Lead Free Interfacial Structures and Their Relationship to Au Plating (Including Accelerated Thermal Cycle Testing of Non-Leaden BGA Spheres)

Toshihiko Taguchi, Rikiya Kato, Satoru Akita
Senju Metal Industry Co., Ltd (SMIC)
405 Yatsuka-cho, Sohka-shi, Saitama, Japan
TEL:81-489-22-1272,FAX:81-489-22-3184

Atsushi Okuno
IEEE Senior Member
Japan Rec Co.Ltd.
5-1,3-Chome Dou-cho, Takatsuki-shi, Osaka, Japan.
TEL:81-726-69-5231,FAX:81-726-69-5230
E-Mail:XLW05557@niftyserve.or.jp

Hiro Suzuki, Tetsuya Okuno
Senju Comtek Corp.
1171-B North Fourth Street, San Jose, California, 95112 USA
TEL: 408-792-3832, FAX: 408-792-3838
E-Mail: teokuno@senjucomtek.com

1. Abstract

As lead is a harmful element, soldering in the electronics industry has moved toward elimination of lead from the solder alloy. Already there are a group of companies who have begun implementation of lead-free solder alloys.

The scope of parts being tested for lead-free processes is not limited to the solder material; the complete absence of lead from electronics parts, including the substrate, parts, and module is being envisioned in the near future.
Therefore, for BGA and/or CSP bumps as well, there is no other option but to evaluate lead-free materials.

First in this paper, the microstructure and the shear strength of the solder bumps were examined. The following lead-free alloys and the alloy containing lead were selected for this first examination: Sn-5Sb, Sn-0.75Cu, Sn-3.5Ag, Sn-3.5Ag-0.75Cu and Pb-63Sn. The bumps were soldered on a copper/nickel substrate with gold plating and were evaluated before and after a thermal cycle test.

Second in this paper, two types of lead-free alloys and the alloy containing lead were selected as CSP bump materials. The mechanical reliability of the soldering joint between the CSP package and PCB was evaluated before and after thermal cycle tests. One of these lead-free alloys is: Sn-Ag-Cu, the most influential candidate for eliminating lead from the current Sn-Pb solder. The other is: Sn-Zn-Bi which has a lower melting temperature than Sn-Ag-Cu. Also, three (3) types of plating on the substrate of PCB (Bare Copper, Alpha Level Silver and Flash Gold) were evaluated with CSP bump materials. The purpose of the evaluation was to select the best material for using lead-free solder alloy as a CSP joint.

The results:

If lead-free and tin/lead alloys are compared, there is a clear difference between each alloy in terms of shear strength. All lead-free solder alloys exhibited greater shear strength than tin/lead solder.

As for the result of the second CSP joint evaluation:

The joint material Sn-Ag-Cu using Alpha Level Silver as the substrate plating demonstrated the best mechanical reliability. Sn-Zn-Bi, with a flash gold plating substrate, exhibited superior mechanical reliability when compared with Sn-Pb. However, Sn-Pb is a more reliable alloy when either bare copper or Alpha level silver are used for the board plating.

2. Introduction

The purpose of this paper is to select the optimum materials to recommend as a lead-free solder alloy for BGA and/or CSP applications.

First, the microstructure and the shear strength of the solder bumps on a copper/nickel substrate with a gold plating were examined before and after a thermal cycle test.

Sn-Sb and Sn-Ag-Cu materials were available for this experiment. However, due to the popularity of the Sn-Ag-Cu alloy it was selected for the second CSP joint evaluation. Also, as the Sn-Zn-Bi solder alloy has a lower melting temperature, Sn-Zn-Bi was selected for the second CSP joint evaluation.

Evaluation method, results and considerations are as follows:

3.1. The microstructure and the shear strength of the solder bumps

3.1.1. Materials and soldering

Table.1 shows the solder alloy type and its melting temperature for this BGA bump examination.

The solder bump was made on a copper/nickel substrate with a gold plating (1um) by reflow soldering with water soluble flux and solder balls. The peak reflow temperature was 250 C in air atmosphere.

Table 1 Bump materials

Solder Type	Melting Range(C)DSC		
	Solidus	Peak	Liquidus
Sn-5Sb	237	241	243
Sn-0.75Cu	226	227	---
Sn-3.5Ag	219	222	---
Sn-3.5Ag-0.75Cu	216	218	220
63Sn-37Pb	183	---	---

*Ball Dia. : 0.76mm
*Flux : WS609 (Water soluble Flux)
*Peak temp : 250C
*Thermo cycle : -65C+/-150C, 15min, 1000cycle

3.1.2. Thermal Cycle Test

Ball Grid Arrays with lead-free bumps were put into the thermal cycle test chamber, set to oscillate between -65 C and +155 C every 15min. After 1000 cycles, the Ball Grid Arrays with lead-free bumps were taken out of the chamber, the bump shear strength was examined and the microstructure analyzed by an SEM (Scanning Electron Microscope).

Fig.1 shows the appearance of shear strength test equipment. The method and cross-section after the test were shown as Fig.2 and Fig.3.

Fig. 1 Photograph of test machine

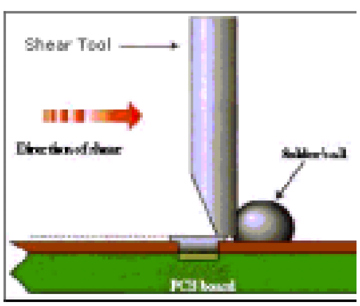


Fig. 2 Test method of Shear strength

(Ni:10um, Au:1um, overresist:35um, bump diameter:0.25mm)

Fig. 3 Cross Section of BGA bump

3.1.3. Results and Discussion

The results of shear strength test were shown at Fig.4.

Between the solder materials, the difference in the initial shear results is small, and concentrated around a range of 13-16 N. However, the results in relation to cycling behavior differ greatly. A quick drop of 30% in strength occurs in the tin/lead solder alloy after 200 cycles. One thousand cycles shows a 50% drop in shear strength with these alloys. As for Sn-5Sb, it differs from the other alloys because Sn-5Sb appears to strengthen during initial cycling. It is believed the increase of heat during cycling is a factor for the strengthening of Sn/Sb alloy. The precipitation of super-saturated Beta phase structures occurs during solidification. [1]

Upon conclusion of the initial cycling Sn/Sb does weaken like all other tested alloys. However at 1000 cycles it continued to maintain the original value. Other lead-free alloys maintain 85% of original strength after the same number of cycles.

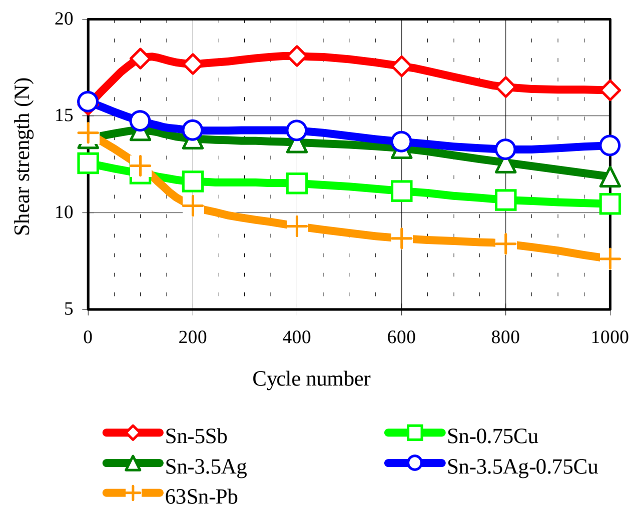
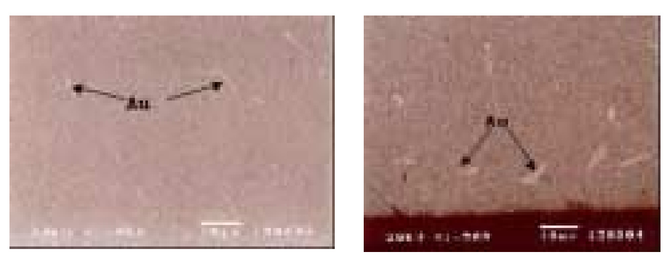


Fig. 4 Shear strength of solder ball bump by the number of cycles.

(a) Sn-5Sb

Basically, there is no change in the microstructure of Sn-5Sb alloy from the first cycle to beyond 1000 cycles.[2]

The reason for the absence of change in the microstructure is the acicular (needle-like) shaped structure present in $AuSn_4$, the intermetallic compound uniformly dispersed in the Sn-Sb base structure. Although the acicular structures around the interface are long and narrow, the structure transforms to a more round shape during thermal cycling. (Fig.5)



Initial After 1000 cycles

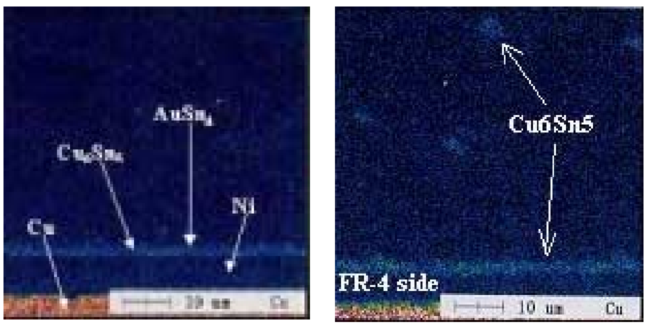
Fig. 5 Micrographs of Sn-5Sb BGA solder joint

More $AuSn_4$ compounds are observed near the interface and the high concentration of Au near the interface is suspected from the beginning of thermal cycling. However this change does not affect shear strength.

In addition, the interface consisted of the intermetallic compound (Sn-Ni).

(b) Sn-0.75Cu

The interface of this solder alloy consists of the intermetallic compound (Sn-Cu). The copper (Cu) portion of this compound precipitates from solder alloy, and the thickness is 1.5~2.0um. After 1000 cycles, it grows to 2~4um (Fig.6). The strength of this alloy during thermal cycling decreases only slightly, because the precipitation of Cu_6Sn_5 and $AuSn_4$ from solder alloy is minimal.

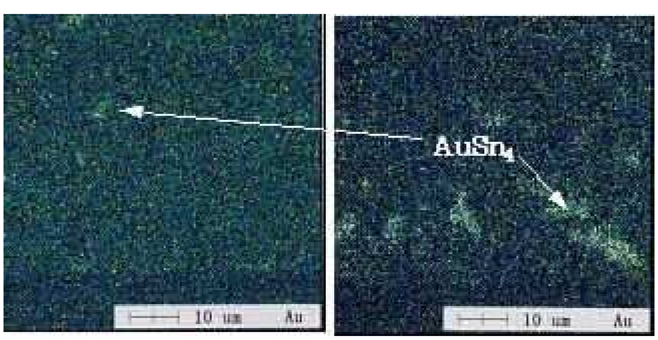


Initial After 1000 cycles

Fig. 6 EPMA image of Sn-Cu BGA solder joint (Analysis of Copper distribution)

(c) Sn-3.5Ag

As the fundamental microstructure of this alloy, the eutectic of Sn and Ag_3Sn is mixed with the interface of the primary crystal (Sn). The crystal of Ag_3Sn is less than 1um long and rod-shape often resembling a granular shape. The precipitation of the primary crystal (Sn) and $AuSn_4$ are non-uniform. During thermal cycling, the shape and size of Ag_3Sn does not change, but $AuSn_4$ change from a needle-shape to a round-shape. (Fig.7)



Initial After 1000 cycles

Fig. 7 EPMA image of Sn-Ag BGA solder ball (Analysis of Au distribution)

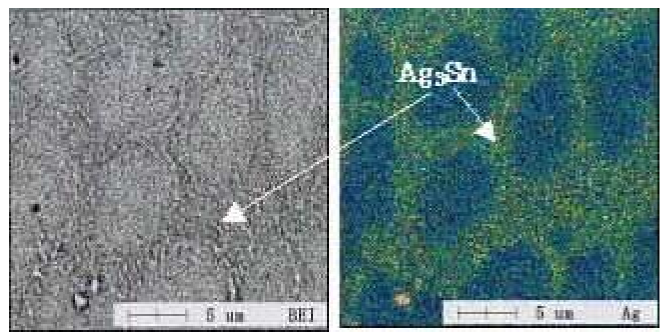
(d) Sn-3.5Ag-0.75Cu

The structure of this alloy consists of the Sn-0.75Cu and Sn-3.5Ag mixture, and the interface consists of Cu_6Sn_5 on Ni substrate. (Fig.8)[3] The intermetallic compound (Ag_3Sn) exists as eutectic around the primary crystal (Sn) with Sn. (Fig.9)

Also present is a little intermetallic compound as Cu_6Sn_5 in the solder bump. During thermal cycling, the microstructure shows little change, and the thickness of the interfacial layer as Cu_6Sn_5 is the same.

Initial

Fig. 8 Micrograph and EPMA image of Sn-3.5Ag-0.75Cu BGA solder ball (Analysis of Cu distribution)



Micrograph EPMA image

Fig. 9 Micrograph and EPMA image of Sn-Ag-Cu solder ball (Analysis of Ag distribution)

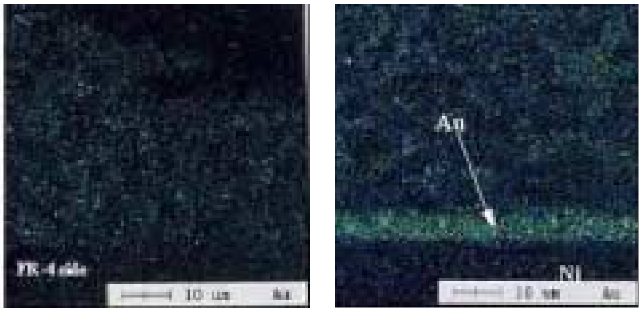
(e) 63Sn-37Pb

The interface layer of this alloy before thermal cycling is 0.5um thick as Sn-Ni-Pb intermetallic compound. Therefore, the shear rupture forms a "zigzag" path along the grain boundary between Sn-phase and Pb-phase.

In this case, the coarsened grain is observed even after 100 cycles. This coarsened grain usually causes a strength deterioration, and cracks inside the solder alloy can be observed. However, in this case, presumably the fracture of the interfacial layer was observed because the interfacial layer is weaker than the coarsened grain.

According to SEM, the fracture occurred at the boundary between the two interfacial layers. Gold (Au) was not initially observed around interfacial area, but Au-phase was evidently observed and increased at the interface area as the number of cycles increased. [4][5] For example, the thickness of Au was initially observed as 0um, 0.3~0.7um at 100 cycles, 2um at 200cycles and 4~6um at 1000 cycles. (Fig.10) The crack between $AuSn_4$ and solder was observed by chance, because the migrating speed of Au from the solder to interface seems high.

This phenomenon suggests an Au compound layer growth may affect the shear strength more strongly than Pb-free solder alloy. However, with the thinner Au plating this phenomenon may be more difficult to occur and the fracture may simply occur between Sn-phase and Pb-phase without a significant deterioration in strength. Even if there is no $AuSn_4$ intermetallic layer, unfortunately, the reaction between Sn and Ni is not clear from this test.



Initial After 1000 cycles

Fig. 10 EPMA image of Sn-Pb BGA solder ball (Analysis of Au distribution)

(f) Au plating control

Identical solder materials are not always used for a package solder bump and solder paste in actual assembly, which is generally more complicated. In the case of Sn-Pb solder, the thickness of Au on a substrate should be controlled at less 0.1um. The thicker the gold on the substrate, the weaker the shear strength. In the case of lead-free solder, even if Au is thick, it does not concentrate around the interface area and does not affect shear strength.

3.2. Joint reliability of assembled CSP with lead-free solder

3.2.1. Procedure

Table.2 shows the scheme used to evaluate CSP. Two types of lead-free solder balls and a Sn-Pb system solder ball were used for CSP solder bumps. (See Table.3) When assembled to the PCB's, three types of solder paste with two types of lead-free alloys or a Sn-Pb system alloy were used. (Table.4) The stencil thickness was 100um. Three types of surface plating of PCB; bare copper, Alpha-level silver and Ni/flash gold were used as Table.5 shows.

Table 2 Detail of CSP

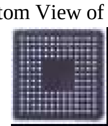
CSP Size	12 x 12 mm	Bottom View of CSP. 
Number of Ball	144	
Ball Pitch	0.8 mm	
Solder Ball Size	0.5 mm dia. Ball	

Table 3 Solder Ball type

Solder type (mass%)	Solidus Temp.	Liquidus Temp.
Sn-1.0Ag-0.5Cu	216	226
Sn-8.0Zn-3.0Bi	188	199
63Sn-2Ag-0.5Sb-Pb	178	210

Table.6 shows the combination of solder joint material evaluated with this test. Test pieces were reflowed 15C above each liquidus temperature as peak temperature in nitrogen atmosphere (Oxygen: 500ppm). The liquidus temperatures are as follows: Sn-Ag-Cu/235C, Sn-Zn-Bi/215C, Sn-Pb-system/200C. Five test pieces were used for each combination.

Table 4 Solder Paste type.

Solder type (mass%)	Solidus Temp.	Liquidus Temp.
Sn-3.9Ag-0.6Cu	217	219
Sn-8.0Zn-3.0Bi	188	199
63Sn-Pb (reference)	183	183

Table 5 FR-4 Board and plating

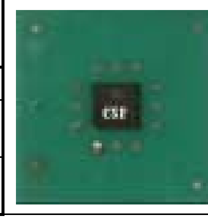
PCB Board	FR-4 Size:5.0 x 5.0mm Thickness:0.8mm	
Plating	*Bare Copper (Cu)	
	*Alpha-level Silver(Ag) (Ag: 0.07~0.15um)	
	*Flash Gold (Au) (Nickel: 3um-Gold:0.03um)	

Table 6 Combination of CSP ball and Solder paste

BGA Ball	Solder Paste	Solder alloy system
Sn-1.0Ag-0.5Cu	Sn-3.9Ag-0.6Cu	Sn-Ag-Cu
Sn-8.0Zn-3.0Bi	Sn-8.0Zn-3.0Bi	Sn-Zn-Bi
Sn-1.0Ag-0.5Cu	Sn-8.0Zn-3.0Bi	Sn-Zn-Bi-Ag-Cu
63Sn-2Ag-0.5Sb-Pb	63Sn-Pb	Sn-Pb

3.2.2. Thermal cycle test

The thermal cycle chamber was set up -55C (10 minutes) and +125C (10 minutes). Assembled CSPs were put into the thermal cycle chamber and run for up to 3000 cycles. The CSP and PCB were designed as a Daisy chain and were able to be monitored for electrical failure. In order to continuously monitor the conditions inside the thermal cycle chamber, a multi point resistance measuring unit was utilized. A joint was considered a failure if measured at over 200 ohm of electrical resistance.

3.2.3 Results and Discussion

3.2.3.1. Initial cross-section of CSP joint

Fig.11 shows initial cross-section of 12 combinations of joint materials. There was no different joint shape for either solder or plating material. In the case of Sn-Ag-Cu, the gold of Au-flash and silver of Alpha-level have dissolved into the solder and cannot be seen around the interface area.

The joint shape and the microstructure of solder joints were uniform, with the exception of the combination of Sn-Ag-Cu ball and Sn-Zn-Bi paste, where two structures were observed. As the melting temperature of the ball was higher than that of paste, only the paste melted. (Fig.12)

Fig.13 shows the microstructure of a cross-section with two types of Sn-Zn systems.In the combination of Sn-1.0Ag-0.5Cu ball and Sn-8Zn-3Bi paste, Zinc exists as the intermetallic compound (Ag/Zn and Sn/Zn) in the solder. However, when Sn-Zn-Bi was used for both ball and paste, Zn was observed as needle-shape and single phase. And some large voids were observed in the joint with Zn.

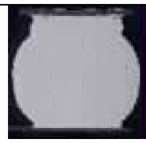
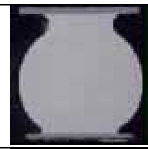
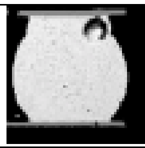
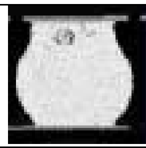
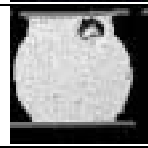
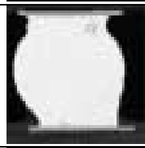
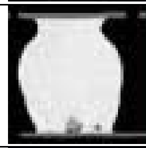
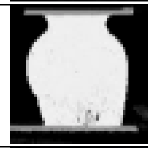
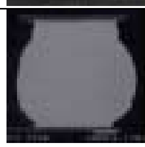
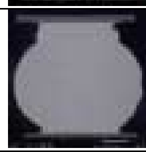
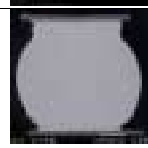
	PCB Plating		
+ Solder Ball * Solder Paste	Cu	Alpha Level Ag	Ni-Au (Flash)
+ Sn-1.0Ag-0.5Cu * Sn-3.9Ag-0.6Cu			
+ Sn-8.0Zn-3.0Bi * Sn-8.0Zn-3.0Bi			
+ Sn-1.0Ag-0.5Cu * Sn-8.0Zn-3.0Bi			
+ 63Sn-2Ag-0.5Sb-Pb * 63Sn-Pb			

Fig.11 Micrograph of initial solder joint

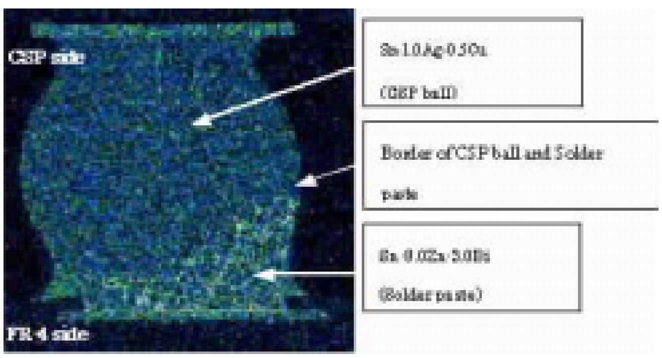
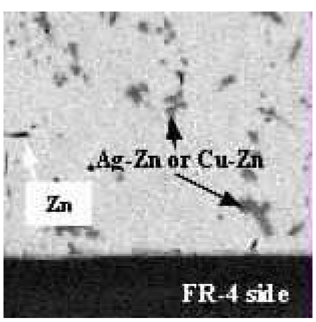
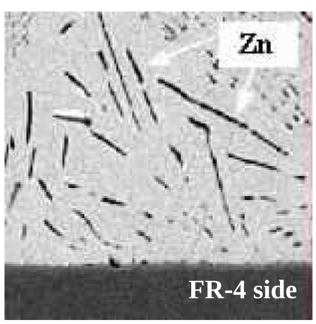


Fig.12 EPMA image of solder joint with Sn-Ag-Cu solder ball and Sn-Zn-Bi solder paste systems (Analysis of Zinc distribution)





Solder Ball	Sn-1.0Ag-0.5Cu	Solder Ball	Sn-8.0Zn-3.0Bi
Solder Paste	Sn-8.0Zn-3.0Bi	Solder Paste	Sn-8.0Zn-3.0Bi

Fig.13 Micrographs of Sn-Zn-Bi system solder joint

3.2.3.2. Thermal Cycle Test Results

Table.7 and Fig.14 show the results. The calculation of the average cycle life was counted from the number of cycle failures. But the joint had not failed after 3000 cycles, it was calculated as 3000.

Fig.15 shows a cross-section of a typical fracture after a thermal cycling test. All of the fractures occurred along the interface and are unrelated to other parameters. Even if the substrate plating was different, there was no difference in the thermal cycling life of solder joints in Sn-Pb system. However, in the case of lead-free solder, significant differences between the type of substrate plating were confirmed.

Table 7 Result of Thermal Cycle Test

Solder Ball	Solder Paste	PCB Plating	Cycle Number of device failed					Mean Number of Cycle to Failure
			1/5	2/5	3/5	4/5	5/5	
Sn-1.0Ag-0.5Cu	Sn-3.9Ag-0.6Cu	Cu	1170	1218	1268	1740		1679
		Alpha Level Ag	2541					2908
		Ni-Au(Flash)	976	1178	1362			1903
Sn-8.0Zn-3.0Bi	Sn-8.0Zn-3.0Bi	Cu	207	235	398	471	476	357
		Alpha Level Ag	453	460	774	937	961	717
		Ni-Au(Flash)	2235	2285	2391	2608		2504
Sn-1.0Ag-0.5Cu	Sn-8.0Zn-3.0Bi	Cu	1043	1081	1093	1409	1538	1233
		Alpha Level Ag	1260	1680	1748	1763	1959	1682
		Ni-Au(Flash)	1806	2229	2377	2676		2418
63Sn-2Ag-0.5Sb-Pb	63Sn-Pb	Cu	1388	1797	1823	1863	2047	1784
		Alpha Level Ag	1421	1688	1869	1903	1987	1774
		Ni-Au(Flash)	1129	1520	1628	1666	1701	1529

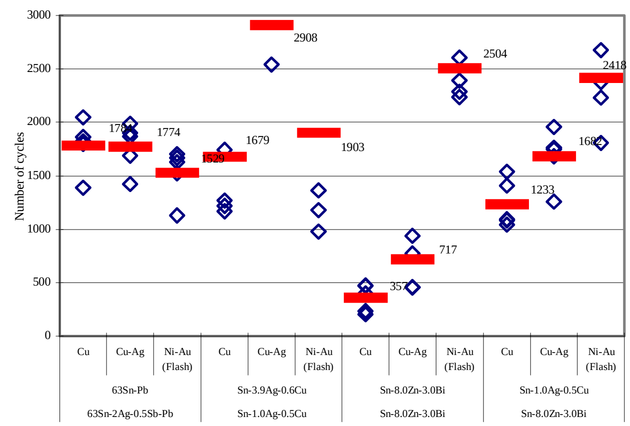


Fig.14 Result of thermal cycle

Fig.15 Typical Fatigue Failure Mode after cycle testing.

(a) Sn-Ag-Cu system

There were significant differences in regard to the substrate plating and the reliability of CSP soldering joint. In the case of Cu and Ni/Au, the thermal cycle life was equivalent or better when compared to the Sn-Pb joint. Furthermore, in the case of Alpha-level silver, excellent results were indicated when compared with Sn-Pb.

Fig.16 shows the cross-section of a fractured joint soldered with Sn-Ag-Cu solder on Alpha-level silver plating at 2541 cycles.

The microstructure and the thickness of the intermetallic compound (Cu_6Sn_5) were equivalent with that of the other combinations. Although the cause of longer life with Sn-Ag-Cu/Silver is under investigation, a strengthening by silver diffusion into the tin-rich solder is presumed as the cause.

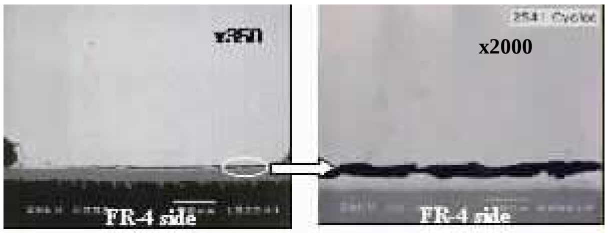
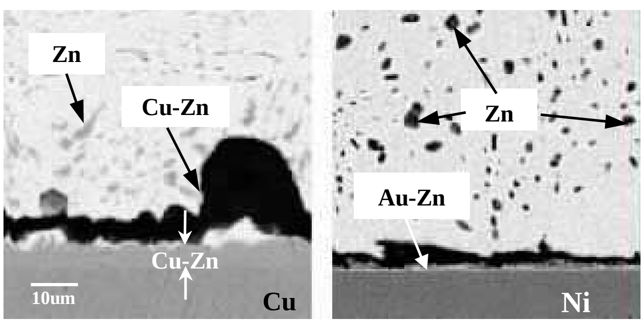


Fig.16 Micrographs of cracked solder joint with Sn-Ag-Cu system and Alpha level Ag plating. (After 2541 Cycles)

(b) Sn-Zn-Bi system [6][7]

In this case, the combination with Ni/Au plating had much better results than a Sn-Pb joint. However, the combinations with Cu or Ag indicated much worse results than with Sn-Pb.

Fig.17 shows the cross-section of a fractured joint soldered with Sn-8Zn-3Bi solder on Cu plating at 235 cycles and Ni/Au plating at 2229 cycles.



Cu	Ni-Au plating
Solder Ball:Sn-8.0Zn-3.0Bi	Solder Paste: Sn-8.0Zn-3.0Bi
After 235 cycles	After 2229 cycles

Fig.17 Micrographs of Sn-8.0Zn-3.0Bi system solder joint with Cu and Ni-Au plating after cycle test.

When the plating was Cu, the intermetallic compound layer as Cu-Zn grew 7um thick and a fracture occurred from this layer. On the other hand, in the case of Ni/Au plating, although gold easily dissolved into the solder, nickel behaves as barrier and prevents the formation of a Cu-Zn layer. Therefore, the fracture was generated from a Au-Zn layer. In this way, a Cu-Zn intermetallic layer may be greatly related to the thermal cycle life. As Fig.13 shows, in the case of the combination with Sn-Ag-Cu ball and Sn-Zn-Bi paste, the Zn concentration near the interface is lower, therefore the life may be longer.

(c) Silver plating within a Lead-Free process

When Sn-Pb solder is used as CSP assembly material, the kind of plating is unrelated to the thermal cycle life. But the plating is greatly related to the thermal cycle life in a lead-free system, for example, Alpha-level silver plating is suitable for Sn-Ag-Cu system and Ni/Au plating is suitable for Sn-Zn-Bi system.

4. Conclusion

4.1. Shear strength

(1) Regarding to the shear strength of BGA substrate and a solder bump, Sn-5Sb, Sn-3.5Ag and Sn-3.5Ag-0.75Cu show better results than Sn-Pb.

(2) In the case of Sn-Pb soldered bumps on 1um of gold plating, gold (Au) was not initially observed around the interfacial area, but the intermetallic compound as $AuSn_4$ was evidently observed and increased at the interface area as the number of cycles increased. However, in the case of lead-free solder evaluated in this paper, even if the Au plating was thick, $AuSn_4$ did not concentrate around the interface area.

4.2. Joint reliability of assembled CSP

(1) All of the fractures occurred along the interface and were unrelated to other parameters.

(2) The plating type greatly affected the joint life in a lead-free system. Alpha-level silver plating is suitable for a Sn-Ag-Cu system and Ni/Au plating is suitable for a Sn-Zn-Bi system.

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