SUPERIOR THERMAL CYCLING RELIABILITY OF PB-FREE SOLDER ALLOY BY ADDITION OF INDIUM AND BISMUTH FOR HARSH ENVIRONMENTS

Takehiro Wada and Kimiaki Mori
Koki Company Ltd.
Hiki-gun, Saitama, Japan
twada@ko-ki.co.jp

Shantanu Joshi and Roberto Garcia
Koki Solder America Inc.
Lake Elsinore, CA, USA
shantanu@kokiamerica.com

ABSTRACT
The consumer electronics industry has widely adopted tin-silver-copper (SAC) solder alloys for lead-free reflow soldering applications. The automotive electronics and power device industry demand high thermal fatigue resistance as compared to consumer electronics. Though SAC solder alloys fulfill most soldering requirements alternative solders are needed to meet more stringent environmental regulations, requirements for greater mechanical reliability, and more demanding high temperature service environments such as under the-hood in automobiles and in avionics systems. The alternative Pb-free solder alloy must satisfy both, the process as well as the reliability requirements. The new solders must form joints with acceptable strength, and, at the same time, must withstand thermal fatigue over the projected operational life of the assembly. Mechanical properties and microstructure are, therefore, among the main parameters to be controlled in the candidate solders in an industrial process.

Development was done on alternative lead-free alloys with varying percentages of tin-bismuth-indium-silver in comparison with a number of conventional lead-free alloys in soldering evaluations. By addition of small amounts of Indium, tin base solder alloys are strengthened without lowering ductility and improves the thermal fatigue resistance. However, adding large amounts of In causes phase transition from β-phase to γ-phase. β-phase consists of a tetragonal crystal structure with many slip planes and directions and it is therefore very easy to deform. On the other hand, γ-phase consists of a hexagonal crystal structure which consists of lesser number of slip planes and directions than β –phase. Therefore, choosing an accurate amount of Indium to maintain a hexagonal crystal lattice was paramount for this study.

As-reflowed and aged samples (1000 hrs. at 150°C in air) were prepared for mechanical and reliability tests. Tests included, tensile tests of solder alloy with micro dumbbell using as cast and after aging, x-ray diffraction was performed on solder powder, cross sections were prepared and microstructure was examined using scanning electron microscopy and energy-dispersive x-ray diffraction.

Accelerated thermal cycling test was performed on the boards assembled with various different alternative alloys and the results were compared with conventional Pb-free alloys. It was seen that indium and bismuth containing alloys lasted as much as 40% more than the conventional SAC alloys. The results of the tests are reported.

Key words: Pb-free solder , Indium , γ- phase, accelerated thermal tests, reliability, mechanical properties

INTRODUCTION
Today, Sn-3.0-Ag-0.5Cu solder alloy, known as SAC305, is the most popular lead-free solder alloy, and most of the industry accommodates this composition. However, according to the result from market research by IPC, although the share among the solder alloy is constantly decreasing, about 25% of the solder paste delivered worldwide in 2015 was leaded solder alloy, as indicated in Fig. 1.

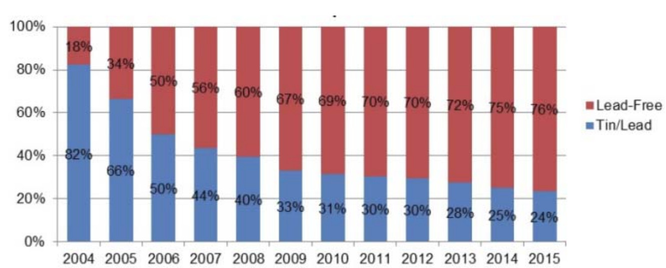


Figure 1. Solder paste delivery ratio, leaded and lead-free [1]

Since the leaded solder alloys have a negative impact on both environment and ecosystem that the transition to lead-free solder alloy has been promoted, it has not been completed yet. The reason for the delayed transition includes but not limited to;

- Increased cost of solder alloy,
- Troubles associated with material change approval procedure for critical parts,
- Concern on more severe thermal stress due to the higher melting point for Sn-Ag-Cu alloy on components with low thermal resistance,
- Higher strength but lower ductility than Sn-Pb solder alloy, SAC-type solder may increase the concern on component breakage

As of now, no solder alloy which solves all issues mentioned above has been developed. However, a Tin-Silver-Bismuth-Indium solder alloy (hereinafter SABI alloy) [2] that has a low melting point as Sn-Pb eutectic solder alloy yet has better ductility than SAC in order to reduce the mechanical damage to the component has been established. These reduced melting point and improved ductility owe largely to Indium addition. SABI alloy has been in the market for about 5 years and been used as a solder alloy with superior thermal cycle resistance.

By keep adding In to Sn, melting point keeps going down until the composition reaches 50wt%. This can be confirmed by looking at the Sn-In binary phase diagram. [3]

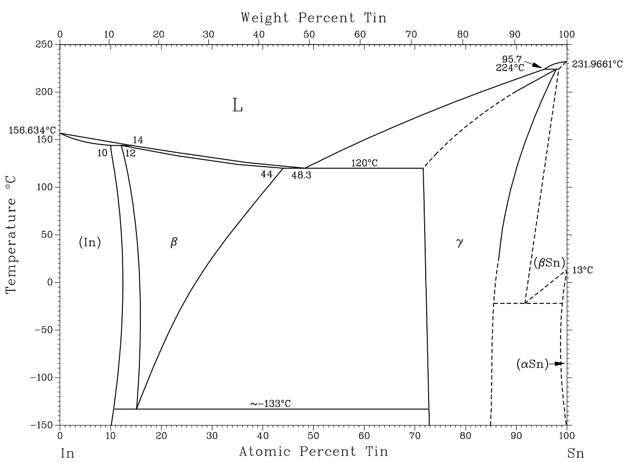


Figure 2. Binary phase diagram of Sn-In

However, Sn-In binary alloy shows formation of γ -phase of $InSn_4$ as the volume of In addition increases in Sn-rich composition[4]. Equivalent phenomena can be found in SABI solder alloy. Solderability performance evaluation has been implemented on SABI solder alloy; however, its mechanical properties have not been studied yet. Thus, in this paper, mechanical properties of SABI solder alloy with variable In addition and its relationship between solder joint reliability are described.

EXPERIMENT PROCEDURE

Evaluate alloy Composition

Table 1 shows the alloy compositions tested and evaluated for the purpose of this paper. The only difference among the tested compositions is the proportion of the In, in order to determine the impact of In amount in SABI solder alloy.

Table1. Solder Alloy Composition

Alloy	Sn	Ag	Cu	Bi	In
SAB4I	Bal.	3.5	-	0.5	4.0
SAB6I	Bal.	3.5	-	0.5	6.0
SAB8I	Bal.	3.5	-	0.5	8.0

Unit: wt%

Solder Alloy Tensile Test

Mechanical properties of the solder alloys were tested by pull test on cast micro-dumbbell, of which the diameter at the section is φ 3mm. Fig. 3 is the image of actual casted micro-dumbbell.

Figure 3. Appearance of micro-dumbbell

Since the microstructure of the solder alloys after soldering is the same as the structure of the casted metal, the micro-dumbbell for the evaluation was casted using a die. Furthermore, to obtain equivalent microstructure as the actual solder joint, molten alloys were casted into a die preheated at 573K. Then the filled die is cooled down in a cooling solution which is formulated to obtain the same cooling rate as actual soldering process, about 5K/second. Observation on the cross section at the gauge marks of the prepared dumbbell revealed uniform microstructure as intended.

Casted micro-dumbbells are divided into 2 groups: As Cast and Aged which have been aged by maintaining at 423K for 1000 hours. Pull tests were performed at a room temperature by applying strain to the micro-dumbbell at a strain speed of $1.0\times10^{-3}s^{-1}$ until the micro-dumbbell breaks .

Evaluate Crystal Structure by X-Ray Diffraction

Crystal structures of the solder alloys listed in Table 1 were identified using X-Ray Diffraction (XRD). The XRD system used is Smart Lab (9kW)-RPA which employs Cu-Kα lines and with rated tube voltage-current of 45kV and 200mA by Rigaku Corporation. Scan speed is 10.000deg./ min and step size is 0.01 deg.

Evaluate Crack on SMT Components after Thermal Cycles

Crack occurrence on solder joints after thermal cycles were evaluated by printing and reflowing solder paste consisting of solder alloys listed in Table 1 in Type 4 powder size and solder flux classified as ROL0 according to IPC J-STD-004 and implementing thermal cycling on the test PCBs.

Test PCBs for this evaluation are made of FR-5 grade material, the dimension of which is 50x50x1.6 mm, and the land's surface finish is Cu-OSP. Mounted component is 72 pin QFN with Sn plated leads, the size is 10x10mm and lead to lead pitch is 0.5mm. Stencil thickness to print the solder paste is 120µm. Reflow profile is shown on Fig. 4. Solder alloy with In addition has lower melting point than SAC type solder paste; therefore, its peak temperature is lower than SAC type, at around 230°C. Picture of the PCB after the reflow is shown on Fig. 5. QFN is located at the center of the test PCB.

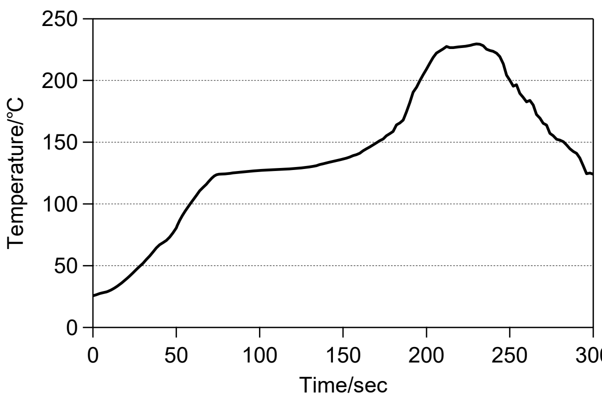


Figure 4. Reflow Profile (Air Atmosphere)

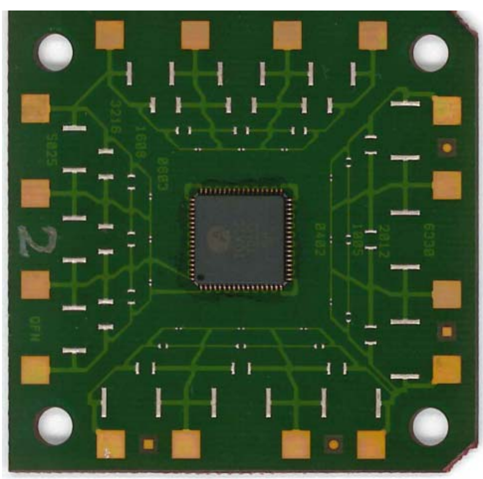


Figure 5. Test PCB for Thermal Cycle Test Evaluation (50x50mm)

Thermal cycle condition is -40/150°C, dwell time is 30 minutes at each temperature extreme. Crack occurrence is examined every 1000 cycles. Cracks on the solder joints were observed using a dye to visualize the cracks. Then, based on the observation, crack occurrence rate was calculated using following formula, Eq. (1).

$$\text{Crack Ratio [\%]} = \frac{\text{Number of cracked plate}}{\text{72 number of total plate}} \times 100 \quad \text{...Eq. (1)}$$

A solder joint is judged as cracked when the crack is propagated more than 50% against its area. 3 samples were prepared for each combination of the condition. Average from 3 samples was compared for crack occurrence evaluation

RESULTS DATA

Solder Alloy Mechanical Property and Microstructure

Fig. 6 shows the Stress-Strain Curve obtained by the pull test on micro-dumbbells. Break elongation declines as the In addition increases. SAB8I, which has 8% In content, shows very little elongation but it shows brittle behavior instead. This brittle behavior is about the same as Sn-Bi eutectic alloy, meaning if the micro-dumbbell is dropped from 1m above the ground, it will break apart at the gauge area.

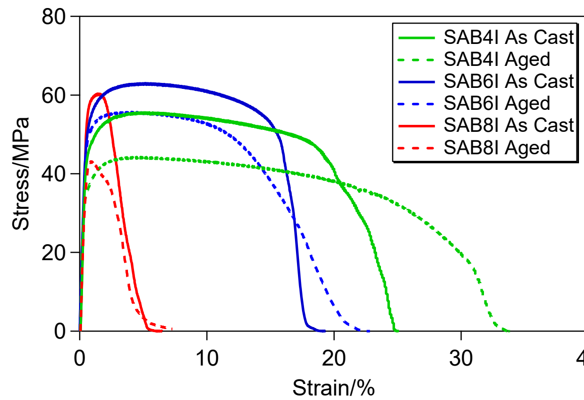
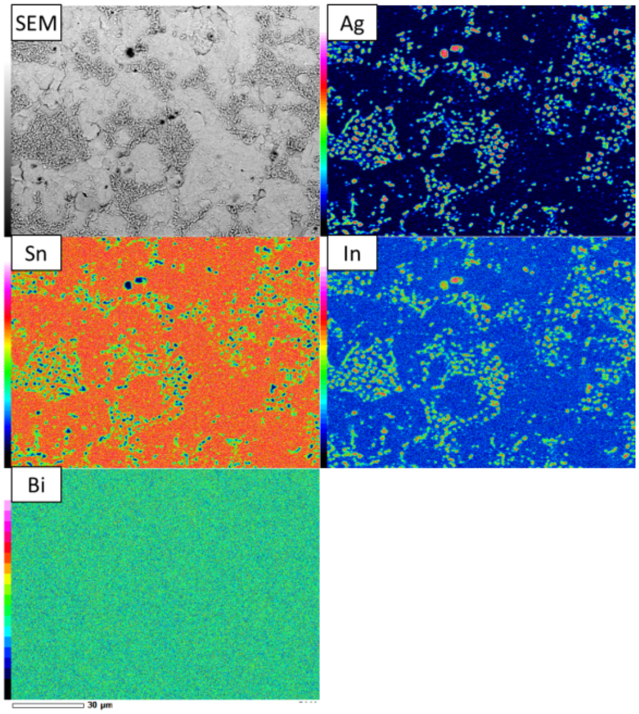


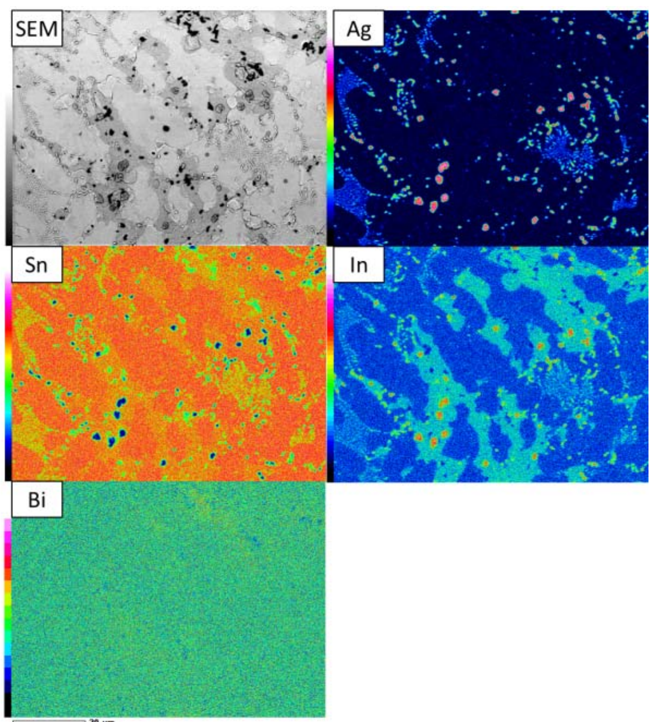
Figure 6. Stress-Strain Curve from Micro-dumbbell Pull Test

Data shows that SAB6I has the highest pull strength, followed by SAB8I and SAB4I. However, SAB8I ductility is so low that it cracks as soon as any load is applied to, making strength evaluation difficult. This is induced by the same reason as the variance in the pull strength data when performing pull strength test on ceramics. For all tested compositions, micro-dumbbells after thermal aging at 150°C tends to perform with lower strength than As Cast ones. In addition, SAB4I and SAB6I show improved elongation, but SAB8I did not show much difference.

Microstructure of SAB6I and SAB8I, compositions with significant difference in the relationship between strength and ductility, were observed using SEM-EDX. SEM image and EDX mapping are shown in Fig. 7 (a) and (b). Since the amount of Bi as additive is very low, it is forming a solid solution with Sn and does not seem to form any compound with other elements. As for In and Ag, they are forming fine Ag-Sn-In compound. This shows as the same form as the micro-precipitates by Ag_3Sn in SAC type solder. Additionally, there are several compound grain that are mainly consisted of Ag and In that are relatively more coarse than Ag-Sn-In grain. Since In also forms solid solution with Sn, it can exist in Sn-rich phase, which is not a compound. As a result, the density contrast of Sn-rich phase and compound is smaller than the Ag. SAB8Is image exhibits a large area with strong In detection aside from Ag concentrated area. This area appears in dark gray in SEM image which is different from Sn phase. Such area cannot be observed on SAB6I.



(a)

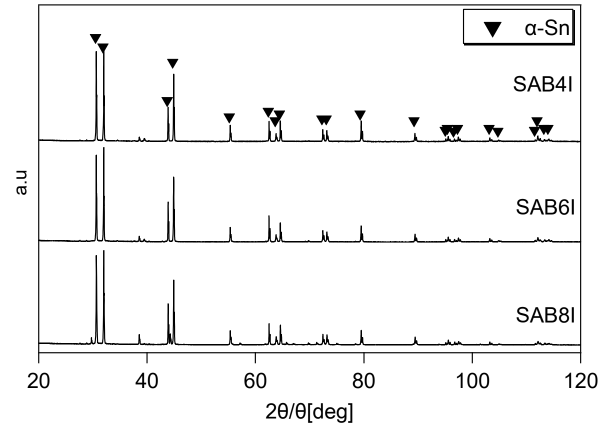


(b)

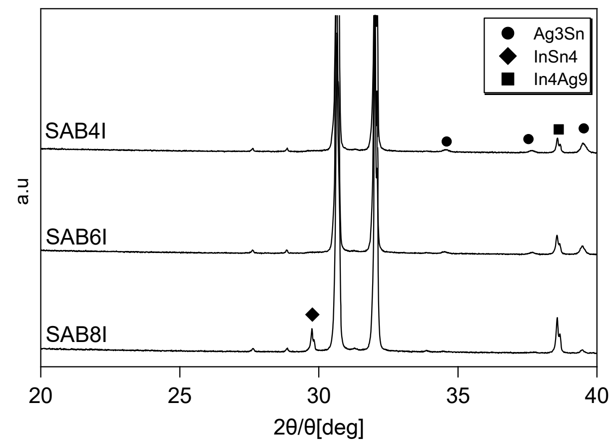
Figure 7. Microstructure and EDX Element Mapping Images at the gauge mark for (a) SAB6I and (b) SAB8I

XRD Patterns of Each Solder Alloys

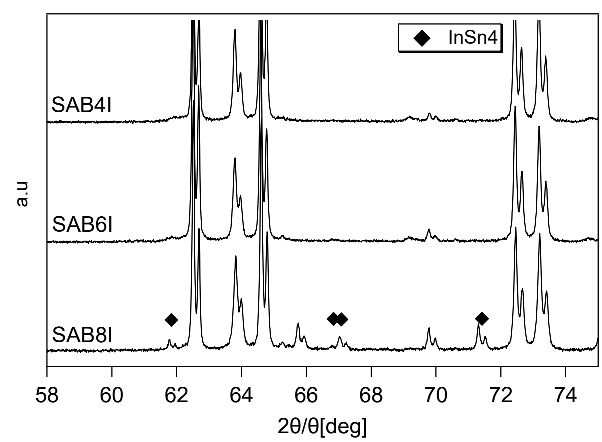
Fig. 8 shows XRD patterns of all tested solder alloy compositions. All alloys show strong detection of a peak which can be identified as α–Sn. By expanding the pattern, peaks for Ag_3Sn and In_4Ag_9 are detected as well. The more In amount in the solder alloy, the stronger In_4Ag_9 peak. A peak which is identified as $InSn_4$ is detected around 30° range and from 60~75°.



(a)



(b)



(c)

Figure 8.XRD Patterns for Each Solder Alloys(a) Overall View, (b) Expanded Micro-peaks at 20~40° and (c) Expanded Micro-peaks at 60~75°

Crack Ratio after Thermal Cycles

Fig. 9 shows the transition of each alloy's crack rate at the solder joint of QFN/BTC after thermal cycle. The crack occurrence order was, from low to high, SAB6I, SAB4I and SAB8I.

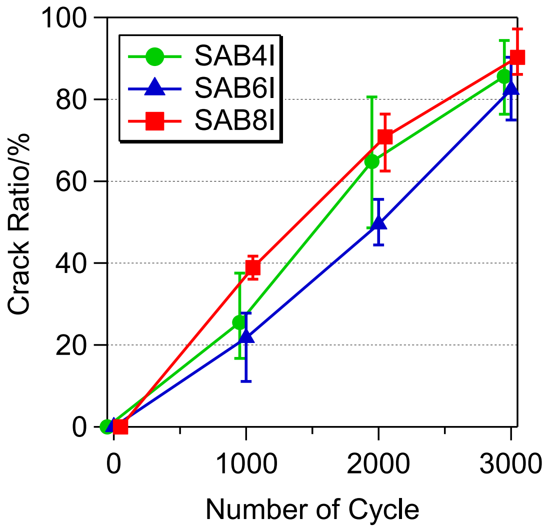


Figure 9. Crack Occurrence Transition on the Solder Joints of Test Solder Alloy and QFN/BTC

DISCUSSION

The Impact of In Addition on Mechanical Properties

In is such a useful element that not only it reduces the melting point, but also it improves ductility. However, it does not necessarily mean the more In is added, the better ductility becomes. According to the Stress-Strain Curve shown in Fig. 6, comparison between SAB4I and SAB6I indicates that SAB6I has better strength but inferior ductility. Although the ductility is lower, SAB6I still maintains about 20% elongation; therefore, it is assumed that SAB6I is sufficiently capable of following the thermal stress the solder joint will be exposed, such as the thermal cycle, etc. On the other hand, comparison between SAB6I and SAB8I suggests concern on SAB8I as a joint material due to its serious loss of ductility. In regards to the loss of strength after thermal aging, as far as the In addition amount this experiment is concerned, there was no notable difference among the tested alloy compositions in heat resistance. It is assumed that diffusion coefficient of In within Sn is significantly larger than the self-diffusion coefficient of Sn[5)]; therefore, In addition does not perform in terms of superiority over structural stability and is not able to prevent Ag_3Sn diffusion.

XRD images in Fig 8 show the distinctive peaks of $InSn_4$ phase, indicating it is a highly crystalline intermetallic compound. Regular Sn-rich phase is tetragonal structure; however, $InSn_4$ has hexagonal structure that characterizes it. [5]. Comparing to the tetragonal structure, hexagonal structure has limited and anisotropic slip plane. This property may be contributing to very low ductility behavior. As a result, SAB8I shows significant loss of ductility in pull test and fastest crack occurrence in thermal cycle tests.

Impact of In Addition to the Solder Structure

Fig. 8(b) shows intensified peak of In_4Ag_9 along with the increased amount of In can be attributed to coarsened compound grain which is observed by EDX mapping on SAB8I.

It is also revealed that $InSn_4$ is barely detected when In addition is 6wt% or less, while it is frequently seen when In addition is 8wt%. Therefore, In content of more than 6wt% is the threshold of massive $InSn_4$ generation. $InSn_4$ also contributes little change in ductility after thermal aging at 150°C, as its γ-phase area is at a higher temperature range, according to the Sn-In phase diagram and stability of $InSn_4$ is rather increased. Since it is difficult to reduce the amount of $InSn_4$ through thermal aging, the ductility is dominated mostly by this phase.

According to the EDX mapping, $InSn_4$ exists in Sn-phase in relatively large form just like Sn-phase, as opposed to the grainy shape of Ag_3Sn or In_4Ag_9. Consequently, when there is strain due to the pull test or temperature change by thermal cycle, the stress will be concentrated at the $InSn_4$ which has very low ductility and the low ductility triggers a crack.

Furthermore, compound grain of In_4Ag_9 is far larger than the micro-precipitates of Sn-Ag-In. This is not desirable from the strength and fatigue resistance point of view. If the amount of In addition increases, Ag which should be strengthening as micro-precipitates will be consumed by coarsened In_4Ag_9 grain that may cause the loss of strength and deteriorated thermal cycle resistance. In_4Ag_9 can be observed in SAB6I, yet the proportion is smaller than that of SAB8I.

CONCLUSIONS

By evaluating Sn-based SABI alloy which contains 4, 6 and 8wt% of In for mechanical properties and thermal cycle resistance after reflowing the following conclusions can be drawn.

Greater than 6wt% In addition causes high presence of $InSn_4$ which has low ductility, reduced Ag_3Sn micro-precipitates and increased In_4Ag_9 compound phase. In consequence, ductility in pull test and crack resistance in thermal cycle test will be impaired. If the In addition is less than 6wt%, there is not enough improvement by solid solution strengthening of In in Sn, and delivers relatively low strength, thus providing relatively low thermal cycle resistance than 6wt% In addition. Based on these results, it is concluded that the proper In addition to Tin-Silver-Bismuth-Indium solder alloy is 6wt%.

REFERENCES

1) IPC Global Solder Statical Program Results for Q4 2015, 2016, PP.7
2) A. Yamaguchi et al., *Mater. Trans.*, **45** 4 (2004) PP. 1282-1289

3) T.B.Massalski et al., "Binary Alloy Phase Diagram" 2nd Edition, (1995)
4) H. Bakker et al., "Diffusion in solid metals and alloys" (1990)
5) G. V. Raynor and J. A. Lee, *Acta Metall.*, **2** (1954) PP. 616-620