Influence of Ni on the refinement and twinning of primary Cu$_6$Sn$_5$ in Sn-0.7Cu-0.05Ni

J.W. Xian$^1$, M.A.A. Mohd Salleh$^2$, S.A. Belyakov$^1$, T.C. Su$^1$, G. Zeng$^{1,3,*}$, K. Nogita$^3$, H. Yasuda$^4$, C.M. Gourlay$^1$

$^1$Department of Materials, Imperial College, London. SW7 2AZ, United Kingdom
$^2$Centre of Excellence Geopolymer and Green Technology, School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), Taman Muhibbah 02600, Jejawi, Arau, Perlis, Malaysia
$^3$Nihon Superior Centre for the Manufacture of Electronic Materials (NS CMEM), School of Mechanical and Mining Engineering, The University of Queensland, 4072 St Lucia, Queensland, Australia
$^4$Department of Materials Science and Engineering, Kyoto University, Sakyoku, Kyoto 606-8501, Japan

Corresponding authors  * j.xian@imperial.ac.uk; ** g.zeng@imperial.ac.uk

Abstract

The influence of Ni on the size and twinning of primary Cu$_6$Sn$_5$ crystals in Sn-0.7Cu-0.05Ni and Sn-xCu (x=0.7, 0.9, 1.1) (mass%) solder joints is studied using synchrotron radiography and SEM-based EBSD. It is shown that the Ni addition does not cause significant refinement of primary Cu$_6$Sn$_5$ if the alloy is fully melted. However, for peak temperatures $\leq$ 250°C relevant to industrial soldering, primary Cu$_6$Sn$_5$ are not completely melted in Sn-0.7Cu-0.05Ni and there are 10-100 times more numerous and smaller crystals than in Sn-0.7Cu. X-shaped Cu$_6$Sn$_5$ crystals with an angle of $\sim$70° commonly formed in Sn-0.7Cu-0.05Ni/Cu joints and are shown to be penetration twins. This type of growth twinning was only found in partially melted samples, both in Sn-0.7Cu-0.05Ni/Cu joints and binary Sn-1.1Cu alloy. The frequency of twinned crystals was significantly higher in Ni-containing solders. The results are discussed in terms of the influence of Ni on the Cu$_6$Sn$_5$ liquidus slope and on the lattice parameters of (Cu,Ni)$_6$Sn$_5$.

Keywords: A. intermetallics; B. twinning; C. crystal growth, joining; F. electron backscatter diffraction
1 Introduction

Pb-free solder compositions commonly contain a dilute Ni addition. For example, the composition Sn-0.7Cu-0.05Ni (mass%) has been in industrial use since 1999 [1], and Ni is increasingly added to Sn-Ag-Cu-X [2] and next-generation solder compositions [3,4]. The addition of Ni significantly affects the intermetallic reaction layers between the solder and copper [5]; a ~500 ppm Ni addition suppresses the formation of the Cu$_3$Sn layer [6–9] and results in a finer and smaller (Cu,Ni)$_6$Sn$_5$ layer after reflow [8,10]. The influence of Ni on the Cu$_6$Sn$_5$ layer has been linked to the substantial solubility of Ni in (Cu,Ni)$_6$Sn$_5$ [6] which can contain up to ~25 at% Ni [11–14]. Ni stabilises the simpler hexagonal polymorph of Cu$_6$Sn$_5$ [15] and improves the high shear rate performance of BGA joints [2,16,17]. Previous work has explored orientation relationships between Cu$_6$Sn$_5$ and the Cu substrate, where the Cu$_6$Sn$_5$ morphology has been shown to depend on the orientation of the underlying copper [18–22]. It has further been shown that Ni can alter the Cu$_6$Sn$_5$ layer growth texture [23].

When tin-based alloys are soldered on copper substrates, Cu dissolution increases the liquid composition such that primary Cu$_6$Sn$_5$ crystals form during solder solidification [24–28] even when Cu-free solders are used [24]. Cu$_6$Sn$_5$ rods can span the entire solder ball diameter [29,30] and large Cu$_6$Sn$_5$ rods have been shown to be deleterious to ball shear impact properties [31]. Similar to the (Cu,Ni)$_6$Sn$_5$ reaction layer, Ni additions significantly influence the formation of primary Cu$_6$Sn$_5$ in the bulk solder. Solders containing nickel usually have significantly smaller and more numerous primary Cu$_6$Sn$_5$ rods/particles in the bulk solder compared with Ni-free solders [14,32–38]; and various papers on Ni-containing solders contain micrographs of primary Cu$_6$Sn$_5$ crystals with an X-shaped morphology [10,39–42].

At present, the mechanism responsible for Cu$_6$Sn$_5$ size refinement is unclear [32] and no explanation was found in the literature for the X-shaped growth of Cu$_6$Sn$_5$ in Ni-containing solders. Therefore, the aims of this work were (i) to quantify the influence of Ni on the size of primary Cu$_6$Sn$_5$; (ii) to uncover the mechanism for the size refinement of Cu$_6$Sn$_5$ due to Ni additions, (iii) to understand X-shaped Cu$_6$Sn$_5$ crystal growth, and (iv) explore links between the size refinement and X-shaped Cu$_6$Sn$_5$ growth in Ni-containing solders. These aims are addressed by combining in situ synchrotron radiography of Cu$_6$Sn$_5$ solidification with post mortem Scanning Electron
Microscopy (SEM)-based Electron Back-Scattered Diffraction (EBSD) and Energy Dispersive Spectroscopy (EDS).

2 Methods

Sn-0.7Cu, Sn-0.9Cu, Sn-1.1Cu and Sn-0.7Cu-0.05Ni solder alloys with compositions in Table 1 were used in this work. Three solder forms were studied: (i) 100µm foils produced by rolling solder ingots; (ii) ~500 µm diameter balls produced by punching foils to discs and remelting under flux; and (iii) commercial solder pastes. Synchrotron radiography of soldering and solidification was conducted on beamlines BL20B2 and XU at the SPring-8 synchrotron in Hyogo, Japan, using techniques described previously [28,32,43]. For freestanding solders, 100µm thick solder foils were held within a polytetrafluoroethylene (PTFE) cavity bounded by a quartz cell with a spacing of ~100µm. A solder foil specimen was inserted into a furnace and heated to 400°C at 0.33 K/s, before being cooled at ~0.33 K/s. The field of view was ~5x5 mm² recorded at 1000 x 1000 pixels at 16 bit-depth, and two samples were placed side by side with each occupying half the field of view. Across the field of view the temperature difference was ~1K. For solder joints, solder paste was used on top of ~100µm thick Copper Organic Solderability Preservative (Cu-OSP) or Electroless Nickel Immersion Gold (ENIG) substrates. The peak temperature was 250°C with a cooling rate of ~0.5 K/s, and the field of view was recorded at 1920x1440 pixels with a pixel size of 0.477µm. In all cases, the radiographs were recorded at 1 frame per second.

To quantify the effect of peak temperature and cooling rate on the size of primary Cu₆Sn₅ in Sn-0.7Cu and Sn-0.7Cu-0.05Ni, ~500µm diameter free standing solder balls, and solder joints made of solder balls and foils were prepared in a Mettler Toledo DSC1 and a LFR400HTX TORNADO reflow oven. Cooling rates of 0.03 and 0.33K/s were applied in the DSC and ~3K/s in the reflow oven. Peak temperatures of 250°C, 300°C and 400°C were studied.

To reveal the 3D distribution of Cu₆Sn₅ crystals in solder joints, βSn was partially etched using a water solution of 5% NaOH and 3.5% 2-nitrophenol. An Auriga field-

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emission gun SEM equipped with an Oxford Instruments INCA x-sight energy dispersive x-ray (EDX) detector and a Bruker electron backscatter diffraction (EBSD) detector was used to study microstructure, compositions and crystallography. EBSD indexing was conducted using the hexagonal Cu$_6$Sn$_5$ phase [44,45] in all cases and to explore the twinning of Cu$_6$Sn$_5$ in Sn-0.7Cu-0.05Ni and Sn-1.1Cu. Note that Ni dissolves in hexagonal Cu$_6$Sn$_5$ as (Cu,Ni)$_6$Sn$_5$, and we refer to this simply as Cu$_6$Sn$_5$ in the rest of the paper.

Synchrotron radiographs were analysed with a combination of Matlab (Mathworks, Natick, MA, USA) and DaVis 8.3 digital image correlation (DIC) software (LaVison Imaging Company, Göettingen, Germany). For stationary Cu$_6$Sn$_5$, Matlab was used to define the solidification time of each pixel in Cu$_6$Sn$_5$ crystals as the sharp change in the intensity vs. time curve of each pixel. The nucleation time of each Cu$_6$Sn$_5$ crystal was defined as the time of the first solidified pixel in that Cu$_6$Sn$_5$ crystal. For moving Cu$_6$Sn$_5$ crystals, shift and rotation correction function in Davis was used to align radiographs accounting for both rotation and translation. The growth of the realigned Cu$_6$Sn$_5$ crystals were then tracked in Matlab. The movement of primary (Cu,Ni)$_6$Sn$_5$ particles due to gravity and liquid flow was analysed using DIC with correlation subset size 161x161 pixels$^2$ and correlation step of 40 pixels.
3 Results and Discussion

3.1 Primary Cu₆Sn₅ formation in bulk solders

Fig. 1 compares the effects of Ni on the formation of primary Cu₆Sn₅ crystals during the solidification of Sn-0.7Cu, Sn-0.9Cu and Sn-0.7Cu-0.05Ni (mass%) bulk solders using in situ synchrotron imaging. The radiographs in Fig. 1(a-c) are at the end of primary Cu₆Sn₅ growth, and the coloured maps in Fig. 1(d-f) are processed images where each Cu₆Sn₅ rod has been segmented and coloured by its nucleation time. Note that t=0s is defined as the last moment prior to βSn nucleation (in undercooled liquid) and ‘hotter’ colours mean that Cu₆Sn₅ nucleation occurs earlier at higher temperatures. The peak temperature was 400°C and the cooling rate was ~0.33 K/s in all three cases. The nucleation kinetics of primary intermetallics were quantified from the radiograph sequences and are shown in Fig. 1(g). It can be seen that new Cu₆Sn₅ crystals nucleate continuously over a range of temperatures during cooling until saturating at a final number density. Note that the finest Cu₆Sn₅ crystals observed in Fig.1 have a length of ~50 μm or a width of ~20μm, which are well above the resolution limit of 5 μm. The final number density of primary Cu₆Sn₅ crystals in Sn-0.7Cu-0.05Ni is slightly higher than that in Sn-0.9Cu and there are approximately 5 times more crystals in Sn-0.9Cu than in Sn-0.7Cu.

In Sn-0.7Cu-0.05Ni, the Ni content in Cu₆Sn₅ rods such as in Fig 1(c) was 7±1 at% Ni (measured by SEM-EDS). The morphology of primary Cu₆Sn₅ was not significantly influenced by Ni in Fig. 1; both with and without Ni, primary Cu₆Sn₅ grew as long rods with near-random rod orientations relative to the field of view. Fig. 1(h-i) show typical SEM images of extracted Cu₆Sn₅ rods and the respective unit cells measured by EBSD. The growth crystallography remains unchanged; the Cu₆Sn₅ grows in the [0001] direction and is bounded by {1010} facets with and without Ni.

It is clear in Fig. 1(g) that the first Cu₆Sn₅ nucleated significantly earlier (at higher temperature) in Sn-0.7Cu-0.05Ni than in Sn-0.9Cu, indicating that Sn-0.7Cu-0.05Ni has a higher Cu₆Sn₅ liquidus temperature. To measure the approximate Cu₆Sn₅ liquidus, ~90g of Sn-0.7Cu-0.05Ni was held in quartz ampoules at various temperatures for 24 hours and was then quenched in water. As shown in Fig. 2, a clear settled layer of Cu₆Sn₅ was present at the bottom of the sample at 262°C, 284°C
and 290°C, and no settled layer was present at 295°C. From a series of such experiments, the Cu₆Sn₅ liquidus temperature of Sn-0.7Cu-0.05Ni was measured to be 292.5 ± 2.5°C. From this it can be seen that the 500 ppm Ni addition moves the alloy into the Cu₆Sn₅ primary phase field and greatly steepens the Cu₆Sn₅ liquidus surface compared with the Cu₆Sn₅ liquidus line in binary Sn-Cu alloys. This is reasonably consistent with predictions from the Thermo-Calc TCSLD3 database [46].

Fig. 3 shows (a) the Sn-Cu phase diagram [46] and (b) the Sn rich corner of the Sn-Cu-Ni liquidus projection using data from [14,47]. The liquid compositions of Sn-0.7Cu-0.05Ni are plotted at various temperatures as an ‘x’ in Fig. 3(b) based on XRF measurements of quenched liquid above the settled Cu₆Sn₅ layers in experiments such as those in Fig.2. Based on Fig. 3(a-b) and Ni contents in Cu₆Sn₅ at different equilibrium temperatures, Fig. 3(c) plots the mass fraction of primary Cu₆Sn₅ versus temperature, assuming that βSn does not nucleate, for the three alloys in Fig. 1 (and Sn-1.1Cu which is discussed later). It can be seen that Sn-0.7Cu-0.05Ni has a high liquidus temperature of ~292.5°C and a much steeper temperature versus mass% primary Cu₆Sn₅ curve than Sn-0.9Cu and Sn-0.7Cu.

The nucleation undercooling of βSn was in the range ~5-25K in synchrotron samples as indicated by the shaded area in Fig. 3(c). At 10K undercooling, Sn-0.7Cu-0.5Ni and Sn-0.9Cu are predicted to have the same mass fraction of primary Cu₆Sn₅ of ~0.4 mass%, and Sn-0.7Cu-0.5Ni has a higher mass% Cu₆Sn₅ than Sn-0.9Cu when the βSn undercooling is smaller than 10K. Sn-0.7Cu is predicted to contain primary Cu₆Sn₅ only when the βSn undercooling exceeds ~15K. Multiple Sn-0.7Cu synchrotron samples were run and one solidified with no primary Cu₆Sn₅ crystals, which is likely to be due to a βSn nucleation undercooling smaller than 15K in that experiment. Thus, the measurements in Fig. 1(g) are in reasonable agreement with the phase diagram calculations in Fig. 3(c). However, the nucleation undercoolings could not be accurately measured in the synchrotron experiment setup used in this work.

The key result in this section is that the Ni addition does not strongly affect the number density of primary Cu₆Sn₅ when bulk alloys are cooled from a peak temperature higher than the Cu₆Sn₅ liquidus temperature.
3.2 Primary Cu$_6$Sn$_5$ in joints on Cu and ENIG substrates

Fig. 4 overviews synchrotron imaging of solder joint solidification on Cu and ENIG substrates. Fig. 4a-b are radiographs of solder joints made of Sn-0.7Cu on Cu and ENIG substrates with a peak temperature of 250°C. The radiographs are at the end of primary Cu$_6$Sn$_5$ growth (t=-1s) in undercooled liquid. It can be seen that most Cu$_6$Sn$_5$ nucleate and grow in the liquid away from the Cu$_6$Sn$_5$ reaction layer and that some Cu$_6$Sn$_5$ grow out from the layer (e.g. in the Sn-0.7Cu/ENIG sample in Fig. 4(b)). Fig. 5(a-b) are processed images of Sn-0.7Cu on Cu and ENIG, and the quantified nucleation kinetics are shown in Fig. 5(c). Each Cu$_6$Sn$_5$ rod has been segmented and coloured by its nucleation time. Note that t=0s is defined as the first frame observed after βSn nucleation and ‘hotter’ colours mean that Cu$_6$Sn$_5$ nucleation occurs earlier at higher temperatures as in Fig. 1. Fig. 5(c) shows, similar to freestanding solders in Fig.1, Cu$_6$Sn$_5$ nucleates over a wide range of temperatures and Fig. 5(a) and (b) show that they only grow in one crystallographic direction, [0001].

Fig. 4c-d are synchrotron radiographs of solder joint solidification of Sn-0.7Cu-0.05Ni on Cu and ENIG with a peak temperature of 250°C. The primary Cu$_6$Sn$_5$ crystals are small and numerous and underwent significant motion due to gravity and convection. The motion was tracked using digital image correlation (DIC) and is shown in Fig. 4(e)-(f), where the arrows are displacement vectors of the crystals based on consecutive frames prior to βSn nucleation. It can be seen that the Cu$_6$Sn$_5$ particles are settling under gravity and are also being swept in a mostly clockwise convective flow.

The final number density of primary Cu$_6$Sn$_5$ in Sn-0.7Cu and Sn-0.7Cu-0.05Ni joints on Cu and ENIG from Fig. 4 are given in Table 2. It can be seen that the number density of Cu$_6$Sn$_5$ crystals in Sn-0.7Cu/ENIG is approximately half that of Sn-0.7Cu/Cu joints, which is related to the larger amount of Cu dissolved from the Cu substrate than Ni from ENIG. This also indicates that dissolved Ni from the ENIG is not effective at triggering primary Cu$_6$Sn$_5$ nucleation events. In contrast, in solders pre-alloyed with Ni, i.e. Sn-0.7Cu-0.05Ni, there are ~10 times more (Table 2) and smaller Cu$_6$Sn$_5$ crystals than in Sn-0.7Cu joints (compare Fig. 4a,b versus Fig. 4c,d). Note that for Sn-0.7Cu-0.05Ni/Cu in Fig.4c, the number density measured in Table 2 is only based on the top half of the sample because the crystals in the bottom half are too small to
quantify with the techniques used. Therefore, the true number density of primary Cu₆Sn₅ in Sn-0.7Cu-0.05Ni/Cu is even higher than in Table 2.

To test the generality of the synchrotron results in Fig. 4 and Table 2, solder foil and BGA joints were studied after reflow soldering in our laboratory. Fig. 6 compares the size and morphology of primary Cu₆Sn₅ crystals cooled from 250°C in 1cm² solder foil joints on Cu substrates. Fig. 6(a) and (b) are typical micrographs of Cu₆Sn₅ crystals, where it is clear that primary Cu₆Sn₅ are significantly smaller in Sn-0.7Cu-0.05Ni/Cu than in Sn-0.7Cu/Cu joints (note the different scale bars in Fig. 6(a) and (b)). The Cu₆Sn₅ size distributions from more than 100 crystals are quantified in Fig. 6(c) and the crystal width/length ratio is shown in Fig. 6(d). It can be seen that the mean crystal length is ~100 times smaller in Sn-0.7Cu-0.05Ni/Cu than in Sn-0.7Cu/Cu when the peak temperature was 250°C.

Fig. 7(a) and (b) show a similar result for freestanding BGA balls of Sn-0.7Cu and Sn-0.7Cu-0.05Ni that were cooled from 250°C: the primary Cu₆Sn₅ are at least an order of magnitude smaller in Sn-0.7Cu-0.05Ni than in Sn-0.7Cu (note the different scale bars in Fig. 7(a) and (b)). Table 2, Fig. 6 and Fig. 7(a) and (b) confirm that the strong grain refinement effect of Cu₆Sn₅ in Sn-0.7Cu-0.05Ni solder and joints is a general phenomenon when the peak temperature is 250°C. In contrast, Ni has no significant grain refining effect on primary Cu₆Sn₅ when freestanding solders are heated to 400°C (Fig. 1) nor when Ni is dissolved in from an ENIG substrate (Fig. 4(b) and Table 2).

Therefore, it seems that the mechanism of primary Cu₆Sn₅ size refinement in Sn-0.7Cu-0.05Ni is related with the partial remelting of Cu₆Sn₅ at 250°C (~40 K below the Cu₆Sn₅ liquidus of Sn-0.7Cu-0.05Ni). To test this interpretation, a further experiment was conducted in which Sn-0.7Cu-0.05Ni solder balls were made by heating balls to 300°C (where all Cu₆Sn₅ melts) with flux and then cooling at either 0.03K/s or ~20K/s. These solder balls containing large or small Cu₆Sn₅ were then soldered to Cu substrates with a peak temperature of 250°C and a cooling rate of ~3K/s in all cases. Typical examples of the resulting joints are shown in Fig. 8(a)-(d). It can be seen that joints made with solder balls initially containing large Cu₆Sn₅, contain large Cu₆Sn₅ after reflow that spans the entire width of the solder joint (Fig. 8(c)); whereas joints made with solder balls initially containing small Cu₆Sn₅, contain numerous small primary Cu₆Sn₅ after reflow (Fig. 8(a) and (b)). This confirms that the mechanism of
Cu₆Sn₅ grain refinement in Sn-0.7Cu-0.05Ni is that pre-existing Cu₆Sn₅ particles are not fully melted during reflow and demonstrates that the size of primary Cu₆Sn₅ in Sn-0.7Cu-0.05Ni can be controlled by controlling the size of Cu₆Sn₅ in the initial solder ball. We note that Cu₆Sn₅ are usually very small in industrial Sn-0.7Cu-0.05Ni/Cu joints because the cooling rate is high in the initial manufacture of solder balls for BGAs, or powder for solder paste.

In contrast, in Ni-free Sn-0.7Cu/Cu joints, primary Cu₆Sn₅ all melts during reflow and the size of primary Cu₆Sn₅ depends only on the reflow profile.

3.3 Twinning in (Cu,Ni)₆Sn₅ and Cu₆Sn₅

A further phenomenon in Sn-0.7Cu-0.05Ni was that the Cu₆Sn₅ crystals were often X-shaped and multi-branched as can be seen in the micrographs in Figs. 4(c), 4(d), 6(b), 7(b), and 8(b). This can be further seen in Fig. 6(d) where the width/length ratio is increased by an order of magnitude in Sn-0.7Cu-0.05Ni, indicating that the shape of primary Cu₆Sn₅ with Ni is more equiaxed and more branched than Cu₆Sn₅ in Sn-0.7Cu/Cu joints.

The formation of branched Cu₆Sn₅ was studied by directly measuring the growth of X-shaped Cu₆Sn₅ crystals in Sn-0.7Cu-0.05Ni/ENIG joints in synchrotron image sequences. Fig. 9(a) shows aligned synchrotron radiographs of a moving crystal in Fig. 4(f) at different times after its nucleation. The moving crystal was aligned and centred using shift and rotation correction function in Davis. The coloured map in Fig. 9(b) has been generated similar to that in Fig. 1 but here each pixel is coloured individually by the time it becomes solid. From Fig. 9(b), it is clear that the X-shaped crystal nucleates from its centre and grows along four directions. Some Cu₆Sn₅ crystals had three branches like the ones shown in Fig. 6(b) and these are likely to have grown along three directions only.

The growth crystallography of X-shaped crystals was explored using extracted crystals such as the one shown in Fig. 10. Fig. 10(a) shows a complete X-shaped Cu₆Sn₅ crystal extracted from a ~Ø500µm Sn-0.7Cu-0.05Ni solder ball and its centre region is magnified in Fig. 10(b). Using EBSD, IPF-Y mapping was performed on the central
area as shown in Fig. 10(c) where the background image is tilt corrected. The measured Cu$_6$Sn$_5$ orientations and corresponding unit cells are superimposed on the crystal in Fig. 10(b). It can be seen that the X-shaped Cu$_6$Sn$_5$ consists of two crystallographic orientations (pink and purple) and the growth crystallography in each arm of the X is the same as that reported previously for hexagonal Cu$_6$Sn$_5$ rods [20,29,30,43,48–51], i.e. growing in the [0001] direction with growth facets of \{10\overline{1}0\}. Fig. 10(d) shows corresponding pole figures of four important planes in hexagonal Cu$_6$Sn$_5$. It can be seen that the two orientations share common \{11\overline{2}0\}, \{10\overline{1}1\} and \{10\overline{1}2\}. From 49 pairs of twinned X-shaped Cu$_6$Sn$_5$ arms, the angle between the two [0001] directions was $\sim70.6\pm0.5^\circ$ and there were always common (shared) \{11\overline{2}0\}, \{10\overline{1}1\} and \{10\overline{1}2\} plane.

The $\sim70^\circ$ angle combined with shared \{11\overline{2}0\}, \{10\overline{1}1\} and \{10\overline{1}2\} common planes is consistent with growth twinning as shown in Fig. 11 based on EBSD measurements. Fig. 11(a) shows an EBSD IPF-X map of the cross section of an X-shaped Cu$_6$Sn$_5$ crystal in Sn-0.7Cu-0.05Ni. Note that apparent X-shaped cross sections were preferentially studied because they have long arms lying in the cross section, which equivalently have <0001> pointing close to the circumference of the pole figure, making it easier to identify common and twin planes as shown in Fig. 11(b). Referring to Fig. 11(a-b), the EBSD mapping plane (i.e. centre of the pole figure) is near-parallel with the marked common plane in the \{11\overline{2}0\} pole figure. The blue and red arrows are along the growth directions <0001> and are superimposed on [0001] poles near the top and right part of the circumference in Fig. 11(b). Two types of twin/interfacial planes are marked in Fig. 11(a) with projected plane normals shown by respective black arrows. Fig. 11(b) shows that the projected twin plane normals are through the common circled \{10\overline{1}2\} and \{10\overline{1}1\} poles, which are necessary conditions for twin planes being the \{10\overline{1}2\} and \{10\overline{1}1\} planes. 20 pairs of Cu$_6$Sn$_5$ crystals with clear boundaries similar to Fig. 11(a) were analysed. 20 out of 20 had \{10\overline{1}1\} as the interfacial plane while 7 out of 20 had \{10\overline{1}2\} coexisting as another interfacial plane. It is very likely that the \{10\overline{1}1\} is the most common twin/interfacial plane, while the \{10\overline{1}2\} twin plane can also coexist with \{10\overline{1}1\}. These two types of twin are common in hexagonal metals [52].
Fig. 11(c) is a low magnification atomic model of Cu$_6$Sn$_5$ growth twinning. The common \{11\overline{2}0\} planes are shown in projection where the two crystal lattices are orientated and coloured according to the IPF-X map in Fig. 11(a) and the macroscopic twin planes are shown. The atoms in Boxes A and B in Fig. 11(c) contain the \{10\overline{1}2\} and \{10\overline{1}1\} twin planes respectively, which are shown in more detail in Fig. 11(d) with two superimposed hexagonal unit cells. This is a type of penetration twinning with two distinct twin planes. If the red and blue rods are perfect single crystals, these twin planes cannot be crystallographically satisfied at the same time because the sum of the $\alpha_1$ and $\alpha_2$ angles in Fig. 11(d), $71.12^\circ+110.06^\circ = 181.18^\circ$ (assuming binary Cu$_6$Sn$_5$ at 250 °C), is larger than $180^\circ$. Note in Fig. 11(d), that the standard twinning angle for the \{10\overline{1}2\} type twin is $180-\alpha_2$, but we use $\alpha_2$ to better indicate the angular mismatch between the two twin types. Since $\alpha_1 + \alpha_2 = 181.2^\circ$ is $1.2^\circ$ from $180^\circ$, it can be compensated by lattice defects/dislocations which enables both \{10\overline{1}2\} and \{10\overline{1}1\} twin planes to coexist in one penetration twinned bicrystal. Coexisting \{10\overline{1}2\} and \{10\overline{1}1\} twins are possible in Cu$_6$Sn$_5$ because this crystal is pseudo-cubic [53], with a $c/a$ ratio of 1.21 which is close to the pseudo-cubic ratio of $\sqrt{3}/2$, $\sim 1.22$.

This type of twinning also led to multi-twinned Cu$_6$Sn$_5$ crystals. An example can be found in Fig. 8(b). Fig. 12 shows that multiple twinning can form following the same twin rules observed in Fig. 11. In Fig. 12(a), the left X-shaped crystal is the same penetration twin-type as Fig. 11 with only two orientations in the arms, while the right crystal has an additional third orientation near the centre of the crystal. The three different orientations are marked ‘1-3’, where ‘1’ and ‘2’ have their [0001] almost in the plane of the screen and ‘3’ has [0001] nearly pointing out of the screen. Fig. 12(b) shows the pole figures of the right multiple twinned crystal. The poles marked with 1 and 2 are the same as ones shown in Fig. 10-11; The [0001] of orientation ‘3’ is also at $70^\circ$ from both ‘1’ and ‘2’, and arm ‘3’ shares common \{11\overline{2}0\} planes with the other two arms respectively. Therefore, the ‘3’rd arm on the right crystal forms the same twinning with arms ‘1-2’, and these three arms are multiple twinned, which is consistent with the morphology of the tri-crystal in Fig. 8(b). Multiple twinning were also found with more than three orientations in one crystal, and each twin segment within each pair was consistent with Fig. 11.
It was found that X-shaped twinned crystals only formed when a peak temperature of \(~250^\circ C\) was used. At peak temperatures of 400°C, freestanding Sn-0.7Cu-0.05Ni solidified with Cu₆Sn₅ that were single crystal hexagonal rods, similar to Fig. 1. This shows that Ni solute is not solely responsible for the twinning and that X-shaped twins are promoted by unmelted Cu₆Sn₅ particles when the peak temperature is \(~250^\circ C\). To prove this concept, a binary Sn-1.1Cu alloy with a liquidus temperature of \(~240^\circ C\) (Fig. 3(a)) was partially melted at 233°C (\(~0.5\) mass% solid in Fig. 3(c)) then cooled at \(~1.8K/s\). The composition of Sn-1.1Cu is shown in Table 1. Twinned X-shaped Cu₆Sn₅ crystals were found in Sn-1.1Cu among a settled layer of intermetallics but the frequency of twinning was \(~53\%\) (10 out of 19), which is much lower than \(~85\%\) (49 out of 58) in Sn-0.7Cu-0.05Ni. Here, the frequency is defined as twinned Cu₆Sn₅ crystals from all analysed touching crystals that seem to have a X-shape cross section. One example is shown in Fig. 13 where the orientations of the two main arms were measured using EBSD. The twinning orientation relationship in binary Sn-1.1Cu is the same as that for Sn-0.7Cu-0.05Ni shown in Fig. 10-11, with twin interfacial planes of \{10\overline{1}1\} and possibly \{10\overline{1}2\}. In Fig. 13, the interfacial planes (shaded) are drawn near the centre of the X-shaped crystal and outlined in the unit cells. The occurrence of twinning in binary Sn-1.1Cu reflowed below the Cu₆Sn₅ liquidus temperature shows that Ni is not necessary for Cu₆Sn₅ growth twinning and confirms that unmelted primary Cu₆Sn₅ particles promote the formation of twinned crystals.

The fact that twinning is more likely to occur when Ni is present might be due to the influence of Ni on the lattice parameters of Cu₆Sn₅. Fig. 11(e-f) shows the influence of Ni and temperature on the c/a ratio and \(\alpha_{1}+\alpha_{2}\) angle (in Fig. 11(d)) using data from ref [45,54]. A temperature change from 30°C to 250°C only yields a marginal \(~0.1^\circ\) difference in the angular mismatch for fixed Ni contents. As more Ni is dissolved, the c/a ratio of Cu₆Sn₅ becomes closer to \(\sqrt{3/2}\) and \(\alpha_{1}+\alpha_{2}\) becomes closer to 180° of pseudo-cubic, improving the angular mismatch between the two twins (zero mismatch occurs at \(~15\) at% Ni at 250 °C). For binary Cu₆Sn₅ (Ni = 0 at%), a \(~1.2^\circ\) mismatch from 180° is sufficiently small for both twin types to coexist, and decreasing this mismatch may promote the increased formation of X-shaped crystals containing two co-existing twin planes.
To further explore the relationship between the Ni content and twinning, EDS measurements were taken along the length of Cu₆Sn₅ arms as shown in Fig. 14(a-b). The Ni EDS map of a multi-twinned Cu₆Sn₅ crystal is shown in Fig. 14(b) where the central area has a higher Ni content than the tips. Fig. 14(c) summarises the Ni content change based on EDS point analysis along the growth directions with a measurement spacing of 1.5 µm and the numbered curves correspond to marked arrows in Fig. 14(a-b). It can be seen that the Ni content generally decreases from ~13at% Ni near the centre of the ‘X’ to ~3at% Ni along the growing arms, but in a few cases the Ni content does not change much, and the mean Ni content remains low at 1-4 at%. Fig. 14(d) shows a weighted interval rank sort (WIRS) plot (developed in ref [55] for the study of microsegregation) of the data in Fig. 14(c) to give an indication of the composition profile along a one-dimensional Cu₆Sn₅ branch. The plot includes more than 240 EDX measurements along Cu₆Sn₅ branches with a 1.5 µm step size. It can be seen that the Sn content in Cu₆Sn₅ is near-constant, and that the Ni content decreases from ~13at% Ni at the start of solidification down to ~0at% Ni. Comparing Fig. 14(d) with Fig 11 (e-f), it can be seen that the Ni content at the centre of X-crystals is ~13 at% Ni which is close to the Ni content (~15 at%) that gives perfectly pseudo-cubic Cu₆Sn₅ at 250°C (the peak reflow temperature) where both {10̅12} and {10̅11} twin planes can coexist without strain or lattice defects.

We note that the common plane in the X-shaped crystals, {11̅20}, is the same as the Cu₆Sn₅-Cu interface plane of the ‘rooftop-type’ Cu₆Sn₅ morphology when Sn is soldered to {100} and/or {111} single crystal Cu substrates [18–22], and both the X-shaped crystals and ‘rooftop-type’ Cu₆Sn₅ have bounding facets of {10̅0}. However, in the case of a ‘rooftop-type’ Cu₆Sn₅ layer, the angle between the Cu₆Sn₅ is 90° or 60° due to the variants of the orientation relationships with Cu whereas, here, the angle between Cu₆Sn₅ is ~70° due to a twin orientation relationship. Note that the branching angle can also be ~40° for in-plane multiple-twinned crystals, e.g. the acute angle between crystal 3 and 5 in Fig. 14(b).
4. Conclusions

The influence of Ni on the solidification of primary Cu₆Sn₅ in Sn-0.7Cu-xNi has been studied in freestanding solders and solder joints on Cu and electroless-nickel-immersion-gold (ENIG) substrates using synchrotron radiography, EBSD and EDS analyses. The refinement and twinning of Cu₆Sn₅ due to a 500ppm Ni addition have been measured and relevant mechanisms explored. The following conclusions can be drawn.

- The 500ppm Ni addition has been shown to only marginally increase the number density of primary Cu₆Sn₅ when the alloy is fully melted at 400°C prior to solidification. Similarly, Ni dissolution from substrates in Sn-0.7Cu/ENIG joints does not refine the primary Cu₆Sn₅ size compared with Sn-0.7Cu/Cu joints. These results prove that Ni solute itself is not the dominant factor in Cu₆Sn₅ refinement in Sn-Cu-Ni solders.
- Ni additions strongly steepen the Cu₆Sn₅ liquidus slope and, in Sn-0.7Cu-0.05Ni, the Cu₆Sn₅ liquidus temperature is ~292.5°C. Therefore, primary Cu₆Sn₅ does not fully remelt at typical reflow temperatures of ≤250°C. As a result, the size of primary Cu₆Sn₅ in Sn-0.7Cu-0.05Ni after solidification strongly depends on the size of preceding primary Cu₆Sn₅ in the original solder ball/paste before melting. In the case of BGA sphere manufacturing, the high cooling rate creates numerous small primary Cu₆Sn₅ that are retained during reflow at 250°C and act as numerous seeds for primary Cu₆Sn₅ growth during cooling. This is the main origin of primary Cu₆Sn₅ refinement in Ni-containing solders.
- X-shaped Cu₆Sn₅ crystals were common in Sn-0.7Cu-0.05Ni. They are observed to grow from the centre of the ‘X’ using synchrotron imaging. EBSD analysis showed that X-shaped Cu₆Sn₅ are a penetration twin with two distinct interfaces, {1012} or {1011}, which generates a fixed branching angle of ~70° around the <1120> twin axis.
- Twinned X-shaped Cu₆Sn₅ crystals were commonly found in Sn-0.7Cu-0.05Ni and were even observed in binary Sn-1.1Cu, provided the peak reflow temperature was below the Cu₆Sn₅ liquidus temperature.
• Cu₆Sn₅ solidification twinning was promoted by Ni additions. The maximum Ni content in Cu₆Sn₅ was shown to be at the centre of the ‘X’ where twinning originates. Reanalysis of past data on the influence of Ni on the Cu₆Sn₅ lattice parameters shows that the Ni content near the centre of twinned ‘X’-crystals gives a c/a ratio that is close to perfectly pseudo-cubic which is expected to facilitate the formation of coexisting \{10\bar{1}2\} and \{10\bar{1}1\} twin planes, that are a key feature of X-shaped penetration twinning.

Acknowledgements

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Table 1: Compositions of Sn-0.7Cu-0.05Ni, Sn-0.7Cu, Sn-0.9Cu and Sn-1.1Cu in mass%, as measured by XRF spectroscopy. Zn, Al, Cd, Ge are all <0.001 mass%.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sn</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Ag</th>
<th>Fe</th>
<th>Sb</th>
<th>Bi</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-0.7Cu-0.05Ni</td>
<td>Bal</td>
<td>0.699</td>
<td>0.053</td>
<td>0.026</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>0.002</td>
<td>0.013</td>
<td>0.004</td>
</tr>
<tr>
<td>Sn-0.7Cu</td>
<td>Bal</td>
<td>0.674</td>
<td>0.002</td>
<td>0.004</td>
<td>0.016</td>
<td>0.003</td>
<td>0.020</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Sn-0.9Cu</td>
<td>Bal</td>
<td>0.852</td>
<td>0.006</td>
<td>0.022</td>
<td>&lt;0.001</td>
<td>0.007</td>
<td>0.006</td>
<td>0.003</td>
<td>0.001</td>
</tr>
<tr>
<td>Sn-1.1Cu</td>
<td>Bal</td>
<td>1.080</td>
<td>0.004</td>
<td>0.013</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>0.018</td>
<td>0.002</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Table 2: Summary of the number density of Cu₆Sn₅ in Sn-0.7Cu/Cu, Sn-0.7Cu/ENIG, Sn-0.7Cu-0.05Ni/Cu, Sn-0.7Cu-0.05Ni/ENIG.

<table>
<thead>
<tr>
<th>Type of solder joint</th>
<th>Cu₆Sn₅ number density, [mm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-0.7Cu/Cu</td>
<td>1769</td>
</tr>
<tr>
<td>Sn-0.7Cu/ENIG</td>
<td>899</td>
</tr>
<tr>
<td>Sn-0.7Cu-0.05Ni/Cu</td>
<td>8595*</td>
</tr>
<tr>
<td>Sn-0.7Cu-0.05Ni/ENIG</td>
<td>7154</td>
</tr>
</tbody>
</table>

*measurement is based on the top half in Fig. 4(c)
Fig. 1 (a)-(c) Synchrotron radiographs of (a) Sn-0.7Cu, (b) Sn-0.9Cu and (c) Sn-0.7Cu-0.05Ni cooled from 400°C at ~0.33K/s. (d)-(f) Processed maps corresponding to (a)-(c) where each Cu₆Sn₅ has been segmented and coloured by its nucleation time. t=0s is the last frame prior to βSn nucleation. (g) Nucleation kinetics of primary Cu₆Sn₅ quantified from (d)-(f). (h-i) Typical extracted Cu₆Sn₅ crystals from Sn-0.7Cu and Sn-0.7Cu-0.05Ni respectively. Unit cell wireframes show orientations measured by EBSD.
Fig. 2 (a) A settled layer of unmelted \((\mathrm{Cu,Ni})_6\mathrm{Sn}_5\) crystals in \(\text{Sn-0.7Cu-0.05Ni}\) held at 262 °C for 24 hours then quenched. (b) The bottom part of samples held at 262 °C, 284 °C, 290 °C and 295 °C. N.B. there is no primary \((\mathrm{Cu,Ni})_6\mathrm{Sn}_5\) at 295 °C.
Fig. 3 (a) Sn-Cu phase diagram from [46] where dashed lines are extended liquidus lines. (b) Sn-rich corner of the Cu-Ni-Sn liquidus projection plotted using data from [14,47]. Datapoints ‘x’ are the measured liquid compositions. (c) Calculated mass fraction of primary Cu₆Sn₅ versus temperature.
Fig. 4 Synchrotron images of (a) Sn-0.7Cu/Cu, (b) Sn-0.7Cu/ENIG, (c) Sn-0.7Cu-0.05Ni/Cu, (d) Sn-0.7Cu-0.05Ni/ENIG cooled at ~0.5K/s from a peak temperature of 250°C. The motion of some Cu₆Sn₅ crystals in (c,d) is tracked in (e,f) using digital image correlation, where yellow arrows are the displacement vectors.
Fig. 5 (a)-(b): Processed maps corresponding to synchrotron image sequences of (a) Sn-0.7Cu/Cu, and (b) Sn-0.7Cu/ENIG from Fig. 4(a)-(b). Each Cu₆Sn₅ has been segmented and coloured by its nucleation time. $t=1\,\text{s}$ is the last frame prior to $\beta\text{Sn}$ nucleation. (c) Nucleation kinetics of primary Cu₆Sn₅ quantified from (a)-(b).
Fig. 6 Quantification of crystal sizes in Sn-0.7Cu/Cu and Sn-0.7Cu-0.05Ni/Cu. (a-b) Deep etched crystals in solder foils. Histogram of the crystal size in the solder foils are shown for (c) Cu₆Sn₅ crystal length and (d) Cu₆Sn₅ crystal width/length ratio.
Fig. 7 Typical primary Cu$_6$Sn$_5$ crystals in freestanding solder balls after cooling at 0.33 K/s from 250 °C.
Fig. 8 Controlling the size of primary Cu$_6$Sn$_5$ in Sn-0.7Cu-0.05Ni / Cu joints. (a) A solder ball was initially fast cooled at ~20 K/s from 300 °C then soldered on Cu with a peak T of 250°C and a cooling rate of ~3K/s. (b) Fine X-shaped and multi-branched primary Cu$_6$Sn$_5$ crystals in (a). (c) A solder ball initially cooled at 0.03K/s from 300 °C then soldered on Cu with a peak T of 250°C and a cooling rate of ~3K/s. A large Cu$_6$Sn$_5$ rod spans the entire joint. (d) Only eutectic Cu$_6$Sn$_5$ exist at higher magnification in (c).
Fig. 9 (a) Aligned images of the X-shaped crystal in Fig. 4(f). (b) The coloured map has been processed with each pixel coloured by the time it becomes solid. Noise has been reduced using a median filter (5x5 pixels).
Fig. 10 (a) An extracted X-shaped Cu₆Sn₅ crystal in Sn-0.7Cu-0.05Ni solder balls. (b) The central part of the crystal with superimposed unit cells. (c) IPF-Y map of the centre superimposed on tilt corrected SE image. (d) Selected pole figures. Circles mark parallel planes.
Fig. 11 (a) EBSD IPF-X map of a sectioned X-shaped Cu$_6$Sn$_5$ crystal. (b) Pole figures of selected planes and directions. Circles mark parallel planes, triangles mark twin interfaces. (c) Atomic model in the common plane. (d) Detailed atomic arrangement and twinning angles of the two twin interfaces \{10\overline{1}2\} and \{10\overline{1}1\}. (e-f) The influence of Ni on the c/a ratio and $\alpha_1+\alpha_2$ at two temperatures using data from Refs [45,54].
Fig. 12 (a) EBSD IPF-X map of sectioned X-shaped Cu₆Sn₅ crystals, the left is a simple X-shaped penetration twin while the right is a multiple twin. (b) Pole figures of the multiple twinning on the right X-shaped cross section.

Fig. 13 Cross section of an X-shaped twinned Cu₆Sn₅ in a binary Sn-1.1Cu alloy, which was partially remelted at 233°C. Wireframe unit cells were measured by EBSD.
Fig. 14 (a) BSE images of X-shaped cross sections. (b) EDS mapping of Ni in a multi-twinned Cu₆Sn₅ crystal. (c) Ni content vs. distance along the arms of X-shaped crystals in Sn-0.7Cu-0.05Ni cooled from 250°C, where the numbered curves correspond to marked arrows in (a-b). (d) Weighted interval ranked sort (WIRS) plot showing the compositional profile along a Cu₆Sn₅ branch.