Influence of cooling conditions on the interfacial Cu₆Sn₅ intermetallic compound in Sn-37Pb/Cu solder joints during reflow

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Abstract. Despite a shift to Pb-free solders in the majority of electronic assemblies, Pb-containing solders are still used in a variety of applications. Recent research has revealed the complexities of the intermetallic Cu₆Sn₅ in terms of its crystal structure and stability when present as the reaction product between Pb-free solders and common substrates. In light of these findings, the effect of multiple reflow cycles with different cooling conditions on the microstructure of the interfacial Cu₆Sn₅ intermetallic compound (IMC) between Sn-Pb solders and Cu substrates was re-examined. For this purpose, the Sn-37Pb (in wt.%) solder was reflowed on a Cu substrate at a temperature of around 240 °C and cooled at a rate of around 30 °C/min under each of two conditions; (i) direct-cooling to room temperature, and (ii) interrupted-cooling with extended isothermal holding periods of 30 and 180 seconds at 140 °C. This second condition was chosen to encourage the polymorphic transformation that occurs in the Cu₆Sn₅ (at an equilibrium temperature of 186 °C) at a temperature which minimises the stresses involved. Smaller cracks and a thinner interfacial IMC layer were observed in the solder joints that were reflowed repeatedly with the interrupted-cooling conditions. However, despite the higher number of cracks in the samples undergoing conventional reflow, the shear strength was not significantly affected.

1 Introduction

Previously, eutectic Sn-37Pb (in wt.%) solder with a melting point of 183 °C found widespread use in the electronic assembly process due to its unique combination of properties and lower cost [1]. However, there are now major restriction on the use of Pb-based solder alloys due to environmental and toxicity concerns [2]. Legislation surrounding the use of Pb-free alloys has granted exemptions [3] for some products whose applications require high long-term reliability, e.g. defense, medical, instrumentation, etc. However, since most electronics companies have already moved towards Pb-free assembly, it is expected that some componentry may be assembled with a combination of both Sn-Pb and Pb-free solders.

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This means the lower melting point Sn-Pb solder joint may be exposed to higher temperatures with multiple thermal cycles in an assembly process designed for Pb-free alloys. One of the major concern with the thermal history during processing is its impact on the stability of the phases of the solder joint, especially the intermetallic Cu₆Sn₅. Above 186 °C the stable form of Cu₆Sn₅ is the hexagonal η phase [4]. At temperatures below 186 °C the stable form of Cu₆Sn₅ is the monoclinic η’ phase [5]. It has been hypothesised that when the Cu₆Sn₅ is constrained within a solder matrix the approximately 2.15% volume change that is associated with the η↔η’ transformation may result in the buildup of stresses that could lead to cracking of Cu₆Sn₅, particularly when the joint is subjected to multiple reflow cycles [6], [7]. Another concern is that coarsening of the Pb phase as a function of time, temperature and mechanical loading, may affect the reliability of the solder joints [8]. Thus, the present study, examines the effect of cooling conditions during the reflow of Sn-37Pb solders on copper (Cu) substrates on the shear strength and initiation of damage in the interfacial intermetallic compounds (IMCs).

2 Materials and Methodology

Solder balls of Sn-37Pb (in wt.%) alloy of approximately 500 μm diameter were reflowed onto 500 μm diameter Cu pads that had an organic solderability preservative (OSP) surface finish. Reflow was carried out in a benchtop reflow simulator with the aid of a small amount of no-clean flux. The time above 220 °C was fixed at ~110 s for all reflow profiles. In the reference reflow profile (see Fig. 1a) the reflowed solder ball cooled from 240 °C to room temperature at a rate of about 30 °C/min.

![Fig. 1.](image)

The cooling rate of 30 °C/min is based on the time-temperature transformation (TTT) curve η↔η+η’ shown in Fig. 2(b) which ensures the solder joint reaches 140 °C prior to the η→η+η’ polymorphic transformation commencing, as determined from the TTT diagram [9]. There will be minimal change in the unit cell volume of Cu₆Sn₅ as it transforms from the η to the η’ form in the temperature range between 140-160 °C as schematically illustrated in Fig. 1(c) [11]. The objective is to confirm that the transformation occurs and to determine the
time required for the completion of the transformation at that temperature. To determine the effect of multiple reflows using the cooling-condition stated in Fig. 1(a), the samples were reflowed 2 and 8 times.

Reflowed samples were cross-sectioned and fine polished perpendicular to the solder/Cu interface. The solder joints were observed using a desktop scanning electron microscope (SEM) (TM3030, Hitachi, Japan). The average thickness of the total IMC layer, \( d_{\text{ave}} \), was determined using the following equation:

\[
d_{\text{ave}} = \frac{A}{L}
\]

where \( A \) is the total hatched IMC area, and \( L \) is the IMC length in the horizontal length of the measurement window. The total crack area was normalized by the total measured area of IMCs in the horizontal length the solder joint, which was typically close to 300 \( \mu \text{m} \). The quantitative image analysis was done using ImageJ software (NIH, USA) [12].

Ball shear tests were performed at a shear speed of 2000 mm/s using a DAGE-4000s bond microtester (Nordson, USA). At least 20 reflowed solder balls were tested for each condition. The hammer height above the substrate was fixed at 50 \( \mu \text{m} \).

The TEM lamella samples were extracted from solder joints using a focused ion beam (FIB) system (FEI Scios Dual-beam FIB/Scanning Electron Microscope, Thermo Fisher Scientific Waltham, MA, USA) and welded with Pt deposition on Cu TEM grids. Energy dispersive x-ray spectroscopy (EDS) mapping was also conducted. TEM characterisation was performed with a JEM-1300NEF (JEOL, Akishima, Japan) at an accelerating voltage of 1250 kV.

3 Results and Discussion

Fig. 2(a, b) show SEM images of the interfacial region of Sn-37Pb/Cu in the single reflowed (1st cycle) and after eight reflow cycles with both direct-cooling (0 s holding at 140 °C) and interrupted-cooling (30 s and 180 s holding at 140 °C). It can be seen that there no obvious differences in the microstructure between the two reflow cooling conditions in the 1st reflow cycle and subsequent reflow cycles. The average interfacial IMC layer thickness growth over multiple reflow cycles is shown in Fig. 2(b). Multiple reflow cycles, in general, increase the interfacial IMC thickness for all cooling conditions. Interestingly, the samples reflowed with interrupted-cooling show less IMC growth after 8 reflow cycles when compared to the direct-cooled samples. As shown in Fig. 2(d), minor cracking was also observed in the interfacial IMC when the solder joints were reflowed repeatedly with longer interrupted-cooling cycles. The results of the shear impact testing at a speed of 2000 mm/s indicate that the variation in reflow cooling conditions does not have any significant effect on the maximum force in Sn-37Pb/Cu solder joints (see Fig. 2(e)). This can be due to the soft Pb distributed along the Cu6Sn5 grain boundaries in the reaction layer [12] that could have accommodated the stress near the IMC area during shear test.

Fig. 2(a) shows the TEM lamella sample that was extracted from the Sn-37Pb/Cu joint after 8 reflow cycles with interrupted-cooling for 180 s at 140 °C. On-zone bright-field TEM images of the sample are shown in Fig. 2(b). As shown in Fig. 2(C), a combination of strong and weak reflections were observed in the selected electron diffraction pattern (SADP) of the chosen Cu6Sn5 grain. The stronger reflections can be indexed as hexagonal \( \eta \)-Cu6Sn5 (P6/mmc) along the [120] zone-axis. The weaker reflections can be indexed as monoclinic \( \eta' \)-Cu6Sn5 (C2\( \bar{1} \)) in the [010]/[0-10] zone-axis. The EDS mapping analysis on the solder joint sample is shown in Fig. 2(d). The formation of the monoclinic phase in the grain shows that the interrupted-cooling for 180 s at 140 °C allows for transformation of the metastable hexagonal structure to a stable monoclinic structure during cooling. Because very minor
cracking was observed in samples held for 180 s, it is assumed the polymorphic transformation has occurred in a controlled fashion in this condition during which the volume change in the unit cell of Cu₆Sn₅ is at a minimum.

**Fig. 2.** Representative backscattered SEM micrographs of cross-sections of Sn-37Pb/Cu after the (a) 1st reflow and (b) 8th reflow cycle; (c) average interfacial IMC thickness; (d) normalized crack area; (e) maximum force in shear impact at a shear speed of 2000 mm/s.

**Fig. 3.** (a) SEM image of the FIB sample obtained from Sn-37Pb/Cu joint after 8 reflow cycles with interrupted-cooling for 180 s at 140 °C; (b) Bright-field TEM image; (c) corresponding selected white circle area diffraction pattern (SADP) in (b); (d) elemental mapping analysis of the FIB sample.
4 Conclusion

The cooling condition with an isothermal holding step of 180 s at ~140 °C during cooling from 240 °C at a cooling rate of 30 °C/min is proposed for Sn-37Pb/Cu solder joints to minimise cracking in solder joints that occurs after exposure to multiple reflow cycles. It is found that multiple reflow cycles with interrupted-cooling cycles are associated with less cracking and thinner IMC layers than what occurs in direct-cooled (uninterrupted) reflow conditions. However, despite the high number of cracks in samples undergoing conventional reflow, the shear strength was not significantly affected in these Pb containing alloys.

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