Applicability Of Bi-42Sn-1Ag Solder For Consumer Products

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Abstract

Eutectic Bi-42Sn solder is a low melting point alternative to lead-based solders, particularly for low cost, consumer electronics. In earlier work, the mechanical properties of this solder have been enhanced by small additions of silver (0.5%-3%). In this study, Bi-42Sn-1Ag solder paste was used to assemble lead-free PBGAs (Sn-0.7Cu, Sn-3.5Ag, and Sn-3.5Ag-0.7Cu ball compositions) on lead-free PCB surfaces (organic solderability preservative (OSP), electroless nickel/immersion gold, and immersion tin). These lead-free assemblies exhibit accelerated thermal cycling (ATC) performance comparable to the performance of assemblies made with Sn-37Pb, surviving 7000 cycles (40 min. cycles between –25°C and 75°C). In addition, with sufficient solder paste these lead-free assemblies have bend strengths approximately equal to the strength of a comparable Sn-37Pb assembly. Moreover, bend failure occurs between the FR-4 and the inlaid copper pad for both solders. To understand the reliability and mechanical behavior, cross-sections of solder joints were evaluated.

Introduction

Pb-free solders that are technically sound and economically viable are needed for microelectronics to satisfy proposed legislation in Europe and potential market pressures in Japan. A wide range of products and applications will require Pb-free solders to meet this challenge. Bi-42Sn-1Ag is a promising Pb-free solder candidate for low cost consumer products for a number of reasons.

For each product type, factors including manufacturability, cost, reliability at high temperatures, and long life must be prioritized. A single replacement to Sn-Pb is desired because of the advantages of standardization, particularly in an industry that depends on outsourcing to contract manufacturers. The single replacement that organizations such as IPC and NEMI are advocating is Sn-3.5Ag-0.7Cu (or similar compositions) with a melting point 34°C greater than eutectic Sn-37Pb.[1] This alloy was selected because the solder joints appear to be reliable for high temperature applications. However, not all products experience high temperature operating environments. Specifically consumer electronics, such as portable products and office products, are designed to be stored below 70°C and operated below 55°C.[2] Although Sn-Ag-Cu joints have good mechanical properties, the overall assembly reliability (not just of the solder joint) may decrease because higher processing temperatures could induce latent damage to components, PCB warpage, and large residual stresses within the PCA. Moreover, the use of Sn-Ag-Cu solder will likely increase assembly and component costs. In particular, the cost of assembly may increase compared to Sn-Pb due to higher material costs, lower yield, increased energy required for reflow, and added preconditioning of components to avoid delamination and "popcorning." In addition, the development required to design, qualify, and produce components to withstand peak reflow temperatures of 240-260°C will likely increase the cost of printed circuit assemblies (PCAs).

For consumer products such as compact disc players, cellular phones and home printers, the design priority is typically to minimize cost while maintaining adequate reliability. A lower melting point solder could be particularly advantageous for consumer electronics because lower cost components and printed circuit boards (PCBs) could be used in a lower energy assembly process. An alternative to eutectic Sn-Pb that provides these advantages is the Bi-Sn system, which exhibits a eutectic Bi-42Sn melting temperature of 138°C (45°C below eutectic Sn-37Pb and 79°C below Sn-3.5Ag-0.7Cu). In earlier studies, small additions of Ag were found to improve mechanical properties,[3,4] increasing thermal fatigue life and shear strain at the maximum shear stress. This earlier work was conducted on bulk tensile specimens[4] or test coupons of ceramic plates bonded to FR-4 boards.[3] In the current study, Bi-42Sn-1Ag solder paste is evaluated with typical electronic components on standard qualification boards, rather than with test coupons. The objective of this study is to establish the feasibility of using Bi-42Sn-1Ag solder in electronic assembly.

Experimental Method

Solder paste: 57Bi-42Sn-1Ag (wt%) paste was used for assembly in a water-clean flux formulation that activates at temperatures below 170°C. The reflow profile that was used is shown in Figure 1. The peak reflow temperature was approximately 170°C, the time over the liquidus temperature was kept below 90 sec, and the soak was near 130°C for about 120 sec. In earlier work, this paste flux was selected for its superior wetting and printing properties after evaluating water clean and no clean pastes from three vendors.[5]

PCB surface finishes

Organic solderability preservative coated Cu (OSP), electroless Ni/ immersion Au, and immersion Sn were used with a Sn-Pb hot air solder leveled (HASL) as a control.

Components

Experimental 256 plastic ball grid array packages (PBGAs) with die bonded test die were provided with Sn-3.5Ag, Sn-3.5Ag-0.7Cu, and Sn-0.7Cu ball alloys and a 63Sn-37Pb control.

Tests

Experiments were conducted on assemblies made from each Pb-free solder ball alloy in combination with each Pb-free surface finish with water-clean Bi-42Sn-1Ag paste. Control experiments were also conducted using 63Sn-37Pb finish, paste and solder balls.

Thermal cycling was conducted with continuous monitoring of daisy-chained parts. Thermal cycles of 40 min. each, –25°C to 75°C, were applied, which included 10 min. at each peak and 10 min. ramps between the peaks.

Four-point bend tests were conducted on as-assembled PCAs with PBGAs. Each assembled PCA was cut so that each BGA was separate and surrounded by about 1.5” of PCB. These tests assemblies were then subjected to 4-point bending at room temperature with a displacement rate of 0.03 in/min.

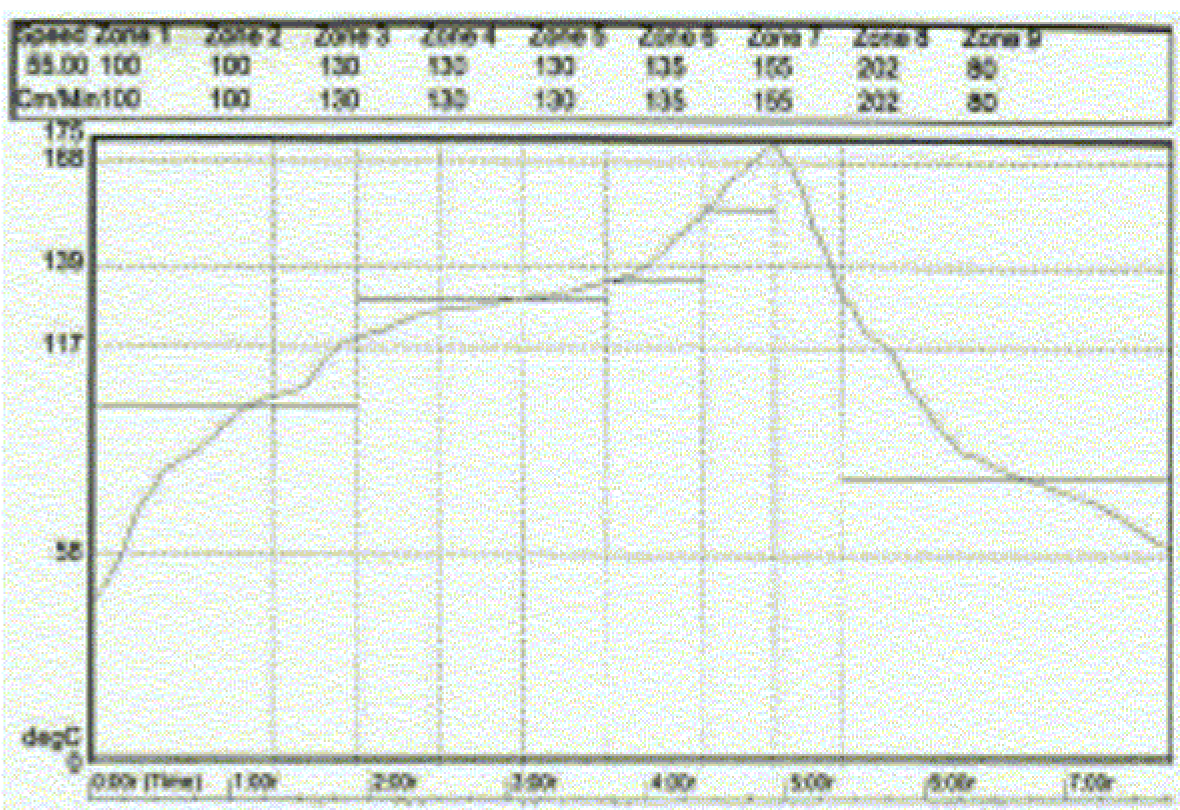

Figure 1 - Representative Reflow Profile for Bi-42Sn–1AgSolder Paste with Temperature in Centigrade on the Vertical Axis and Time in Minutes on the Horizontal Axis

Cross-sectional analysis was conducted with a scanning electron microscope (SEM) on as-assembled PCAs and PCAs aged for 10 days at 110°C. On these cross-sections, energy dispersive spectroscopy (EDS) was also performed to determine which elements were present in different regions of the microstructure.

Results and Discussion

This section will be divided into three parts: PCA bend strength, thermal fatigue resistance, and microstructural analysis. For these experiments, 256 PBGA components of three metallurgies, Sn-3.5Ag, Sn-3.5Ag-0.7Cu, and Sn-0.7Cu, were assembled with Bi-42Sn-1Ag water-clean paste on boards with OSP, Sn, and Ni/Au surface finishes.

Solder Joint Strength

Four-point bend testing of assembled BGAs was used to evaluate resistance of the BGA assemblies to fracture at room temperature, simulating operations such as inserting connectors, shipping, and handling. In this test, loads were applied mechanically rather than thermally.

Results from this four-point bend testing showed that the bend strength and failure mode for 256 PBGAs assembled with Bi-Sn-Ag solder paste and high-Sn solder balls depended strongly on the volume of paste applied. In fact, the failure modes observed in this work indicate that Bi-Sn-Ag joints with volume exceeding a critical level are comparable to Sn-Pb joints. With adequate paste, Sn-Pb and Pb-free joints failed by pullout of the copper pad from the FR-4 of the PCB. In this study, joints printed with approximately 4250 mils^3 of paste per pad failed at the intermetallic/solder interface, while joints with 9500 mils^3 or greater paste volume were barrel shaped and failed by pull out of the copper pad. This means that the Sn-Pb and Bi-Sn-Ag joints are stronger in bending than the interface between copper and FR-4. The specific values measured in the bend testing will not be presented because these values indicate the strength of the copper/FR-4 interface, not the bulk solder or any solder/intermetallic interface.

As presented below, four-point bend test results suggested that a critical volume of Bi-42Sn-1Ag paste was required to obtain PCAs with comparable bend strengths and bend failure modes to Sn-Pb. The shape of the solder joints also indicated that a critical paste volume was necessary. In particular, the Pb-free BGA joints assembled with 4000-4500 mils^3 paste volume had an hourglass shape, Figure 2a. Conversely, the eutectic Sn-Pb solder balls and paste melted during assembly, yielding barrel-shaped joints. This difference in shape is related to use of high melting point, high-Sn solder balls (T_{mp} ~ 220°C) in a low temperature reflow process ($T_{peak\ reflow}$ ~170°C). To obtain a barrel-shaped joint with a non-melting solder ball, 8000-10,000 mils^3 was required with a 30 mil ball. A joint assembled with about 9500 mils^3 of Bi-42Sn-1Ag paste and a Sn-3.5Ag-0.7Cu ball is shown in Figure 2b.

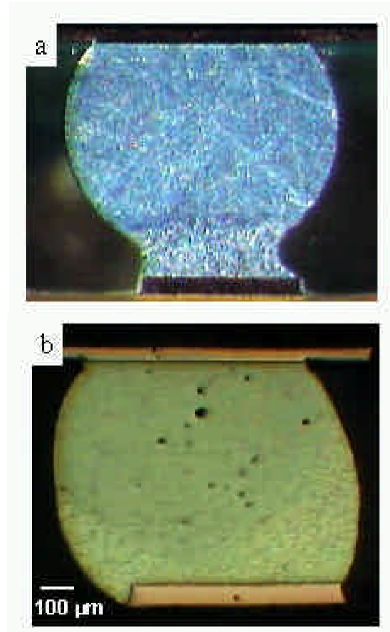

Figure 2 - SEM Micrograph of the PCB Side of a Pb-free BGA Assembly, Showing the Cu pad, the Bi-42Sn-1Ag Solder Paste and the High-Sn Ball After Reflow for (a) About 4000 mils^3 of Bi-42Sn-1Ag Solder Paste and (b) About 9500 mils^3 of Solder Paste

Earlier work on ceramic BGAs with non-melting balls can be used as a point of reference for the current work of Bi-42Sn-1Ag solder paste and high-Sn, non-melting solder balls. For ceramic BGAs, non-melting, high-Pb solder balls and eutectic Sn-Pb paste are commonly used with these heavy components to maintain a reasonable height between the component and the PCB.[6] Work on ceramic BGAs also suggests that reliability of the solder joints is improved with a larger paste volume.

In work that preceded this study,[7] 256 PBGAs with high-Sn solder balls were assembled with about 4000-4500 mils^3 of Bi-42Sn-1Ag paste. All of these Pb-free 256 PBGA assemblies failed primarily in the solder between the PCB and the BGA. Specifically, fracture surfaces created during bend testing revealed two types of failure: cleavage of the Bi-rich phases and "pull out" of the Cu-Sn intermetallic nodules from the Sn phase. This behavior differed from that of BGA assemblies using Sn-Pb[7,8] and Sn-Ag-Cu[8] solder paste, for which failure occurred primarily between the FR-4 board and the copper inlaid in the board. In the current study, this inferior behavior of BGA joints made with Bi-Sn-Ag paste and high Sn balls such as Sn-3.5Ag-0.5Cu has been linked to low paste volume with a non-melting BGA ball. To summarize, the joint shape rather than the metallurgy had the largest effect on failure mode.

It is important to evaluate mechanical behavior of Bi-42Sn-1Ag joints because of the high yield strength and low ductility measured in the eutectic Bi-42Sn alloy. In earlier work by Tomlinson and Collier, Bi-42Sn was considered brittle.[9]. Interestingly in that work, the *bulk* Bi-42Sn specimens tested in tension were relatively brittle with a lower fracture energy and higher yield strength than Sn-Pb.[9] However, solder *joints* on copper or brass coupons had similar shear strength and work of fracture to Sn-Pb. Thus in the constrained condition of the solder joint Bi-42Sn was not significantly brittle. Furthermore, preliminary shock and vibration testing of PCAs assembled with Bi-42Sn-1Ag solder suggests that Bi-42Sn-1Ag joints perform well under high strain rate conditions.[10] It has also been shown that Bi-42Sn performs better than Sn-3.3Ag-4.8Bi in thermal shock, but worse than Sn-3.5Ag.[11]

Thermal Fatigue Resistance

Temperature changes imposed during thermal cycling induce stresses in the solder joints because of thermal expansion variations between the layers of the assembly, i.e. the solder joint, board, and package. These temperature changes simulate the service environment of a PCA when a product is turned on and off or stored at different temperatures. A thermal cycle profile of –25°C to 75°C was selected to accelerate the thermal fatigue degradation of the solder joints in service. Typically, a thermal profile of 0°C-100° C is used to evaluate Sn-Pb PCAs. In the current study, lower temperatures of -25°C to 75°C were selected so that the peak homologous temperature for Bi-42Sn-1Ag (T_{peak}/T_{mp} ~0.85) would be similar to that of Sn-37Pb, subjected to the conventional thermal test profile (T_{peak}/T_{mp} ~0.82). Moreover, this -25°C to 75°C temperature range is representative of extreme possible product storage temperatures.[2]

All of the Pb-free 256 PBGA assemblies have survived 7000 thermal cycles. This excellent thermal fatigue resistance is consistent with coupon-level testing of near-eutectic Bi-Sn-Ag alloys.[3,4] In particular, Bi-Sn-Ag outperformed Sn-Pb and Bi-Sn in coupon level tests.[3] One hypothesis for the superior properties of Bi-Sn-Ag near-eutectic alloys is based on the influence of silver on microstructural evolution during thermal fatigue. Silver is believed to decrease the grain size and stabilize the microstructure of Bi-42Sn eutectic during aging.[4] Typically, a fine microstructure results in better mechanical properties for a solder. In the current work, some evidence supports the role of silver in stabilizing the microstructure because Ag_3Sn particles appear to pin the Bi-rich phase.

The good fatigue behavior of Bi-42Sn-1Ag joints is also consistent with fatigue testing of PCAs assembled with the eutectic Bi-42Sn solder paste.[11-12] NCMS found that Bi-42Sn surface mount assemblies had better fatigue resistance than Sn-Pb even for high temperature cycles (0°C to 100°C and –55°C to 125°C).[12] In fact, a smaller[12] or equivalent[11] amount of microstructural damage was observed following thermal fatigue for the Bi-42Sn assemblies compared to other solders.

Another reason for the good fatigue resistance of Bi-42Sn and Bi-42Sn-1Ag solder is the small coefficient of thermal expansion (CTE) mismatch in joints made with these Bi-containing alloys.[13] The residual stresses in the joints depend on the global and local CTE mismatch, the reflow temperature, and the service temperature, as well as the geometry of the joint and PCA and the type, size, and order of the material layers in the PCA. The CTE of Bi-42Sn is significantly lower than that of Sn-Pb and Sn-3.5Ag-0.7Cu solder. This means the CTE mismatch between Bi-42Sn and components of the PCB and packages is smaller than for most other solders.[11,13-14] Thus for the same temperature cycle, the stresses in a Bi-42Sn joint may be smaller than the stresses in a Sn-Pb or Sn-Ag-Cu joint.

The data acquired in this study and in earlier work indicate that Bi-42Sn and Bi-42Sn-1Ag alloys provide acceptable thermal cycle reliability relative to eutectic Sn-Pb. The influence of the well-known low-melting 52Bi-30Pb-18Sn phase arising from the presence of Pb on components or PCBs is currently under investigation. Earlier work has shown that Bi-42Sn assemblies, which contain Pb, survived 7000 thermal cycles from –18°C to 75°C. However, when cycled from 0°C to 100°C, similar Pb-containing assemblies failed prematurely due to grain growth.[3,15]

In the current study, failures have not occurred. Hence, these test assemblies will stay in the thermal cycle chamber to obtain future failures, create Weibull failure distributions, and compare the reliability of joints made with different ball alloys and PCB surface finishes. Since this testing was initiated, cross-sectional analysis and bend testing revealed that these BGAs have insufficient paste volume for use with a solder ball that does not melt during reflow. This insufficient paste volume and resulting reduced cross-section may affect the thermal fatigue behavior. As discussed in this previous section, insufficient paste volume significantly decreased the bend strength and changed the failure mode to solder fracture from copper pad pullout. This bend test finding further supports the conclusion that the thermal fatigue life of Pb-free Bi-Sn-Ag solder joints is adequate for electronic assemblies; even with insufficient solder volume and a resulting small cross-section, the BGA assemblies have survived 7000 thermal cycles of -25°C to +75°C.

Microstructural Analysis

The most significant microstructural observation was the appearance of a degraded eutectic microstructure, where the Bi-42Sn-1Ag had been soldered to the high-Sn solder ball. It appears that the Bi dissolved into the Sn matrix of the BGA ball during reflow and isothermal aging. Based on the Bi-Sn phase diagram, the Bi from the near-eutectic solder paste is highly soluble in the Sn-rich phase of the high-Sn BGA ball.[16] The microstructure with excess tin (Figure 3b) can be compared to the microstructure of the Bi-42Sn-1Ag paste reflowed on a Cu pad (Figure 3a), which has a fine-grained microstructure similar to a eutectic. The dissolution of Bi from the paste is apparent in the as-reflowed joint, Figure 4a and becomes more pronounced after aging at high temperatures, Figure 4b. Since these BGAs were assembled with Sn-3.5Ag, Sn-0.7Cu, or Sn-3.5Ag-0.7Cu, there was effectively an unlimited source of Sn in which Bi could dissolve to reduce its chemical potential.

After aging at high temperatures, the Bi-rich phase appeared both to dissolve into the Sn matrix and to agglomerate in large Bi-rich phase regions. EDS analysis confirmed that there was a decay of bismuth concentration in the Sn-phase matrix between the paste region and the BGA ball region. This finding of Bi in the Sn-phase matrix in the region that was initially the solder ball is consistent with the observation of a decrease in the amount of Bi-phase present in the solder paste region after isothermal aging. Thus using BGAs of high-Sn content with the Bi-42Sn-1Ag solder degraded the near eutectic microstructure, which could adversely affect thermal fatigue, creep and strength behavior. To avoid this type of microstructural degradation, Bi-Sn or Bi-Sn-Ag solder balls could be used. In a similar example, the Bi-Sn-Ag microstructure is not as significantly affected by soldering to a Sn-coated lead, shown in Figure 3c. In this case, a much smaller amount of Sn is present to diffuse into the Bi-Sn-Ag paste than in the case of soldering to a high-Sn BGA solder ball.

The location of the Ag in the microstructure was also studied. Based on the phase diagram for Bi-Sn-Ag, Ag is most likely present in the Ag_3Sn phase and is practically insoluble in Bi or Sn-rich phases.[16] In addition, EDS analysis confirmed that Ag was present in high concentration when larger particles of the Ag-Sn phase were found. However, most of the Ag-Sn particles were so small that the EDS beam picked up surrounding material making confirmation of the Ag_3Sn phase difficult.

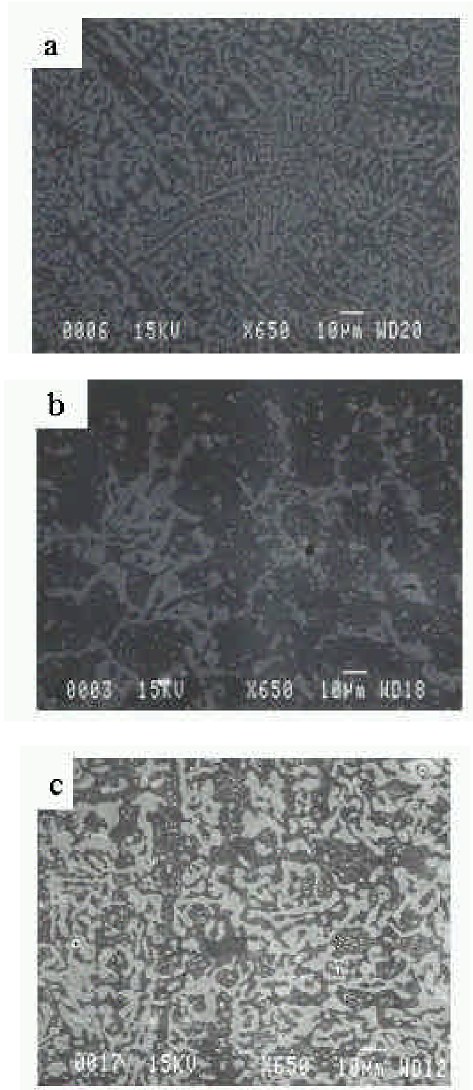

Figure 3 - As-Reflowed Bi-42Sn-1Ag Solder Paste (a) On a Bare Cu pad (b) Attaching a Cu Pad to a Sn-0.7Cu BGA, and (c)Attaching a Cu Pad to a Sn-Coated SOL 18 Lead

After aging for 10 days at 110°C, there is a significant microstructural change in the Bi-Sn-Ag region of the joint (Figure 4). First, there is less of the Bi-rich phase. This is not surprising since the Bi is dissolving into the Sn-rich phase. Secondly, after aging there is a bimodal distribution in the size of the Bi-rich phases. Specifically, phase regions on the order 1 μm^2 are observed, scattered evenly throughout the paste layer. Also large regions, on the order of 100 μm^2, are present in higher density near the PCB-solder interface. One hypothesis for this bimodal distribution is as follows. For the large Bi-rich regions, the large radius of curvature may reduce the chemical potential of the Bi atoms in a large region compared to the chemical potential in a small region with a small radius of curvature. For the small phase regions, the proximity of Ag_3Sn may lower the surface energy of the Bi-rich phase. Other researchers have found Ag_3Sn to be persistent in the microstructure.[17] In addition, McCormack and co-workers showed that evenly distributed, insoluble Fe particles were able to stabilize a fine Bi-Sn microstructure.[18] The effectively insoluble Ag_3Sn phase may perform the same role as insoluble Fe particles.

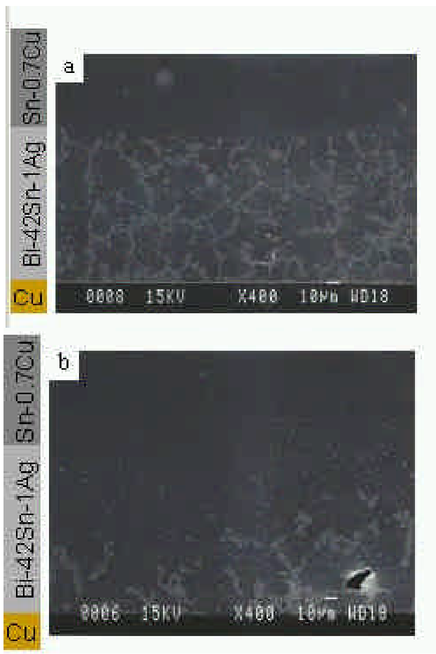

Figure 4 - SEM Micrographs of BGA Assemblies Showing aCu PCB Pad, Reflowed Bi-42Sn-1Ag Solder Paste, and a Sn-0.7 Cu BGA Ball (a) as Reflowed and (b) After Aging at 110°C for 10 Days

Conclusions

Bi-42Sn-1Ag is a lead-free, low melting point alternative to lead-based solders, particularly suitable for consumer electronics applications. In this paper, an evaluation of the BGA thermal fatigue resistance and bend strength of 57Bi-42Sn-1Ag alloy was presented. The main results were:

- Pb-free PCAs assembled with Bi-42Sn-1Ag solder paste survived 7000 thermal cycles of –25°C to 75°C. These ATC test results show that Bi-42Sn-1Ag has excellent thermal fatigue resistance, and that thermal fatigue does not present a barrier for the use of Bi-42Sn-1Ag solder paste. An increase in paste volume or a Bi-42Sn solder ball may improve the already acceptable thermal fatigue behavior of joints assembled with Bi-42Sn-1Ag solder paste.
- BGA bend strength is optimized with a paste volume of 9500 $mils^3$ for a 30-mil diameter solder ball, such that the strength and failure path is comparable to Sn-Pb joints.
- The near-eutectic microstructure of Bi-42Sn-1Ag is broken down by the high-Sn BGA balls by diffusion of Bi into the Sn-rich matrix and agglomeration of the Bi-rich phase. Bi-Sn or Bi-Sn-Ag BGA ball alloys may improve the mechanical properties of joints assembled with Bi-42Sn-1Ag.

Future Work

In further testing, we plan to evaluate Bi-Sn BGAs to understand any change in strength or fatigue resistance with large changes in joint shape, microstructure and standoff height. With a Bi-Sn ball, the joint microstructure would likely be improved because grains would be smaller and the microstructure would be more stable during aging. However, the stand off height of the BGA, which is known to improve fatigue resistance, would decrease with a melting Bi-Sn BGA ball.

Further shock and vibration testing is needed to evaluate the response of Bi-42Sn-1Ag joints under high strain rates. An initial assessment has shown promising results. However, there is some earlier evidence of brittle behavior of Bi-42Sn, so shock and vibration behavior should be thoroughly evaluated.

References

1. Bath, J., C. Handwerker, and E. Bradley, Research update: Lead free solder alternatives. Circuits Assembly, 2000. 11(5): p. 30-40.
2. Environmental Test Manual. 1986, Hewlett Packard internal report.
3. Hua, F., et al. Eutectic Sn-Bi as an alternative Pb-free solder. in IPC Works '99. 1999. Minneapolis: IPC.
4. McCormack, M., et al., Significantly improved mechanical properties of Bi-Sn solder alloys by Ag-doping. Journal of Electronic Materials, 1997. 26(8): p. 954-958.
5. Schroeder, V. and F. Hua. Feasibility study of 57Bi-42Sn-1Ag solder. in APEX. 2001. San Diego: IPC.
6. Guo, Y. and J.S. Corbin, Reliability of ceramic ball grid array assembly, in Ball Grid Array Technology, J.H. Lau, Editor. 1995, McGraw-Hill, Inc.: San Francisco. p. 223-265.
7. V. Schroeder and F. Hua, Proceedings of SMTA Boston, June 2001 pp.
8. Roubaud, P., et al. Impact of intermetallic growth on the mechanical strength of Pb-free assemblies. in APEX. 2001. San Diego: IPC.
9. Tomlinson, W.J. and I. Collier, The mechanical properties and microstructures of copper and brass joints soldered with tin-bismuth solder. Journal of Materials Science, 1987. 22: p. 1835-1839.
10. Gleason, J. and V. Schroeder, to be published. 2001.
11. Vianco, P.T. and C. May, Evaluation of prototype surface mount circuit boards assembled with three non-lead bearing solders. Surface mount International, 1995: p. 481-494.
12. NCMS, Lead free solder project final report. 1997, NCMS: Ann Arbor.
13. Hua, F., Z. Mei, and J. Glazer. Eutectic Sn-Bi as an alternative Pb-free solder. in Electronic Components and Technology Conference. 1998. Seattle: IPC.
14. Lide, D.R., ed. Handbook of Chemistry and Physics. 73 ed. 1992-1993, CRC: Ann Arbor.
15. Z. Mei, F. Hua, and J. Glazer. Thermal reliability of 58Bi-42Sn solder joints on Pb-containing surfaces. Proceedings of TMS Symposium: Design and Reliability of Solders and Solder Interconnections. 1997. pp229-39.
16. Kattner, U.R. and W.J. Boettinger, On the Sn-Bi-Ag ternary phase diagram. Journal of Electronic Materials, 1994. 23(7): p. 603-610.
17. Chen, S.W. and Y.-W. Yen. Interfacial reactions in the Ag-Sn/Au couples. in TMS. 2001. New Orleans.
18. McCormack, M., J. S, and G.W. Kammlott, Suppression of microstructural coarsening and creep deformation in a lead-free solder. Applied Physics Letters, 1994. 64(5): p. 580-582.

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