Controlling bulk Cu₆Sn₅ nucleation in Sn0.7Cu/Cu joints with Al micro-alloying

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Abstract

We show that dilute Al additions can control the size of primary Cu₆Sn₅ rods in Sn-0.7Cu/Cu ball grid array (BGA) joints. In Sn-0.7Cu-0.05Al/Cu joints, the number of primary Cu₆Sn₅ per mm² is ~7 times higher and the mean three dimensional (3D) length of rods is ~4 times smaller than in Al-free Sn-0.7Cu/Cu joints, while the area fraction of primary Cu₆Sn₅ is similar. It is shown that epitaxial nucleation of primary Cu₆Sn₅ occurs on δ-Cu₃₃Al₁₇ or γ₁-Cu₉Al₄ particles, which are stable in the Sn-0.7Cu-0.05Al melt during holding at 250°C. The observed facet relationships agree well with previously determined orientation relationships between δ-Cu₃₃Al₁₇ and Cu₆Sn₅ in hypereutectic Sn-Cu-Al alloys and result in a good lattice match with <=2.5% lattice mismatch on two different interfacial planes.
1. Introduction

In the pursuit of next-generation Pb-free solders, there is ongoing interest in microalloying solders with Al [1-6]. Potential benefits of dilute Al additions include (i) the suppression of nucleation undercooling for βSn in Sn-Ag-Cu [1, 2] and Sn-Ag [3] solders, which has been linked to a reduction in primary (pro-eutectoid) Ag₃Sn blade formation [4] and may have the potential to grain refine the βSn phase in solder joints [5]; (ii) the suppression of Cu₆Sn₅ layer growth on Cu substrates [6]; and (iii) the introduction of small, hard Cu-Al intermetallics that could be harnessed as a dispersion in the βSn matrix to improve the performance and reliability of solder joints [5].

It has also been found that Al additions have a substantial influence on Cu₆Sn₅ in bulk solders [2, 4, 5, 7, 8]. Reeve et al. [5] and Boesenberg et al. [4] found that Cu₆Sn₅ often shared an interface with δ-Cu₃₃Al₁₇ in Sn-3.5Ag-0.95Cu, Kantarcıoğlu and Kalay [2] observed that 0.05 wt% Al additions reduce the size of Cu₆Sn₅ in Sn-3.5Ag-0.9Cu/Cu joints, and McDonald et al. [8] and Xian et al. [7] reported that Al micro-alloying decreased the size of primary Cu₆Sn₅ in hypereutectic Sn-4Cu alloys. The grain refinement and reduced nucleation undercooling of primary Cu₆Sn₅ due to Al additions has been deduced to be due to heterogeneous epitaxial nucleation of Cu₆Sn₅ on either δ-Cu₃₃Al₁₇ or γ₁-Cu₉Al₄ [7]. These two Al-Cu intermetallics have very similar crystal structure [7, 9, 10] and it was shown that both can form interfaces with only ~2.5% lattice mismatch to the first order and second order prism planes of Cu₆Sn₅ (i.e. the {1̅100} and {11̅20}-type planes of Cu₆Sn₅) [7].

The crystallographic study on the nucleation of Cu₆Sn₅ on δ-Cu₃₃Al₁₇ or γ₁-Cu₉Al₄ particles was performed on large (0.5g) samples of Sn-4Cu-xAl and did not involve a solder substrate [7]. Common solders such as Sn-0.7Cu and Sn-3Ag-0.5Cu are
hypoeutectic (i.e. are in the βSn primary phase field of the liquidus projection) and primary Cu$_6$Sn$_5$ can only form if the nucleation undercooling for βSn is sufficiently high. In joints on Cu substrates, primary Cu$_6$Sn$_5$ formation is more complex because Cu-dissolution from the substrate produces a Cu$_6$Sn$_5$ reaction layer and also increases the Cu content in the liquid prior to solidification.

This paper builds on [7] to investigate whether dilute Al additions can be used to control the size of primary Cu$_6$Sn$_5$ in the more complex situation of Sn-0.7Cu/Cu ball grid array (BGA) solder joints. Since primary Cu$_6$Sn$_5$ formation is expected to depend on Cu dissolution from the substrate, the presence of a Cu$_6$Sn$_5$ layer and on Al additions, both (i) Sn-0.7Cu and Sn-0.7Cu-0.05Al freestanding BGA balls and (ii) Sn-0.7Cu/Cu and Sn-0.7Cu-0.05Al/Cu BGA joints are studied.

2. Methods

Sn-0.7Cu and Sn-0.7Cu-0.05Al (in mass%) solder balls were prepared by mixing 99.9 Sn ingots with Sn-10Cu and/or Sn-1Al master alloys in a graphite crucible and heating to 450°C in a resistance furnace. Molten samples were held for 60 minutes before being cast into a steel chill mould. The casts were then rolled down to foil ~30µm thick and punched into Ø1.6mm discs. Utilizing surface tension, ~500µm solder balls were then produced by melting the ~0.5mg discs with RM-5 flux on a hot plate at 350°C.

Using lithography, 0.5mm thick Cu substrates were covered with a solder mask patterned with circular holes 500µm wide. The solder balls were placed on the Cu substrates fluxed with RM-5 flux. Samples were then reflowed through a LFR400HTX TORNARDO reflow oven (Surface Mount Technology, Isle of Wight, UK). The thermal history was recorded by thermocouples attached to the carrier plate on the conveyor, showing that the samples were heated at ~2K/s up to a peak temperature of
248°C, spent ~58 seconds above the Sn-Cu₆Sn₅ eutectic temperature and were cooled at ~4.5K/s from 240-200°C. The joints were washed in ethanol to remove residual flux in an ultrasonic bath for 20 min.

Both freestanding solder balls and BGA joints were solidified in a Mettler Toledo DSC. The solder balls were placed in Al₂O₃ pans and cycled twice with a heating rate of 0.16K/s, a peak temperature of 250°C and a cooling rate of 0.33K/s. Solder joints underwent a final controlled reflow cycle in the DSC following the same thermal profile as the freestanding solder balls.

In order to test whether any solid phases were present at the peak reflow temperature, a holding experiment at 250°C using ~40g Sn-0.7Cu-0.05Al alloy was also performed. The alloy was cast into a cylindrical graphite mould which was then sealed in a quartz tube filled with Ar gas. The sample was then put in a forced air convection oven at 250°C for one week before being cooled at room temperature.

Samples were mounted in Struers VersoCit acrylic cold mounting resin and ground and polished following standard procedures. An Olympus DP70 optical microscope and a Zeiss Auriga field emission gun scanning electron microscope (FEG-SEM) were used to investigate the microstructure. The SEM is equipped with an Oxford Instruments INCA 80mm² x-sight energy dispersive X-ray (EDX) detector and a Bruker electron backscatter diffraction (EBSD) detector. Kikuchi patterns were analysed using Bruker Esprit software.

The three-dimensional morphology of Cu₆Sn₅ was investigated by selectively etching the Sn-0.7Cu and Sn-0.7Cu-0.05Al BGA balls and joints. A solution of 5% NaOH and 3.5% orthonitrophenol in distilled H₂O was used at 60°C for 15~30 min. Only the Sn
matrix was dissolved in the etchant and the single crystal intermetallics (both primary and eutectic) were later tipped onto a stub and studied in the FEG-SEM.
3. Results and Discussion

3.1. Sn-0.7Cu and Sn-0.7Cu-0.05Al BGA balls

Figure 1 shows optical micrographs of cross sections of Sn-0.7Cu and Sn-0.7Cu-0.05Al freestanding solder balls. Primary Cu$_6$Sn$_5$ crystals can be observed clearly in Sn-0.7Cu as labelled by the arrows in Figure 1 (A), but it is not obvious whether there are any primary Cu$_6$Sn$_5$ crystals in the cross section of Sn-0.7Cu-0.05Al in Figure 1 (B). Figure 1 (C) and (D) show typical Cu$_6$Sn$_5$ single crystals after the tin matrix was dissolved. The Cu$_6$Sn$_5$ crystals extracted from Sn-0.7Cu solder balls in Figure 1 (C) are long faceted rods and are clearly a primary (i.e. pro-eutectic) phase. The largest Cu$_6$Sn$_5$ in Sn-0.7Cu-0.05Al are much smaller and only weakly-faceted (Figure 1 (D)). Care was taken to check that no larger Cu$_6$Sn$_5$ crystals exist than the ones shown in Figure 1 (D).

To compare the extracted Cu$_6$Sn$_5$ with eutectic Cu$_6$Sn$_5$, a cross section of a Sn-0.7Cu-0.05Al freestanding ball was shallow etched for <1 min and is shown in Figure 2. From the higher magnification micrograph in Figure 2(B), it can be seen that the eutectic Cu$_6$Sn$_5$ has typical morphologies of both long needles and thin sheets, some of which are as long as ~60 µm. Additionally, in some regions the eutectic morphology is similar to the extracted Cu$_6$Sn$_5$ in Figure 1(D). Therefore, it can be concluded that there is no primary Cu$_6$Sn$_5$ and only eutectic Cu$_6$Sn$_5$ in the Sn-0.7Cu-0.05Al freestanding solder balls.

Table 1. Averaged value and standard deviation of measured area fraction of primary Cu$_6$Sn$_5$ and nucleation undercooling of βSn in BGA balls and joints. Values in brackets are the number of samples measured.

<table>
<thead>
<tr>
<th></th>
<th>Freestanding solder balls</th>
<th>Joints on Cu substrates</th>
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<tbody>
<tr>
<td></td>
<td>Sn-0.7Cu</td>
<td>Sn-0.7Cu-0.05Al</td>
</tr>
<tr>
<td>Area fraction of Primary Cu$_6$Sn$_5$ [%]</td>
<td>0.24±0.11 (15)</td>
<td>N/A</td>
</tr>
<tr>
<td>Nucleation undercooling of βSn [K]</td>
<td>46.3±5.1 (30)</td>
<td>3.6±0.9 (20)</td>
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</table>
Table 1 summaries the measured area fraction of primary Cu$_6$Sn$_5$ in BGA balls. Note that there is zero % primary Cu$_6$Sn$_5$ in Sn-0.7Cu-0.05Al balls. The presence of primary Cu$_6$Sn$_5$ in hypoeutectic Sn-0.7Cu balls is due to a large nucleation undercooling of $\beta$Sn, which was measured to be $46.3 \pm 5.1$ K based on 30 experiments. The mass fraction of primary Cu$_6$Sn$_5$ ($W_{Cu6Sn5}$) in Sn-0.7Cu balls would increase as the $\beta$Sn nucleation temperature ($T_{nuc}^{\beta Sn}$) decreases according to Equation 1:

$$W_{Cu6Sn5} = \frac{c_0 - f(T_{nuc}^{\beta Sn})}{c_{Cu6Sn5} - f(T_{nuc}^{\beta Sn})} \times 100\%$$  \hspace{1cm} \text{Equation 1}$$

Where $c_0 = 0.7$ mass% Cu is the bulk alloy composition, $c_{Cu6Sn5} = 38.7$ mass% Cu is the composition of Cu$_6$Sn$_5$, and $f(T_{nuc}^{\beta Sn}) = 6.5 \times 10^{-9} \times (T_{nuc}^{\beta Sn})^{3.456}$ is the fitted extended liquidus line of Cu$_6$Sn$_5$ from the Sn-Cu phase diagram in [11]. Using Equation 1, there is a driving force to nucleate primary Cu$_6$Sn$_5$ in Sn-0.7Cu once the undercooling reaches 16.9 K and, for the measured nucleation undercooling of $46.3 \pm 5.1$ K, the mass fraction of Cu$_6$Sn$_5$ is predicted to be 0.74 mass% (0.64 vol% Cu$_6$Sn$_5$). The somewhat lower measured area fraction in Table 1 might be due to a required nucleation undercooling for Cu$_6$Sn$_5$, a required growth undercooling for faceted Cu$_6$Sn$_5$ crystal growth and stereology issues related to measuring area fraction in cross-sections through a small number of long rods within a sphere.

The lack of primary Cu$_6$Sn$_5$ in Sn-0.7Cu-0.05Al freestanding balls (Figures 1(B) and 2) is due to (i) the reaction of Al with Cu to form Cu$_x$Al$_y$ intermetallic, reducing the Cu content of the remaining liquid and (ii) the influence of Al on the nucleation undercooling for $\beta$Sn. For example, samples held isothermally at 250°C for one week contained a layer of particles segregated on the top region due to buoyancy as shown in
Figure 3 (A). SEM-EDX measurements of 15 of the largest black particles (e.g. Figure 3 (B)) gave a mean composition of Al-61at%Cu with a standard deviation of 2 at% and no Sn peaks were present in the EDX spectra. Referring to the most recent Al-Cu phase diagram by Ponweiser et. al. [12], this composition is near the centre of the δ-Cu33Al17 phase field.

In addition to causing δ-Cu33Al17 to form, Al additions reduced the nucleation undercooling from 46.3 to 3.6 K (see Table 1), similar to past work [1-3]. With an undercooling of only ~4K, only a very slightly hypoeutectic alloy would form primary Cu6Sn5 and it is not surprising that primary Cu6Sn5 does not form in Sn-0.7Cu-0.05Al freestanding balls. This interpretation is consistent with calculations made using Thermo-Calc software [11], which predicts that δ-Cu33Al17 is a primary phase in Sn-0.7Cu-0.05Al and that Cu6Sn5 only forms before βSn if the nucleation undercooling for βSn is 44K or higher.

3.2. Sn-0.7Cu freestanding balls and Sn-0.7Cu/Cu BGA joints

Examining Table 1, it can be seen that the area fraction of primary Cu6Sn5 is higher in Sn-0.7Cu/Cu joints than in Sn-0.7Cu freestanding balls due to substrate dissolution. Also, it can be seen in Table 1 that the nucleation undercooling for βSn is significantly less in Sn-0.7Cu/Cu joints than in freestanding Sn-0.7Cu balls, which is similar to past studies [13, 14]. The combined influence of Cu dissolution and nucleation undercooling of βSn on the amount of primary Cu6Sn5 that forms in Sn-0.7Cu and Sn-0.7Cu/Cu can be understood from the Sn-rich end of the Sn-Cu phase diagram as shown in Figure 4 using data from reference [11]. Note from Equation 1 that the fraction of primary Cu6Sn5 depends on the difference between the bulk alloy composition, C0, and the extended Cu6Sn5 liquidus line, which implicitly depends on the nucleation
undercooling of βSn. Figure 4 is a plot of the data for the βSn nucleation temperature in Sn-0.7Cu freestanding balls and in Sn-0.7Cu/Cu joints superimposed on the Sn-Cu phase diagram. The liquid composition for Sn-0.7Cu/Cu joints is plotted as \( C_{\text{Liq}} \) at 250°C = ~1.25 wt%Cu which is the maximum composition of the liquid above the Cu₆Sn₅ reaction layer (i.e. assuming complete mixing in the liquid). Although the nucleation undercooling of βSn is smaller in Sn-0.7Cu/Cu joints than in Sn-0.7Cu freestanding solder balls (Figure 4) which would result in less primary Cu₆Sn₅ if the two samples had the same Cu content, the increased Cu content in the joints due to substrate dissolution is a more dominant factor and leads to an increase in primary Cu₆Sn₅ fraction as shown in Table 1. Primary Cu₆Sn₅ formation in joints is further complicated by the fact that a portion of the Cu₆Sn₅ that forms on cooling from the peak temperature grows onto the Cu₆Sn₅ reaction layer and the remainder nucleates and grows in the bulk liquid as primary Cu₆Sn₅ rods.

3.3. Sn-0.7Cu/Cu and Sn-0.7Cu-0.05Al/Cu BGA joints

Figure 5 shows that both Sn-0.7Cu/Cu and Sn-0.7Cu-0.05Al/Cu BGA joints contain primary Cu₆Sn₅ crystals in the bulk solder. Figure 5 (A-B) shows typical BSE micrographs of the two BGA joint systems, where the darker particles are primary Cu₆Sn₅ and the brighter background are tin dendrite and eutectic regions. In Figure 5 (A-B) it can be seen that there are more Cu₆Sn₅ crystals in the Al-containing cross-section. Measurements on 5 joints for each composition gave the number of primary Cu₆Sn₅ crystals per mm² in Sn-0.7Cu-0.05Al/Cu to be ~7 times more than in Sn-0.7Cu/Cu. Figure 5 (C-D) show the top view of partially etched solder joints, revealing Cu₆Sn₅ crystals protruding from undissolved Sn. In both the cross-sections of Figure 5(A-B) and the etched three dimensional (3D) images of Figure 5(C-D), it can be seen that there are significantly more Cu₆Sn₅ rods in the Al containing sample where they
are also thinner. However, whether the Al addition has caused any significant change in Cu₆Sn₅ length is not clear from two dimensional (2D) sections such as Figure 5(A-B) or partially etched images such as Figure 5(C-D). In particular, note that any small Cu₆Sn₅ rods are likely to have been washed away as the tin dissolved in Figure 5(C-D) and this partial etching technique will be biased towards revealing longer Cu₆Sn₅ rods that still are partially-embedded in the tin.

Therefore, to compare the true 3D length of the primary Cu₆Sn₅ in Sn-0.7Cu/Cu versus Sn-0.7Cu-0.05Al/Cu joints, the length of numerous individual extracted Cu₆Sn₅ crystals, e.g. crystals shown in Figure 5(E-F), were measured. 212 Cu₆Sn₅ rods were measured in Al containing joints and 28 Cu₆Sn₅ rods in Sn-0.7Cu/Cu joints in 8 samples of each composition. The data are summarised as a histogram of primary Cu₆Sn₅ rod length in Figure 6. The number of primary Cu₆Sn₅ rods in Figure 6 cannot be used to quantify the number of Cu₆Sn₅ crystals per unit volume because some rods were lost during the etc...hing and washing process. However, the fact that the mean length of Cu₆Sn₅ rods decreased by a factor of ~4 after Al additions is apparent, as are the significantly more numerous Cu₆Sn₅ rods in Sn-0.7Cu-0.05Al/Cu joints. Care was taken to check whether rods had fractured during dissolution and extraction: most ends of the measured rods had the morphology expected of a faceted growth tip rather than a fracture surface. The only exception was that some rods in Sn-0.7Cu/Cu samples were fractured, indicating that the mean Cu₆Sn₅ rod length in Sn-0.7Cu/Cu is actually even higher than that shown in Figure 6. Note also from Figure 6 that, in Sn-0.7Cu/Cu joints and Sn-0.7Cu balls, some Cu₆Sn₅ rods grow to nearly 90% of the solder ball diameter, which was not apparent in 2D sections such as Figure 5(A-B).
A challenge in studying grain refinement of primary intermetallics in solder joints is that additions often affect the volume fraction of intermetallic that forms in addition to their influence on the number of nucleation events. However, in the case of Sn-0.7Cu/Cu and Sn-0.7Cu-0.05Al/Cu joints, the fraction of primary Cu₆Sn₅ is similar with and without the Al additions (Table 1) and it can be concluded that the decreased Cu₆Sn₅ size and increased number of Cu₆Sn₅ crystals (Figure 6) is due to an increased number of Cu₆Sn₅ nucleation events per unit volume with the Al addition.

Figure 5(E) shows a SE-SEM micrograph of typical extracted primary Cu₆Sn₅ crystals in Sn-0.7Cu/Cu joints, showing the long (100s of µm) hexagonal rod morphology. The Cu₆Sn₅ rods in Sn-0.7Cu/Cu joints have similar morphologies to those in the freestanding solder balls as shown in Figure 1 (C). Figure 5(F) shows two types of typical morphologies of primary Cu₆Sn₅ in Sn-0.7Cu-0.05Al/Cu joints. The top two crystals in Figure 5(F) has the morphology of a hexagonal rod similar to those in Sn-0.7Cu BGA balls and joints, while the bottom crystal in Figure 5(F) has an ‘X-shape’. Note that the angle between arms of the X-shape here is quite constant, which is different to the reported X-shape of Cu₆Sn₅ in binary Sn-Cu system [15], where the angles between arms are more random. Note that Figure 5 (E-F) are at the same magnification.

In Table 1, it can be seen that the area fraction of primary Cu₆Sn₅ is similar in joints with and without Al. This shows that substrate dissolution compensates for the Cu that reacts with Al to form δ-Cu₃Al₁₇. Note also that the nucleation undercooling for βSn is similar in Sn-0.7Cu-0.05Al freestanding balls and Sn-0.7Cu-0.05Al/Cu joints, and that the undercooling is less in Sn-0.7Cu-0.05Al/Cu joints than in Sn-0.7Cu/Cu joints.
A quantitative understanding of the combined influence of Cu dissolution and nucleation undercooling of βSn on primary Cu₆Sn₅ formation in Sn-0.7Cu-0.05Al/Cu joints can be obtained from Figure 7, which is based on Thermo-Calc calculations assuming the Sn-Cu-Al phase equilibria in the TCSLD v.3 database [11].

Figure 7 (A) is the Sn-Cu-Al isothermal section at 250°C based on ref [11]. With the TCSLD3 database, Thermo-Calc predicts that β Cu-Al phase (BCC_B2) should be an equilibrium phase at 250°C but, since it was not observed in Sn-0.7Cu-0.05Al/Cu joints, this phase was omitted from the calculations. In Figure 7(A), the “□” symbol denotes the composition Sn-0.7Cu-0.05Al which is in the L+δCu₃₃Al₁₇ two-phase region at 250°C. The relevant L+δCu₃₃Al₁₇ tie line is plotted as a dashed line and the equilibrium liquid composition of freestanding balls at 250°C is marked with a “○” symbol. During reactive dissolution of the Cu substrate, the liquid will become enriched in Cu, following the 250°C contour of the liquidus surface until it reaches the corner of the L+CuₓAlᵧ+Cu₆Sn₅ tie-triangle when the liquid is in equilibrium with both the CuₓAlᵧ particles and the Cu₆Sn₅ reaction layer. This liquid composition is marked with a “△” symbol. Note that Thermo-Calc also predicts that there is a transformation from δCu₃₃Al₁₇ to γ₁-Cu₉Al₄ as the liquid becomes enriched in Cu. However, these phases are crystallographically very similar (as discussed in ref [7]) and it is not important for this paper whether or not δ transforms into γ₁-Cu₉Al₄. Figure 7(B) is a plot of the development of primary Cu₆Sn₅ during cooling from the peak reflow temperature of 250°C for Sn-0.7Cu-0.05Al/Cu joints (assuming a liquid composition marked with a “△” symbol from Figure 7(A)) as well as for Sn-0.7Cu/Cu joints and Sn-0.7Cu and Sn-0.7Cu-0.05Al freestanding balls. The βSn phase has been omitted to calculate the development of primary Cu₆Sn₅ as the liquid supercools with respect to βSn. ‘X’
symbols denote the mean measured nucleation undercooling for βSn in each solder/substrate combination. The Thermo-Calc predictions in Figure 7(B) are in reasonable agreement with our results. For example, primary Cu₆Sn₅ is predicted to form in Sn-0.7Cu but not Sn-0.7Cu-0.05Al freestanding balls, and the fraction of primary Cu₆Sn₅ in Sn-0.7Cu/Cu and Sn-0.7Cu-0.05Al/Cu joints are similar for the levels of undercooling measured.

3.4. Heterogeneous nucleation mechanism of Cu₆Sn₅

Microstructural analysis suggested that the smaller and more numerous primary Cu₆Sn₅ crystals in Sn-0.7Cu-0.05Al/Cu joints (Figure 6) are due to heterogeneous nucleation of Cu₆Sn₅ on δ-Cu₃₃Al₁₇ particles. Figure 8 shows a series of BSE micrographs of primary Cu₆Sn₅ particles in Sn-0.7Cu-0.05Al/Cu containing or sharing an interface with some black particles. These particles have similar morphology to those in the holding sample in Figure 3 and are very likely to be the same δ-Cu₃₃Al₁₇ phase. They are, however, too small for accurate SEM-EDX and it is possible that δ-Cu₃₃Al₁₇ has transformed into γ₁-Cu₉Al₄ as predicted by Figure 7(A). As we have shown previously, the crystallographic similarities between δ-Cu₃₃Al₁₇ and γ₁-Cu₉Al₄ mean that both phases form a similar lattice match to Cu₆Sn₅ and we will refer to the phase as δ-Cu₃₃Al₁₇ for the remainder of this paper.

Examination of cross-sections of Cu₆Sn₅ crystals containing δ-Cu₃₃Al₁₇ showed that there were often reproducible facet relationships between the Cu₆Sn₅ and δ-Cu₃₃Al₁₇ particles. A typical example can be found in Figure 8(E), where the shorter edge (marked by red dashed line) of the rectangular δ-Cu₃₃Al₁₇ is parallel to a Cu₆Sn₅ facet, and the longer edge (blue dashed line) is parallel to the second nearest corners of the
Cu₆Sn₅ crystal. It is possible to infer the Cu₆Sn₅ habit planes at δ-Cu₃₃Al₁₇ - Cu₆Sn₅ interfaces from this commonly-found geometrical observation because hexagonal rods of Cu₆Sn₅ grow with reproducible growth facets. Figure 9 shows the indexing of the facets of a primary Cu₆Sn₅ rod. According to the EBSD pattern in Figure 9(B) and measured unit cell orientation in Figure 9(A), it can be seen that the facets of the hexagonal Cu₆Sn₅ rods are the \{1\overline{1}00\}-type prism planes. In Figure 9(C), the hexagonal facets of an extracted Cu₆Sn₅ rod are labelled as \{1\overline{1}00\}, and the growth direction can be seen to be [0001].

Therefore, the habit plane marked by the short red dashed line in Figure 8(E) is parallel to a \{1\overline{1}00\} of Cu₆Sn₅ and the habit plane marked by the blue dashed line is parallel to a \{1\overline{1}20\} of Cu₆Sn₅. These two families of planes in Cu₆Sn₅ are exactly those found to nucleate on δ-Cu₃₃Al₁₇ and γ₁-Cu₉Al₄ in Sn-4Cu-0.2Al in our previous detailed crystallographic study [7]. Therefore, similar to Sn-4Cu-0.2Al, it can be concluded that a nucleation orientation relationship between δ-Cu₃₃Al₁₇ and Cu₆Sn₅, OR₁, is:

\[ \{1\overline{1}00\}_{\text{Cu₃₃Al₁₇}} \parallel \{1\overline{1}00\}_{\text{Cu₆Sn₅}} \text{ with } [0001]_{\text{Cu₃₃Al₁₇}} \parallel [0001]_{\text{Cu₆Sn₅}} \]

with \{1\overline{1}00\} and \{1\overline{1}20\} as the two interfacial planes (habit planes), using the hexagonal setting for rhombohedral δ-Cu₃₃Al₁₇.

If the rhombohedral setting is used instead for δ-Cu₃₃Al₁₇, the same OR₁ is:

\[ (1\overline{2}10)_{\text{Cu₃₃Al₁₇}} \parallel (1\overline{2}10)_{\text{Cu₆Sn₅}} \text{ with } [1\overline{1}1]_{\text{Cu₃₃Al₁₇}} \parallel [0001]_{\text{Cu₆Sn₅}} \]

with \(1\overline{2}10\) and \(2\overline{1}\overline{1}0\) as the two interfacial planes (habit planes), using the hexagonal setting for rhombohedral δ-Cu₃₃Al₁₇.

A second orientation relationship, OR₂, is also consistent with the facet relationship, as follows:

\[ (1\overline{2}10)_{\text{Cu₃₃Al₁₇}} \parallel (1\overline{2}10)_{\text{Cu₆Sn₅}} \text{ with } [\overline{2}0\overline{2}1]_{\text{Cu₃₃Al₁₇}} \parallel [0001]_{\text{Cu₆Sn₅}} \]
with interfacial plane as $(\bar{1}210)_{\text{Cu}_33\text{Al}_{17}}|\!(\bar{1}210)_{\text{Cu}_6\text{Sn}_5}$ in the hexagonal form;

or $(10\bar{1})_{\text{Cu}_33\text{Al}_{17}}|\!(\bar{1}210)_{\text{Cu}_6\text{Sn}_5}$ and $[1\bar{1}1]_{\text{Cu}_33\text{Al}_{17}}|\![0001]_{\text{Cu}_6\text{Sn}_5}$

with interfacial plane $(10\bar{1})_{\text{Cu}_33\text{Al}_{17}}|\!(\bar{1}210)_{\text{Cu}_6\text{Sn}_5}$ in the rhombohedral form.

Note that the ORs are presented using hexagonal $\eta$-$\text{Cu}_6\text{Sn}_5$ [16, 17] because this phase is expected to have been present during primary $\text{Cu}_6\text{Sn}_5$ prior to superstructure ordering to monoclinic $\eta'$-$\text{Cu}_6\text{Sn}_5$ at lower temperature [18, 19].

The two ORs offer an interesting insight into the ‘X-shape’ of primary $\text{Cu}_6\text{Sn}_5$ crystals in Figure 5(F), which are commonly seen in Sn-0.7Cu-0.05Al/Cu joints and not in Sn-0.7Cu/Cu joints. The acute angle between arms of the ‘X-shaped’ $\text{Cu}_6\text{Sn}_5$ is $70^\circ \pm 2^\circ$ from more than 10 measured crystals similar to that in Figure 5(F). Assuming that the four arms of the X-shape all nucleate on one single $\delta$-$\text{Cu}_{33}\text{Al}_{17}$ particle and the growth direction of the four arms are all $[0001]_{\text{Cu}_6\text{Sn}_5}$, then one of the $\text{Cu}_6\text{Sn}_5$ arms is parallel with $[111]_{\text{Cu}_33\text{Al}_{17}}$, i.e. OR1, and the other nearest arm would be parallel with $[1\bar{1}1]_{\text{Cu}_33\text{Al}_{17}}$, i.e. OR2. Because the rhombohedral $\delta$-$\text{Cu}_{33}\text{Al}_{17}$ has a very nearly cubic unit cell, the angle between $[111]_{\text{Cu}_33\text{Al}_{17}}$ and $[1\bar{1}1]_{\text{Cu}_33\text{Al}_{17}}$ in the rhombohedral unit cell is $\approx 70.5^\circ$, which is consistent with the measured angle between the ‘X-shaped’ $\text{Cu}_6\text{Sn}_5$ arms. Therefore, the formation of the ‘X-shaped’ $\text{Cu}_6\text{Sn}_5$ is likely to be due to multiple nucleation events on a single $\delta$-$\text{Cu}_{33}\text{Al}_{17}$ particle with two different nucleation ORs. Further work is required to prove this idea.

The interfacial planes between $\delta$-$\text{Cu}_{33}\text{Al}_{17}$ and $\text{Cu}_6\text{Sn}_5$ in these ORs give a good planar lattice match with only $\approx 2.5\%$ mismatch as shown in ref [7]. This is consistent with $\delta$-$\text{Cu}_{33}\text{Al}_{17}$ being a potent nucleant for $\text{Cu}_6\text{Sn}_5$ with low interfacial energy and suggests
that the epitaxial nucleation of Cu₆Sn₅ on δ-Cu₃₃Al₁₇ is the main cause of the Cu₆Sn₅ grain refinement. The presence of δ-Cu₃₃Al₁₇ in samples held for one week at 250°C (Figure 3) also shows that δ-Cu₃₃Al₁₇ particles do not fully-melt during reflow with a peak temperature of 250°C and, therefore, δ-Cu₃₃Al₁₇ are present in the liquid prior to primary Cu₆Sn₅ nucleation. The average size of δ-Cu₃₃Al₁₇ in Sn-0.7Cu-0.05Al/Cu joints is ~1µm (Figure 8) and the average size of floating δ-Cu₃₃Al₁₇ particles after one week at 250°C is only slightly larger at ~1-2 µm (Figure 3). This shows that the δ-Cu₃₃Al₁₇ particles are stable in the melt and coarsen particularly slowly, even when in a liquid matrix.

While heterogeneous nucleation on δ-Cu₃₃Al₁₇ seems to be the main cause of Cu₆Sn₅ grain refinement in Sn-0.7Cu-0.05Al/Cu joints, it is probable that other factors play some role. For example, it is not known how Al alters the Cu₆Sn₅-L interfacial energy.
4. Conclusions

The formation of primary (pro-eutectoid) \( \text{Cu}_6\text{Sn}_5 \) rods has been studied in Sn-0.7Cu and Sn-0.7Cu-0.05Al freestanding BGA balls and in Sn-0.7Cu/Cu and Sn-0.7Cu-0.05Al/Cu joints. For a constant reflow profile (time liquid, peak temperature and cooling rate), primary \( \text{Cu}_6\text{Sn}_5 \) formation in the bulk solder is shown to be affected by three main factors:

(i) the increasing Cu content of the liquid due to substrate dissolution
(ii) the change in phase equilibria due to the Al and Cu addition. In particular, the reaction of Al with Cu to form \( \delta-\text{Cu}_{33}\text{Al}_{17} \) in the liquid prior to \( \text{Cu}_6\text{Sn}_5 \) nucleation.
(iii) the degree of nucleation undercooling for \( \beta \text{Sn} \) (similar to large \( \text{Ag}_3\text{Sn} \) blades in SAC solders)

It is demonstrated that the size of primary \( \text{Cu}_6\text{Sn}_5 \) rods in BGA balls and joints can be greatly underestimated by analysing 2D sections and that the true 3D length of primary \( \text{Cu}_6\text{Sn}_5 \) rods can span almost the entire 500µm solder ball in Sn-0.7Cu/Cu joints and Sn-0.7Cu balls.

A key result from this work is that a 0.05wt% Al addition to Sn-0.7Cu solder can significantly reduce the size of primary \( \text{Cu}_6\text{Sn}_5 \) crystals during soldering to Cu substrates. The reduced size of primary \( \text{Cu}_6\text{Sn}_5 \) is accompanied by an increase in the number of \( \text{Cu}_6\text{Sn}_5 \) particles per unit volume and the total fraction of \( \text{Cu}_6\text{Sn}_5 \) is similar in Sn-0.7Cu/Cu and Sn-0.7Cu-0.05Al/Cu joints. The grain refinement mechanism is heterogeneous epitaxial nucleation of \( \text{Cu}_6\text{Sn}_5 \) on \( \delta-\text{Cu}_{33}\text{Al}_{17} \) particles. These phases are found to form interfaces with a lattice mismatch of ~2.5% and it is likely that the nucleation interface is coherent and of low interfacial energy. The \( \delta-\text{Cu}_{33}\text{Al}_{17} \) particles
are found to be stable in the melt at 250°C and, therefore, do not melt during reflow. The size of active $\delta$-Cu$_{33}$Al$_{17}$ nuclei was $<1\mu$m in Sn-0.7Cu-0.05Al/Cu joints and $\delta$-Cu$_{33}$Al$_{17}$ are shown to coarsen very slowly in the melt.

These findings indicate that Al additions might be useful at decreasing the size of primary Cu$_6$Sn$_5$ crystals in BGA/Cu joints.

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6. References

Figure 1. (A)-(B): Typical microstructures of freestanding ~500µm solder balls cooled at 0.33K/s in a DSC. (A) Sn-0.7Cu, (B) Sn-0.7Cu-0.05Al. (C)-(D) Typical extracted Cu₆Sn₅ crystals from freestanding solder balls. (C) Sn-0.7Cu and (D) Sn-0.7Cu-0.05Al. N.B. crystals in (D) are eutectic Cu₆Sn₅.
Figure 2. Typical BSE images of Sn-0.7Cu-0.05Al BGA balls after shallow etching. (A) A whole solder ball and (B) a high magnification micrograph of eutectic Cu₆Sn₅ of similar lengthscale to Fig. 1(D).

Figure 3. (A) Optical image of the top region of a Sn-0.7Cu-0.05Al alloy held at 250°C for one week. (B)-(E) Typical higher magnification BSE micrographs of the δ-Cu₃₃Al₁₇ particles segregated at the top due to buoyancy.
Figure 4. Partial Sn-Cu phase diagram with best-fit extended Cu₆Sn₅ liquidus line based on data from [11]. Measured nucleation temperatures of βSn in ~500µm BGA balls and joints are marked, and boxplots summarise the statistics from >30 experiments. The Sn-0.7Cu/Cu joint data is plotted assuming a liquid composition that is saturated in Cu at the DSC peak temperature.
Figure 5. (A-B) Typical microstructures of ~500µm BGA/Cu joints cooled at 0.33K/s in a DSC. (C-D) Top view of partially etched solder joints. (E-F) Typical extracted primary Cu₆Sn₅ crystals. (A-C,E) Sn-0.7Cu/Cu, (B,D,F) Sn-0.7Cu-0.05Al/Cu.
Figure 6. A histogram of the length of primary Cu₆Sn₅ rods in BGA freestanding balls and BGA/Cu joints cooled at 0.33K/s from 250°C in a DSC. Note that freestanding Sn-0.7Cu-0.05Al balls contained no primary Cu₆Sn₅.
Figure 7. (A) Sn-Cu-Al isothermal section at 250°C based on [11]. (B) Solidification path of primary Cu₆Sn₅ during cooling from 250°C in Sn-0.7Cu-0.05Al, Sn-0.7Cu BGA balls and Sn-0.7Cu-0.05Al/Cu, Sn-0.7Cu/Cu joints.
Figure 8. Typical BSE micrographs of Cu₆Sn₅ particles containing Cu-Al particles in Sn-0.7Cu-0.05Al/Cu joints. Facet relationships between δ-Cu₃₃Al₁₇ particles and Cu₆Sn₅ are drawn in (D) and (E).
Figure 9. (A) BSE micrograph of the cross section of a primary Cu$_6$Sn$_5$ in a Sn-0.7Cu/Cu BGA joint. (B) EBSD pattern of the Cu$_6$Sn$_5$ in (A) which is indexed as hexagonal η-Cu$_6$Sn$_5$ [16,17]. Note that the measured orientation of the unit cell is outlined in (A) showing the facets in the micrograph are $\{1\bar{1}00\}$-type. (C) An extracted hollow Cu$_6$Sn$_5$ hexagonal-rod in Sn-0.7Cu with labelled facets.