Effects of Fe, Ni and Sn on Reaction Diffusion at the Solder/Cu-Base Alloy Interface*

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Copper base alloys, containing Fe, Ni and Sn up to 2.0 mass%, were soldered using 37 mass% Pb–Sn soft solder and then heated at 423K for 1.08 Ms (300 h) to grow intermetallic compounds at the solder/alloy interface. Diffusion of additional elements at the interface was analyzed by EPMA. The fractured interface, where the solder was peeled off after repeating the 90° bending test twice, was observed by SEM, and concentrated elements were analyzed by IMA.

Intermetallic compounds formed at the interface were the typical η-Cu₆Sn₅ and ε-Cu₃Sn from the solder side to the alloy side. Fe and Ni were concentrated at the ε-phase/alloy interface, and the Fe₃Sn or Ni₃Sn phase containing Cu was observed. On the basis of the observation of the peeled surface, peeling phenomena were roughly classified into 3 types. The first one which was observed on the alloys containing only Fe (or Ni) without Sn, was a type of peeling at boundaries of the η-phase and/or the η-phase/ε-phase interface. The second one which was observed on the alloys containing Fe (or Ni) and Sn above 0.5 mass%, respectively, was a type of peeling at the Fe₃Sn (or Ni₃Sn) phase where many voids were formed. The third type was a mixed peeling of the above two types, which was observed on the alloys containing a few mass percent of Fe (or Ni) or Sn. The diffusion of Cu into the ε-phase resulted in the formation of many voids in the Fe₃Sn or Ni₃Sn phase and the peeling of the solder.

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I. Introduction

Recently, Cu-base alloys with excellent mechanical strength and high heat conductivity have been developed for uses as the lead frame material in IC and the lead wire material in transistors and diodes. The soldering and plating properties of the Cu-base alloys have also been improved(1)(2). The reliability of the soldered part of these Cu-base alloys was evaluated by various methods. The most prevalent method is that a soldered Cu-base alloy heated for a long time is subjected to the 90° bending test. The reliability of joining depends on the strength of the diffusion layer formed.

The intermetallic compound formed by the reaction diffusion of pure copper and solder has long been identified(3). According to the recent results by Kay(4), Unsworth(5) and Mackay(6) et al., selective diffusion between Sn in solder and Cu contained in a base material occurs when an intermetallic compound formed at the interface is heated at less than 500 K. At that time, two intermetallic compounds, ε-Cu₃Sn and η-Cu₆Sn₅ from the pure copper side, are formed at the interface. The phase is identical to that estimated from the Cu–Sn equilibrium diagram(7). This phase also agrees with that formed when tin-plated pure copper(8)(9) is heated. Unsworth et al. demonstrated that there are no differences in growing rates of the η and ε phases at 408 K by reactions between copper and solder and between copper and tin. However, these studies(4–6)(8)(9) are related to the research on the formation or reaction diffusion of the phase and the growth of its layer by use of pure copper as the
base material, except for the experiment of Miyashita et al.\(^{(9)}\) by use of bronze. These results have not dealt with the strength of the joints. In effect, the Cu-base alloy used for the lead frame and lead wire material contains Fe, Ni or Sn as an additive element to increase the strength. Little is known about the effects of these elements on the layer growth for the \(\eta\) phase and the \(\epsilon\) phase during the reaction with the solder and also on the strength of the joint. Therefore, it is necessary to study the effects of these elements on the reaction diffusion at the interface.

In this paper this problem was examined by using several kinds of tin-plated Cu base alloys containing Fe and Sn. The effects of the additive elements on the layer growth of the compound formed by heat treatment\(^{(10)}\)\(^{(11)}\) have already been reported. A Cu-base alloy containing Fe and Ni was soldered and heated. Then, the growth of the reaction diffusion layer on the joint was studied, together with the effect of the additive elements on the strength of the joints. In addition, the 90° bending test was performed on the Cu-base alloy and analyzed its peeling pattern on the fractured surfaces.

II. Experimental Procedure

1. Sample preparation

The compositions of the specimens used in this study are shown in Table 1. The pure copper and copper alloys were cut to a size of 10 mm \(\times\) 20 mm \(\times\) 2 mm. Before soldering, the surfaces of the base metal were polished with diamond paste to remove the surface segregated layer of the additional element. Then, the metal was degreased and cleaned sonically with trichloroethylene and pure water. The cleanliness of the surface was confirmed by checking the absence of S or Cl with Parkin Elmer's Auger electron spectrometer SAM 590-A. This base metal was dipped in a eutectic solder bath of 37% mass Pb–Sn, held at 533 K (hereinafter referred to as 37 Pb–Sn or simply solder) for 5 s, to solder the base metal to a thickness of about 10 \(\mu\)m. The soldered copper alloy was mounted on an alumina board with the surface facing upwards for the analysis. Then, the sample was heated in an electronic oven controlled at 423±0.5 K for 1.08 Ms (300 h).

2. Analysis for solder-joined interface

Test samples prepared in the above manner were subjected to various tests such as the observation of diffusion profiles for the elements in the cross-section of the joint, identification of intermetallic compounds in the reaction diffusion layer, a 90° bending test and elemental analysis of the peeled-off solder after bending. In order to examine diffusion profiles of the additive elements in the diffusion direction of the test sample, the concentration distribution was determined from the results of X-ray plane analysis and point analysis with EPMA JXA-50A (JEOL). To identify the intermetallic compound phase, the X-ray diffraction spectrometer RV-100 (Rigaku Denki) was used. The vertical plane for the sample against the diffusion direction was polished with emery paper to 1 to 3 \(\mu\)m, while the plane was analyzed by the spectrometer to identify the compound by reference to the ASTM card. The result was compared with the results obtained by EPMA, and thereby the laminar structure for the reaction diffusion layer formed between solder and base material was determined. For the bending test, one end of the test sample was fixed in a vice, the sample was bent to 90° and then bent back into place. This cycle was repeated twice. The peeled-off surface was observed with SEM F-310A (Hitachi Ltd.). In addition, IMA-2 (Hitachi Ltd.) was used to determine depth profiles for Fe, Ni, Cu and Sn on the peeled-off surfaces of the solder and the copper alloy. The profiles on the solder side and the base material side were connected by using a program developed by the authors, and

| Denotation | Sn | Fe | Ni | Zn | Cu  |
|------------|----|----|----|----|-----|
| 2 4Fe–0 1Zn–Cu | 2.4 | 0.1 | Bal. |
| 0 7Fe–1 1Sn–Cu | 1.1 | 0.7 | Bal. |
| 0 2Ni–2.0Sn–Cu | 2.0 | 0.2 | Bal. |
| 0.9Ni–0 5Sn–Cu | 0.5 | 0.9 | Bal. |
the distribution of concentrated elements on the peeled-off plane was investigated.

III. Experimental Results

1. Diffusion reaction at the interface between pure copper and solder

After heating, the total thickness of 5.2 μm of the ε and η diffusion phases shown in the Cu–Sn equilibrium phase diagram was formed at the interface between pure copper and solder. Mackay et al. proved that, even when either 37 Pb–Sn or Sn is attached to the surface of pure copper and heated, the total thickness of the two phases does not differ. Onishi et al. has proposed an equation for calculating the thickness of layer growth for Sn plating. This equation gives a thickness of 5 μm for the ε and η phases in the present experimental condition, which agrees well with the experimental value.

2. Diffusion reaction and peeling action at the interface between 2.4 Fe–0.1 Zn–Cu and solder

Figure 1 shows diffusion profiles of the interface between 2.4 Fe–0.1 Zn–Cu and solder after heating, in terms of composition and the Fe–Kα X-ray images. As with pure copper, the formation of the ε and η phases is proved. However, the total thickness of the two phases is as thick as 8 μm. In addition, the concentrated Fe is observed on the interface between the ε phase and the base material. From the X-ray diffraction analysis, this is understood to come from the layer growth of the Fe3Sn phase. The amount of Fe added is so low that the concentration of concentrated Fe remains at about 6 to 8 mass% 11. This layer also contains Cu, but its chemical state is not sufficiently known. The presence of Cu in the

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![Composition and Fe-Kα X-ray images at interface between solder and alloy containing Fe after heating at 423 K for 1.08 Ms. (300 h).](Image)
Fe₃Sn layer has also been proved by the analysis with the Auger spectrometer, and it is hereinafter referred to as Fe₃Sn(Cu). The Zn content is too small to be measured.

Figure 2 shows the interface of solder peeled-off after heating and the bending test. It comprises the secondary electron images observed by SEM, denoting figures on the solder side peel-off surface, the alloy side peel-off surface and the peel-off interface. Obviously, as shown in these figures, peel-off occurs in the grain boundaries of the phase and the interface.
Effects of Fe, Ni and Sn on Reaction Diffusion at the Solder/Cu-Base Alloy Interface

Figure 3 shows the result of IMA investigations on the concentrated elements in the interface. In Fig. 3, the positive direction of the sputtering time relates to the direction of the depth of peeling on the metal side in Fig. 2. The negative direction agrees with the depth direction of peeling on the solder side. Two profiles for the peeling surfaces are connected at sputtering time 0. Figure 3 reveals that Fe, Sn and Cu are not highly concentrated on the peel-off surface. This also indicates that no peeling occurs in the Fe$_3$Sn(Cu) phase layer. In addition, peeling occurs in 2 positions, namely in the $\eta$ phase layer or in the interface between the $\varepsilon$ and $\eta$ phases. As the result, the sharpness of the profile disappears. Such a significantly concentrated Fe as shown in Fig. 1, cannot be observed apparently. In the $\eta$ phase, Fe is dissolved at about $10^{-2}$ mass% according to a calculation from the profile. The presence of Fe is not clear. This may be explained by the fact that Fe melted during soldering is left on the joint face (melting of Fe has been confirmed in a sample taken immediately after soldering)\(^{(12)(13)}\) or Fe is diffused into the grain boundary of the $\eta$ phase.

3. Diffusion reaction and peeling action at the interface between 0.7 Fe–1.1 Sn–Cu and solder

Figure 1 shows the composition and Fe–K X-ray images at the interface between 0.7Fe–1.1Sn–Cu and the solder after heating. Trends of the phase formation are substantially the same as those with the 2.4Fe–0.1Zn–Cu. The thicknesses of the $\varepsilon$ and $\eta$ phases are about 5 $\mu$m as in the case with pure copper.

Figure 4 shows SEM fractographs of the 0.7Fe–1.1Sn–Cu solder joint. Obviously, peeling occurs in the layer Fe$_3$Sn(Cu). Many voids from 0.1 to 3 $\mu$m exist on the peeled-off surface. In the case of the 0.7Fe–1.1Sn–Cu, Fe$_3$Sn(Cu) is significantly brittle, so that it is easily peeled after one bending test. Figure 5 shows the IMA results of the depth profile for the elements on the peeled-off surface as shown in Fig. 3. On the peeled-off surface, the concentrated Fe and Sn are observed, implying the presence of peeling in the Fe$_3$Sn(Cu) layer.

As described above, it is revealed that, even with the same copper-base alloy with Fe additions, the joint strength of the solder and the peel-off type differ depending on whether Sn is added or not.

4. Copper-base alloys with Fe and Sn additions vs peeling types at the alloy/solder interface

The peeling phenomena were studied with two kinds of copper-base alloys with Fe additions. The types are classified as shown in Fig. 6. Type 1 is defined by a case in which peeling occurs in the Fe$_3$Sn(Cu) phase layer. Type 2 is the case of peeling taking place in the Fe$_3$Sn(Cu) layer as shown in the case of 0.7Fe–1.1Sn–Cu. However, another type is expected to occur when either Fe or Sn is added in smaller quantities. This type is considered as a mixture of types 1 and 2. As in the case of Fe, Ni forms an intermetallic compound with Sn. Therefore, the peeling of solder in copper-base alloys with
Ni additions could be one of these three types.

5. **Peeling action at the interface between solder and 0.9Ni–0.5Sn–Cu and 0.2Ni–2.0Sn–Cu**

Figure 7 shows the result of the SEM observation on the interface between 0.9Ni–0.5Sn–Cu and solder when the solder is peeled-off by the bending test. As with 0.7Fe–1.1Sn–Cu, the peeling belongs to type 2, where peel-off occurs in the Ni$_3$Sn(Cu) layer. In addition, many voids are observed on the peeled-off surfaces, as in the case of 0.7Fe–1.1Sn–Cu. Figure 8 shows the result of SEM observations on the in-

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Fig. 4 SEM fractographs of soldered 0.7Fe–1.1Sn–Cu alloy after heating and bending. (Notice that the peeling occurred at Fe$_3$Sn where many voids were formed.)
Effects of Fe, Ni and Sn on Reaction Diffusion at the Solder/Cu-Base Alloy Interface

From the figure it is apparent that the type of peeling belongs to a mixture of types 1 and 2. These results indicate that the effect of Ni on peeling of the solder is the same as that of Fe. Peeling types can be classified according to the additional amounts of Ni or Fe and Sn.

6. Peeling type vs Fe, Ni and Sn additions in copper-base alloys

To study the effect of the additional amounts of Fe, Ni and Sn on the 3 peeling types shown in Fig. 6, the further experiments were performed on several kinds of copper-base alloys. Figure 9 shows the relationship between the peeling type and the concentration of Fe, Ni or Sn in Cu-base alloys. The samples used in the experiments are shown by the arrow. As seen from the figure, no peeling occurs even with an alloy containing both Fe or Ni and Sn provided that the additions are small. When each addition is 0.5 mass% or more, the type-2 peeling tends to occur. When only Fe or Ni is added, the type-1 peeling occurs. When only Sn is added, no peeling occurs. Moreover, the copper-base alloy of type-2 peeling has lower strength of solder-joints than that of the copper-base alloy of type-1 peeling, thus easily causing a peeling action.

IV. Discussion

Figure 10 shows a simple qualitative model for the diffusion phenomena with an example of a copper-base alloy with Fe addition. The diffusion coefficients of the additional elements at 423 K in the copper-base alloy or in the \( \eta \) and \( \epsilon \) phases available at present are so small that the temperature-variation of the diffusion coefficients in the figure was obtained by extrapolating, up to 423 K, the values obtained at 473–1473 K by Hoshino\(^{(14)(15)}\), Smithells (Handbook),\(^{(16)}\) Lubyova\(^{(17)}\) and Starke et al.\(^{(18)}\). The grain diameter is neglected here, because the grain diameters for all the experimental alloys are substantially the same.

As shown in Fig. 10, the diffusion coefficients for Cu and Sn are represented by \( D_{Cu} \)
and $D_{Sn}$, respectively. These coefficients are larger than those for any other elements in the model in the related phase. Therefore, Cu and Sn are quickly and selectively diffused in the solder to form the $\eta$ and $\varepsilon$ phases. As the result, Pb is left on the surface of the solder. Fe and Sn in the alloy remain in the $\varepsilon$ phase and alloy interface because of the low $D_{Fe}$ and $D_{Sn}$ in Sn in the solder. The remaining Fe and Sn contents gradually exceed the solid solution limit in the copper-base alloy and are precipitated as Fe$_3$Sn. However, as the Fe$_3$Sn cannot form a single layer, it contains much Cu. This layer significantly grows when the
amount of Sn in the copper-base alloy is large. Consequently, it is understood that the addition of Sn in the alloy contributes largely to the growth rate of the Fe₃Sn layer. According to the measurement with the EPMA by Inaba et al., the thickness of the Fe₃Sn(Cu) layer is less than 1 micron in the case of Sn plating. Therefore, it is difficult to precisely determine the concentration from a cross section. However, the Cu concentration in the ε phase

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**Fig. 8** SEM fractographs of soldered 0.2Ni–0.2Sn–Cu alloy after heating and binding (The mixed type of types 1 and 2).
is about 2 to 5 mass% higher than that for the \( \text{Fe}_3\text{Sn}(\text{Cu}) \) phase. In other words, the Cu concentration is slightly reversed between these 2 layers, due to \( D_{\text{Cu}} > D_{\text{Sn}} \) in \( \text{Fe}_3\text{Sn} \). In the present experiment, the Cu in the \( \text{Fe}_3\text{Sn}(\text{Cu}) \) phase is promptly diffused into the \( \varepsilon \) phase, while the \( \text{Fe}_3\text{Sn}(\text{Cu}) \) phase becomes brittle with many Kirkendall voids. In the case of a copper-base alloy without Sn or with a smaller addition of Fe, the layer growth of the \( \text{Fe}_3\text{Sn}(\text{Cu}) \) phase becomes slower. Therefore, no peeling occurs in this phase. With a copper-base alloy containing Fe only, peeling occurs in the phase containing Fe. However, the bonding strength of the alloy becomes higher compared with peeling in the \( \text{Fe}_3\text{Sn}(\text{Cu}) \) phase.

These phenomena take place with copper-base alloys with Fe or Ni additions. In a broader sense, this rule seems to be applicable to copper-base alloys containing an element which forms an intermetallic compound with Sn.

V. Conclusions

Copper-base alloys containing Fe, Ni and Sn were soldered and heat treated at 423 K for 1.08 Ms. Thereafter, the diffusion profiles and peel-off phenomena were observed on the solder/alloy interfaces, with the following results:

1. Intermetallic compounds formed at the solder/alloy interfaces consisted of, from the solder side, \( \eta - \text{Cu}_6\text{Sn}_5 \) and \( \varepsilon - \text{Cu}_3\text{Sn} \) in the copper-base alloys containing Fe, Ni and Sn. Fe and Ni were concentrated at the interface between the \( \varepsilon \) phase and the alloy, forming the \( \text{Fe}_3\text{Sn} \) and \( \text{Ni}_3\text{Sn} \) phases containing Cu, respectively.

2. In copper-base alloys containing Fe, Ni and Sn, peeling of the solder occurred by a 90° bending. The type of peeling can be roughly classified into 3 types. For the copper-base alloys containing Fe or Ni, with no Sn, peeling occurred in the grain boundary of the \( \eta \) phase and the interface between the \( \varepsilon \) and \( \eta \) phases. For the copper-base alloys containing more than 0.5 mass% Fe or Ni and Sn, peeling occurred in the \( \text{Fe}_3\text{Sn}(\text{Cu}) \) or \( \text{Ni}_3\text{Sn}(\text{Cu}) \) phase which contained voids and became brittle. In the copper-base alloys containing a smaller amount of Fe(Ni) or Sn, the mixed-type peeling occurred.

3. Voids in the \( \text{Fe}_3\text{Sn}(\text{Cu}) \) and \( \text{Ni}_3\text{Sn}(\text{Cu}) \) were Kirkendall voids, because Cu in these phases diffused at a much faster rate than Sn. In the copper-base alloy with the element form-
ing an intermetallic compound with Sn, the same peeling action of the solder may occur when $D_{\text{Cu}} > D_{\text{Sn}}$ holds true in the phase.

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