[Technical Paper]

Effects of Bismuth in Sn-Cu Based Solder Alloys and Interconnects

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Abstract

Additions of 1.5wt%Bi to Sn-0.7wt%Cu-0.05wt%Ni (SN100C) were investigated for their influence on mechanical properties and the intermetallic (IMC) layer formed between the solder and Cu substrates. Solder balls of Sn-0.7wt%Cu (Sn07Cu), SN100C, Sn-0.7wt%Cu-0.05wt%Ni-1.5wt%Bi (SN100CV) and Sn-3wt%Ag-0.5wt%Cu (SAC) were reflowed onto Cu ball grid arrays (BGAs). They were examined in the as reflowed condition and after a heat treatment of annealing at 150°C up to 1,500 hours. The mechanical properties of SN100C, SN100CV and SAC solder balls were investigated by nano-indentation, and cross-sections of the interfacial IMC layer were observed by SEM to determine the morphology and average interfacial IMC layer thickness. It was found that the effect of Bi additions was to increase the lattice parameters and alter the mechanical properties. The near-eutectic microstructure and suppression of Cu₃Sn at the IMC layer that are associated with Ni additions are not altered by the presence of 1.5wt%Bi.

Keywords: Lead-free Solders, Solid Solution Strengthening, Intermetallics, Hardness, Elastic Modulus, Ball Grid Arrays, Nano-indentation

1. Introduction

Sn-0.7wt%Cu-0.05wt%Ni (SN100C) is a well-known standard solder alloy used in Pb-free soldering. While it exhibits good soldering properties due to its eutectic microstructure,[1, 2] stable (Cu,Ni)₆Sn₅ intermetallics (IMCs) [2–7] and suppression of Cu₃Sn growth,[2] further modifications in terms of increasing hardness via elemental additions could potentially improve performance during thermal cycling. In general, to improve the performance of Sn based solders in thermal cycling, a barrier to the move-

ment of dislocations through the bulk of the solder alloy is required. This can be achieved through solid solution strengthening. Bismuth (Bi) is known to be an element that can improve the mechanical properties of tin due to solid solution strengthening.[8, 9] However, little research has been presented on the effect of Bi in Sn-Cu alloys. The main Sn-Cu alloy used for Pb-free soldering is Sn-0.7Cu (Sn07Cu) and a common commercial variant in this system is SN100C (also containing Ni as shown in Table 1). Hence, minor additions of Bi (1.5 wt. %) were added to

Table 1 Sample nominal compositions and testings.

Samples	Nominal compositions	Testings		
		Lattice parameters	Mechanical properties	IMC thickness
Sn	Sn	x		
Sn07Cu	Sn-0.7wt%Cu			x
SN100C	Sn-0.7wt%Cu-0.05wt%Ni	x	x	x
SN100CV	Sn-0.7wt%Cu-0.05wt%Ni-1.5wt%Bi	x	x	x
SAC	Sn-3wt%Ag-0.5wt%Cu		x	x

SN100C to investigate the solid solution strengthening effects on these alloys.

2. Experimental Procedure

2.1 Samples

Table 1 shows the list of samples with nominal compositions and details the characterisation that was performed for each sample. Tin lattice parameter measurements were conducted for 3N Tin (Sn), Sn-0.7wt%Cu-0.05wt%Ni (SN100C) and Sn-0.7wt%Cu-0.05wt%Ni-1.5wt%Bi (SN100CV) samples. Mechanical property experiments were for SN100C, SN100CV and Sn-3wt%Ag-0.5wt%Cu (SAC) samples, then Cu_6Sn_5 and Cu_3Sn intermetallics (IMCs) thickness measurements were for Sn-0.7wt%Cu (Sn07Cu), SN100C, SN100CV and SAC samples.

2.2 Lattice parameter measurements

Sn (99.9%), SN100C and SN100CV 30 μm powders supplied by Nihon Superior Co. were tested at the Australian Synchrotron by XRD (beam energy = 16.01 KeV). The reference data was collected at 25°C. This was followed by a thermal profile from -100 to 200°C with data collected at 10°C intervals. Rietveld refinement was performed with the software TOPAS v4.2 and calibration of a LaB_6 standard was used to fix the wavelength, zero error and instrument effect on the peak shape. R_{wp} values below 10 were obtained for each refinement to ensure accuracy of the fit. The CTE values were calculated on the difference in the lattice parameters measured between adjacent temperature steps. (10°C intervals).

2.3 Annealed BGA ball sample preparation for mechanical properties of solders and IMC thickness

Samples were 500 μm diameter BGA balls of SN100C, SN100CV and SAC supplied by Nihon Superior Co. The solder reflow temperature profile used in preparing the solder joints is shown in Fig. 1. The sample solder balls

were placed on a Cu substrate printed circuit board (PCB) with an organic soldering preservative (OSP) surface finish and were solder reflowed for 127s with 250°C maximum temperature with the aid of small amount of flux using a desktop reflow oven with N_2 gas flow. The soldered samples were then annealed at 150°C for 0, 500, 1,000 and 1,500 hours. Cross-sectioned samples were tested for hardness and elastic modulus using nano-indentation, and had the IMC thickness characterised as described below.

2.4 Hardness and elastic modulus

The mechanical properties (hardness and elastic modulus) of the Sn phase in solder balls with different solder compositions (SN100C, SN100CV and SAC) were tested along with the effect of heat treatment on these properties. The experiments were performed using nanoindentation using a Triboindenter (Hysitron Inc., Minneapolis, MN) equipped with a three-sided Berkovich indenter with a nominal radius of 100 nm and a total included angle of 142.3°. The polished samples were observed using the optical microscope associated with the Triboindenter. The indentations were made in tin-rich regions avoiding intermetallic precipitates. A peak load of 400 μN was used and at least 20 indents were made for each sample.

2.5 IMC formation and growth

Cross sectional microstructure at the interface of the solder joints were observed and analysed. The effect of aging at 150°C on the thickness of Cu_6Sn_5 and Cu_3Sn in three different Sn solder alloys (SN100C, SN100CV and SAC) was observed. The thickness of the IMC for each sample was analysed from three images of three different areas to get the average thickness of the IMC layer across the joint. The images were taken using a backscattered Scanning Electron Microscope (SEM) to enable contrast between different layers and facilitate image analysis.

Fig. 1 Reflow temperature profile for BGA balls of Sn07Cu, SN100C, SN100CV and SAC samples.

3. Results and Discussion

3.1 Lattice parameter

Solid solution hardening is a type of technique to improve the strength of a pure metal by alloying with additional elements that occupy the crystalline lattice of the base metal, forming either a substitutional or interstitial

solid solution.[10] The local nonuniformity in the lattice due to the alloying element makes plastic deformation more difficult by impeding dislocation motion. In contrast, alloying beyond the solubility limit can form a second phase, leading to strengthening via other mechanisms (e.g. the precipitation of intermetallic compounds). Figure

Fig. 2 XRD results of Sn, SN100C and SN100CV. (a) Sn lattice parameter 'a', (b) Sn lattice parameter 'c', (c) Sn cell volume, (d) Sn c/a lattice parameter ratio, (e) Sn linear CTE along axis 'a', (f) Sn linear CTE along axis 'c'.

2 shows XRD results with respect to the temperature profile: (a) Sn lattice parameter 'a', (b) Sn lattice parameter 'c', (c) Sn cell volume, (d) Sn c/a lattice parameter ratio, (e) Sn linear CTE along axis 'a', (f) Sn linear CTE along axis 'c'. All graphs are consistent with the legend shown in (a). Sn data is overlapped by SN100C data in graphs (a)–(d).

Comparison of SN100C with Sn shows no significant difference in the lattice parameters of the Sn phase, which may be due to the minor alloying additions in SN100C not dissolving into the Sn lattice. Comparison of SN100CV with Sn shows the added 1.5wt%Bi is in solution in the Sn phase, increasing the lattice parameters. Lattice parameter 'a' increases by approximately 0.07% and 'c' increases by approximately 0.05%. The addition of 1.5wt%Bi reduces the c/a ratio, meaning the anisotropy of the crystal structure is increased, compared to pure Sn. No new Bi phase is detected in SN100CV in the temperature range of -100 to 200°C . 1.5wt%Bi has negligible effect on the linear coefficients of thermal expansion (CTE) along the 'a' and 'c' axes. The βSn solidus line in Sn-Bi alloys has been re-measured recently and confirmed that the maximum solubility of Bi in βSn at the eutectic temperature (138.5°C) was 20.6%Bi.[11] Figure 2 demonstrates that 1.5wt%Bi addition was in solution in the Sn phase and increased the lattice parameters of Sn. It is noted that a Sn07Cu alloy was not included in the experimental matrix for this study as Ni is known to have zero solubility in Sn.[1, 2]

The source of the discontinuity in the linear CTE in Fig. 2 (e) Sn, axis 'a' and (f) Sn axis 'c' at around 80 – 90°C in all three alloys is unclear however it is likely to be an aberration of the method of calculation (coarse temperature step) and may have no physical significance.

3.2 Hardness and elastic modulus

Hardness, elastic modulus and creep performance of

hypoeutectic and hypereutectic Sn-Bi alloys have been evaluated and compared with that of the eutectic structure, by using a nanoindentation constant strain rate technique. [12] The concentrations of the Sn-Bi alloys under evaluation in reference[12] were Sn-3Bi, Sn-10Bi, Sn-50Bi, Sn-57Bi (eutectic) and Sn-70Bi. Solid solutions of Sn-Bi alloy with Bi concentrations up to 10 wt% showed a much higher hardness and modulus than the Sn matrix. Small amounts of Bi precipitates at or near grain boundaries of the Sn-rich phase effectively enhance the hardness and creep resistance of the alloy while having little effect on the elastic modulus. For Sn-Bi alloys with a Bi concentration greater than 10%, three stress regions are generally identifiable, which are dominated by different rate-controlling mechanisms respectively in the explored stress range from 90 to 450 MPa. The eutectic alloy with the lowest creep resistance shows the lowest transition stress; while the Sn-10Bi alloy shows the highest transition stress. At the high stress region (>370 MPa), dislocation glide dominates the deformation of the Sn-Bi alloys with a stress exponent greater than 10. At the intermediate stress region (200–370 MPa), dislocation climb is the dominant creep mechanism with stress exponents of 5–8. When a fine lamellar structure is the main constituent microstructure, phase boundary sliding is identified as the rate-controlling mechanism in the low stress region (<200 MPa). The steady-state creep properties of Sn-1wt%Bi, Sn-2wt%Bi, and Sn-5wt%Bi have also been investigated.[13] An equation was employed to describe steady-state creep where at low strain rates there is linear stress dependence and at high strain rates there is an exponential stress dependence. Observations suggested that for Sn-xBi alloys ($x = 1, 2, 5$), dislocation climb is the rate-limiting mechanism in the nonlinear region. The stress sensitivity of the steady-state strain rate data is simi-

Fig. 3 The average (a) hardness and (b) elastic modulus for three series of samples with different heat treatment time. (AR = as reflowed).

lar to that of pure Sn, where dislocation climb is known to be the rate-limiting mechanism. Secondly, primary creep is observed throughout the tested stress range. Thirdly, incremental additions of Bi decrease the steady-state creep rates, even though Bi has a higher diffusivity in Sn than self-diffusion of Sn.

Figure 3 shows (a) the hardness and (b) the elastic modulus of BGA balls of SN100C, SN100CV and SAC. For the as-reflowed samples, SN100C has the lowest hardness value for Sn phase in the solder balls, SAC is in the middle and SN100CV has the highest. The effects of annealing (150°C) are quite different for different solder compositions. For SN100C, the hardness decreases after heat treatment for 500 hours and then increases after 1,000 and 1,500 hours of annealing. Another important phenomenon is that the hardness values are significantly scattered after 1,500 hours of heat treatment. The reasons for this are unclear and may relate to changes in the grain size and interdiffusion of the solder and substrate. In contrast, the hardness values are scattered for the as-reflowed SN100CV sample with the magnitude decreasing and becoming more stable after 1,500 hours of heat treatment, meaning that the microstructure of the Sn phase in SAC solder balls is becoming more uniform. The hardness of SAC samples decreases after 500, 1,000 and 1,500 hours of heat treatment. There is little difference in the elastic modulus between the samples regardless of the heat treatment. The formation of Ag_3Sn in SAC solders does not strictly occur by traditional heat treatment processes. However, most of the existing studies of lead-free solders regard Ag_3Sn as a precipitate phase and therefore the strengthening effect by Ag_3Sn is referred to as “precipitation strengthening” in much of the literature. The arrangement and morphology of the Ag_3Sn phase found in SAC alloys affects their mechanical properties.[14] Further studies relating to grain size, anisotropy and trace element distribution are required to fully understand the behavior of mechanical properties as a function of composition and thermal history.

3.3 IMC formation and growth

Figure 4 shows cross-sectioned BGA balls (Sn07Cu, SN100C, SN100CV and SAC) after 1,500 hr annealing at 150°C. Figure 5 shows (a) The total IMC thickness ($\text{Cu}_6\text{Sn}_5 + \text{Cu}_3\text{Sn}$), (b) the Cu_3Sn thickness, (c) the Cu_6Sn_5 thickness and (d) the ratio of $\text{Cu}_3\text{Sn}/\text{Cu}_6\text{Sn}_5$. The total thickness of the IMC in the as-reflowed samples is 2.67 times thicker for Sn07Cu ($5.67 \pm 0.91 \mu\text{m}$) compared to SN100CV ($2.20 \pm 0.16 \mu\text{m}$) while after 1,500 hours anneal-

Fig. 4 SEM back-scattered images of cross-sectioned BGA balls (Sn07Cu, SN100C, SN100CV and SAC) after 1,500 hr annealing at 150°C.

ing, all sample thicknesses are within 1.27 times with the thickest being SN100CV ($11.56 \pm 0.53 \mu\text{m}$) and thinnest being SAC ($9.10 \pm 1.08 \mu\text{m}$). The $\text{Cu}_3\text{Sn}/\text{Cu}_6\text{Sn}_5$ thickness ratio is significantly reduced in SN100CV and SN100C as shown in Figs. 4 and 5. From Fig. 5(b) it is clear that the thickness of the Cu_3Sn layer is reduced in both SN100C and SN100CV. This is likely an effect of Ni in the SN100C, however, in the SN100CV sample it can be concluded only that Bi does not interfere with the suppression of Cu_3Sn thickness that is associated with Ni. Further studies on the effect of Bi in isolation are required to separate the effect of these two elements.

Fig. 5 (a) The total IMC thickness ($\text{Cu}_6\text{Sn}_5 + \text{Cu}_3\text{Sn}$), (b) the Cu_3Sn thickness, (c) the Cu_6Sn_5 thickness and (d) the ratio of $\text{Cu}_3\text{Sn}/\text{Cu}_6\text{Sn}_5$

4. Conclusions

The benefits of 0.05wt%Ni in Sn-0.7wt%Cu alloy have been well reported in previous studies. The Ni addition refines the microstructure of the solder joint, stabilises the Cu_6Sn_5 and inhibits its growth. The addition of 1.5wt%Bi to the Sn-0.7wt%Cu-0.05wt%Ni system can further improve its behaviour and properties. The benefits of 1.5wt%Bi addition include improving mechanical properties due to solid solution hardening and it is seen that Bi does not interfere with the suppression of Cu_3Sn formation/growth at the Cu substrate and solder interface that is associated with the presence of Ni.

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