Inhibiting Cracking of Interfacial Cu_6Sn_5 by Ni Additions to Sn-based Lead-free Solders

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Abstract

The authors found inhibition of cracking in the interfacial Cu_6Sn_5 intermetallic when Ni containing Sn-0.7Cu alloy was used for soldering. It is thought that this crack inhibition occurred due to the stabilisation of the high temperature hexagonal Cu_6Sn_5 phase through the presence of Ni from a Sn-0.7Cu-0.05Ni solder alloy. To explore the mechanisms associated with the differences in joint integrity, in-situ synchrotron X-ray diffraction (XRD) at the Australian Synchrotron was conducted in the temperature range of 25 to 200°C. The results show that Ni stabilises a high-temperature allotrope of the Cu_6Sn_5 phase, avoiding stresses induced by a volumetric change that would otherwise occur on phase transformation.

Keywords: Lead-Free Solder, Cracking, Intermetallics, Cu_6Sn_5 , Phase Transformation, Synchrotron X-ray Diffraction

1. Introduction

In the last few decades significant research has been directed at developing lead-free solders for the electronics industry.[1] One attractive group of lead-free solder alloys are those based on the Sn-Cu-Ni system which have found applications in wave-, dip-, and iron-soldering processes and are cheaper than most other candidate alloys due to the omission of expensive elements such as silver or rare earths.[2-5] The intermetallic compound (IMC) of Cu_6Sn_5 that forms between Sn-based lead-free solder alloys and Cu substrates influences the soldering process and the subsequent joint properties. Figure 1 shows the Sn-Cu binary phase diagram.[6] Cu_6Sn_5 exists in at least two crystal structures, with an allotropic transformation at temperatures lower than 186°C from monoclinic η' - Cu_6Sn_5 to hexagonal η - Cu_6Sn_5 . [7-9] In conventional Sn-Cu lead-free solder alloys, the brittle Cu_6Sn_5 intermetallic is often associated with the presence of a large number of micro-cracks[10] which may form in response to thermomechanically induced stresses associated with the phase transformation. The authors find that cracking in the Cu_6Sn_5 IMC is inhibited by stabilising the high-temperature hexagonal Cu_6Sn_5 phase with Ni additions.[10-13] The phase stability induced by the presence of Ni in the Cu_6Sn_5 phase and its possible implications are discussed with ref-

erence to the experimental results.

2. Experimental Procedure

2.1 Cracking measurements

The nature of cracking in the reaction layer present in two types of samples, soldered ball-grid-array (BGA) type and dipped Cu plate type interfaces, was investigated. Three compositions of lead-free solder were used, Sn-0.7wt%Cu (SC), Sn-3wt%Ag-0.5wt%Cu (SAC) and Sn-0.7wt%Cu-0.05wt%Ni (SCN). Table 1 shows the chemical composition of the three solder alloys investigated, the soldering methods used, and the solder bath temperatures used for the dip tests. BGA type samples were obtained from 500 μm diameter solder balls on organic solderability protection (OSP) Cu boards with a common reflow process using RMA-type organic flux containing halogen. Figure 2 shows the reflow profile for the BGA process. This cycle was conducted twice for each BGA-type specimen. Dipped Cu type samples were obtained by dipping a Cu plate (C1220P), 10 mm $\times$ 30 mm $\times$ 0.3 mm, with standard Flux B, into a molten solder at 250°C for 10 seconds. Selected samples were subsequently annealed at 120°C for 1000 hours.

All samples were embedded in resin and polished in cross-section to observe the solder joint IMC using SEM/

Fig. 1 (a) Reported Sn-Cu phase diagram and (b) magnified in the Sn-rich corner.

Table 1 Chemical compositions of solder alloys, soldering methods and temperatures.

Sample name	Sample type	Chemical composition	Methods	Temp. (°C)
SC	BGA type	Sn-0.7wt%Cu	Reflow	Max. 250
SAC	BGA type	Sn-3wt%Ag-0.5wt%Cu	Reflow	Max. 250
SCN	BGA type	Sn-0.7wt%Cu-0.05wt%Ni	Reflow	Max. 250
SC	Dipped Cu type	Sn-0.7wt%Cu	Dipped	250
SAC	Dipped Cu type	Sn-3wt%Ag-0.5wt%Cu	Dipped	250
SCN	Dipped Cu type	Sn-0.7wt%Cu-0.5wt%Ni	Dipped	250

Fig. 2 Temperature profile for the reflow process used with the BGA samples.

EDS. The microstructures of the samples were studied using SEM (JEOL JSM-6460LA, Japan) at 20 kV in back-scatter image mode. The crack length and crack number of IMCs were measured by digital imaging using commercial SEM image analysis software, JEOL AnalysisStation.

The crack number and crack length were normalised by the total measured length of the solder joint, which was typically close to 300 μm . SEM/EDS point elemental analysis of Sn, Cu and Ni in the intermetallics layer of the BGA type and dipped Cu type SCN samples was conducted by averaging five measurements with 5at% of Ni present in the intermetallic for each case.[12]

To avoid any mechanical damage during sample preparation the morphology of the Sn-IMC interface of BGA-type samples was observed in secondary image mode after dissolving the tin phase in a solution of 35 g ortho-nitrophenol and 50 g NaOH in 1 liter of water at 80°C.

2.2 Phase stabilisation

To obtain Cu_6Sn_5 and $(\text{Cu},\text{Ni})_6\text{Sn}_5$ particles for these experiments, pre-alloyed Sn-3Cu and Sn-0.7Cu-0.05Ni ingot bars supplied by Nihon Superior Co. were placed in a clay-graphite crucible and heated to 290°C in an electric resistance furnace. The melt was held at this temperature for a minimum of two hours. Using stainless steel cups, approximately 80 g of each alloy was taken from the melt

and allowed to solidify while cooling in air at a rate of $0.5^{\circ}\text{C}/\text{sec}$. Approximately 30 g of the solid sample was placed in a solution of 35 g of ortho-nitro-phenol and 50 g of NaOH in 1 liter of water at 80°C for twenty four hours during which all the Sn phase was dissolved. The remaining eutectic Cu_6Sn_5 and $(\text{Cu},\text{Ni})_6\text{Sn}_5$ particles were then collected using a paper filter, rinsed in ethanol, and dried. TEM-EDS elemental point analysis results from the central region of seven independent $(\text{Cu},\text{Ni})_6\text{Sn}_5$ particles showed an average Ni content of 5.1at%. [10]

The samples were crushed in an agate mortar to obtain powder for the X-ray diffraction (XRD) experiments. The samples were powdered and loaded into a quartz capillary sample cell ($0.3\text{ }\mu\text{m}$ in diameter) in preparation for exposure to temperatures between 25 and 200°C in the Powder Diffraction beam line at the Australian Synchrotron. XRD measurements were performed using 15 kV in the 2θ range 10 to 60 degrees to obtain peak counts. Samples were kept at 25°C (room temperature) for 40 min then 20min for measurement (total 60 min), then heated using a hot-air stream from 25 to 120, 150, 180, 190 and 200°C at a rate of $6^{\circ}\text{C}/\text{min}$. The experimental conditions are shown in Fig. 3. The samples were maintained at each experimental temperature for 40 min for stabilisation purposes followed by 20 min for data collection. For calibration, a Si standard (NIST600C) cell was measured at room temperature for 5 min and an empty capillary cell was measured for 5 min at each experimental temperature. The wave length calibrated by the Si standard at room temperature is 0.082708 nm. The phase identification and volume fraction of monoclinic and hexagonal Cu_6Sn_5 was estimated using X-ray peak data obtained from the Cu_6Sn_5 sample at each temperature using the EVA X-ray diffraction analysis software (Bruker-AXS, Germany). As a reference crystallography, the ICDD (International Centre for Diffraction Data)

Fig. 3 Temperature profile used in the synchrotron XRD experiments.

number of 045-1488 (for Monoclinic)[7] and 047-1575 (for Hexagonal)[14] were used in association with the EVA.

3. Results and Discussion

3.1 Observation and quantification of cracking at the soldered interface

Figures 4 to 6 show SEM micrographs of (a) cross-sectioned BGA-type samples and (b) the Sn-IMC interfaces of the SC, SAC, and SCN, respectively. Arrows in the figures indicate cracking. Cracks can be seen in the IMC layer between the solder alloy and the Cu substrate on the SC and SAC alloys but there are few cracks visible in the SCN alloys where Ni is present at 5at%. It is conceivable that the observed cracking is influenced by sample preparation (sectioning, grinding, and polishing), because the hard, brittle IMC phases are embedded in the soft Sn and Cu matrix. However, the specimen preparation procedures were the same in all cases in this study and systematic variations in cracking propensity were measured for differ-

(a)

(b)

Fig. 4 (a) Cross-sectional SEM image of BGA-type SC sample. (b) Sn-IMC interface SEM image of BGA-type SC sample (chemically prepared).

(a)

(b)

Fig. 5 (a) Cross-sectional SEM image of BGA-type SAC sample. (b) Sn-IMC interface SEM image of BGA-type SAC sample (chemically prepared).

(a)

(b)

Fig. 6 (a) Cross-sectional SEM image of BGA-type SCN sample. (b) Sn-IMC interface SEM image of BGA-type SCN sample (chemically prepared).

ent solder alloy compositions. In addition, Figs 4 to 6 show SEM micrographs with the same apparent trend in cracking, and these samples were regions of the Sn-IMC interface prepared using a deformation-free chemical method.

Figure 7 shows SEM micrographs of cross-sectioned, dipped Cu-type samples and dipped Cu samples that have undergone a subsequent anneal at 120°C for the alloys SC, SAC and SCN, respectively. It is noted that all the cracks formed in the IMC layer are nearly parallel to the Cu substrate, but none are perpendicular or present in other directions. This tendency may be due to the direction of growth of the IMC[15] as determined by the interface crystallography, or possibly due to thermal conditions combined with a preferred habit plane for cracking, or it may be otherwise related to the direction of stresses during thermal expansion. It has previously been reported that Cu_6Sn_5 formed at the interface between Sn37Pb solder and a polycrystalline Cu substrate has a strong grain orientation in the directions $\langle 102 \rangle$ and $\langle 101 \rangle$. [16] Further

investigations on the crack orientation are required. The IMC present in this layer is commonly known to be Cu_6Sn_5 and, it is apparent that significantly fewer cracks are present in the Cu_6Sn_5 layer when Ni is present in the solder. According to the literature, a Cu_3Sn layer may be present between the Cu substrate and the Cu_6Sn_5 IMC in all samples; [17] however, this must be very thin and was not detectable in the current study at the limits of SEM magnification. The chemical compositions of the IMCs found in this study are Cu_6Sn_5 and $(\text{Cu},\text{Ni})_6\text{Sn}_5$. It is obvious that the IMC in the SCN samples of BGA and dipped Cu contains about 5at% Ni and is best represented by $(\text{Cu},\text{Ni})_6\text{Sn}_5$. [12] Since the only source of Ni for the SCN samples is in the solder, it is believed that the 5at% Ni migrates from the solder during growth of the IMC layer.

Figure 8 indicates the normalized crack length and crack number in these IMC sample types: (a) BGA-type, (b) dipped Cu-type and (c) dipped Cu-type with subsequent annealing. The IMC layers in the SCN solders,

Fig. 7 Cross-sectional SEM image of Cu dipped-type samples.

Fig. 8 The normalised crack number and length in the IMC layer for (a) BGA-type samples, (b) dipped Cu-type samples, and (c) dipped Cu-type samples after annealing at 120°C. The total measured length of the solder joint for the normalising is typically close to 300 μm .

which contain around 5 at% Ni, experience less cracking than those without Ni in all solder conditions and there are no cracks present in the dipped Cu samples using the SCN solder. Therefore, by including Ni in the solder, cracking in the IMC layer at the interface can be inhibited. In the next section, we use synchrotron powder XRD for Cu_6Sn_5 and $(\text{Cu},\text{Ni})_6\text{Sn}_5$ with 5 at% Ni samples to demonstrate that the mechanism of crack inhabitation is likely to be related to phase stabilisation.

3.2 Crystallography and phase stability of Cu_6Sn_5 and $(\text{Cu},\text{Ni})_6\text{Sn}_5$

Table 2 show the fractional coordinates of (a) hexagonal $\eta\text{-Cu}_6\text{Sn}_5$ ($P6_3/\text{mmc}$) and (b) monoclinic $\eta'\text{-Cu}_6\text{Sn}_5$ ($C2/c$). There are very small differences in the X-ray diffraction peaks between the two except for the strong peak height ratio and the presence of several relatively weak peaks[9] in the 2θ range of 15–30° when using X-ray energy of 15 keV. Therefore, a strong synchrotron X-ray source was required to distinguish between the two allotropes.

To compare the effects of Ni on the crystallography at 120°C, the XRD patterns obtained from the Cu_6Sn_5 and $(\text{Cu},\text{Ni})_6\text{Sn}_5$ samples are shown in Fig. 9(a) and (b). In the figures, each diffraction peak has been indexed according to monoclinic symmetry models (ICDD number of 045-

Table 2 Unit cell-external parameters (fractional coordinates) of (a) hexagonal η -Cu₆Sn₅ (P6₃/mmc) and (b) monoclinic η' -Cu₆Sn₅ (C2/c).

(a) P6 ₃ /mmc					
Atom	Site	Occ	x	y	z
Sn1	2(c)	1	0.333	0.667	0.250
Cu1	2(a)	1	0.000	0.000	0.000
Cu2	2(d)	0.2	0.333	0.667	0.750
(b) C2/c					
Atom	Site	Occ	x	y	z
Cu1	8(f)	1	0.101	0.473	0.202
Cu2	8(f)	1	0.306	0.504	0.610
Cu3	4(a)	1	0.000	0.000	0.000
Cu4	4(e)	1	0.000	0.160	0.250
Sn1	8(f)	1	0.391	0.162	0.529
Sn2	8(f)	1	0.285	0.655	0.358
Sn3	4(e)	1	0.000	0.799	0.250

Fig. 9 (a) XRD peaks of Cu₆Sn₅ sample at 120°C. (b) XRD peaks of (Cu,Ni)₆Sn₅ sample at 120°C.

1488)[7] and the hexagonal structure (047-1575).[14] The XRD peaks for the Ni-free samples in Fig. 9(a) clearly indicate small peaks, which are expected from the monoclinic

phase according to report by Lidin and Larsson.[7] These previous researchers also found two different phases of η^8 -Cu₅Sn₄ and η^6 -Cu₅Sn₄:[8] however, these were not present in this current research with only the η' -Cu₆Sn₅ monoclinic phase being present. Figure 9(b) clearly shows a hexagonal (Cu,Ni)₆Sn₅ structure in a Ni-containing sample but no monoclinic phase was detected.

Figure 10(a) and (b) shows all the temperature diffraction peaks of Cu₆Sn₅ and (Cu,Ni)₆Sn₅ in 2θ between 15 and 20° to magnify the small peaks from the monoclinic phase. In Fig. 10(a), for the Cu₆Sn₅ sample without Ni, there are small monoclinic peaks at 25°C; however, the intensities of the weak monoclinic peaks are higher at 180°C than at 25°C. This suggests the sample at 25°C may contain a mixture of hexagonal and monoclinic as a result of being quenched from 290°C at a cooling rate of 0.5°C/sec and/or during sample preparations at 80°C. XRD analysis showing monoclinic Cu₆Sn₅ in Ni-free alloys has been reported by Ghosh and Asta[9] in samples annealed at 150°C for 80 days. They reported several relatively weak peaks in the 2θ range of 25–50° (at Cu target X-ray energy) clearly characteristic of monoclinic Cu₆Sn₅. In the Ni-containing samples of the present, the XRD pattern from the IMC (Cu,Ni)₆Sn₅ displayed no peaks characteristic of the monoclinic structure at any temperature range between 25 to 200°C as shown in Fig. 10(b). It is concluded that in the current study for this condition, around 5 at% of Ni in Cu₆Sn₅ stabilised the high-temperature hexagonal phase. Furthermore, the cracking of the IMCs in the SC and SAC samples shown in Figs 4, 5 and 7 are possibly related to the phase transformation from hexagonal to monoclinic during cooling and/or annealing at 120°C. Importantly, it is likely that the degree of cracking in the SC and SAC samples and the potential for more cracking during loading depends on the cooling rate, phase transformation kinetics, and the mechanical conditions at the joint, and it is believed that the transformation is incomplete at 25°C.

3.3 The relationship between cracking at the solder joint and the transformation of monoclinic to/from hexagonal Cu₆Sn₅

According to reviews by Laurila *et al.*, [17, 18] during soldering and subsequent cooling, the time available for transformation into the low-temperature monoclinic structure is not sufficient and high-temperature hexagonal Cu₆Sn₅ remains as a metastable phase. If the solder is then held near room temperature, the transformation does not occur easily because of kinetic constraints. Figure 11

Fig. 10 (a) XRD peaks of Cu_6Sn_5 between 15–25° in 2θ for a range of temperatures. Arrows indicate monoclinic peaks. (b) XRD peaks of $(\text{Cu,Ni})_6\text{Sn}_5$ between 15–25° in 2θ for a range of temperatures.

shows analysis results of the volume % of hexagonal Cu_6Sn_5 present as a function of temperature for a Cu_6Sn_5 sample. The analysis indicates around 80–90 vol.% of

Fig. 11 Volume of hexagonal Cu_6Sn_5 vs. temperature for a Ni-free alloy.

Cu_6Sn_5 is hexagonal at 25°C. This means even at the relatively slow 0.5°C/sec cooling rate and subsequent experimental treatment of 80°C for two weeks, the hexagonal Cu_6Sn_5 is still stable. However, importantly, when the structure is at relatively high temperatures, a transformation begins to occur in reasonably short timeframes. Such high temperatures are readily reached in many electronic devices, because of the strong local heating effect of power components. The data of Fig. 11 shows that by 120°C the volume % of hexagonal IMC is zero, which means all the Cu_6Sn_5 has transformed from metastable hexagonal to monoclinic during only the 16 min of heating from 25 to 120°C and subsequent 60 min of measuring at 120°C. With continued heating, there is a further allotropic phase transformation, from monoclinic to hexagonal at 190°C, which is in good agreement with published data from a differential scanning calorimeter (DSC) at a heating rate of 1–5°C/min.[9, 12]

From the reported phase diagram,[17] Cu_6Sn_5 exists in at least two crystal structures with an allotropic transformation from monoclinic η' - Cu_6Sn_5 at temperatures lower than 186°C to hexagonal η - Cu_6Sn_5 . Theoretical ambient temperature densities of monoclinic and hexagonal are evaluated as 8.270 g/cm³ and 8.448 g/cm³, respectively.[9] This means that if the IMC makes a phase transformation from the quenched hexagonal phase to the monoclinic phase during operation, there will theoretically be a 2.15% volume expansion, which would conceivably be accompanied by significant stress in the IMC layer. It is likely that the decreased cracking in $(\text{Cu,Ni})_6\text{Sn}_5$ compared with Cu_6Sn_5 reaction layers is, at least in part, related to the stabilization of hexagonal $(\text{Cu,Ni})_6\text{Sn}_5$ that occurs with Ni additions. The data in Fig. 8 clearly show inhibition of cracking in the Cu_6Sn_5 intermetallic layers with 5at% Ni

present and the fundamental phase stability of Cu₆Sn₅ with 5at% Ni, independently. The lack of phase stability in the Ni-free SAC solder joints may be related to the higher rate of interfacial failure in these alloys.[19] While phase stability, or lack thereof, may be related to joint integrity, this is an area requiring further research and the authors acknowledge there are other changes that may contribute to the mechanical properties of the joint such as the (Cu,Ni)₆Sn₅ grain size,[17, 18, 20] the mechanical properties of (Cu,Ni)₆Sn₅,[21] the thickness of the IMC reaction layer,[18, 20, 22] and also growth orientations of the IMC.[15]

4. Conclusions

A method of limiting cracking in the Cu₆Sn₅ intermetallic compounds found at the interface of lead-free solder alloys and their substrates has been successfully developed by adding small amounts of Ni to a Sn–Cu lead-free solder. The intermetallic layers in Sn–Cu–Ni solders experience less cracking than those without Ni present. Synchrotron XRD was used to show that one role of Ni in these solder alloys is to stabilise the hexagonal (Cu,Ni)₆Sn₅ phase. This phase stabilisation prevents volume changes that may contribute to the cracking process in the IMC layer in Ni-free alloys where the hexagonal-monoclinic transformation occurs at approximately 186°C or at lower temperatures if a metastable hexagonal structure is present. Further research is required to clarify the relationships between the cracking behavior and the phase stability of the Cu₆Sn₅ layer with or without Ni and it is possible Ni has additional roles in improving the mechanical integrity of the solder joint.

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