Effects of Zn, Zn-Al and Zn-P Additions on the Tensile Properties of Sn-Bi Solder

Xiaojing Wang · Yanlai Wang · Fengjiang Wang · Ning Liu · Jianxin Wang

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Abstract Effects of Zn, Zn-Al and Zn-P additions on melting points, microstructures, tensile properties, and oxidation behaviors of Sn-40Bi lead-free solder were investigated. The experimental results show that the addition of these three types of elements can refine the microstructures and improve the ultimate tensile strength (UTS) of solder alloys. The fractographic analysis illustrates that ductile fracture is the dominant failure mode in tensile tests of Sn-40Bi-2Zn (SBZ) and Sn-40Bi-2Zn-0.005Al (SBZA) specimens, while brittle fracture is the controlled manner in Sn-40Bi-2Zn-0.005P (SBZP) and Sn-58Bi solders. XPS analysis indicates that trace amounts of both Al and P additives in solder can improve the antioxidant capacity, whereas only the additive of Al in solder can reduce the thickness of oxidation film.

KEY WORDS: Sn-Bi; Tensile test; Microstructure

1 Introduction

Sn-58Bi eutectic solder has been used as thermal interface material in notebook thermal module, for lower melting temperature ($\sim 137^\circ\text{C}$), superior wettability, and almost void-free bonding [1–3]. It dramatically reduces the mismatch of coefficient of thermal expansion among various materials of components in a package assembly using the lower soldering temperature. However, the existence of excessive Bi in Sn-Bi solder will deteriorate the thermal conductivity of Sn-Bi solders [4]. Therefore, in order to improve the thermal

conductivity of Sn-Bi solder, two other kinds of solders, Sn-35Bi-1Ag and Sn-17Bi-0.5Cu [5] are also used in manufacture by considering product function, technical process, cost, and so on. Another problem of Sn-Bi solder is the microstructural coarsening phenomenon, which will seriously affect its mechanical properties during thermal aging [6–8]. The microstructural coarsening mainly comes from two aspects, the grain growth in eutectic field and the Bi-rich phase segregation at the interface caused by the reaction between Cu and Sn [9]. It has been reported that the instability of microstructure at high temperature can be inhibited by introducing fine dispersive particles to solder base [10].

Zn has been paid much attention in Pb-free alloys study for the cheapness and effectiveness as additive. It has been reported that minor Zn addition into Pb-free solders can pronouncedly inhibit the growth of intermetallic compounds (IMCs), especially restraining the growth of Cu_3Sn and the formation of Kirkendall voids during isothermal aging [11–13]. Being very active, Zn preferentially reacts with the substrate metals to produce IMC layer rather than Sn, and the Zn-containing IMCs layer will retard the reaction between Sn and substrate metals. In addition, the addition of about 0.5 wt% Zn to Sn-Ag-Cu-Ce solder can depress the growth of

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X. Wang (✉) · F. Wang · N. Liu · J. Wang
School of Material and Science Engineering, Jiangsu University
of Science and Technology, Zhenjiang 212003, China
e-mail: xjwang120089@gmail.com

Y. Wang
Key Laboratory of Semiconductor Photovoltaic Technology of
Inner Mongolia Autonomous Region, School of Physical Science
and Technology, Inner Mongolia University, Hohhot 010021,
China

whisker on surface [14]. However, it is unfortunate that the Zn addition in solder will initiate a new problem of liquid oxidation during soldering [15]. The addition of alloying elements, such as Al, Ag, and P, can improve the oxidation resistance of Zn-containing system solders [16–19]. Among all the alloying elements, Al and P have been paid much more attention. Moreover, the addition of P may also affect other properties of the solder joint. Therefore, in the present paper, trace amount of Al and P will be added into SBZ alloy; their effects on the mechanical properties and surface element distribution will be investigated in this work.

2 Experimental

The ingots of Sn-58Bi, Sn-40Bi, Sn-40Bi-2Zn (SBZ), Sn-40Bi-2Zn-0.005Al (SBZA), and Sn-40Bi-2Zn-0.005P (SBZP) were prepared by melting high purity of Sn, Bi, Zn, Al, and Sn-2.5 wt% P master alloy in vacuum furnace at 800 °C for 60 min. The obtained ingots were remelted and stirred at 200 °C for 15 min with an anti-oxidation agent covering on the surface, then casted into a plate followed by two-week aging to get a stabilized microstructure.

2.1 Melting Temperature

About 3–5 mg samples were cut directly from the ingot plates for differential scanning calorimetry (DSC) analysis to test the melting behavior of the solder alloys. The heating rate of test was 2 °C/min, and the melting process was carried out in Ar flow protection of 20 mL/min.

2.2 Metallographic Observation

The samples for the microstructural observations were cut to small buttons from the plates, which were cross-sectioned and etched gently after grinding and polishing. The microstructures and the fracture surfaces after tensile tests were investigated by scanning electron microscopy (SEM).

2.3 Mechanical Properties

Tensile test were carried out on an electronic universal testing machine CMT5205 at room temperature. All the specimens were machined from cast ingots based on the GB/T228.1-2010 standard tensile sample size. The tensile tests were conducted three times each at the strain rate of 0.005/s.

2.4 Surface Test

The SBZ, SBZA, and SBZP solder alloys with the weight of about 50 g were heated up to 170 °C. The oxidation layer on liquid solder surface was scraped away to expose a

fresh surface, and then the alloys were kept at 170 °C for 7 min. The outer surface was prepared for x-ray photoelectron spectroscopy (XPS) analysis with an achromatic AlK_{α} X-ray and the vacuum of 10^{-6} Pa.

3 Results and Discussion

3.1 Melting Temperature

Figure 1 shows the DSC curves of SBZ, SBZA, and SBZP solder alloys. It is presented that there are no significant differences in the melting temperature among the three solders. For example, the melting temperature of SBZ is 137.01 °C. After adding a small amount of Al/P element, the melting points of SBZA and SBZP solder alloy are still kept at round 137 °C. Therefore, the addition of trace amount of Al/P into Sn-Bi-Zn alloy does not apparently affect the melting temperature of Sn-Bi-Zn alloy.

3.2 Microstructure

Figure 2 shows the SEM micrographs of Sn-58Bi, Sn-40Bi, SBZ, SBZA, and SBZP alloys. The microstructure of Sn-58Bi alloy in Fig. 2a represents a typical eutectic structure which is composed of Sn-rich phase (gray contrast) and Bi-rich phase (white contrast). The microstructure of Sn-40Bi alloy is quite different from that of eutectic Sn-Bi alloy. The 18 wt% Bi withdrawn from the Sn-58Bi alloy destroys the uniformity of eutectic structure and the fishbone-like Bi precipitate (Fig. 2b). The Bi-rich phase is much coarser in Sn-40Bi alloy than that in Sn-58Bi alloy. And also the Sn-rich domains are interspersed with larger thin white or granular Bi-rich phase compared to Sn-58Bi alloy. The microstructure reveals that the phase transformation during cooling of Sn-40Bi alloy from 170 °C is liquid → Sn matrix and Bi/Sn coexistence area.

Fig. 1 DSC curves of the solder alloys

Fig. 2 SEM micrographs of the lead-free solders: **a** Sn-58Bi; **b** Sn-40Bi; **c** Sn-40Bi-2Zn; **d** Sn-40Bi-2Zn-0.005Al; **e** Sn-40Bi-2Zn-0.005P

2 wt% Zn doping into Sn-40Bi alloy, exhibited in Fig. 2c, induces the microstructure refinement which includes Sn base and coexistent areas. Moreover, it is observed that the Zn-rich phase with a grainy or short rod-like shape mainly presents along with Sn/Bi eutectic structures in Fig. 2c. It is predicted that the cooling reaction for SBZ alloy from 170 °C is liquid $\rightarrow$ Sn matrix + Bi/Sn eutectic + Zn-rich primary phase. The additives of trace amount of Al and P in SBZ alloy make further microstructural refinement on Bi-rich phase, as shown in Fig. 2e, f, respectively. The Zn-rich phase transformed into needle-like shape. However, the overall microstructures of SBZA and SBZP are highly similar. It indicated that although the trace amount of Al/P could not be detected by SEM observation, it did affect the microstructure of SBZ alloys. As we know, the solubility of Al in Sn and Sn in Al are near zero and 0.025 at% at 300 °C, respectively [20]. The solid solubility of Al in Sn is lower than that of Al in Zn. Therefore, Al may form an intermetallic compound, $\text{Al}_6\text{Zn}_3\text{Sn}$, with Zn and Sn as it has been reported by Lin *et al.* [21] in Sn-9Zn-0.45Al alloy. Zhou *et al.* [21] reported that the addition of 0.5 wt% P addition to Sn-8Zn-3Bi alloy promoted needle-like Zn-rich phase growth and refined Bi-rich phase; the XRD analysis indicated that the SnP_3 existed around the grain boundary of solder alloy. Therefore, more attention should be paid to the grain boundary, Sn/Bi and Sn/Zn phase interfaces during deformation.

3.3 Strength and Fracture Strain

Engineering stress–strain curves of all five solder alloys obtained at room temperature and at strain rate of 0.005 s^{-1} , are shown in Fig. 3. It is noted that the shapes of curves are quite similar, which look like a dome consisting of a linear elastic region, a plastic falling dome including the steady state flow and a decay followed by the fracture. The ultimate tensile strength (UTS), ε_{Eu} (the maximum strain for uniform plastic deformation along the sample length) and elongation values are summarized in Table 1.

It is also noted that the stress–strain curve of Sn-58Bi has a much steeper slope than Sn-40Bi alloy after UTS point. It indicates that the microstructure nonuniformity seriously deteriorates the performance of plastic deformation of solder alloy before fracture. Compared to the higher brittleness and hardness of Bi phase with Sn phase, Sn/Bi interface must be the weakest region during tensile testing, especially after the strain higher than ε_{Eu} . The deformation mismatch between Sn and Bi interface may induce the concentration of stress and strain and then gives rise to the initiation of micro crack. It also exhibited that although the UTS, comparing the Sn-40Bi alloy with Sn-58Bi alloy, decreased from 57.3 to 51 MPa, the fracture strain increased almost twice to 0.24. It can be interpreted by the thick microstructure and extra Sn content.

There is no obvious difference in terms of UTSs among SBZ, SBZA, and SBZP. However, the fracture strain drops

Fig. 3 Engineering stress–strain curves of Sn-Bi series of alloys

suddenly from 0.34 to 0.15 with the addition of P. It was predicted that the intermetallic compound (IMC) of Sn-P may be formed at the grain boundary and the interface between Sn and Bi, as mentioned above. During the tensile process, the pinning effects of SnP IMC on the phase interface or grain boundary will be enhanced. On the other hand, the addition of a small amount of Al to SBZ alloy increases the fracture strain almost twice the original value, as shown in Table 1.

The significant increase in the UTSs of the Bi-containing solders can be attributed to the microstructures. Zn and Al are strengthening elements for Sn-Bi base alloy, which induce a much finer microstructure.

3.4 Fracture Surfaces

Figure 4 shows the SEM fractures of the five solder alloys after tensile tests. From the fractures, it is noted that the fracture surfaces of Sn-58Bi and Sn-40Bi alloys are granular. In detail, the fractograph of Sn-58Bi comprises the small fracture humps or terraces, while it mainly shows large granular particles in Sn-40Bi alloy, the size of particles is in correspondence with the size range of Bi-rich phases in Fig. 2b. As there are several regions revealing sticky surface in Fig. 4b, Sn-40Bi shows a complicated fracture manner which has both intergranular fracture and ductile character. This phenomenon reflects an increase in ductility of the solder, and also results in a longer non-uniform stress decay stage before fracture, as shown in Fig. 3. Therefore, the phase interface should be the weakest part in Sn-58Bi and Sn-40Bi alloys.

The fractographs of SBZ and SBZA alloys, as shown in Fig. 4c, e, mainly display ductile fracture. There is no obvious difference between the fractographs of SBZ and SBZA alloys except that several smooth steps and cracks are observed in SBZA which indicate that the Sn/Bi

Table 1 Mechanical properties of the Sn-58Bi, Sn-40Bi, Sn-40Bi-2Zn, Sn-40Bi-2Zn-0.005Al, and Sn-40Bi-2Zn-0.005P alloys

Materials	Tensile strength (MPa)	Strain at UTS, ϵ_{Eu}	Elongation (%)
Sn-58Bi	57.3	0.017	0.12
Sn-40Bi	51	0.029	0.24
Sn-40Bi-2Zn	65	0.048	0.25
Sn-40Bi-2Zn-0.005Al	70	0.045	0.33
Sn-40Bi-2Zn-0.005P	68	0.036	0.15

interface and grain boundaries may be the local stress concentration regions [22].

It should be pointed out that the layer-like structure comes up in SBZP, as shown in Fig. 4d, which verified that P addition did weaken the phase interface due to the smaller cohesion of the layer-like structure compared to others. The SnP IMC existing in between interface will pin the motion of interface during tensile process and provide more crack sources. Micro-crack initiation, propagation, and junction may occur under loading with a following failure. It also explains the decrease of fracture strain observed in Fig. 3.

3.5 Surface Analysis

The XPS investigation was carried out to collect the surface elemental information of SBZ, SBZA, and SBZP solder alloys exposed at 170 °C for 7 min. The XPS surface analysis and depth profiles of Oxygen and Zinc are presented in Fig. 5. Figure 5a is the survey spectra of SBZ, with a range of 0–1400 eV. It is found that Zn, Bi, O, and Sn can be detected on the surface. In order to show more details, the selected sub-range of 0–200 eV, which is concerning three Zn peaks and an Al peak, is collected (Fig. 5b). The C1 peak in Fig. 5b can be considered as a contamination.

The relative composition analysis of XPS concerning core levels of O1 s, Zn 2p versus spray time is presented in Fig. 6. The oxygen contents on the outer surface of SBZ, SBZP, and SBZA solder alloys are about 71.6, 60.4, and 46.2 at%, respectively (see Fig. 6a), which indicates that the addition of trace amount of Al/P can improve the antioxidant capacity of Zinc-containing solder. Moreover, the addition of Al is even better on the antioxidant capacity than that of P. The total thickness of the oxide films in the three samples after oxidation at 170 °C for 7 min is measured based on the sputter test showing in Fig. 6a; it can be seen that the thickness of oxygen films on the surface of SBZ, SBZP, and SBZA solder alloys are about 216, 198, and 156 nm, respectively, as shown in Fig. 6c.

For all of the three alloys, the surface concentration of Zn is very high, and then decreases quickly toward the solder base direction, as observed in Fig. 6b. Moreover, it is worth noting that the Zn concentrations on the surface of

Fig. 4 Fracture surfaces of the lead-free solders: **a** Sn-58Bi; **b** Sn-40Bi; **c** Sn-40Bi-2Zn; **d** Sn-40Bi-2Zn-0.005P; **e** Sn-40Bi-2Zn-0.005Al

Fig. 5 XPS surface analysis results of **a** Sn-Bi-Zn, **b** Sn-Bi-Zn-Al solders after exposure at 170 °C for 7 min

solder alloys decrease by the turn of SBZA, SBZP to SBZ solder alloys from 40.4 at. % to 36.9 at. %, then 24.6 at. % respectively. It is suggested that a trace amount of Al/P added into SBZ solder may protect Zn from over-oxidation. Al addition can not only change the Zn oxidation in outer surface, but also reduce the thickness of the oxidation film.

3.6 Discussion

The Bi content in Sn-Bi solder will affect the microstructure. As we can see that with the decrease of Bi content in Sn-Bi solder, the percentage of eutectic Sn-Bi structure decreases. And also the liquid–solid two-phase region becomes wide during cooling process, producing a relatively coarse

microstructure, as shown in Fig. 2b. Additive of Zn into Sn-40Bi alloy refines the microstructure and significantly improves the mechanical properties. This behavior was attributed to the competing effects of work hardening and dynamic recovery processes [23]. The Zn-containing Sn-Bi solder consistently displayed the higher mechanical properties due to the formation of finer eutectic regions and the refinement of β -Sn grain size, which could provide more obstacles for dislocation pile-up in the adjacent grains [24].

Although there is no big difference between the microstructures of SBZA and SBZP solders, the fracture morphology transfers from ductile to brittle mode. A layer-like structure with some visible cracks was observed on the fracture surface of SBZP. The IMC particles and P prefer to

Fig. 6 XPS depth profiles for **a** oxygen **b** zinc, **c** the thickness of oxidation films for the SBZ, SBZA, and SBZP specimens after oxidation at 170 °C for 7 min

segregate at the interface, which will pin the movement of interface and make the interface become weakened during the tensile process. This is consistent with the stress–strain curves. Moreover, it has been reported that a small amount of P doped into Sn–Cu eutectic alloy can enhance the void forming rate in the Sn0.7Cu solder joint [25]. The voids can potentially lead to crack initiation or propagation in the solder joint.

As known, Zn-containing solder often exhibits inferior anti-oxidation properties. Therefore, a trace amount of Al/P was doped in SBZ solder for comprehensive performance in mechanical and anti-oxidation abilities. The XPS data show that Al/P can relieve the over-oxidation of SBZ by reducing the oxidation film thickness and increasing the Zn content in the outer surface of oxidation film of SBZ.

4 Conclusions

- 1) The addition of Zn to Sn–40Bi alloy refines the microstructure and improves the UTS of solders. The addition of Al to Sn–40Bi–2Zn alloy can improve the antioxidant capacity and decrease the thickness of oxygen film on the surface of solder alloy.
- 2) The fractographic analysis indicates that the fracture mechanism of Sn–40Bi solder is controlled by both of ductile and brittle fractures at the same time. And the ductile fracture dominates the tensile failure in the test of SBZ and SBZA solder alloys. The brittle failure mode appears in SBZP and Sn–58Bi solders.
- 3) The XPS analysis reveals that trace amount of Al/P addition will definitely reduce the over-oxidation of Zn, but only Al can decrease the thickness of oxidation film at 170 °C.

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References

- [1] X.C. Tong, *Advanced Materials for Thermal Management of Electronic Packaging*, vol. 30 (Springer-Verlag, New York, 2011), pp. 305–371
- [2] L. Zhang, Z. Yuan, Y. Zhu, B. Xu, H. Matsuura, F. Tsukihashi, *Colloids Surf. A* **44**, 57 (2012)
- [3] G.F. Ma, H.L. Zhang, H.F. Zhang, H. Li, Z.Q. Hu, *Mater. Lett.* **62**, 1853 (2008)
- [4] Y.I. Dutchak, V.P. Osipenko, P.V. Panasyuk, *Sov. Phys. J.* **11**, 145 (1968)
- [5] J. Shen, C. Wu, S. Li, *J. Mater. Sci.* **23**, 156 (2012)
- [6] T.Y. Kang, Y.Y. Xiu, L. Hui, J.J. Wang, W.P. Tong, C.Z. Liu, *J. Mater. Sci. Technol.* **27**, 741 (2011)
- [7] M. McCormack, S. Jin, G.W. Kammlott, *Appl. Phys. Lett.* **64**, 580 (1994)
- [8] C.H. Raeder, L.E. Felton, V.A. Tanzi, D.B. Knorr, *J. Electron. Mater.* **23**, 611 (1994)
- [9] S. Chen, L. Zhang, J. Liu, Y. Gao, Q. Zhai, *Mater. Trans.* **51**, 1720 (2010)
- [10] Q. S. Zhu, H. Y. Song, in *Proceedings of the 9th ICEPT-HDP*, Beijing, 10–13 Aug. 2009, p. 1043
- [11] Y.M. Kim, T.J. Kim, M.Y. Choi, Y.H. Kim, *J. Alloys Compd.* **575**, 350 (2013)
- [12] I. Shohji, T. Nakamura, F. Mori, S. Fujiuchi, *Mater. Trans.* **43**, 1797 (2002)
- [13] F. Wang, F. Gao, Y. Qian, *J. Electron. Mater.* **35**, 1818 (2006)
- [14] T.H. Chuang, H.J. Lin, *J. Electron. Mater.* **38**, 420 (2009)
- [15] H.Z. Huang, X.Q. Wei, L. Zhou, X.D. Liu, G.L. Guo, *Acta Metall. Sin. (Engl. Lett.)* **19**, 251 (2006)
- [16] K.L. Lin, T.P. Liu, *Oxid. Met.* **50**, 255 (1998)
- [17] T.C. Chang, J.W. Wang, M.C. Wang, M.H. Hon, *J. Alloys Compd.* **422**, 239 (2006)
- [18] M.L. Huang, N. Kang, Q. Zhou, Y.Z. Huang, *J. Mater. Sci. Technol.* **28**, 844 (2012)
- [19] M. Kitajima, T. Shono, *FUJITSU Sci. Technol. J.* **2**, 225 (2005)
- [20] M. Hansen, *Constitution of Binary Alloys*, 2nd edn. (McGraw-Hill Book Co., New York, 1958)
- [21] K.L. Lin, L.H. Wen, T.P. Liu, *J. Electron. Mater.* **27**, 97 (1998)
- [22] J. Han, H. Chen, M. Li, *Acta Metall. Sin. (Engl. Lett.)* **25**, 214 (2012)
- [23] J.W. Martin, *Precipitation Hardening*, 2nd edn. (Butterworth-Heinemann, London, 1998)
- [24] A.A. El-Daly, A.M. El-Taher, *Mater. Des.* **47**, 607 (2013)
- [25] G. Li, Y. Shi, H. Hao, Z. Xia, Y. Lei, F. Guo, *J. Alloys Compd.* **491**, 382 (2010)