Prediction of Intermetallic Compound Formation Sequences in Pseudo Binary Diffusion Couples: Experimental Examinations for (Sn-xZn)/Cu (x = 2, 5, 10, 15, 20 and 25 mass%) by a Kinetic Model with Thermodynamic Data Using MDR Diagram

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A kinetic model based on the principle of maximum degradation rate of the total system free energy, MDR law, using thermodynamic data is applied to (Sn-Zn)/Cu diffusion couples to predict intermetallic compound phases and their order to be formed. According to this model, only γ-Cu5Zn8 is predicted to appear when Zn content is less than 10 mass%, while both γ-Cu5Zn8 and ε-CuZn4 can exist with 10 mass%Zn or more, which was in a good agreement with EPMA and TEM observations of Cu plates dipped into Sn-Zn baths. Therefore, it is concluded that the phase prediction based on the MDR law can also be applied to pseudo binary diffusion systems. [doi:10.2320/matertrans.M2014151]

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1. Introduction

Because of a wide use of mobile electronic devices, a risk of failure of these devices is increasing by dropping them accidentally. Usually, long term reliabilities against these accidents are evaluated by drop tests.

Regulations to evaluate drop reliabilities for electronic devices (JESD22-B1101 and JESD22-B1112) are proposed by Joint Electron Device Engineering Council (JEDEC), where evaluations are carried out using an impact pulse with a peak acceleration of 1500 G and a pulse duration of 0.5 ms. In the literature, many researchers have evaluated drop reliabilities of lead free solder interconnects under above regulations, and reported that cracks caused by the drop test propagate through inside or near brittle intermetallic compound phases, which form between lead-free solders and electrodes.3,4)

Namely, intermetallic compound phases formed between a lead-free Sn-based solder and electrodes on an electric device or a printed circuit board plays an important role especially for mobile electronic products.

In order to clarify the relationship between intermetallic compound phases and drop reliabilities, a formation of these phases should be well understood. In most studies, intermetallic compound phases to be formed at a diffusion couple are predicted based on a diffusion path derived with thermodynamical calculations.5-9) However, phases formed at some diffusion couples cannot be predicted precisely by these calculations. For instance, ε-CuZn4 is predicted as a major phase at (eutectic Sn-8.8 mass%Zn)/Cu diffusion couple,5) but γ-Cu5Zn8 is observed as the first phase or ε-CuZn4 cannot be seen from experimental results in the literature.5,10)

Hence, there have been several attempts using above thermodynamic calculations to predict the first intermetallic compound phase or intermetallic compound formation sequence by comparing driving forces of homogeneous nucleation of intermetallic compound phases,7,8) activation energies for homogeneous nucleation of intermetallic compound phases,9) effective heat of formation of an intermetallic compound phase (EHF model),11) or by applying modified Jonson-Mehl-Avrami-Kolmogorov kinetic equation for precipitation.12) Except EHF model, competitive aspect of these models leads to a conclusion that a couple of intermetallic compound phases could form first at the interface simultaneously while one intermetallic compound phase forms first then another intermetallic compound phase forms next in experimental observations. With EHF model, one can avoid this competitiveness with successful predictions of the first intermetallic compound phases. However, this model requires a special treatment for the predictions mentioned above, that is to say, this model uses two values of composition even at the reaction interface between two phases.

It is expected these differences can be solved if a reaction rate of a system is taken into account to the model. Sasaki et al. has proposed a kinetic model based on the principle of Maximum Degradation Rate of the total system free energy (MDR law) using thermodynamic data, and reported its successful application to both Cu/Sn and Ni/Sn diffusion couples by revealing good agreements of the predicted first and second phases based on this model with those observed experimentally.13-15)

In this paper, MDR law is applied to (Sn-xZn)/Cu (x = 2, 5, 10, 15, 20 and 25 mass%) diffusion couples, and the first and the second phases predicted by this model are compared with those observed experimentally (at 613,653 and 673 K) in order to reveal an effectiveness of the MDR law even in the pseudo binary diffusion system.

2. Experimental Procedure

Cu plates (width: 10 mm, length: 50 mm, thickness: 2 mm) were cleaned by 10% diluted hydrochloric acid, and were dipped for 90 s into one of the melted Sn-xZn (x = 2, 5, 10, 15, 20 and 25 mass%) baths which were kept at 613 K under
an Ar atmosphere in our previous paper. In the present paper, specimens were also prepared in Sn-10 mass%Zn and Sn-15 mass%Zn baths which were kept at 653 or 673 K under an Ar atmosphere.

After dipping, phases formed at the soldered interface were characterised by electron probe micro analyzer (EPMA), JEOL JXA-8230, operated with an LaB6 filament at 20 kV under 100 nm steps using cross sections of metallographically prepared samples. In order to identify the crystal structures of the phases, a field-emission transmission electron microscopy (FE-TEM, type: JEM-2100F) operated at 200 kV was employed. Specimens for TEM observation were prepared by a focused ion beam (FIB) apparatus.

3. Model for Intermetallic Compound Phase Formation

In this section, MDR law is explained briefly and the model for intermetallic compound phase formation at the interfaces of diffusion couples is explained.

MDR law is an assumption that a system chooses a path which gives the largest degradation rate of free energy of the system among feasible paths. In other words, a path with the most negative value of $\frac{\partial G}{\partial t}$ is realized, where $G$ is the system Gibbs free energy. Cahn proposed a model based on MDR to explain lamella structures observed in carbon steel. Recently, MDR law was applied to silicide formation on MDR to explain lamella structures observed in carbon for silicide formation prediction and is supported by the binary phase diagram.

In this model, intermetallic compound phase formation is described as a chemical reaction at the interface of a diffusion couple of metals X and Y, where intermetallic compound phases X$_A$Y$_B$, X$_C$Y$_D$, and so on are formed at X/Y interface. The reactions are expressed as follows;

$$X + \frac{B}{A} Y = \frac{1}{A} X_A Y_B , X + \frac{D}{C} Y = \frac{1}{C} X_C Y_D, \ldots \quad (1)$$

For these reactions, supply rates of both metals to the reaction region, X/Y interface, are introduced as $r_X$ and $r_Y$, respectively.

In addition to the MDR law, the following assumptions are postulated.

1. The reaction of intermetallic compound formation at the interface gives the largest change in the system total free energy of a diffusion couple.
2. The reaction is limited by the supply of a metal with lower supply rate. Here, the ratio of the supply rates is assumed to be the ratio of X/Y at liquidus minimum in X-Y binary phase diagram.

The second assumption is the Walser-Bené rule successful for silicide formation prediction and is supported by the thermodynamic discussion by Bené in which an interface composition is likely to be that of liquidus minimum. This well coincides to the assumption that the supply rate of a metal with higher melting point is lower than that of a metal with lower melting point as shown in the previous paper, in which the first phases are predicted for Cu/Sn and Ni/Sn interfaces. It seems to be reasonable to consider that in the case of a metal with higher melting point atoms of the metal at the interface, i.e., at the surface exposed to the reaction region, are more tightly bound to their matrix compared to another metal with lower melting point. In the present (Sn-Zn)/Cu system, Cu is assumed as the atom which limits the reaction of intermetallic compound formation since Cu has the higher melting point ($\sim 1358$ K) than Sn ($\sim 469$ K) or Zn ($\sim 963$ K).

Assuming metal X to be the rate limiting one, the supply rate of X to the interface, $r_X$, is smaller than that of Y, $r_Y$ X atoms at the surface exposed to the reaction region, namely X/Y interface, are released from their matrix to the reaction region at the rate of $r_X$, while Y atoms are sufficiently supplied to X/Y interface at the rate of $r_Y$, which is larger than $r_X$.

When one X atom is supplied to the reaction region and react with Y atoms of an amount of B/A, the system energy changes by $\Delta G = \Delta G_f (X_A Y_B; per X atom)$.

$$\frac{\partial G}{\partial t} = r_X \cdot \Delta G_f (X_A Y_B; per X atom). \quad (2)$$

Similarly, for another intermetallic compound phase X$_C$Y$_D$, the energy change in a unit time is

$$\frac{\partial G}{\partial t} = r_X \cdot \Delta G_f (X_C Y_D; per X atom). \quad (3)$$

In order to predict which phase forms first at the interface, X$_A$Y$_B$ or X$_C$Y$_D$, the products in eqs. (2) and (3) are compared. In this model, the phase with more negative value of the product is predicted to be the first phase. If $r_X \Delta G_f (X_A Y_B per X atoms)$ is more negative, the intermetallic compound phase X$_A$Y$_B$ is predicted to be formed first.

Applying this model to Cu/Sn and Ni/Sn interfaces, the first intermetallic compound phases are successfully predicted. In these cases, instead of the formation energy $\Delta G_f$ of the formation enthalpy $\Delta H_f$ at 298 K is obtained from $\Delta H_f$ at 298 K is more easily available in the literatures for many intermetallic compound phases and this approximation is also successful in other first intermetallic compound phase predictions. Therefore, in this paper, the products $r_X \Delta H_f$ are compared for intermetallic compound phase formation in MDR diagrams explained in the next section. Because intermetallic compound phases formed at the temperature (613, 653 and 673 K), $\Delta H_f$ of the exact reaction temperature should be utilized to draw MDR diagrams ideally. However, $\Delta H_f$ of the near reaction temperature were used in this paper. Namely, $\Delta H_f$ at 723 K is used for $\varepsilon$-Cu$_5$Zn$_8$ formation, and $\Delta H_f$ at 773 K is utilized for $\gamma$-Cu$_5$Zn$_8$ and $\gamma$-Cu$_3$Zn$_4$ formations.

4. Results and Discussions

Figure 1 shows cross sectional SEM images of (Sn-xZn)/Cu (x = 2, 5, 10, 15, 20 and 25 mass%) diffusion couples prepared at 613 K. Arrows in Fig. 1 indicate lines for EPMA line measurements shown in Fig. 2.

Figure 2 shows the EPMA line profiles of the (Sn-xZn)/Cu (x = 2, 5, 10, 15, 20 and 25 mass%) diffusion couples. As seen from the figure, the diffusion couples with x = 2, 5 and 10 mass% showed a single phase of $\gamma$-Cu$_5$Zn$_8$, while those with x = 15, 20 and 25 mass% had two phases of $\varepsilon$-Cu$_5$Zn$_8$ and $\gamma$-Cu$_5$Zn$_8$ between Sn-Zn solder and Cu.
Table 1 shows values of $A/B$ and the formation enthalpy, $\Delta H_f$, for $\gamma$-Cu$_3$Sn (at 723 K) and for $\varepsilon$-Cu$_5$Zn$_8$ and $\gamma$-CuZn$_4$ (at 773 K). $A/B$ was calculated as a ratio of $A$ and $B$ of a $XAYB$ phase, and $\Delta H_f$ per Cu was calculated using the value of $\Delta H_f$ per formula shown in the literature.

If we assume $r_{Cu}$ is constant when ($r_{Sn}$ or $r_{Zn}$) / $r_{Cu} > A/B$, $\partial G/\partial t$ can be described as a constant value of $r_{Cu} \Delta H_f$ per Cu, while $\partial G/\partial t$ linearly changes along with $r_{Sn}$ or $r_{Zn}$ when ($r_{Sn}$ or $r_{Zn}$) / $r_{Cu} < A/B$. Figure 3 shows the relationship between $r \Delta H_f$ and $r_{Zn}$ / $r_{Cu}$ or $r_{Sn}$ / $r_{Cu}$ for $\gamma$-Cu$_3$Sn (at 723 K) and for $\gamma$-Cu$_5$Zn$_8$ and $\varepsilon$-CuZn$_4$ (at 773 K), which is called as MDR diagram plotted under above assumptions.

### Table 1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A/B$</th>
<th>$\Delta H_f$ per formula/cal g-atm$^{-1}$</th>
<th>$\Delta H_f$ per Cu/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3Cu + Sn = Cu_3Sn$</td>
<td>0.33</td>
<td>-1800$^{(26)}$</td>
<td>-10.0</td>
</tr>
<tr>
<td>$5Cu + 8Zn = Cu_5Zn_8$</td>
<td>1.6</td>
<td>-2718$^{(26)}$</td>
<td>-29.6</td>
</tr>
<tr>
<td>$Cu + 4Zn = CuZn_4$</td>
<td>4.0</td>
<td>-1484$^{(26)}$</td>
<td>-31.0</td>
</tr>
</tbody>
</table>

#### 4.1 (Sn-xZn)/Cu ($x = 2, 5$ and $10$ mass%)

According to Walser-Bené rule, an initial chemical composition at a reaction interface of a diffusion couple at
the beginning of the reaction can be considered as the composition where the temperature becomes the lowest in the liquidus line. If it is assumed that an initial $r_{Zn}/r_{Cu}$ is related with its initial composition, an initial $r_{Zn}/r_{Cu}$ of Zn/Cu diffusion couple can be calculated as 32 (= 97/3) because its initial composition is about Zn-3 mass% Cu according to Walser-Bené rule.

In Fig. 3, $\gamma$-Cu$_{3}$Zn$_{8}$ and $\epsilon$-CuZn$_{4}$ can be considered as two major phases to be formed in the present diffusion system since they have smaller $\Delta H_f$ than $\epsilon$-Cu$_5$Sn. An intersection point between two lines of $\gamma$-Cu$_{3}$Zn$_{8}$ and $\epsilon$-CuZn$_{4}$ can be seen when $r_{Zn}/r_{Cu}$ or $r_{Sn}/r_{Cu}$ is about 5.3. In the present (Sn-Zn)/Cu system, it can be considered that Zn is diluted by Sn. Hence, Zn concentration of the (Sn-Zn)/Cu whose $r_{Zn}/r_{Cu}$ is 5.3 can be estimated as 9.9 mass% Zn (= 16.6 at% Zn = 5.3/32). Therefore, the diffusion couple of (Sn-x mass% Zn)/Cu is predicted to reveal a single phase of $\gamma$-Cu$_{3}$Zn$_{8}$ if x is smaller than about 10 according to the MDR law. $\epsilon$-CuZn$_{4}$ can only appear as the second phase when the reaction proceeds further. This corresponds to the results shown in Fig. 1, namely, the diffusion couples of (Sn-xZn)/Cu (x = 2, 5 and 10 mass%), which had lower Zn concentration than the intersection point in Fig. 3, showed a single phase of $\gamma$-Cu$_{3}$Zn$_{8}$.

4.2 (Sn-xZn)/Cu (x = 15, 20 and 25 mass%)

When the initial $r_{Zn}/r_{Cu}$ is higher than the intersection point in Fig. 3 (namely, $r_{Zn}/r_{Cu}$ < 5.3, $\epsilon$-Cu$_{3}$Zn$_{8}$ grows as the first phase because $\epsilon$-Cu$_{3}$Zn$_{8}$ has the lowest $r\Delta H_f$ when $r_{Zn}/r_{Cu}$ < 5.3 in Fig. 3. After the reaction proceeds, $r_{Zn}/r_{Cu}$ decreases with Cu diffusion toward the reaction surface, and $\gamma$-Cu$_{3}$Zn$_{8}$ appears as the second phase when $r_{Zn}/r_{Cu}$ fell below 5.3 since $\gamma$-Cu$_{3}$Zn$_{8}$ has the lowest $r\Delta H_f$ when $r_{Zn}/r_{Cu}$ < 5.3. Namely, the diffusion couples of (Sn-xZn)/Cu (x = 15, 20 and 25 mass%), which had higher Zn concentration than the intersection point in Fig. 3 show two phases of $\epsilon$-CuZn$_{4}$ and $\gamma$-Cu$_{3}$Zn$_{8}$. This again corresponds to the results shown in Fig. 2.

4.3 (Sn-10Zn)/Cu and (Sn-15Zn)/Cu at 653 or 673 K

In order to confirm that (Sn-10 mass% Zn)/Cu shows a single phase of $\gamma$-Cu$_{3}$Zn$_{8}$ and that (Sn-15 mass% Zn)/Cu shows two phases of $\epsilon$-Cu$_{3}$Zn$_{8}$ and $\gamma$-Cu$_{3}$Zn$_{8}$, further observation was performed even at elevated temperatures.

Figure 4 shows the EPMA line profiles of (Sn-10 mass% Zn)/Cu and (Sn-15 mass% Zn)/Cu diffusion couples prepared at 613, 653 or 673 K. Figure 5 shows TEM images and diffraction patterns of (Sn-10 mass% Zn)/Cu diffusion couple prepared at 673 K. As seen from the figures, the diffusion couple of (Sn-10 mass% Zn)/Cu showed a single phase of $\gamma$-Cu$_{3}$Zn$_{8}$, while that for (Sn-15 mass% Zn)/Cu had two phases of $\epsilon$-Cu$_{3}$Zn$_{8}$ and $\gamma$-Cu$_{3}$Zn$_{8}$ between Sn-Zn solder and Cu even at elevated temperatures of 653 or 673 K. The results at elevated temperatures again correspond to the predictions from the MDR diagram shown in Fig. 3.

Therefore, it can be concluded that the phase prediction based on the MDR law is also effective in pseudo binary diffusion systems such as (Sn-Zn)/Cu diffusion couple.
5. Conclusions

In this paper, MDR law is applied to \((\text{Sn-}x\text{Zn})/\text{Cu}\) diffusion couples and the first and the second intermetallic compound phases predicted by this model were compared with those observed experimentally. Assuming that a supply of Cu, which has the higher melting point than Sn or Zn, limits a reaction of an intermetallic compound phase formation at a soldered interface, and that the reaction brings about the largest free energy change to the system in this model, the first and the second phases predicted well agreed with those observed experimentally. Namely, only \(\gamma\text{-Cu}_{2}\text{Zn}_8\) was observed when Zn content was 10 mass% or less, while both \(\gamma\text{-Cu}_{2}\text{Zn}_8\) and \(\delta\text{-CuZn}_4\) were indentified with 15 mass% Zn or more. Therefore, it can be said that the phase prediction based on the MDR law is also effective in pseudo binary diffusion systems such as \((\text{Sn-Zn})/\text{Cu}\) diffusion couple.

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REFERENCES