1. Introduction

RoHS Directive issued by European Union in 2003 increased the demand for Pb free solder alloy in the industry. As of 2015, Sn-Ag-Cu solder alloy group has been the standard Pb free solder alloy. However, due to the constantly increasing silver prices, the demand for low-Ag Pb free solder alloy with high electric reliability for application to the power device is increasing.

Currently, researchers from all over the world are actively conducting experiments in order to develop a solder alloy with improved joint strength, good wettability and higher joint reliability solder paste by adding different elements into Sn-base solder. However, since the Sn-Pb solder alloy has been in use for an extensive period of time, information regarding Sn-base alloy and various additive elements, such as multi-phase diagrams or their alloyed microstructures, etc… is not as readily available as other frequently used Fe-base, Cu-base and Al-base alloys. This makes it difficult for the solder alloy users to properly select the appropriate Sn-base solder alloy and to understand the solder alloy structure depending on the application condition.

This paper describes the alloy structure from the metallurgical point of view and describes the alloy structure of the additive elements which are frequently used with Sn-base alloys, based on the research data.

2. Alloy Structure

In general, solidified additive elements show up in the base metal, which is commonly referred as matrix (in the case of Sn solder alloy, the Sn matrix), as either a solid solution or a precipitation (in single phase or in compounds).

2.1 Solid Solution

Solid solution is the solid to which the additive element is dissolved into the matrix. It is similar to solving a little bit sugar (solute) into a glass of pure water (solvent) then solidifying it (note that, if you “freeze” the sugar water, sugar and water would freeze separately, so freezing would not serve the purpose here…). In the sugar water, sugar molecules and water molecules are forming homogeneous mixture; therefore, it is difficult to distinguish a glass of pure water and a glass of sugar water. Metals form mixture at the atomic lattice field level and form single phase matrix as a whole. There are two kinds of solid solution: (a) substantial and (b) interstitial.

Fig. 1(a) shows the structure of substantial solid solution which is consisted of the additive element with equivalent or slightly smaller atom radius and the base metal. Part of the base metal matrix has been replaced by the additive element. Unlike the lattice field consisted of only base metal matrix, this structure gives strain to the replacing atom derived from the difference of atom radius which prevents the atom dislocation from the mitigating and improves alloy’s strength. In this case, the larger the strain in the lattice field which further improves strengthening. Alloying structure of popular additive elements for Sn-matrix such as Bi, In and Sb typically form substantial solid solution.

On the other hand, if the atom radius of the additive element is significantly smaller than the radius of the base metal atom, additive element forms solid solution by invading in the lattice spacing of the base metal. Similar to (a) substantial solid solution, strengthening is obtained by invaded atom preventing the deformation of lattice force. However, there are not many additive elements which form this type of solid solution. Nonmetals, such as P, B and C, etc… to name a few, form this type of solid solution; however, application on the solder alloy is relatively small.

2.2 Precipitations (Intermetallic Compound)

Precipitates will not be integrated into the lattice field of the base metal but form separate lattice field; therefore, it precipitate as different phase by forming interface with base metal.

For the Sn-matrix, Ag or Cu forms InterMetallic Compounds such as Ag₃Sn or Cu₆Sn₅, and disperse into the base metal as precipitates in grain, plate or stick shape. In general, compound phase has stronger bonds among the atoms and derives higher strength and melt point. Therefore, the IMC may have been formed in the molten base metal. In addition, IMC displays
brittle characteristics owing to the atom’s low degree of freedom.

2.3. Alloy Phase Diagram and Alloy Form

Looking at the alloy phase diagram gives some idea on which alloy form Sn-matrix and additive element may take. For instance, when adding Bi into Sn, Fig. 2(a) Sn-Bi phase diagram show the existence of large solid solution range for Sn-rich phase (β-Sn area appears to the left side of the diagram). This indicates that the Bi is element which forms solid solution with Sn rather easily. In contrast, there is almost no solid solution range for the Bi-rich side, meaning Sn would hardly form solid solution into Bi.

Next scenario is adding Ag in Sn. According to Fig. 2(b) Ag-Sn phase diagram shows no solid solution range on the Sn rich side and ε phase (Ag₃Sn phase) can be seen around Sn 25 wt%. Therefore, the solidification structure of the Sn with a few wt% Ag additions will be eutectic structure of almost pure Sn phase and Ag₃Sn. Ag₃Sn will disperse into eutectic structure as fine particles in Sn at the solidification rate during reflow. In general, precipitation form will diverse as it is affected by solidification condition, ratio of additive element and other additive elements.

This report introduces alloying form of major additive elements for Pb-free solder alloys: Ag, Cu, In and Ni.

3.1 Test Method

Distribution of the additive elements was analyzed using element mapping on microstructure and X-ray diffraction pattern of solder alloy powder. Solder alloy composition investigated are listed in Table 1.

<table>
<thead>
<tr>
<th>Table 1 Solder Alloy Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solder Alloy</td>
</tr>
<tr>
<td>---------------</td>
</tr>
<tr>
<td>S1X*</td>
</tr>
<tr>
<td>S1XBIG</td>
</tr>
<tr>
<td>SB6N</td>
</tr>
</tbody>
</table>

* S1X is tested for XRD only.

3.1.1 Solder Sample and Element Mapping

Screen print each solder paste on test PCB with OSP treatment, mount 6330 chip resistors and reflow in hot air oven under air atmosphere. Cut the solder fillet vertically, grind and polish the sectioned plane and observed microstructure using SEM imaging and element mapping. Reflow profile is shown in Fig. 3.

3.1.2 X-Ray Diffraction on Solder Powder

It is extremely difficult to observe the change in lattice with high magnification microscope as the change is very little to the order of the atom size. Thus, evaluation of the alloy lattice change is conducted by using X-ray diffraction which is frequently used to identify the crystal structure of the alloys.

As Fig.4 indicates that the synchrotron incident beams directed at lattice field with crystalline will partially be reflected by the atom in lattice plane. When directed at a given angle θ0, if the difference of X-ray’s optical distance between surface and interstitial reflection (indicated in red in Fig. 4) is a multiple of an integer, diffraction occurs and reflects intensified X-ray. This is calculated by Bragg’s law \(^{21}\):
Changing the incident beam angle $\theta$ to obtain various diffraction patterns of the specimen enables evaluating the crystal structure and crystalline. Interstitial spacing is not uniform but varies by the direction; therefore, several diffraction patterns are observed. Powdered specimen is preferred to average out the grating measuring of the planes which X-ray is directed.

The solder alloys used in this X-ray diffraction evaluation is produced using a centrifugal atomizer and filtered by 20-38 µm thieves.

The X-ray tube with 45kV, 200mA Cu-Ka emission line was used. The scanning speed was 10.000deg/min and step size was 0.01 degrees.

3.2 Observation and Discussion

3.2.1 Distribution of additive element in solder alloy

Fig. 5 shows the element mapping of SB6N and S1XBIG. For SB6N, Ag contrast is higher at compound as oppose to Sn which shows lower contrast at the same area. This indicates that Sn and Ag is forming grain IMC ($Ag_3Sn$) in Sn-base solder and is distributed as a group. Same phenomena can be observed on S1XBIG as well.

Concentration of In can be seen on the same location as Ag; however, unlike Ag, In is also detected at Sn phase and its contrast ratio is smaller than Ag. Although its content is not comparable to Sn, its distribution appears to be similar to Sn. This means that In can exist in Sn phase as solid solution.

As for Cu, it shows higher contrast ratio with Sn at the compound location, which is an indication of Sn-Cu compound. Sn-Cu compound is detected in SB6N as well. The source of Cu in this Sn-Cu compound is the Cu eluted from the pads on the PCB.

Ni is S1XBIG has been detected in Sn-Cu compound; therefore, it is forming Sn-Cu-Ni compound.

As for Bi, although it exhibits slight variance in the contrast, it is distributed uniformly to almost entire Sn phase and no compound can be observed. This observation implies that Bi is forming solid solution in Sn phase. On the other hand, Bi content is smaller in precipitations such as Ag-Sn and Cu-Ni-Sn. It appears that there is hardly any Bi in these precipitations. Similar tendency can be seen on SB6N, with small contrast ratio at the precipitations, owing to its small amount in the solder alloy.

![Fig. 4 Principle Diagram of X-Ray Diffraction](image-url)
3.2.2 XRD Pattern of the Solder Alloys

Fig. 6 shows the X-Ray Diffraction patterns of respective solder alloys. On each solder alloy, similar peaks derived from β-Sn and Ag₃Sn are detected. Therefore, Bi in S1XBIG or Bi and In in SB6N does not form compounds or precipitations but exists as solid solution in Sn phase. As for Cu and Ni in S1XBIG, since its content is very low, despite the element mapping image indicates the formation of the Compound with Sn, no diffraction peak is detected.

Figure 7 lists enhanced images of each solder alloy’s β-Sn peaks around θ=32° and 44°. When taking the S1X as nominal, S1XBIG is shifted toward the lower angle on both 32° and 44°. In contrast, SB6N shows that peak is shifted to lower angle at 32° while it is shifted to the higher angle for 44°. According to formula (1), lowered peak θ was indication of increase in lattice spacing; therefore, by adding Bi, whose atomic radius is greater than Sn, lattice structure has been deformed and evenly increased lattice spacing. In Fig. 6, Sn peak in S1XBIG is shifted toward lower angle.

On the contrary, In lattice spacing appears to expand and contract according to θ. By adding given % of In to Sn, γ-phase (hexagonal crystal system) is partially generated as a middle range layer from β-Sn phase (tetragonal crystal system) which puts crystalline structure of β-Sn in a transitioning state.

Thus, it is assumed that not all unit cells are concurrently transitioning by expansion and contraction but rather doing one or the other depending on the direction of the lattice plane.

### 4. Conclusion

This report contains study on alloying structure of each additive element by analyzing solder alloys with element mapping and X-Ray diffraction.
- Ag, Cu and Ni ... Precipitates as compound phase
- Bi, In ... Formed solid solution in Sn phase.

In addition, X-ray diffraction revealed that Bi in the S1XBIG formed solid solution which increases the lattice spacing while the In in the SB6N formed solid solution which changes the crystalline structure of β-Sn.

However, additive elements which precipitate by forming compounds may form non-equilibrium solid solution in the base metal if the solidification rate was too fast to precipitate. It should be noted that the microstructure of the precipitates are largely depends on the solidification condition.

### Reference