Development of Sn-Zn-Al Lead-Free Solder Alloys

● Masayuki Kitajima ● Tadaaki Shono

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Fujitsu has implemented a company-wide effort to progressively reduce the use of lead (Pb) and eventually eliminate this environmental pollutant from its products. As part of this effort, we have developed a new lead-free solder that consists of tin (Sn), zinc (Zn), and aluminum (Al) and yet offers superior productivity and joint reliability. The new lead-free solder has a melting point equivalent to that of an Sn-Pb eutectic solder and enables devices to be packaged at a lower temperature than with the increasingly popular Sn, silver (Ag), copper (Cu) solder. The new lead-free solder, therefore, accelerates the elimination of Pb from products. We have already used printed circuit boards containing the new lead-free solder in some products and plan to extend its use to other products. We made a solder composed of Sn, Zn, and Al and investigated its mechanical characteristics and the effects of adding Al. A tension test was conducted in air at 25°C and 60%RH at a tensile speed of 60 mm/min. The results showed favorable elongations in the following order: Sn-9wt%Zn < Sn-7wt%Zn < Sn-7wt%Zn-Al < Sn-9wt%Zn-Al. Al-added specimens showed better stress values than specimens without Al. Observation of the periphery of fractured specimens without Al revealed numerous, deep cracks and the contraction was smaller than in the Al-added specimens.

We also joined Sn-Zn-Al solder balls to a Cu/nickel (Ni)/gold (Au) plated substrate at 215°C for Chip Size Package (CSP) applications. After 1000 hours of aging at 150°C, no deterioration was detected in the ball shear strength compared with the initial value. This paper describes a study and the characteristics of the new lead-free solders.

1. Introduction

Although electronic equipment manufacturers have steadily gained experience in the application of lead-free solders to commercial products, there still remains a serious obstacle to achieving full application of lead-free solders to all products. In terms of manufacturing, the greatest problem regarding Sn-Ag-Cu solders, which are the current mainstream solders, is that their use may deteriorate component reliability because of over-heating during soldering. Although this problem could be overcome by improving the heat tolerance of components, such an improvement is not progressing. As a result, product manufacturers are looking forward to the advent of new solders with lower melting points.

Recently, bismuth (Bi) added Sn-Zn solders with low melting points have come into use in some cases (**Table 1**).[1] However, their use is limited to certain fields due to a joint-reliability problem caused by the reaction of Bi and tin (Sn) with the lead (Pb) commonly contained on the terminals of components.

We developed a medium-temperature solder with a suppressed melting point of 199°C by adding aluminum (Al) to an Sn-Zn-based material to help reduce its oxidization. This new lead-free solder ensures good reliability for the terminals of various components and has been used in commercial products since 2002.

Table 1
Characteristics of lead-free solder.

Solder	Sn-Zn-Bi family	Sn-Ag-family	Sn-Pb eutectic
Melting point	199°C	218°C	183°C
Merit	Low melting point & low price	High reliability	Low melting point & low price
Demerit	Very high oxidization & low reliability	High melting point	Environmental pollutant

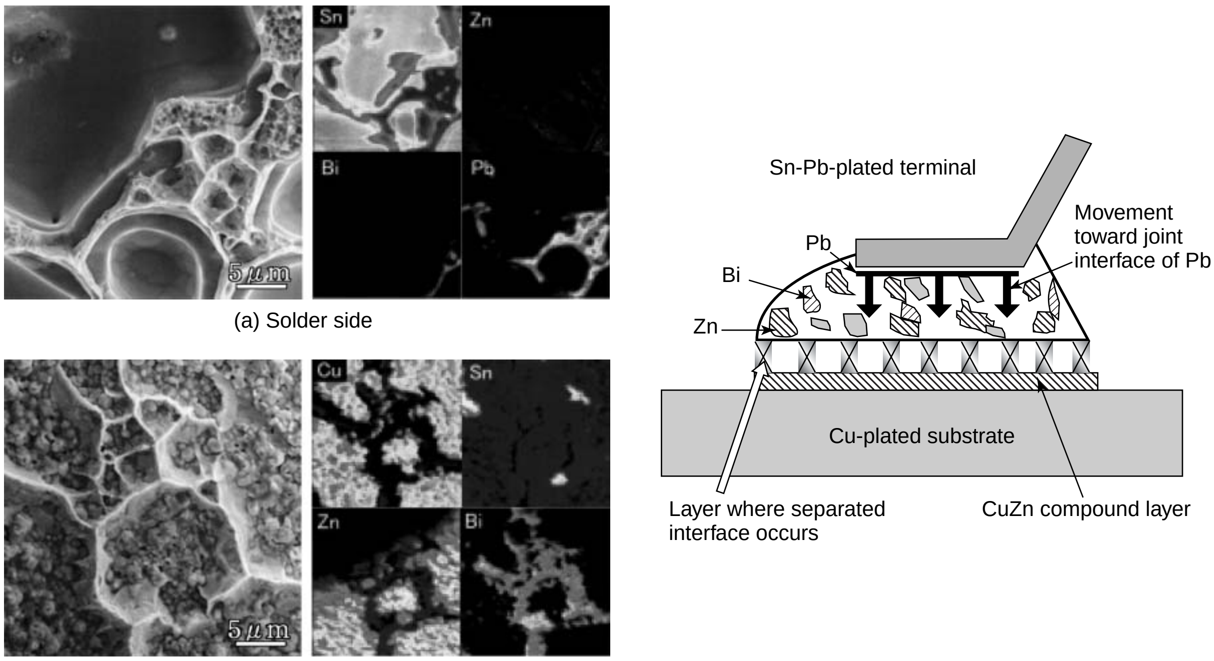
2. Problems with Sn-Zn-Bi solders

Because joints between Sn-Pb-plated terminals and lead-free solder will be common during the transition to lead-free solder, we assessed the reliability of joints between Sn-Zn-Bi solders and Sn-Pb-plated terminals. Using a solder paste composed of Sn-8wt%Zn-3wt%Bi at a peak temperature of 215°C, we packaged a 0.5 mm-pitch Low Quad Flat Package (LQFP) component having Sn-Pb-plated terminals on a substrate that was plated with copper (Cu) and then nickel (Ni: 3 microns)/gold (Au: 0.05 micron). During soldering of this component, the following occurred: 1) the Au plating covered the surface of the solder and then completely diffused into the solder so that none of the Au remained in the substrate plating and 2) about a 2-micron layer of NiZn intermetallic compound with voids on its upper and lower sides was formed on the Ni plate. Moreover, exposure to high temperature increased the thickness of the NiZn layer and the number of voids but did not significantly reduce the joint strength.

We also used this solder paste to solder Sn-Pb-plated terminals to a Cu-plated substrate. Immediately after soldering, the tensile strength of the terminals was approximately 10 N. However, after aging for 100 hours at 150°C, interface separations occurred. These separations weakened the joints so much that their tensile strength could not be measured. Electron Probe Micro-Analysis (EPMA) of the joint interface immediately after soldering revealed a 6-micron layer of CuZn intermetallic compound at the interface with the Cu-plated substrate. The EPMA also revealed that Bi, which is a component of the solder, and Pb, a component of the terminals, had entered the solder. After aging at high temperature, the thickness of the CuZn layer increased by about 8 microns, and the interface separated from the solder. We found a mixed layer of Pb and Bi scattered around the area of separation. As shown in **Figure 1**, a layer of CuZn intermetallic compound of less than 2 microns with an irregular surface spread over the entire side of the Cu-plated substrate, and there was a belt of Bi on the upper side. At the solder-side of the interface, there was a band of Pb. When an Sn-Pb solder-plated terminal is joined to a Cu-plated substrate using Sn-Zn-Bi solder, a mixed layer of Pb/Bi/Sn is formed by heating at the joint interface, which is a belt-shaped Sn-Pb-Bi ternary-eutectic alloy having a melting point of 99.5°C. It is considered that the separation of the joint interface occurs because the interface is maintained only through this alloy.[2)]

3. Oxidation of Sn-Zn-Al solder: theoretical discussion

The phenomenon of the addition of Al significantly improving the wettability of an Sn-Zn solder is considered to be due to inhibited oxidization of the solder by Al substitution of zinc (Zn) as a reactive atom to combine with oxygen molecules. Atmospheric oxygen molecules adsorb to the Zn on the surface of the molten solder and then attract electrons from the Zn to form a zinc oxide film. Furthermore, other atmospheric oxygen molecules pass through this oxide and promote a diffusion reaction within the solder to form a thick oxide layer. Therefore, the wettability of the



(a) Solder side

(b) Cu-plated substrate side

(c) Mechanism of interfacial separation

Figure 1
Rupture side at junction with Sn-8wt%Zn-3wt%Bi solder.

Table 2
Ionization energy of Zn, Al, and Cu atoms.

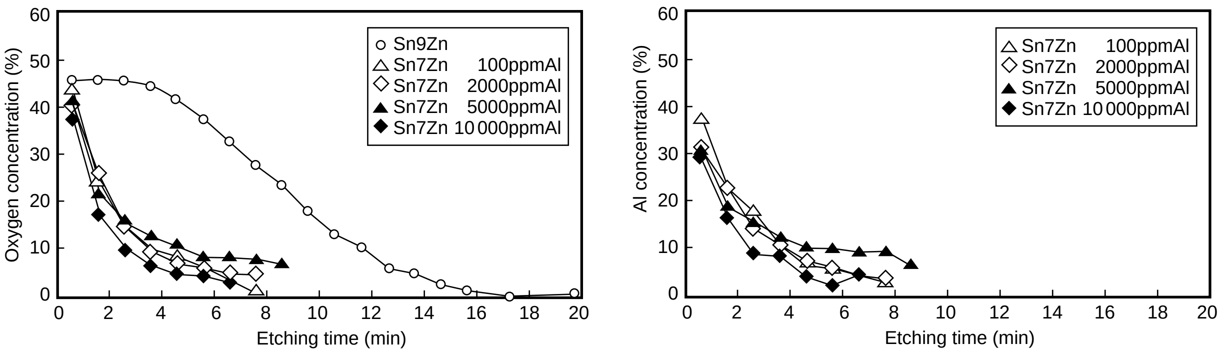
Atom	Zn	Al	Cu
Ionization energy (kcal/mol)	217	138	178

solder in air significantly deteriorates. However, when Al atoms are added in place of the Zn, the Al atoms oxidize, and a dense Al_2O_3 oxide film is instantly formed. It is known that Al atoms are liable to release electrons partially due to their chemical properties (**Table 2**) and react with oxygen molecules. Al atoms contained in an Sn-Zn alloy segregate to the surface of the metal and prevent the contact of Zn atoms with oxygen molecules. We consider that electron-releasing Al atoms are continuously supplied to the metal surface because an interfacial state is maintained between oxygen molecules on the positive side and the metal surface on the negative side.

Furthermore, because an Al_2O_3 oxide film consisting of Al restrains the entry of moisture, corrosion resistance will be improved in a high-temperature, high-humidity environment. This clearly indicates the specific oxidization-restraining effect of Al in an Sn-Zn solder.[3)]

4. Oxidation of Sn-Zn-Al solder: surface element analysis

To clarify the behavior of Al and Zn atoms during oxidization, a surface element analysis in the depth direction of the alloy was made on the Sn-Zn-Al solders (**Figure 2**). Micro-Auger Electron Spectroscopy (μ - AES) analysis showed that even when an Sn-Zn-Al solder ball 760 microns in diameter was formed, oxygen and aluminum diffused into a specific area in the depth direction from the solder-ball's surface. Also, Al was detected only less than several hundreds of angstroms from the surface, and surface segregation of Al could not be confirmed. This analysis showed that a very small addition of Al to Sn-Zn solder can greatly reduce the oxygen diffusion in the depth direction. The analysis conditions of the



(a) Depth direction surface analysis of oxygen.

(b) Depth direction surface analysis of Al.

Figure 2
Depth direction surface analysis of Sn-Zn-Al solders.

micro-Auger Electron Spectroscopy (μ - AES) apparatus are shown in **Table 3**.

Table 3
Analysis parameters of Micro-Auger Electron Spectroscopy apparatus.

Acceleration voltage	10 kV
Irradiation current	3 nA
Measuring time	300 ms × 5 sweep
Etching speed	10 nm/min (SiO_2 conversion)

5. Wettability of Sn-Zn solder and effects of Al addition

Thanks to the Al oxide film that is preferentially formed on the surface of Zn solder, it is possible to obtain favorable solder wettability. Unlike a Zn oxide film, an Al oxide film has no progressive oxidizability toward the interior.

We made an Sn-7wt%Zn-60ppmAl solder and measured its wetting time in air using a meniscus tester. The wetting time was measured by coating Cu plates with an RMA type flux and then dipping them into a bath of molten solder heated to 230°C, 240°C, or 250°C at 20 mm/sec. The measurement time was up to 8 seconds. At each of the bath temperatures, we found that the wetting time of this solder was 1.5 seconds, which is equivalent to that of Sn-Pb eutectic solder (**Figure 3**). At 230°C, Sn-Zn-Al solder shows even more favorable wettability than Sn-3wt%Ag-0.5wt%Cu solder.

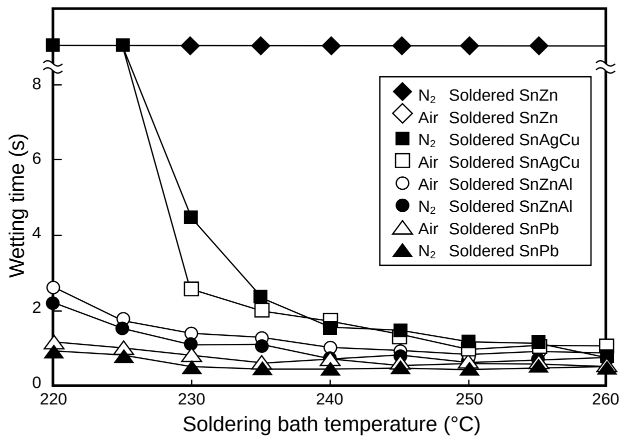


Figure 3
Wetting time of Sn-Zn-Al solder in air.

6. Mechanical characteristics of Sn-Zn solder and effects of Al addition

We prepared test specimens of Sn-7wt%Zn, Sn-9wt%Zn, Sn-7wt%Zn-120ppmAl, and Sn-9wt%Zn-120ppmAl solders. The molten temperature was maintained at 600°C for 40 minutes in a melting furnace, and the mold was pre-heated to 320°C using a hot plate. The molten solders were then poured from the down gate and casted into plate-shaped test specimens 200 mm long, 20 mm wide, and 3 mm thick. The moldings were placed on a block to cool at about 0.26°C/sec. Then, a quantitative analysis of Zn and Al was conducted on the specimens using plasma emission spectrophotometry. Although there was a slight discrepancy in composition, the compositions of the specimens were almost equivalent to the target composition.

As shown in **Figure 4**, Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) revealed the presence of Al in the Sn grain boundaries of the Sn-Zn-Al solder. Tension tests of five samples of each composition were conducted in air at 25°C, 60%RH, and a tensile speed of 60 mm/min. **Figure 5** shows the stress-strain diagram obtained from these tests. The figure shows favorable elongations in the following order: Sn-9wt%Zn < Sn-7wt%Zn < Sn-7wt%Zn-Al < Sn-9wt%Zn-Al. Note that, whereas the elongation of Sn-7wt%Zn was superior to that of Sn-9wt%Zn, the addition of Al reversed this relationship: that is, the elongation of Sn-9wt%Zn-Al was superior to that of Sn-7wt%Zn-Al. The improvement in elongation was 86% for Sn-7wt%Zn and 109% for Sn-9wt%Zn. Also, Al-added specimens showed better stress values than the specimens without Al. Observation of the periphery of fractured specimens without Al showed numerous, deep cracks, and the contractions were smaller than those of the Al-added specimens.[4] As shown in **Figure 6**, Secondary Electron Microscope (SEM) observation of the fractured cross-section in the tensile test revealed that ruptures occurred at the

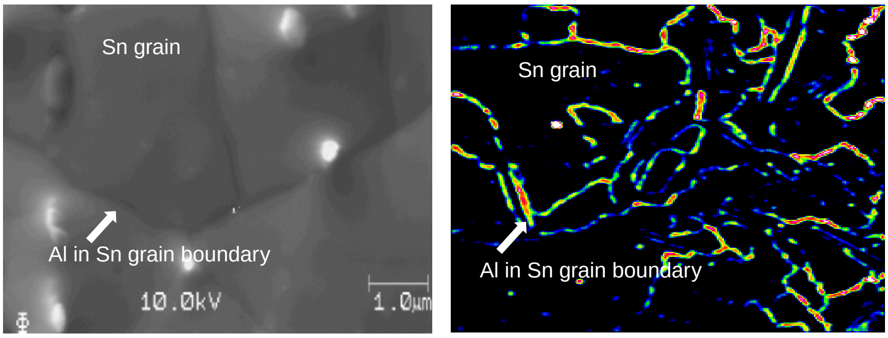


Figure 4
Analyzed Al positions on surface of sputter-etched Sn-9wt%Zn-Al solders.

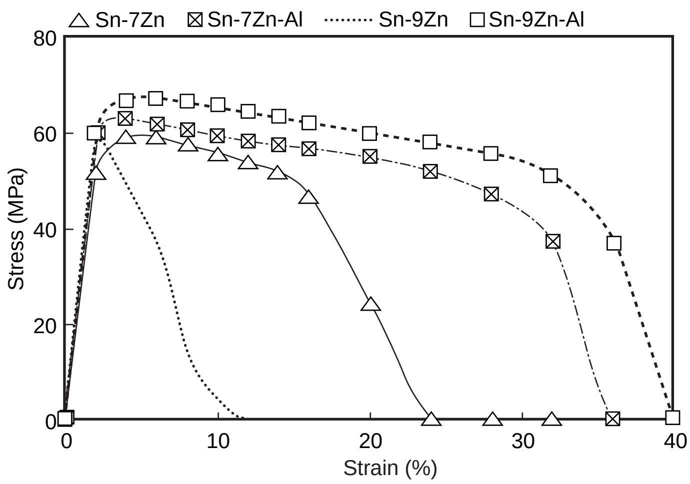
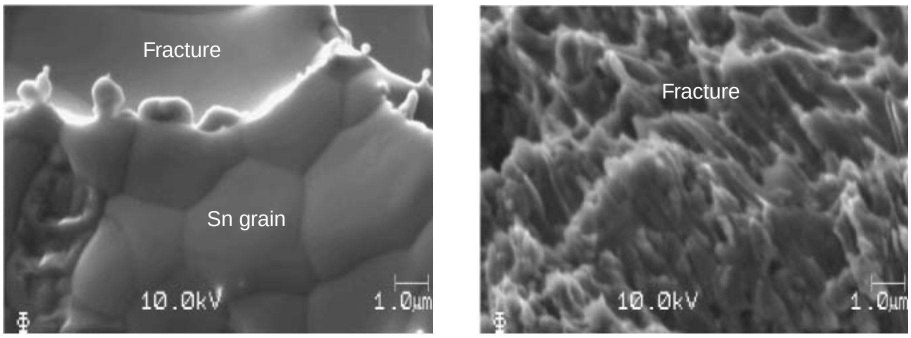


Figure 5
Stress-strain diagram of Sn-Zn-Al solders.



Sn-Zn solder

(a) Fractures easily at Sn grain boundaries.

Sn-Zn-Al solder

(b) Sn grains deform and then fracture.

Figure 6
Fracture in solders.

Sn grain boundaries in the Sn-Zn eutectic solders; while, in the case of Al-added solders, typical ductile fractured cross-sections were observed. In the Al-added solders, favorable fractured cross-sections similar to those of Sn were observed.

7. Joint reliability of Sn-Zn-Al solder

Using a traditional Sn-Zn eutectic solder and an Sn-Zn-Al solder, we soldered a Low Quad Flat Package (LQFP) with Sn-Pb-plated terminals to a Cu-plated substrate at a peak temperature of 215°C and observed the cross-sections of the joint interfaces. In the Sn-Zn eutectic solder, the intermetallic compound layer was 6 microns thick immediately after soldering, and voids were observed at the interface with the terminals. During aging at high temperature, both the thickness of the layer and number of voids increased. In the Sn-Zn-Al solder, the intermetallic compound layer was only about 1 micron thick immediately after soldering and about 2 microns thick after adding heat. The number of voids was nominal, and a favorable joint interface was obtained (**Figure 7**). We consider that the Sn-Zn-Al solder results were obtained because the added Al inhibited Zn from reacting to form an intermetallic compound layer and also suppressed the formation of voids. First, a layer of CuAl inter-metallic compounds is formed at the Al/Cu joint interface, and on the surface of that layer, a layer of ZnCu inter-metallic compound is formed. At the Cu/solder joint interface, a layer of $CuAl_2$ inter-metallic compound is formed that suppresses the growth of CuZn inter-metallic compounds and further eliminates the generation of voids (**Figure 8**).

We measured the tensile strength of the LQFP's terminals after exposure to 150°C for 1000 hours and found no serious deterioration in tensile strength.

8. Evaluation of product joint reliability

We soldered components onto Cu-plated substrates using Sn-Zn-Al solder paste in nitrogen with a peak reflow temperature of 215°C. The soldered components were evaluated using several reliability tests. As indicated in **Table 4**, good results were obtained. The performance of Sn-Zn-Al solder is now sufficient for use in commercial Fujitsu products. We have already finished evaluations of volume productivity and reliability tests in commercial products and have used the new lead-free solder in several products (**Figure 9**). A new solder paste flux enables continuous printing of the solder paste at 0.4 mm for 24 hours and can be preserved for more than 3

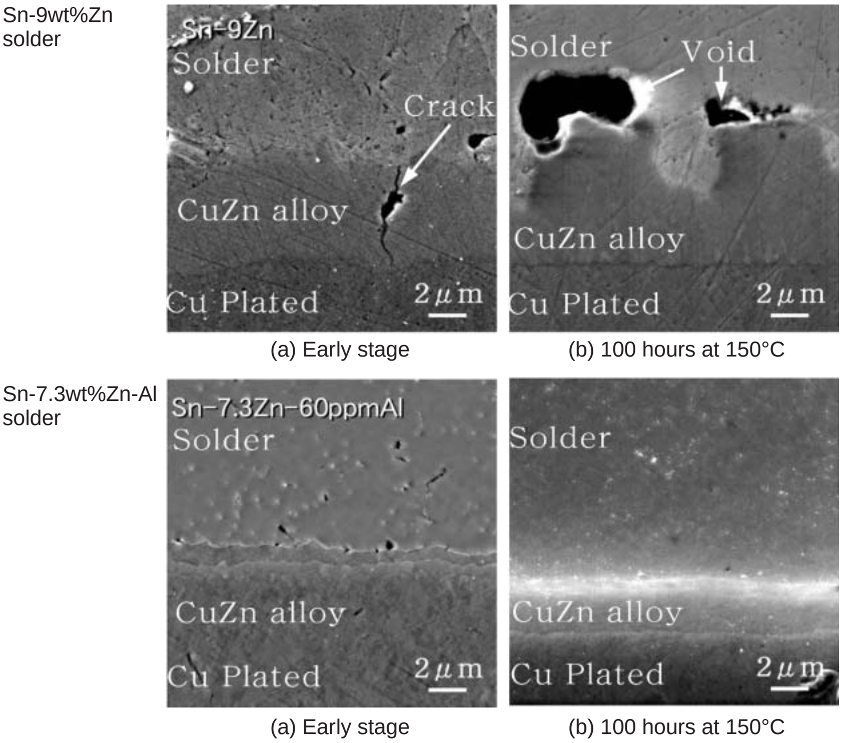
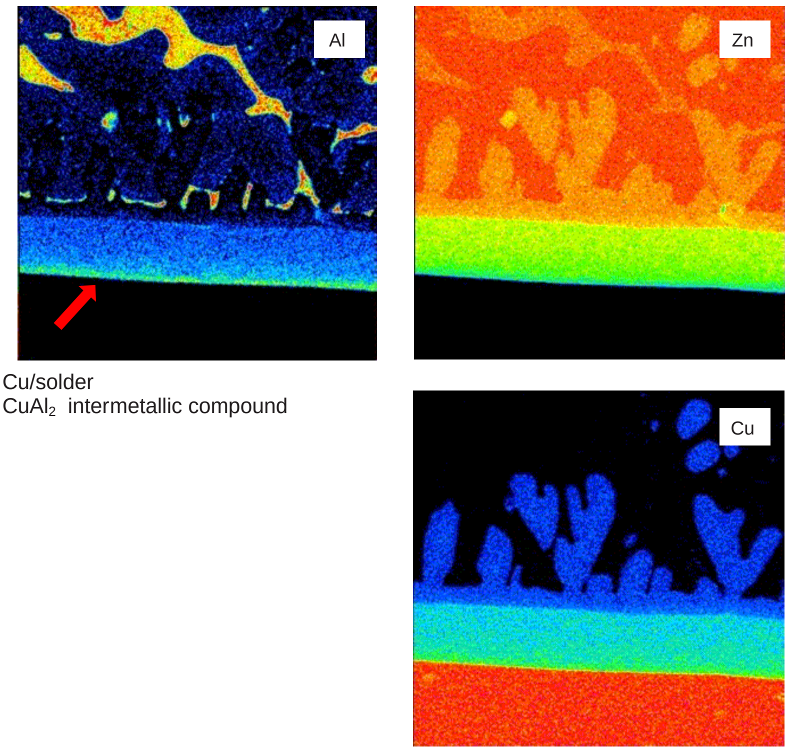


Figure 7
Cu-plated substrate interface with Sn-Zn-Al solder.



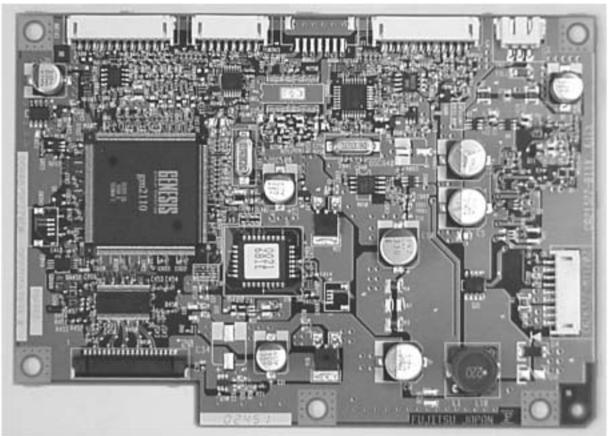
(Analyzed by Electron Probe Micro Analyzer: EPMA)

Figure 8
Improved joint interface of Sn-Zn solders by addition of Al.

Table 4
Joint reliability of printed circuit board assemblies.

Test item	Test condition	Result	N
MIL damping cycle	-10 to 65°C/80%RH × 5 cycles	Accepted	20
High temp. creep	80°C × 500 h	Accepted	20
Temperature cycle	-30 to 80°C × 3000 cycles	Accepted	20
Vibration test	10 to 500 Hz, 1.5 mm peak-peak	Accepted	20
Drop test	Dropped in packaged state	Accepted	20
SO_2 exposure	200 ppm × 10 days	Accepted	20
Electro-corrosion test	40°C/90%RH × 1000 h	Accepted	5

N: Number



(a) Printed Wiring Board (PWB)

(b) 17-inch LCD display: VL-170VS

Figure 9
PWB assemblies in products.

months at 5°C.

9. Experimental manufacture of Chip Size Package using Sn-Zn-Al solder balls

We manufactured a batch of the experimental Chip Size Package (CSP) shown in **Figure 10** and soldered them using Sn-Zn-Al solder balls. We then investigated how the solder joints aged and measured their shear strength. The substrate is coated with polyimide film on the package side and Cu/Ni/Au plating on the pad side. **Figure 11** shows two of these CSPs with, respectively, 130-micron and 300-micron diameter solder balls. To compare the solder reliability, we also used eutectic solder balls. The specifications of the specimens are listed in **Table 5**. The soldering was conducted with flux in nitrogen and air with a peak reflow temperature of 215°C.

10. Ageing of Sn-Zn-Al solder-ball joints

The CSPs with Sn-Zn-Al solder balls were soldered in nitrogen and air at a peak reflow temperature of 215°C. Element distribution analysis using an Electron Probe Micro Analyzer (EPMA) showed that the interface between the solder balls and substrate immediately after soldering consisted of two layers: an AuZnSn inter-metallic layer on the solder side and a ZnSnNi inter-metallic layer on the substrate side. After 1000 hours of aging at 150°C, these two layers became a single

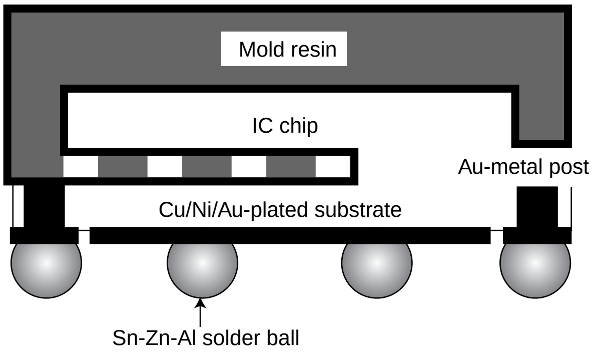


Figure 10
Experimental plastic CSP.

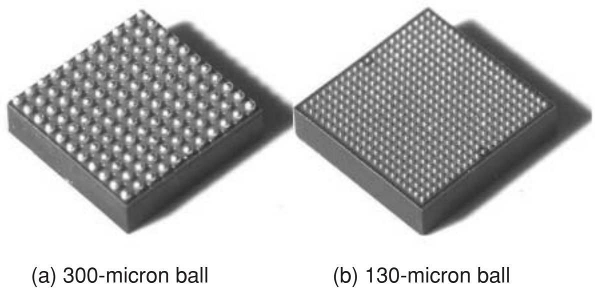


Figure 11
Fabricated CSPs.

Table 5
Specifications of CSPs and evaluation substrate.

Items		Specifications	
CSP	Ball diameter (µm)	300	130
	Ball composition	Sn-7wt%Zn-100ppmAl	Sn-7wt%Zn-100ppmAl
	Pad diameter (µm)	200	100
	Pad plating (µm)	Cu/Ni/Au 15/2/0.1	Cu/Ni/Au 15/2/0.1
	Pitch (mm)	0.5	0.25
	Number of balls	121	441
	Size (mm)	5.5 × 5.5 × 1.1	5.5 × 5.5 × 1.1
Substrate	Materials	Polyimide	Polyimide
	Pad diameter (µm)	200	90
	Pad plating (µm)	Cu/Ni/Au 15/2/0.1	Cu/Ni/Au 15/2/0.1
	Size (mm)	9.1 × 9.1 × 1.1	9.1 × 9.1 × 1.1

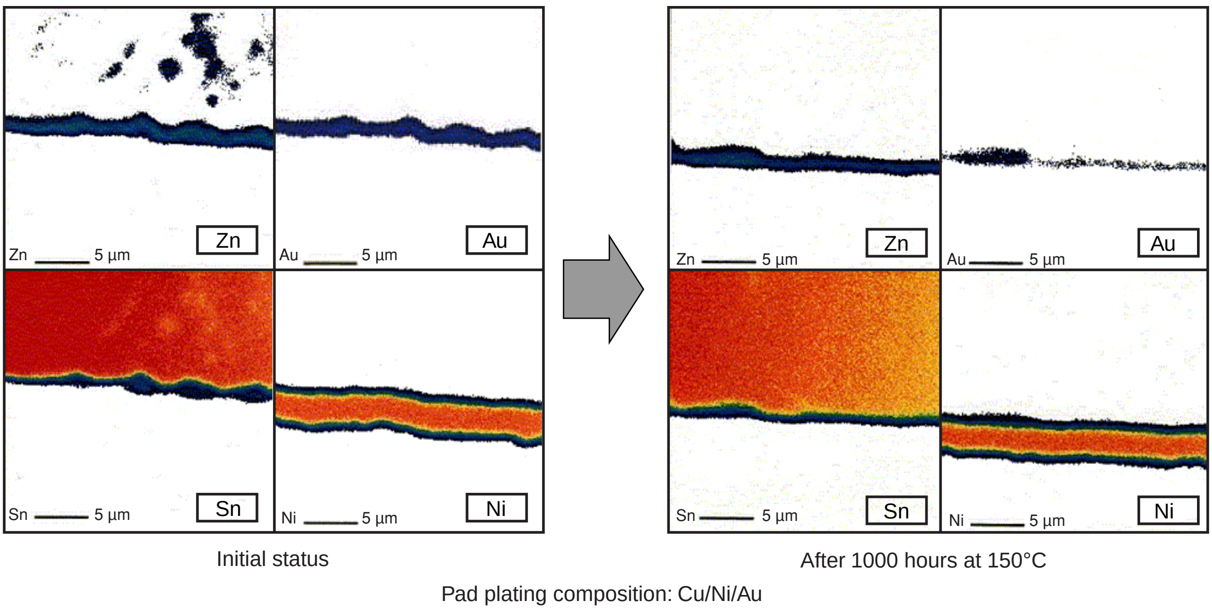


Figure 12
Electron Probe Micro Analyzer results of Sn-Zn-Al 130-micron solder ball.

layer of a ZnSnNiAu compound (**Figure 12**).

11. Shear-strength evaluation of Sn-Zn-Al CSP solder joints

We evaluated the reliability of the solder ball joints of the experimental CSPs. We measured the shear strength of solder joints made with the 300-micron solder balls after various aging conditions (**Table 6**). The shear strength was measured using the method shown in **Figure 13**. More than 20 balls for each case were measured. In general, favorable soldering strengths were found compared with the Sn-Pb eutectic solder joints (**Figures 14** and **15**). However, after the 85°C/85%RH aging in air, the strength of the Sn-Zn-Al solder joints was inferior to that of the Sn-Pb eutectic solder joints (**Figure 16**).

It is considered that, due to the invasion of high-temperature vapor, the Zn in the solder interface became oxidized and thus lost its metallic properties, resulting in the deterioration of shear strength. The solder reliability after high-temperature, high-moisture aging is an important factor in determining suitable application environments for Sn-Zn-Al solder. However, no deterioration in strength occurred after 40°C/90%RH aging (**Figure 17**).

12. Conclusions

We have investigated the properties of Sn-Zn-Al solders and found the following:

1) A minimal addition of Al to Sn-Zn solder reduces the oxygen concentration at the solder surface.
2) A minimal addition of Al to Sn-Zn solder improves its wetting properties.
3) By adding traces of Al to Sn-Zn solders,

Table 6
Aging conditions before shearing test.

Test items	Test condition	N
High-temperature release	150°C × 600 to 1300 h	20
Temperature cycle release	-40 to 125°C × 600 cycles	20
High-temperature high-humidity aging	40°C/90%RH × 600 h	20
	85°C/85%RH × 600 h	20

N: Number

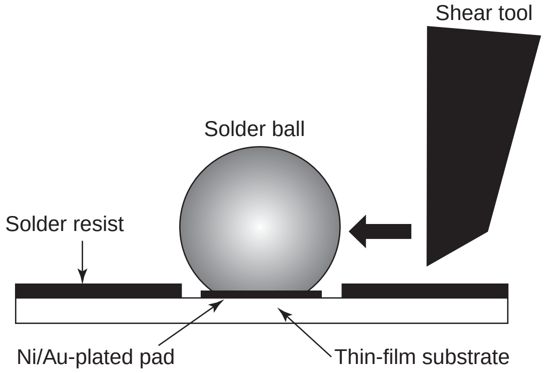


Figure 13
Solder ball shear-strength measuring method.

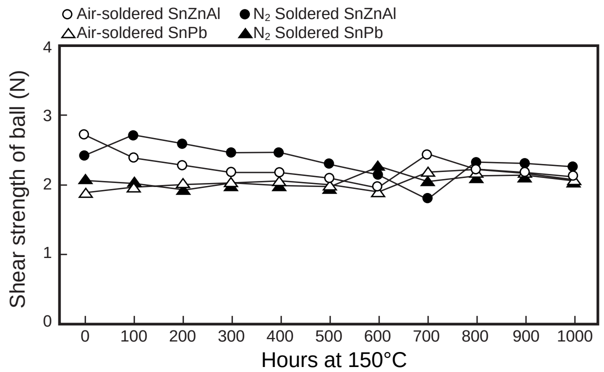


Figure 14
Shear strength of Sn-Zn-Al solder joints after high-temperature aging at 150°C.

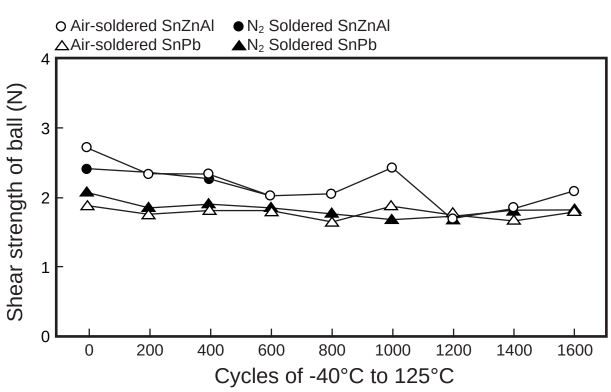


Figure 15
Shear strength of Sn-Zn-Al solder joints after temperature cycling.

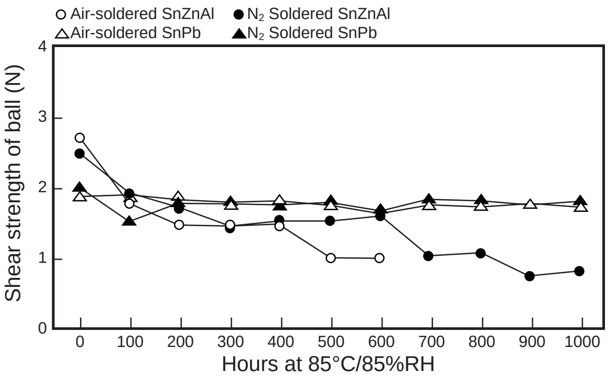


Figure 16
Shear strength of Sn-Zn-Al solder joints after high-temperature, high-humidity aging at 85°C/85%RH.

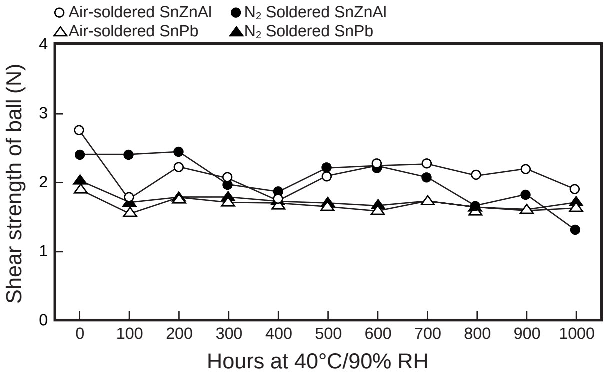


Figure 17
Shear strength of Sn-Zn-Al solder joints after high-temperature, high-humidity aging at 40°C/90%RH.

favorable elongation was achieved with no decline in strength.

4) The Al and Zn were highly concentrated at the Sn grain boundaries, which is assumed to have improved the boundaries' bonding strength.
5) No soldering problems occur with a peak reflow temperature of 215°C.
6) No remarkable voids were detected in solder joints evaluated immediately after mounting.
7) Except in the case of 85°C/85%RH aging, the Sn-Zn-Al solder-ball joints with a Cu/Ni/Au-plated substrate were stronger than Sn-Pb eutectic solder joints with the same substrate.

We started commercial use of Sn-Zn-Al solder in 2002 and have already shipped more than 100000 products that use it. We will continue to make pioneering efforts in eco-activities. Further comments and cooperation by interested parties would be highly appreciated.

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Masayuki Kitajima was born in Saitama, Japan, in 1960. He received the B.E. degree from Chuo University, Tokyo, Japan in 1983. He joined Fujitsu Limited, Kanagawa, Japan in 1983, where he has been researching and developing soldering. His current research interests include developing Pb-free solder alloys consisting of Sn-Zn-Al and new industrial chemical materials. He is a member of the Japan Institute of Electronics Packaging (JIEP). He received the Best Paper Award at the 2003 JIEP Annual Meeting.

E-mail: kitajima.mas-01@jp.fujitsu.com

Tadaaki Shono was born in Saga, Japan in 1974. He received the M.A. degree from Saga University, Saga, Japan in 1999. He joined Fujitsu Limited, Kanagawa, Japan in 1999, where he has been researching and developing soldering. Currently, he is developing Pb-free solder alloys consisting of Sn-Zn-Al with Mr. Kitajima.

E-mail: shono@transtron.fujitsu.com