The Effect of Indium and Bismuth Addition on IMC Formation of $SN_{96}AG_{3.5}CU_{0.5}$ Solder

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This work focused on the effect of adding indium and bismuth to wettability and the IMCs that form at the surface before and after aging to the ternary $Sn_{96}Ag_{3.5}Cu_{0.5}$ solder. *Solders (SAC-9In and SAC-5In4Bi) were prepared by melting the components together at 500⁰C. Solders were then re-flowed on Cu substrate at temperature 20⁰C and 40⁰C above melting point for each solder. The microstructural characteristics of IMCs formed at solder joint before and after aging were carried out using Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-Ray (EDX). The DSC result shows that the melting point of SAC solder was reduced from 217⁰C to 202⁰C and 214⁰C with addition of 9% In and 4% Bi respectively. Adding In increases* F_{max} *and lower wetting time and thus indicates better wettability. Addition of Bi results in lower thickness of IMC and this indicates better reliability of solder joint.*

Keywords: lead-free solder, SAC, mechanical properties, ball shear

INTRODUCTION

In the current industrial world, soldering has become indispensable for the interconnection and packaging of virtually all electronic devices and circuits. The fast changing technology and increasing miniaturization of electronic devices place a challenge for obtaining reliable and successful component joints. This is another reason which has pressed researchers to investigate and develop novel solder materials to meet the requirements and goal of the modern day solder interconnects. Almost all the potential lead-free solder materials are high Sn-containing alloys, including the most promising Sn-Ag-Cu (SAC) alloy of eutectic composition.

However the greatest problem with these solder are there is a fear of bad effect on reliability of solders caused by over-heating part at the time of melting the solder because of higher re-flow temperature. During soldering process, the metallization layer of the printed circuit board (PCB) or the component pins react with Sn in the solder to form an inter-metallic compound (IMC) layer at the metallization/solder interface. Although the formation of the IMCs layer is desirable for good wetting and necessary bonding, an excessively thick layer is detrimental to the health and reliability of solder joints. Thus, reliability issues are usually closely related to the solder joints' inter-metallic compounds. Excessive thickness of IMCs will embrittle the solder joint due to its hard and brittle properties in nature which makes it prone to mechanical failure even at low loads [1]. A thicker IMCs layer would also increase the heterogeneity in the physical properties of material across the joint. Therefore, the growth rate of the IMCs layer and subsequent dissolution of the metallization (substrate) must be under control during soldering. In these Sn-Ag-Cu solder alloys, two types of inter-metallic will generally form, Ag_3Sn and Cu_6Sn_5.

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These IMCs are relatively large and brittle and may lead to serious problems under stressed conditions.

Some researchers reported that a small amount of other elemental addition such as Bi and In will reduce melting point, improves strength, thermal resistance or fatigue life due to its solid solution strengthening effect [2-4]. This investigation aimed at exploring the effect of Bi and In addition on the formation and growth of the IMCs layer of SAC solder on copper substrate before and after aging process.

EXPERIMENTAL

Sample Preparation

All alloy components were melted together in muffle furnace in argon environment to avoid oxidation of the solder. Table 1 shows the composition of the solder.

TABLE 1
Compositions of solder alloys

Solder	Sn	Ag	Cu	In	Bi
SAC	Balance	3.5	0.5	-	-
SAC-Bi	Balance	3.5	0.5	-	4
SAC-In	Balance	3.5	0.5	9	-

Solder were re-melted three times at 350°C to ensure homogeneity of alloy components. The microstructure observation and phase identification were carried out by means of optical microscopy (OM), scanning electron microscopy (SEM) model SUPRA 35VP equipped with energy dispersive X-ray spectroscopy (EDAX). The wetting behavior is evaluated by means of wetting angle measurement of the solder on copper substrate using microscope zoom stereo. The wetting force and wetting time were determined by solder checker equipment (RHESCA).

Preparation for Solder Reflows

The solder alloys were cast in round mold and produced into sheet form with approximately 2 mm thickness. The sheet was then punched into a disk 6 mm in diameter and 2 mm in thickness. The copper substrate used in reflow was 10 mm x10 mm with 0.5 mm in thickness. Copper substrate was ground and polished using Si-C grit paper to mirror-like finish without any obvious scratch under magnification 20x using optical microscope. $ZnCl_2$ was used as flux and applied to the copper substrate and also on the surface of solder sample. Reflow was done at a temperature 20% higher than the melting point of each solder.

Aging

After re-flow process, aging was done by heating samples in oven at temperature 160°C for 100 hours.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry measurements were performed on milligram size alloy using DSC equipment model METTLER TOLEDO. Each sample was placed into an Al pan/lid assembly. For melting property data, the sample was initially scanned from room temperature to 300^0C at rate 10^0C/min and cooled at same rate.

Dipping Test

The dipping test was done using the Solder Checker Instrument model SAT-5100 Rhesca. $Sn_{96}Ag_{3.5}Cu_{0.5}$, $Sn_{87}Ag_{3.5}Cu_{0.5}In_9$ and $Sn_{92}Ag_{3.5}Cu_{0.5}Bi_4$ solder were tested using Cu substrate with (5.0 ± 0.5) mm in width, (50.0 ± 0.5) in length and 0.4 mm in thickness. $ZnCl_2$ was used as flux for all solder. The wetting balance tests were performed at immersion rate 5mm/s at immersion depth 5 mm for 30 second with temperature between 200°C to 250°C depending of the types of solder.

Samples Preparation for SEM and EDX Analysis

Samples of as-reflowed and after aging were then cross sectioned and cold mounted with epoxy and hardener. Samples were ground using silicon carbide paper with grid 600, 800, 1000 and 1200 and polished using alumina to get mirror-like finish without any scratches under magnification 20x of optical microscope. Then the cross sectional samples need to be etched using aqueous ferric chloride etchant with formulation (5g $FeCl_2$ + 20ml HCL + 15ml HNO_3 + 100ml distilled water) for 2-4 seconds. It is recommended to add small amount of ethanol into the etchant solution for a better etching. After deep etching, the samples were ultrasonically cleaned followed by sputtering with a thin coated gold before the specimens were characterized using SEM and EDX.

RESULTS AND DISCUSSIONS

DSC Analysis

The DSC analysis of $Sn_{96}Ag_{3.5}Cu_{0.5}$, $Sn_{92}Ag_{3.5}Cu_{0.5}Bi_4$ and $Sn_{87}Ag_{3.5}Cu_{0.5}In_9$ solder are shown in Table 2.

TABLE 2
DSC analysis of (a) $Sn_{96}Ag_{3.5}Cu_{0.5}$ solder
(b) $Sn_{92}Ag_{3.5}Cu_{0.5}Bi_4$ solder
(c) $Sn_{87}Ag_{3.5}Cu_{0.5}In_9$ solder

Solder	Onset (°C)	Peak (°C)
$Sn_{96}Ag_{3.5}Cu_{0.5}$	217.57	218.54
$Sn_{92}Ag_{3.5}Cu_{0.5}Bi_4$	214.29	216.94
$Sn_{87}Ag_{3.5}Cu_{0.5}In_9$	202.41	209.87

Table 2 shows onset temperature of $Sn_{96}Ag_{3.5}Cu_{0.5}$ solder at 217.57°C. The onset temperature of the DSC wetting curve is the temperature at which solder start to melt, or it can be marked as a solidus temperature of the solders. The addition of 4%Bi in SAC solder lowered the onset temperature from 217.57°C to 214.29°C. The addition of 9% In further lowered the onset temperature from 217.57°C to 202.41°C due to lower melting of Indium itself, which is 157°C.

Wettability Test

Three of the most commonly applied wetting indicates are the wetting time (T_0), the maximum wetting force (F_{MAX}) and the withdrawal force (F_W). The (T_0) is the time to cross the zero axis of wetting force. This point indicates the transition from non-wetting ($F<0$) to wetting ($F>0$). In a static equilibrium condition, the wetting force F can be expressed as follows [5-6].

$$F = P \sigma_{lV} \cos \theta_e - \rho g V_b \qquad (1)$$

Where P is the parameter of copper substrates, σ_{lV} is surface tension, is the contact angle, ρ is the density of the solder, g is acceleration of gravity constant and V_b is the buoyancy volume.

From the analysis of SAT/WET graph, it is shown that addition of Bi, In and Zn reduces wetting time of solder as can been seen in Table 3. Addition of In result in higher F_{MAX} and shorter wetting time. Whereas Bi slightly lower F_{MAX} and shorter wetting time as compared to SAC solder. Addition of Zn reduces the wetting time further given the lowest wetting time. There is a generally accepted measure for quantitative value of wetting time based on wetting balance parameters and suggested evaluation criteria for wettability was $\leq$1second for wave soldering and $\leq$2 second for the reflow. The shortest wetting time indicate the greatest tendency to wet rapidly. According to equation 1 higher F_{max} and lower surface tension give lower contact angle and good wettability due to cosine value.

TABLE 3
The result of F_{MAX}, F_W and wetting time from solder checker analysis

Solder	F_{MAX} (mN)	F_W (mN)	T_0 (s)
SAC	2.25	5.05	1.18
SAC-Bi	2.16	4.79	1.15
SAC-In	3.35	5.37	0.40

Fig. 1 shows the wetting angle of $Sn_{96}Ag_{3.5}Cu_{0.5}$ decrease with adding Bi and In. Increasing re-flow temperature also reduce the wetting angle due to better fluidity of alloys at high temperature. From the result of solder re-flow, it can be related that higher F_{MAX} of

$Sn_{87}Ag_{3.5}Cu_{0.5}In_9$ solder and lower surface tension of $Sn_{92}Ag_{3.5}Cu_{0.5}Bi_4$ given lower wetting angle compared to $Sn_{96}Ag_{3.5}Cu_{0.5}$.

TABLE 4
Calculated surface tension from eq. 2

Solder	F_{MAX} (mN)	F_W (mN)
SAC	12	420.8
SAC-Bi	12	399.2
SAC-In	12	447.5

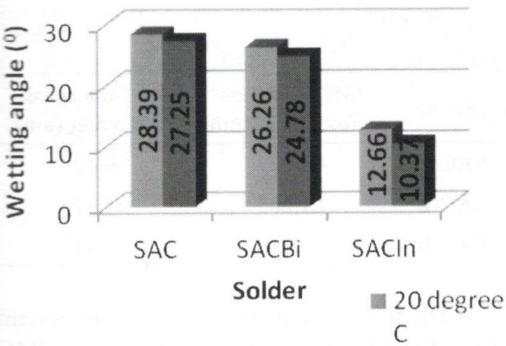

Fig. 1: Comparison of wetting angle of $Sn_{96}Ag_{3.5}Cu_{0.5}$, $Sn_{92}Ag_{3.5}Cu_{0.5}Bi_4$ and $Sn_{87}Ag_{3.5}Cu_{0.5}In_9$ solder at temperature 20°C and 40°C above melting point

Microstructure of Solder Alloys on Copper Substrate Before Aging

Both backscattered electron and secondary image were used to identify phase boundary of IMC layer. During initial reflow, the Cu substrate in contact with solder will dissolve into the molten solder to form IMC. For a solder alloy based on Sn as matrix, Cu_6Sn_5 IMC layer will easily form between solder and copper substrate. The Cu atoms diffuse easily into Sn by rapid interstitial mechanism whereas Sn diffuses into Cu by a slower substitutional mechanism [7]. From the observation on interfacial microstructures of $Sn_{96}Ag_{3.5}Cu_{0.5}$, it can be seen that the IMC layer on solder joints have round scallop-type morphology. The interfacial IMC layers are mainly composed of Cu_6Sn_5 and Cu_3Sn but Cu_3Sn layers are too thin to be observed. In *Fig. 2(b)* shows that the microstructure of SAC after adding 4% Bi. Adding Bi contributes to refinement of grain structure of SAC alloys [8] as we can see in *Fig. 2(a)* and *2(b)*. Addition of bismuth increase activation energy in solder Bi does not take place in formation of IMC but accumulate near the solder joint. *Fig. 2(c)* shows the morphology of $Sn_{87}Ag_{3.5}Cu_{0.5}In_9$ solder after re-flow on copper substrates. It show that $Ag_3(Sn,In)$ phases appear in solder region and γ-InSn diffuses into Sn matrix with increasing the quantity of In from 6.91At% to 8.25At%.

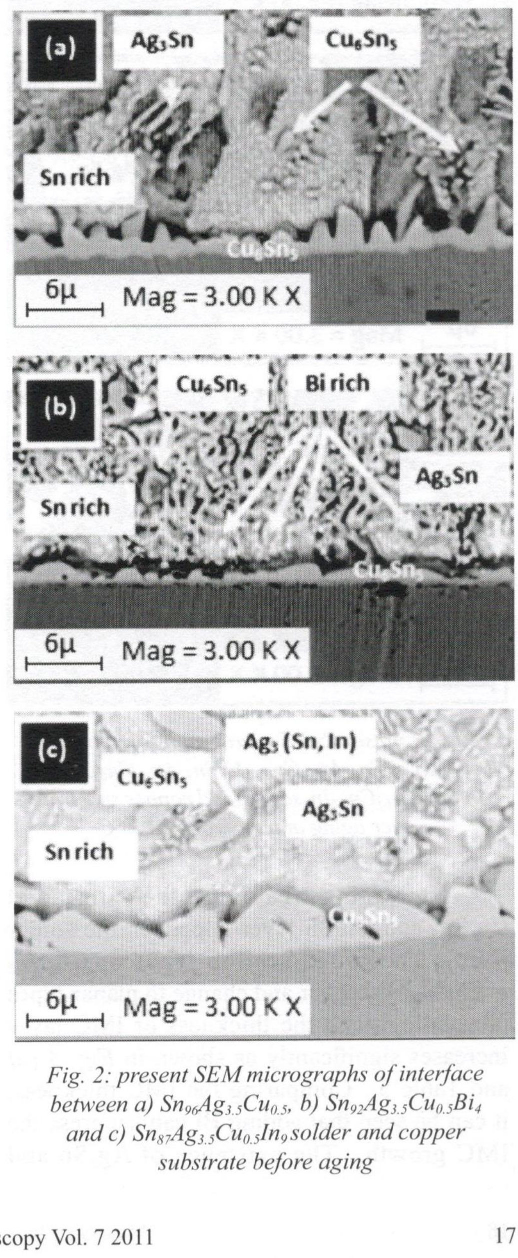

Fig. 2: present SEM micrographs of interface between a) $Sn_{96}Ag_{3.5}Cu_{0.5}$, b) $Sn_{92}Ag_{3.5}Cu_{0.5}Bi_4$ and c) $Sn_{87}Ag_{3.5}Cu_{0.5}In_9$ solder and copper substrate before aging

Microstructure of Solder Alloys on Copper Substrate After Aging

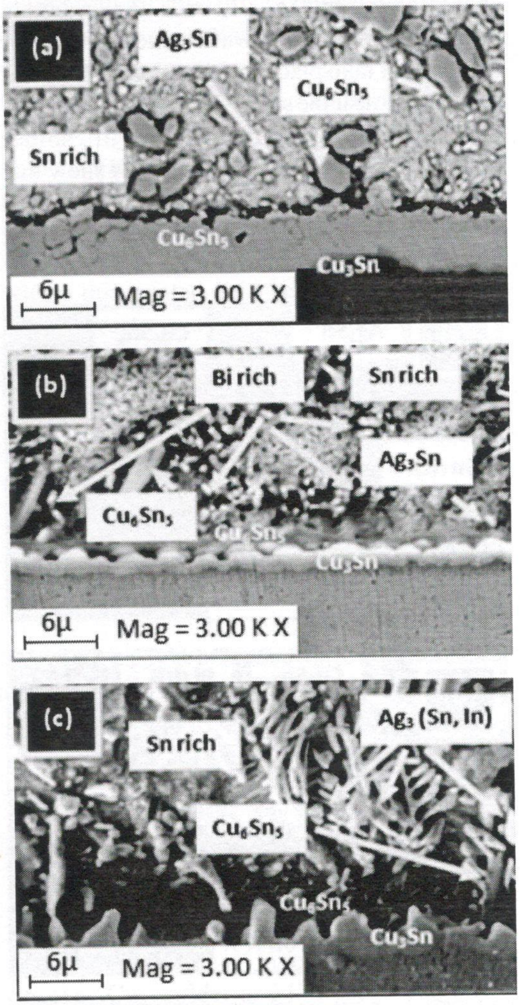

Fig. 3: present SEM micrographs of interface between a) $Sn_{96}Ag_{3.5}Cu_{0.5}$, b) $Sn_{92}Ag_{3.5}Cu_{0.5}Bi_4$ and c) $Sn_{87}Ag_{3.5}Cu_{0.5}In_9$ solder and copper substrate after aging at temperature 160^0C

After aging treatment, the interfacial Cu_6Sn_5 and Cu_3Sn layer appear in the solder joint. The round scallop types of Cu_6Sn_5 gradually disappear and change to planar-types morphology and the thickness of IMC layer increases significantly as shown in *Fig. 3 (a)* and Table 5. Comparing the IMC thickness, it can be seen that adding Bi can suppress the IMC growth. The existence of Ag_3Sn and Bi rich particles in $Sn_{92}Ag_{3.5}Cu_{0.5}Bi_4$ solder obstruct the grain boundary diffusion of Cu and Sn via IMC layer leading to suppression of the growth of IMCs. Adding Bi has been found to increase the activation energy of solder alloy thus reduce diffusion rate and inhibit the excessive growth of IMC [8]. Table 5 shows the comparison of IMC thickness after and before aging of $Sn_{96}Ag_{3.5}Cu_{0.5}$, $Sn_{92}Ag_{3.5}Cu_{0.5}Bi_4$, and $Sn_{87}Ag_{3.5}Cu_{0.5}In_9$ solder alloys.

TABLE 5
Comparison IMC thickness of solder joints before and after aging

Solder	IMC thickness before aging (µm)	IMC thickness after aging (µm)
SAC	≈2.029	≈6.407
SAC-Bi	≈1.285	≈1.378
SAC-In	≈2.848	≈2.943

The thickness of IMC layer was important for reliability of solder joint. Excessive IMC growth may weaken the strength of solder joint due to its brittleness.

CONCLUSION

From the result of adding In and Bi in SAC solder on the melting points, IMCs growth, wettability and shear properties, several conclusions can be made:

- Addition of In and Bi in SAC solder reduce the melting points and give better wettability.
- Addition of In and Bi resulted in lower IMCs thickness and slower growth rate after aging.
- The thickness of inter-metallic layer at soldered/Cu interface increases with aging and addition of Bi is more significant in reducing the thickness of IMC.

AKNOWLEDGEMENTS

The authors would like to thank Universiti Sains Malaysia for providing funding through the FRGS and USM-RU-PGRS grant in order to carry out this project.

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