reactive diffusion between solid Ni and liquid Zn was experimentally observed by Kong et al.³⁹ in the temperature range of \( T = 723–923 \) K. In their experiment, however, an immersion technique was used to prepare Ni/Zn diffusion couples. At \( T = 723 \) K, an intermetallic layer composed of the \( \gamma \) and \( \delta \) phases formed at the original interface in the Ni/Zn diffusion couple. On the other hand, at \( T = 823–923 \) K, the \( \delta \) phase was not recognized in the intermetallic layer. According to an equilibrium phase diagram in the binary Ni–Zn system,⁴⁰ the \( \beta_1 \) phase as well as the \( \gamma \) and \( \delta \) phases is stable in this temperature range.

*Corresponding author, E-mail: kajihara@materia.titech.ac.jp
Nevertheless, the $\beta_1$ phase was not recognized in their annealed diffusion couples. They reported that a parabolic relationship held between the thickness of the intermetallic layer and the annealing time. If we carefully look at the experimental values of the layer thickness, however, the experimental values are slightly scattered. Thus, the parabolic relationship may not necessarily hold between the layer thickness and the annealing time. In the present study, the IB technique was used to examine experimentally the kinetics of reactive diffusion between solid Ni and liquid Zn. Diffusion couples consisting of pure Ni and Zn specimens were prepared by the IB technique and then isothermally annealed in the temperature range of $T = 773$–$923$ K. In this temperature range, only the $\beta_1$ and $\gamma$ phases are the stable compounds. Thus, attention was focused on these compounds in the present study. The microstructure evolution in the diffusion couple during isothermal annealing was observed in a metallographical manner. The kinetic features of the compound growth were discussed from information on the microstructure evolution.

2. Experimental

A polycrystalline commercial rod of pure Ni with diameter of 8 mm and purity higher than 99% were cut into columnar specimens with length of 5 mm as previously described. The annealing and the mechanical polishing of each columnar Ni specimen were conducted by the technique reported in a previous article. Polycrystalline columnar specimens with length of 30 mm were cut from a commercial rod of pure Zn with diameter of 6 mm and purity of 99.9%. A pair of the columnar Zn specimen and the polished Ni specimen was encapsulated in an evacuated silica capsule with inner diameter of 8.5 mm. The silica capsule was isothermally preheated and bonded to prepare a solid-Ni/liquid-Zn diffusion couple by an isothermal bonding (IB) technique in the temperature range between 773 K and 923 K. The diffusion couple was isothermally annealed for various times up to 10.8 ks (3 h) at each constant temperature in this temperature range, followed by water quenching with breaking the capsule. Hereafter, $T$ shows the annealing temperature, and $t$ indicates the annealing time.

Cross-sections of the annealed diffusion couple were mechanically polished in a manner similar to a previous study. For each cross-section, the microstructure was observed by differential interference contrast optical microscopy (DICOM) and with a back-scattered electron image (BEI) by scanning electron microscopy (SEM), and the concentrations of Ni and Zn in each phase were measured by electron probe microanalysis (EPMA). The EPMA measurement was conducted using pure Ni and Zn with purity of 99.99% as standard specimens in a manner similar to a previous study.

3. Results and Discussion

3.1 Microstructure

A typical DICOM image for the cross-section of the diffusion couple annealed at 863 K for 1.8 ks (0.5 h) is shown in Fig. 1; here the top region corresponds to the Zn specimen and the bottom region is the Ni specimen. A compound layer is observed at the original Ni/Zn interface. To identify this layer, the concentration profiles of Ni and Zn were measured by EPMA along the direction perpendicular to the original interface. A result for the diffusion couple annealed at 803 K for 1.8 ks (0.5 h) is indicated in Fig. 2. Here, the vertical axis represents the mol fraction $y_i$ of component $i$, and the horizontal axis shows the distance $x$ measured from an arbitrary origin; open squares and circles are correspondent with $i = \text{Ni}$ and $\text{Zn}$, respectively. The result shows that the layer consists of only the $\gamma$ phase. For all the annealed diffusion couples, the $\gamma$ phase is only the visible compound. Hereafter, the layer composed of the $\gamma$ phase is referred to as the ‘intermetallic layer’. An examination of the edge of the diffusion couple on the cross-section permitted the determination of the location of the original Ni/Zn interface. This showed that the intermetallic layer grew mainly into the Zn and slightly into the Ni.

According to an equilibrium phase diagram in the binary Ni–Zn system, the $\beta_1$ and $\gamma$ phases are stable at the annealing temperatures of $T = 773$–$923$ K. Nevertheless, as
mentioned above, only the γ phase was recognized in all the annealed diffusion couples. If the thickness of a compound is much smaller than the spatial resolution of EPMA with about 1 µm, the compound is invisible in the EPMA measurement. Within realistic annealing times, compounds with very small interdiffusion coefficients cannot grow to detectable thicknesses.²⁵⁻³⁷ For determination of phase diagrams in multicomponent systems, a diffusion couple (DC) technique has been easily utilized by many investigators. However, all the stable compounds may not be necessarily observed under experimental conditions in this technique.²⁵,⁴¹ Hence, stable compounds with very small interdiffusion coefficients are missing in the phase diagram. For instance, only Ni₃Sn₄ was detected in the solid-Ni/liquid-Sn diffusion couples annealed at \( T = 533–623 \) K for \( t = 14.4 \) ks, though Ni₅Sn and Ni₅Sn₂ as well as Ni₃Sn₃ are the stable compounds at these annealing temperatures in the binary Ni–Sn system.²⁵

On the other hand, the \( β_1, γ, γ_1 \) and \( γ_2 \) phases are the stable compounds at \( T = 523–573 \) K in the binary Co–Zn system.⁶² Nevertheless, the \( β_1 \) phase was not found in the solid-Co/solid-Zn diffusion couples annealed for \( t = 759.6 \) ks in this temperature range.⁶² As a consequence, it is not recommended to determine the phase diagram only by the DC technique. A conventional equilibration technique is necessary to determine reliably equilibrium phase diagrams. According to the microstructure observation of the annealed Ni/Zn diffusion couple, it is concluded that the interdiffusion coefficient is much smaller for the \( β_1 \) phase than for the γ phase.

### 3.2 Growth behavior of intermetallic layer

Figure 3 is a schematic representation of the microstructure for the intermetallic layer at cross-section \( i \) corresponding to the DICOM image shown in Fig. 1. At cross-section \( i \) in Fig. 3, \( w_i \) is the length of the original Ni/Zn interface, and \( A_i \) is the area of the intermetallic layer correlated with \( w_i \). From such cross-sectional DICOM images, \( A_i \) and \( w_i \) were measured for cross-section \( i \), and then the sums \( A \) and \( w \) were calculated from \( A_i \) and \( w_i \), respectively, by using the equations below:²⁵

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

and

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

where \( w_i \) is 422 µm and \( m \) is greater than 5. For each annealing time \( t \), the mean thickness \( l \) of the intermetallic layer was evaluated from the values of \( A \) and \( w \), as follows:²⁵

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

The values of \( l \) for \( T = 773–923 \) K are plotted against the annealing time \( t \) as various open symbols in Fig. 4, where the vertical and horizontal axes are shown in logarithmic scales. According to Fig. 4, \( l \) is a monotonically increasing function of \( t \), and the open symbols for each annealing temperature \( T \) show a near-linear relationship to \( t \). Consequently, \( l \) is expressed as a power function of \( t \) as follows:

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

In eq. (3), \( k \) is the proportionality coefficient, \( n \) is the exponent, and \( t_0 \) is the unit time (1 s). Here, \( k \) has the same dimension as \( l \), \( n \) is dimensionless, and \( t_0 \) is adopted to make the argument \( t/t_0 \) of the power function dimensionless. It is essential that the argument of the power function is dimensionless, as otherwise the dimension of \( k \) will vary depending on the value of \( n \). Such \( n \)-value dependence of the dimension of \( k \) may violate the mathematical consistency of the power function. From the open symbols plotted in Fig. 4, values of \( k \) and \( n \) in eq. (3) were calculated by the least-squares method and are shown by the various straight lines in the figure.

![Fig. 3 Schematic of morphology for the intermetallic layer on cross-section \( i \).](Image)

![Fig. 4 The thickness \( l \) of the intermetallic layer versus the annealing time \( t \) at \( T = 733, 803, 863 \) and 923 K shown as open triangles, rhombuses, squares and circles, respectively. Various lines represent the calculations from eq. (3).](Image)
3.3 Rate-controlling process of intermetallic growth

Figure 5 shows a plot of the value of $n$ against $T$ as open circles with error bars. Hereafter, the error bar shows the standard error. For the layer growth of the intermetallic layer controlled by volume diffusion, $n = 0.5$. This is a parabolic relationship. In contrast, for the layer growth governed by interface reaction, $n = 1$. If volume diffusion is frozen out at low temperatures, however, boundary diffusion can control the layer growth. For the layer growth controlled by boundary diffusion across the intermetallic layer, grain growth may occur in the intermetallic layer. In such a case, $n < 0.5$. As grain growth slows down, the volume fraction of grain boundary in the intermetallic layer remains almost constant and therefore the effective cross-section for boundary diffusion hardly varies during annealing. In this case, $n = 0.5$, even if the layer growth is governed purely by boundary diffusion. Consequently, in the case where $n = 0.5$, there are two possibilities for the rate-controlling process.

Figure 5 indicates that $n$ is equal to 0.5 within experimental uncertainty at $T = 773$ and 863 K. However, $n$ is slightly greater than 0.5 at $T = 803$ K but lightly smaller than 0.5 at $T = 923$ K. Nevertheless, there is no systematic dependence of $n$ on $T$. Thus, we may consider that $n$ is close to 0.5 at $T = 773–923$ K. As previously mentioned, there are two possibilities for the rate-controlling process in the case of $n = 0.5$. To confirm experimentally the presence of grain growth, we attempted to use various chemicals to etch the intermetallic layer, but we were unable to find an appropriate etchant in the present study. The confirmation was also attempted by an electron back scatter diffraction (EBSD) method. For this method, the cross-sectional surface of the intermetallic layer was carefully polished by various techniques. Although polycrystalline microstructure was partially recognized in the intermetallic layer, the whole cross-sectional surface was not observed reproducibly. Thus, we could not conclusively determine the rate-controlling process of the layer growth.

3.4 Comparison with other results

The result for $T = 923$ K in Fig. 4 is represented again as open squares with a solid line. The corresponding result reported by Kong et al. is shown as open squares. A dashed line indicates the calculation from eq. (3).

![Image](image.png)

Fig. 5 The exponent $n$ versus the annealing temperature $T$ for the result in Fig. 4 shown as open circles with error bars.

![Image](image.png)

Fig. 6 The result for $T = 923$ K in Fig. 4 is represented again as open squares with a solid line. The corresponding result reported by Kong et al. is shown as open squares. A dashed line indicates the calculation from eq. (3).
with a dashed line in Fig. 7. The calculation provides $Q_k = 117 \text{kJ/mol}$. However, it should be noted that the δ phase appears at $T = 723 \text{K}$ but not at $T = 823–923 \text{K}$.

As shown in Fig. 5, $n$ is not so different from 0.5 at $T = 773–923 \text{K}$ also in the present study. Therefore, from the open symbols plotted in Fig. 4, values of $K$ in eq. (4) were calculated by the least-squares method and are indicated as open circles with error bars in Fig. 7. In this figure, the open circles are located well on a straight line. Hence, eq. (5) is valid to express the dependence of $K$ on $T$. Values of $K$ and $Q_k$ in eq. (5) were evaluated by the least-squares method as shown in a solid line in Fig. 7. The evaluation gives $Q_k = 40 \text{kJ/mol}$. In Fig. 7, the dashed line located below the solid line. The difference in $K$ between the solid and dashed lines remarkably increases with decreasing annealing temperature $T$. This yields that $Q_k$ is about three times greater for the dashed line than for the solid line.

As previously mentioned, an immersion technique was used to prepare Ni/Zn diffusion couples by Kong et al. In their experiment, each solid Ni wire specimen with diameter of 1 mm and length of 50 mm was immersed in molten Zn with $T = 723–923 \text{K}$ in an open chamber filled with Ar gas. During immersion, the following reactions may occur in the open chamber.

\[
\begin{align*}
2\text{Ni} + \text{O}_2 & \rightleftharpoons 2\text{NiO} \quad (6) \\
2\text{Zn} + \text{O}_2 & \rightleftharpoons 2\text{ZnO} \quad (7)
\end{align*}
\]

The equilibrium partial pressure of $\text{O}_2$ is denoted by $P_{\text{O}_2}^{\text{NiO}}$ and $P_{\text{O}_2}^{\text{ZnO}}$ for eqs. (6) and (7), respectively. At $T = 923 \text{K}$, $P_{\text{O}_2}^{\text{NiO}} = 10^{-18} \text{atm}$ and $P_{\text{O}_2}^{\text{ZnO}} = 10^{-29} \text{atm}$. The values of $P_{\text{O}_2}^{\text{NiO}}$ and $P_{\text{O}_2}^{\text{ZnO}}$ remarkably decrease with decreasing temperature from $T = 923 \text{K}$ to $T = 723 \text{K}$. Although the partial pressure $P_{\text{O}_2}$ of $\text{O}_2$ is not reported for the open chamber filled with Ar gas by Kong et al., it is very difficult for $P_{\text{O}_2}$ to reach not only the value of $P_{\text{O}_2}^{\text{NiO}}$ but also that of $P_{\text{O}_2}^{\text{ZnO}}$ in such an open chamber. Hence, the value of $P_{\text{O}_2}$ in this open chamber should be practically much higher than those of $P_{\text{O}_2}^{\text{NiO}}$ and $P_{\text{O}_2}^{\text{ZnO}}$. As a consequence, thin films of NiO and ZnO will form on the surfaces of the solid Ni and the molten Zn, respectively. Such NiO and ZnO films cover the Ni/Zn interface and thus block interdiffusion of Ni and Zn atoms across the interface. This interdiffusion block decelerates the growth of the intermetallic layer.

In contrast, in the present study, Ni/Zn diffusion couples were prepared by the IB technique. For this technique, a Ni specimen was encapsulated together with a Zn specimen in an evacuated silica capsule as mentioned in Section 2. During isothermal preheating of the evacuated silica capsule, the molten Zn will be covered with a very thin layer of ZnO, and hence $P_{\text{O}_2}$ will diminish to $P_{\text{O}_2}^{\text{ZnO}}$. For $P_{\text{O}_2} = P_{\text{O}_2}^{\text{ZnO}}$, the solid Ni cannot be oxidized at all. After isothermal preheating, the surface of the solid Ni is immediately contacted with that of the molten Zn, and therefore the thin ZnO layer is broken down by mechanical impact. As a result, a sound Ni/Zn interface will be realized by direct touch between fresh surfaces of the solid Ni and the molten Zn. Consequently, unlike the immersion technique, interdiffusion of Ni and Zn atoms across the Ni/Zn interface occurs without any obstacles in the IB technique. This is the reason why the dashed line lies below the solid line in Fig. 7. As shown in Fig. 7, $Q_k = 40 \text{kJ/mol}$ for the solid line. This value of $Q_k$ corresponds to the activation enthalpy for the intermetallic growth. Assuming the rate-controlling process of volume diffusion, the interdiffusion coefficient of the $\gamma$ phase was evaluated using a diffusion model in a previous study. The evaluation will be reported in detail elsewhere.

4. Conclusions

The growth behavior of compound during the isothermal reactive diffusion in the solid-Ni/liquid-Zn system was experimentally examined in a metallographical manner. The semi-infinite solid-Ni/liquid-Zn diffusion couples were bonded by the isothermal bonding technique and then isothermally annealed at each temperature in the range of $T = 773–923 \text{K}$ for various times up to $t = 10.8 \text{ks}$ (3 h). Owing to isothermal annealing, a compound layer of the $\gamma$ phase is formed at the original Ni/Zn interface in the diffusion couple. The compound layer grows mainly into the liquid Zn specimen and slightly towards the solid Ni specimen. The mean thickness of the compound layer is denoted as a power function of the annealing time. Although the exponent $n$ of the power function takes values between 0.44 and 0.60, there is no formulated dependence of $n$ on $T$. Consequently, within the experimental annealing temperatures, $n$ is considered insensitive to $T$. Assuming that the square of the layer thickness is proportional to the annealing temperature, we may evaluate the dependence of the proportionality coefficient on the annealing temperature. The evaluation provides the activation enthalpy of 40 kJ/mol for the layer growth.

Acknowledgements

The present study was supported by the jet engine triangle (JET) project at Tokyo Institute of Technology, Japan.
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