

Cu₆Sn₅ crystal growth mechanisms during solidification of electronic interconnections

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Abstract

The growth mechanisms of primary Cu₆Sn₅ are studied in Sn-Cu alloys and solder joints by combining EBSD, FIB-tomography and synchrotron radiography. With increasing cooling rate and Cu content, Cu₆Sn₅ crystals developed from faceted hexagonal rods to grooved rods, in-plane branched faceted crystals and, finally, to nonfaceted dendrites. This range of growth morphologies has been rationalised into a kinetic microstructure map. Cu₆Sn₅ hexagonal rods grew along [0001] bounded by {10 $\bar{1}$ 0} facets and Cu₆Sn₅ dendrites branched along <405> in the {10 $\bar{1}$ 0} planes. The faceted to nonfaceted transition indicates a kinetic interface roughening transition and a gradual change in mechanism from lateral growth governed by anisotropic attachment kinetics to continuous growth governed by diffusion and curvature. Finally, it is shown that the full range of Cu₆Sn₅ morphologies that grew for different composition and cooling rate combinations in bulk alloys can be engineered to grow in solder joints made with a single composition (Sn-0.7wt%Cu/Cu) by altering the peak temperature and the cooling rate.

Keywords:

Crystal growth; 3D characterization; EBSD; Soldering; Synchrotron radiation

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1 Introduction

With the miniaturization of Pb-free solder joints, intermetallics occupy an increasing proportion of the solder joint volume and impact more significantly on the reliability of electronics [1]. In some cases, fully intermetallic interconnections are favoured and can be made by micro-bumps or transient liquid phase soldering [2-5]. Cu_6Sn_5 is of particular interest because it is commonly found as primary crystals in the bulk solder and as the interfacial reaction layer in joints between Cu substrates and most Sn-rich solders. Thus, there has been increasing interest in methods to control the size and morphology of primary Cu_6Sn_5 [6-9].

Primary Cu_6Sn_5 has been reported to grow with various morphologies such as needles [10-12], hollow rods [11, 13], X-shapes [9, 14, 15], Y-shapes [8, 9], H- and M- shapes [16, 17] and as dendrites [6, 18]. Since many of these studies have been based on arbitrary 2D cross sections, it is not clear how many of these morphologies are separate growth forms in 3D. The growth direction of the rod-like Cu_6Sn_5 is reported to be [0001] and the growth facets are usually $\{1\bar{1}00\}$ -type Cu_6Sn_5 planes [15, 16, 19, 20]. The crystallographic directions and facets of the other growth forms are not known. Although markedly different primary Cu_6Sn_5 morphologies have been observed [8-11, 13-17], there has been little work on the transitions between these growth forms nor on the mechanisms responsible for the range of Cu_6Sn_5 morphologies.

In this work, we grow primary Cu_6Sn_5 with a wide range of morphologies by altering the Cu content and cooling rate during equiaxed solidification. We characterise the 3D morphology, the crystallographic growth directions and facets, and study the growth mechanisms for each morphology. The results are then rationalised into a kinetic

microstructure map including a faceted to nonfaceted growth transition. Finally, we explore how this understanding can be applied to control the primary Cu_6Sn_5 morphology in Sn-0.7Cu/Cu joints (all compositions are given in wt% unless otherwise stated).

2 Experimental Methods

Alloys containing 0-4.2Cu were prepared by mixing 99.9%Sn with a Sn-10Cu master alloy in a graphite crucible, melting in a resistance furnace and holding at 450°C for 1 hour. The melt was then drawn into borosilicate glass tubes of inner diameter 4 mm with vacuum. 500±0.5 mg samples were made by cutting the resulting rods and Ø500 µm solder BGA balls and joints were made following procedures detailed in [15].

The Sn-xCu alloys were solidified at controlled cooling rates in the range 0.03-100 K/s using the following procedures. 500±0.5 mg samples were first placed in two quartz tubes held vertically at the same level in a forced air convection oven in order to ensure similar thermal profiles. Both samples were melted and held at 450°C before a BN-coated 0.5mm K-type thermocouple was inserted into one of the samples. After 30 min holding at 450°C, the samples were cooled by opening the door to different positions generating different reproducible cooling rates. Faster cooling rates were achieved by submerging the bottom of the quartz tubes in media with higher thermal conductivity, i.e. sand or water. Cooling rates were measured from the cooling curves recorded by the immersed thermocouple and microstructure analysis was performed on the samples without a thermocouple.

For real-time observation by synchrotron radiography at the BL20XU beamline of the SPring-8 synchrotron, Sn-1.1Cu, Sn-4.2Cu and Sn-10Cu alloys were rolled to ~50 µm thickness.

Samples were fixed between two SiO₂ sheets and a ~50 µm thick polytetrafluoroethylene (PTFE) sheet was used as a spacer. The experimental set-up was similar to previous research [7, 10, 21-23] and a 21 keV beam was used. The transmission imaging field of view was 877 µm x 658 µm (1920x1440 pixels) with a resolution of 0.457 µm per pixel. The exposure time was 150ms per frame and the frames were recorded at 6.67 frames per second.

To study primary Cu_6Sn_5 in Sn-0.7Cu/Cu solder joints, samples were held at different peak temperatures ranging from 240°C to 390°C for 5 mins before being cooled at one of two cooling rates. A cooling rate at ~30 K/s was applied by removing a joint from the oven and placing rapidly under an extraction fan. The cooling rate was measured by a thermocouple attached to the Cu substrate near the joint. Cooling at 0.67 K/s was performed in a DSC by heating at 0.33 K/s up to the same peak temperatures, holding for 5 mins and cooling at 0.67 K/s.

Samples were mounted in Struers VersoCit acrylic cold mounting resin and prepared following standard metallographic procedures. A Zeiss Auriga field emission gun scanning electron microscope (FEG-SEM) was used to investigate the cross sections and a Bruker e-Flash electron backscatter diffraction (EBSD) detector and Bruker ESPRIT 2.1 software were used to measure the crystal orientations. For the investigation of the three-dimensional morphology and growth directions of Cu_6Sn_5 , some samples were etched in a solution of 5% NaOH and 3.5% orthonitrophenol in distilled H_2O at 60°C for approximately 15 min to selectively dissolve the matrix βSn . Single crystal intermetallics were then placed on a stub and studied by analytical SEM. For 3-dimensional (3D) characterisation of Cu_6Sn_5 dendrites, ~30x30x50 μm volumes were serially-sliced using a dual column focused ion beam/SEM microscope (FIB-SEM, FEI Helios NanoLab 600). The slice step was 100 nm and the milling current was 2.8 nA. Raw images were segmented using Image J and Matlab, and 3D reconstruction was performed in Avizo 9.

3 Results and Discussion

3.1 Solidification microstructure map for primary Cu_6Sn_5

Fig. 1 shows the range of primary Cu_6Sn_5 growth morphologies that developed in samples with Cu contents in the range 0.7-4.2Cu solidified at cooling rates in the range 0.03-100 K/s. The top row shows the typical appearance of these morphologies in 2D sections. The bottom row shows the equivalent 3D morphologies after selective dissolution of the βSn matrix. These morphologies can be classified into three major categories, (i) faceted hexagonal rods (e.g. Fig. 1A), (ii) grooved and/or branched faceted crystals (e.g. Fig. 1B and C), and (iii) dendrites (e.g. Figs. 1D and E).

Fig. 2A is a solidification microstructure map, summarising the cooling rate and composition combinations where the different primary Cu_6Sn_5 morphologies were observed. It can be seen that faceted growth (e.g. Figs. 1A-C) occurs at fairly slow cooling rates $<\sim 3.7$ K/s, whereas dendritic growth (e.g. Fig. 1D-E) occurs for Cu contents $>2.3\text{wt}\%$ and cooling rates $\geq \sim 3.7$ K/s. This map shows that there is a transition from hexagonal rods to grooved and branched faceted crystals as the Cu content increases from 0.7Cu to 4.2Cu at low cooling rate, and that there is a faceted (blue symbols) to dendritic (red symbols) growth transition with increasing cooling rate in Sn-2.3Cu and Sn-4.2Cu. The growth mechanisms for each morphology and the transitions between them are discussed in sections 3.2-3.4.

Fig. 2A also shows the composition and cooling rate combinations that produced no primary Cu_6Sn_5 (i.e. microstructures that were either fully-eutectic or βSn dendrites plus eutectic). Note in Fig. 2A that, at low cooling rate, some primary Cu_6Sn_5 formed in hypoeutectic compositions (e.g. Sn-0.7Cu at 0.03 K/s) and, at high cooling rate, primary Cu_6Sn_5 did not form in some hypereutectic compositions (e.g. Sn-1.1Cu at >28 K/s). The boundary between

microstructures without primary Cu₆Sn₅ and those containing primary Cu₆Sn₅ can be understood and calculated from cooling curve measurements and a simple competitive solidification model, as shown next.

Fig. 2B is a typical cooling curve and its derivative for a Sn-4.2Cu sample. The release of latent heat as Cu₆Sn₅ nucleates and grows is clearly detected in the green derivative curve in Fig. 2B, and the onset of Cu₆Sn₅ latent heat release, $T_{onset}^{Cu_6Sn_5}$ was found from the departure of the derivative curve from the baseline. Here the measured temperature at which latent heat release was first detected is a combination of the nucleation undercooling and growth undercooling for primary Cu₆Sn₅. The onset of Cu₆Sn₅ latent heat release, $T_{onset}^{Cu_6Sn_5}$ is plotted against cooling rate in Fig. 2D. It can be seen that $T_{onset}^{Cu_6Sn_5}$ decreases strongly with increasing cooling rate. $T_{onset}^{Cu_6Sn_5}$ was converted to an undercooling using $\Delta T_{onset}^{Cu_6Sn_5} = T_{Liq}^{Cu_6Sn_5} - T_{onset}^{Cu_6Sn_5}$ and an empirical exponential fit was found as shown on Fig. 2D.

The nucleation of β Sn and subsequent recalescence is also clearly detected in Fig. 2B and the nucleation undercooling for β Sn, $\Delta T_n^{\beta Sn}$, was defined as the β Sn-Cu₆Sn₅ eutectic temperature (226.9°C) minus the nucleation temperature prior to recalescence. $\Delta T_n^{\beta Sn}$ was found to be relatively high and near-constant at 19-25 K for all compositions and cooling rates studied [24]; any influence of cooling rate on this undercooling was masked by the scatter in the data.

To calculate the boundary between microstructures without primary Cu₆Sn₅ and those containing primary Cu₆Sn₅, the following competitive solidification condition was applied: primary Cu₆Sn₅ forms if it can nucleate and grow before β Sn nucleates. This is equivalent to: Cu₆Sn₅ forms if the primary Cu₆Sn₅ onset temperature is higher than the β Sn nucleation temperature, i.e. if $T_{onset}^{Cu_6Sn_5}$ in Eq. 1 is larger than $T_n^{\beta Sn}$ in Eq. 2.

$$T_{onset}^{Cu_6Sn_5} = T_{Liq}^{Cu_6Sn_5} - \Delta T_{onset}^{Cu_6Sn_5} \quad \text{Eq. 1}$$

$$T_n^{\beta Sn} = T_E - \Delta T_n^{\beta Sn} \quad \text{Eq. 2}$$

Where the Cu_6Sn_5 liquidus temperature, $T_{Liq}^{Cu_6Sn_5}$, was expressed as a function of bulk composition, C_0 , using a polynomial fit to the Sn-Cu phase diagram in Fig. 2C based on ThermoCalc database TCSD3.0 [25], $T_E = 226.9^\circ C$ is the βSn - Cu_6Sn_5 eutectic temperature and $T_{onset}^{Cu_6Sn_5}$ is given by the exponential fit in Fig. 2D. The microstructure transition occurs when $T_{onset}^{Cu_6Sn_5} = T_n^{\beta Sn}$ as given in Eq. 3.

$$T_{Liq}^{Cu_6Sn_5} - 9.411 \left(\frac{dT}{dt} \right)_{crit}^{0.3398} = 226.9 - \Delta T_n^{\beta Sn} \quad \text{Eq. 3}$$

Eq. 3 is plotted on Fig. 2A as two grey curves, one for $\Delta T_n^{\beta Sn} = 19 K$ and one for $\Delta T_n^{\beta Sn} = 25 K$ according to the scattering of the measurement. It can be seen that the calculated transition lines and the experimental data are in reasonable agreement. From this, it can be understood that primary Cu_6Sn_5 forms in Sn-0.7Cu cooled at 0.03 K/s because the βSn nucleation temperature lies below the extended Cu_6Sn_5 liquidus line at this composition and the undercooling for Cu_6Sn_5 is low at this cooling rate. On the other hand, the lack of primary Cu_6Sn_5 in Sn-1.1Cu cooled at >28 K/s occurs because the calculated primary Cu_6Sn_5 onset temperature lies below the βSn nucleation temperature for this combination of composition and cooling rate. In this latter case, once βSn nucleates, either a fully eutectic microstructure or a βSn dendrite plus eutectic microstructure grows depending on the growth competition between a eutectic βSn - Cu_6Sn_5 front and βSn dendrite tips for the combination of undercooling and composition.

3.2 Faceted growth mechanisms

Primary Cu_6Sn_5 grew as faceted crystals when the cooling rate was less than $\sim 4 \text{ K/s}$, as shown in the microstructure map in Fig. 2A. The crystallography of faceted Cu_6Sn_5 growth was found to be similar for hexagonal rods, grooved and branched faceted morphologies. Fig. 3 overviews this for hexagonal rods and branched faceted morphologies using EBSD analysis of extracted crystals that have been laid flat on an SEM stub (imaged in Figs. 3A and D). The stub was then tilted 70° and the EBSD patterns in Fig. 3C and F were collected by a camera with a $\sim 20^\circ$ difference against the tilted SEM stub, so the viewing angle in Fig. 3C and F is slightly different from that in Fig. 3AB and DE. Comparing Fig. 3C and F shows that $\{10\bar{1}0\}$ bands of both crystals are near parallel. The orientations of crystals with respect to sample surface (Fig. 3A,D) were calculated and are shown by the hexagonal unit cells and pole figures. Note that the Cu_6Sn_5 phase has been indexed as hexagonal ‘high temperature’ $\eta\text{-Cu}_6\text{Sn}_5$ based on the structure in [26-28] because this is the polymorph that was stable during solidification [29]. Comparison of the pole figures with the crystal morphologies in Fig. 3A and D shows that each crystal grows along $[0001]$ and is bounded by $\{10\bar{1}0\}$ growth facets. Note that, in both crystals, one facet is near-parallel with the page (marked with a triangle on crystals and in the $\{10\bar{1}0\}$ pole figures).

The growth kinetics of Cu_6Sn_5 faceted hexagonal rods were studied by in-situ radiography of Sn-1.1Cu. Fig. 4A shows two images coloured by the time each pixel becomes solid and Fig. 4B are images of the same areas where each Cu_6Sn_5 crystal has been assigned a unique colour and the growth direction is marked with an arrow. The $[0001]$ growth distance vs time data are summarised for each crystal in Fig. 4C using colours corresponding to Fig. 4B.

In Fig. 4C, the initial steady growth velocities of different crystals were near-constant at $16.2 \pm 3.8 \mu\text{m/s}$, and then usually became slower gradually (e.g. the purple curve in Fig. 4C). The steady growth rate in Fig. 4C is calculated from a linear fit of the near-linear region (i.e. growth distance $< 100 \mu\text{m}$). This gradual decrease of growth velocity is linked with the solute field in the liquid ahead of the growing tips. For example, in Fig. 4B, the purple crystal grows towards two other Cu_6Sn_5 crystals (yellow and cyan). The purple crystal was measured to slow as it approaches the two crystals where there is a depleted Cu solute field. For free growing Cu_6Sn_5 crystals such as the long teal crystal, the [0001] growth velocity remained near-constant. Similarly, the kinetics of Cu_6Sn_5 growth perpendicular to [0001] (i.e. $\sim \langle 10\bar{1}0 \rangle$ direction) is shown in Fig. 4D and E, from which it can be seen that the $\sim \langle 10\bar{1}0 \rangle$ growth rate is initially $\sim 1.87 \pm 0.64 \mu\text{m/s}$ (i.e. when growth distance $< 2 \mu\text{m}$) and then becomes steady at $\sim 0.57 \pm 0.21 \mu\text{m/s}$ from 8 measurements. Note that the steady growth rate in Fig. 4E is difficult to measure and is estimated from a linear fit of the region with a growth distance between $2 \mu\text{m}$ and $< 6 \mu\text{m}$. Note that the arrows in Fig. 4D are longer than the actual growth distance to help discriminate the different colours. The anisotropy of Cu_6Sn_5 rod growth can be quantified from the ratio of the steady-state growth rates along the main growth direction [0001] and directions perpendicular to [0001] which is $\sim 16.2/0.57 = 28.4$. Fig. 4F is a histogram of the final length to width ratio of 53 Cu_6Sn_5 rods extracted from bulk samples such as that in Fig. 1A; it can be seen that the histogram from bulk samples has a mean between 20 and 30 which is comparable with the growth anisotropy of rods in the thin radiography samples (~ 28).

Many faceted hexagonal rods had a hollow core, similar to the example in Fig. 1A. The formation of hollow cores was observed in the synchrotron image sequences such as that in

Fig. 4G. It can be seen that the Cu_6Sn_5 crystals grew as filled rods initially and became hollow by melting of the core later during growth. For example, the melting of the core begins between 4.5s and 30s in the left part of Fig. 4G and between 12s and 24s in the right part. Note that the melting direction is opposite to the $[0001]$ crystal growth direction indicating that the hollowness starts at the growth tip. Frank et al. [30] linked the formation of hollow-core rod-like crystals to an axial screw dislocation where the core remelts when the strain energy of the dislocation core exceeds the new surface energy required to create a hollow [31]. Frear et al. [13] suggested that Cu_6Sn_5 rods develop hollow cores by a similar mechanism.

This predicts that Cu_6Sn_5 rod growth occurs by a $[0001]$ axial screw dislocation providing a perpetual ledge onto which atoms attach to the crystal-liquid interface. Examination of the growth tips of numerous Cu_6Sn_5 hexagonal rods such as those in Fig. 1A gave little evidence for spiral ledge growth in most cases. However, in some cases, there was evidence of spiral growth as shown in Fig. 5A-B, which contains a large spiral ledge. Further evidence for spiral growth was found when $\sim 50\text{ }\mu\text{m}$ thick samples were solidified with some Cu_6Sn_5 crystals having $[0001]$ near-perpendicular with the sample plane so that they were constrained to grow along $\langle 10\bar{1}0 \rangle$. In this case, numerous faceted ledges formed on (0001) as shown in Fig. 5C-D. These resemble typical screw dislocation growth [32-36] although they are not perfect closed screws.

3.3 Transition to grooved, branched or dendritic Cu₆Sn₅ crystals

It can be seen in the microstructure map of Fig. 2A that there was a transition from hexagonal rods to grooved and branched-faceted crystals when either (i) the composition was increased from 0.7Cu-4.2Cu at 0.03K/s or (ii) the cooling rate was increased from 0.03-3.7K/s at 0.9Cu.

A typical grooved crystal is shown in Fig. 1B. Grooved crystals are similar to hollow hexagonal rods except that the hollowness has 'broken through' one or more of the $\{10\bar{1}0\}$ facets, internal fins commonly develop, and the relative surface area of the six $\{10\bar{1}0\}$ facets is often unequal so that the crystal loses its simple hexagonal shape. It is likely that these grooved crystals began growing as a rod and developed into a grooved crystal with continued growth, which is similar to the proposed mechanism by Tian et al. [37].

The development of the in-plane branching morphology (e.g. Fig. 1C and Fig. 3D) can be understood from Fig. 6, which shows extracted crystals from Sn-4.2Cu cooled at ~ 1.7 K/s. Fig. 6A-E show the in-plane branching mechanism at a range of magnifications and at different stages of growth. In Fig. 6A, tip splitting can be observed. Fig. 6B-C show how split tips develop into in-plane faceted branches, and Fig. 6D-E show how multiple in-plane branching events lead to the macroscopic crystal shape. Note that, as the Cu₆Sn₅ branches split sideways, they continue growing in the [0001] direction and all the branches have common $\{10\bar{1}0\}$ facets.

The faceted growth ledges in Fig. 5 indicate stepwise lateral growth by a terrace-ledge kink (TLK) type mechanism where growth is governed by the interface attachment kinetics, whereas the nonfaceted, curved and split tip in Fig. 6A indicates continuous growth of an atomically rough interface governed by diffusion and curvature. This suggests that Cu₆Sn₅

undergoes an atomic roughening transition of the S-L interface with increasing cooling rate and/or Cu content. Jackson presented a simple model for the equilibrium atomic roughness of a stationary S-L interface [38]. This model highlighted the importance of two factors in determining the interface roughness: the difference in structure and bonding between the crystal and liquid via the dimensionless entropy of fusion ($\Delta S_f/R$), and the crystallographic plane at the interface via a term (ξ) that is always less than 1 and is usually larger for more closely packed interfacial planes. The product of these two terms is Jackson's alpha factor [38] as given in Eq. 4:

$$\alpha = \frac{\Delta S_f}{R} \xi \quad \text{Eq. 4}$$

Jackson's model predicts that interfaces should be atomically smooth with few ledge/kink sites when $\alpha \gg 2$. Experimentally, it is now well known that generally crystals with $\Delta S_f/R < 2$ have atomically rough interfaces and grow with a nonfaceted front, whereas crystals with $\Delta S_f/R \gg 2$ have atomically smooth interfaces with ledges and grow with a faceted front. To find the dimensionless entropy of fusion of an intermetallic compound that melts by a peritectic reaction (such as Cu_6Sn_5), a CALPHAD approach can be used to suppress some solid phases and calculate the metastable congruent melting point and the associated enthalpy of fusion [39]. Performing this calculation using Thermo-Calc TSLD3.0 [25], gave a metastable congruent melting point of Sn-44.57Cu at 523.31°C and an enthalpy of fusion of 13231 J mol⁻¹, which gives a dimensionless entropy of fusion of $\Delta H_f/RT_m = \Delta S_f/R = 2.0$. Thus, Cu_6Sn_5 is predicted to be close to the transition between an atomically smooth and rough interface.

The factor ξ in Eq. 4 is larger for the most close-packed planes which, therefore, have the most atomically smooth interface, the fewest low energy attachment sites and grow the slowest for a given driving force. Since the crystal growth shape is bounded by the slowest growing planes, the growth facets are expected to be the most closely packed planes. The planar atomic density of closely packed planes in Cu_6Sn_5 are summarised in Table 1 and Fig. 7, assuming the high temperature hexagonal structure from references [26-28] with 20% occupancy on the Cu_2 sites. Note that parallel planes with different atomic arrangements (e.g. $(10\bar{1}0)$ and $(30\bar{3}0)$) need to be considered separately to calculate individual close-packedness and high-index planes (with low d-spacings) can be either less closely packed (e.g. $(30\bar{3}0) < (10\bar{1}0)$) or more closely packed (e.g. $(20\bar{2}2) > (10\bar{1}1)$ in Fig. 7). Therefore, the closed-packedness in Cu_6Sn_5 will not be accurately ranked by d-spacing or by an estimation involving generalised structure factors [40] and requires careful measurements from plane to plane in the unit cell as illustrated in Fig. 7. It can be seen in Fig. 7 that, although the atomic densities of $(1\bar{1}02)$ and $(20\bar{2}2)$ appear high, they are exaggerated due to the projection of zig-zag planes. These zig-zag planes (highlighted in yellow in Fig. 7) are intrinsically rough and, therefore, are ranked at the bottom of the list in Table 1. For the atomically flat planes, the close-packedness is in the order of $(11\bar{2}0) > (10\bar{1}0) > (0004) > (11\bar{2}4)$. Thus, from Eq. 4 and the discussion above, it might be expected that $(11\bar{2}0)$ would be a growth facet which was not the case (Fig. 3). One reason may be that the partially occupied Cu_2 sites on $\{11\bar{2}0\}$ planes (Fig. 7) introduce an inherent roughness, more attachment sites and faster attachment kinetics than if it were a fully-occupied flat plane. Thus, the atomically smoothest plane is expected to be $(10\bar{1}0)$ (i.e. the closest-packed fully-occupied flat plane) and the roughest planes are expected to be the intrinsically rough zig-zag pyramidal planes (Table 1 and Fig. 7D-E). The presence of $(10\bar{1}0)$ growth facets and a

growth anisotropy of ~28 times faster along $\sim[0001]$ than perpendicular to $[0001]$ (Fig. 4) is consistent with this.

The transition from faceted growth (Fig. 5) to a nonfaceted tip of an otherwise faceted crystal (Fig. 6A) to fully nonfaceted dendrites (Fig. 1E) with increasing cooling rate (Fig. 2A) indicates that the S-L interface undergoes an atomic roughening transition as the driving force is increased. A smooth transition from an atomically smooth to a rough S-L interface with increasing driving force is predicted by Cahn [41, 42], although it is somewhat unusual for this transition to be experimentally accessible. The occurrence of a kinetic roughening transition in Cu_6Sn_5 may be related to the value of $\Delta S_f/R=2.0$ being close to the limit between a faceted and nonfaceted crystal and, therefore, requiring only a small driving force to cause the transition. However, we caution that other phases with similar $\Delta S_f/R$ grow as faceted crystals under all conditions studied here (e.g. Ni_3Sn_4 [43]).

The occurrence of faceting and branching shows that Cu_6Sn_5 crystal growth is both interface controlled and diffusion controlled. For example, the grooves and in-plane branching can be understood from the total interface growth undercooling, ΔT_{growth} , given in Eq. 5. This depends on the solute undercooling, ΔT_{solute} , due to the build up of Sn at the Cu_6Sn_5 -liquid interface, a curvature undercooling, ΔT_{curv} due to the Gibbs-Thomson effect, and a kinetic undercooling, $\Delta T_{kinetic}$, to drive the anisotropic atomic attachment process.

$$\Delta T_{growth} = \Delta T_{solute} + \Delta T_{curv} + \Delta T_{kinetic} \quad \text{Eq. 5}$$

As Cu_6Sn_5 crystals grow they reject Sn atoms and a diffusion profile develops in the liquid. The solute undercooling can be large for Cu_6Sn_5 crystals because the liquidus slope is steep and $\Delta T_{solute} = m_L(C_0 - C_L^*)$ where m_L is the liquidus slope and $C_0 - C_L^*$ is the deviation of

the interface composition from the bulk alloy composition. Grooves, internal fins and in-plane branching are all efficient ways for a faceted crystal to reject solute while maintaining the preferred $\{10\bar{1}0\}$ growth facets and $[0001]$ growth direction. Presumably these shapes give an optimal balance of solute, curvature and kinetic undercoolings. With reference to the microstructure map in Fig. 2A, the grooves and in-plane branching are promoted by (i) a higher Cu content because each crystal grows further when the volume fraction of Cu_6Sn_5 is higher allowing more solute to build up at the interface and (ii) higher cooling rate because this increases the interface velocity which gives less time for solute diffusion and can trigger interface roughening.

3.4 Cu₆Sn₅ dendrite growth

When the Cu content was greater than 2.3wt% and the cooling rate was higher than ~4 K/s, primary Cu₆Sn₅ developed into fully dendritic structures as summarized in Fig. 2A. To determine the 3D growth crystallography of Cu₆Sn₅ dendrites, EBSD and FIB tomography were combined. The procedures are summarized in Fig. 8 for a dendrite in Sn-4.2Cu cooled at ~100 K/s. First, the orientation of a dendrite was measured on a 2D section by EBSD. Fig. 8A and B show the corresponding IPF-z map and [0001] pole figure. It can be seen that the orientation of the Cu₆Sn₅ dendrite is slightly scattered but most regions have a common 'red' orientation whose [0001] direction is nearly out of the screen. The median orientation of the red data in the pole figure is plotted as a unit cell in Fig. 8B. Fig. 8C shows a 3D reconstruction of the Cu₆Sn₅ dendrite from more than 300 FIB slices with 100nm slice thickness occupying a volume of ~30x30x50 μm . With the knowledge of the crystal coordinates relative to the FIB coordinate system, the unit cell has been plotted within the reconstructed volume in Fig. 8C which enables the sectioning plane and viewing direction to be selected relative to the crystal coordinate system. Fig. 8D is the same dendrite rotated to have [0001] pointing out of the page. By comparing the dendrite morphology with the unit cell in Fig. 8D, it can be seen that Cu₆Sn₅ dendrites grow with primary, secondary and tertiary arms in the $\{10\bar{1}0\}$ planes. In order to measure the preferred growth directions, 3D datasets were sectioned along the $\{10\bar{1}0\}$ planes containing the primary dendrite arms as marked by dashed lines in Fig. 8D and a normal view of these sectioning planes is shown in Fig. 8E. In Fig. 8E, the white arrows denote primary dendrite arms and dashed arrows denote secondary dendrite arms in the same $\{10\bar{1}0\}$ plane as the primary arm. The dendrite arms in Fig. 8E are symmetrical about [0001] which are marked by dash-dot lines. The half-

angle, α , between the branch directions and [0001] was measured to have a mean value of $\alpha=34.2^\circ$ with an uncertainty of $\sim\pm 3^\circ$ from >30 measurements. The relatively large uncertainty is due to the width of the dendrite arms in 2D sections as can be seen in Fig. 8E. Based on this measurement, Fig. 8F shows the 12 symmetrically equivalent growth directions (white arrows) of Cu_6Sn_5 within a unit cell. Fig. 8G shows the atomic arrangement in the $\{10\bar{1}0\}$ plane with the mean measured dendrite growth directions superimposed in white arrows. The mean measured dendrite growth direction is 0.75° off $\langle 405 \rangle$ but the uncertainty of $\sim\pm 3^\circ$ allows for other possibilities. Therefore, Fig. 8G includes a range of possible directions as a grey wedge which is bounded by two simpler crystallographic directions, $\langle 101 \rangle$ (5.35° off the mean measured) and the $\{1\bar{2}14\}$ plane normal (3.01° off the mean measured). To better illustrate the $\{1\bar{2}14\}$ plane (a less closed-packed plane in Table 1), it is highlighted in the hexagonal Cu_6Sn_5 unit cell in Fig. 7F and Fig. 8G. Since there are 12 $\langle 405 \rangle$ branching directions, a primary arm has 10 possible directions for secondary arm branching. However, the secondary branches from one primary arm were often only in three directions. This can be seen in Fig. 8H in which the arms are coloured according to their rank: primary (red), secondary (blue) or tertiary (yellow). The directions are plotted in a pole figure (northern hemisphere only) where solid symbols denote the out-of-page growth directions and open symbols denote the opposite of into-page growth directions. Note that in Fig. 8H the secondary arms are labelled by “1-3” where “1 and 2” grew with a component out of the page and “3” grew with a component into the page. It can be seen in Fig. 8H that branch “3” is in the same $\{10\bar{1}0\}$ plane as the primary arm and that branches “1” and “2” are in the other two $\{10\bar{1}0\}$ planes.

2D sections of Cu_6Sn_5 dendrites can be understood with knowledge of the 3D growth crystallography. Fig. 9 shows an orientation map of a typical cross-section in Sn-2.3Cu cooled at ~ 4 K/s. In this plot, colour does not correlate with orientation and has been selected simply to discriminate between grains. The orientations are shown by superimposed Cu_6Sn_5 unit cells which were measured by EBSD. It can be seen that when [0001] of Cu_6Sn_5 is near perpendicular to the sample surface (e.g. the red grain), 2D sections appear as regular triangular arrays. On the other hand, if [0001] is near parallel to the cross-section, elongated irregular dendritic arrays are observed such as the green grain in Fig. 9.

Fig. 10 shows a purely geometrical 3D model of Cu_6Sn_5 dendrite growth generated in Matlab based on the crystallography of branching measured by EBSD coupled with FIB-tomography in Fig. 8. Fig. 10A and C show two common dendrite geometries observed on 2D sections when {0001} is near-parallel with the sample surface. Fig. 10A is a hexagon section and Fig. 10C is a hexagram section (with corners towards the primary dendrite arms). Fig. 10B shows a 3D geometrical model based on Fig. 8H, where the three secondary dendrite arms “1, 2 and 3” were considered in this 3D model. The red lines are 3D vectors representing the primary and secondary dendrite arms and blue points mark where the vectors intersect a slice of the (0001) plane. The blue points form a hexagon with six lines emanating from the vertices, similar to the cross section in Fig. 10A. Fig. 10D shows another combination of possible secondary dendrite arms, “4, 5 and 3”, in a similar 3D model. This combination of secondary arms creates a hexagram in 2D section consistent with Fig. 10C. It was found that the different secondary dendrite arms in Fig. 10A-D can coexist on one primary Cu_6Sn_5 dendrite arm (i.e. all of “1-5” secondary dendrite arms growing from one primary arm). An example is shown in the SEM image in Fig. 10E. Note that secondary arm “3” is not obvious in the SEM image due to the viewing angle.

It was found that all dendrites had a secondary dendrite arm along “3” and that the other secondary dendrite arm growth directions changed from “4 and 5” (Fig. 10C-D) to “1 and 2” (Fig. 10A-B) and then to “1, 2, 4 and 5” when the cooling rate and Cu content increased. This is likely due to the different angles between the possible <405> secondary arms and the primary trunk. Referring to Fig. 10, the angle between secondary arm “3” and primary arm “P” is 113° , between “4 or 5” and “P” is 57° , and between “1 or 2” and “P” is 32° . The higher the angle, the less the rejected solute from the primary tip will retard the growth of the secondary tip and, therefore, destabilisation of the trunk behind the primary tip will occur first for the secondary arms with higher angle. A high interface velocity and/or high solute content increases the degree of constitutional supercooling and may lead to branching with more of the angles from the <405> family.

Fig. 11A-F show in-situ synchrotron images of a Cu_6Sn_5 dendrite growing vertically in Sn-4.2Cu. The vertical dendrite tip velocity is $\sim 123 \pm 5 \mu\text{m/s}$ which is 7.6 times faster than that in Fig. 4C. For each of Fig. 11A-F, there are two images; the larger ones are raw x-ray images and the smaller images (labelled a-f) are repeats of the right primary dendrite arm with superimposed arrows indicating the secondary arm growth directions. Accurate 3D angular information is not accessible from projection imaging but it can be seen that there is complex 3D branching with three secondary arms growing from the right primary arm that likely follow the branching mechanisms (hexagram 2D section) shown in Fig. 10C-D.

The dendrite in Fig. 8 was cooled at $\sim 100 \text{ K/s}$ and is nonfaceted, but dendrites solidified at lower cooling rate were often partly-faceted (e.g. Fig. 1D). Synchrotron radiography was used to study when the faceting occurs during solidification. It was found that Cu_6Sn_5

dendrites initially grew as nonfaceted dendrites and then developed facets as the tip velocity slowed and the dendrites coarsened in the later stages of solidification. Two examples are shown in Fig. 12 for Sn-10Cu where this effect was the most dramatic. Pixels have been coloured by the time at which they became solid to show the changing dendrite shape during growth. Note that Fig. 12A-C share the same colour scale. Fig. 12A shows a nonfaceted dendrite at an early stage (<15s) of solidification and the tip velocity is $11.1 \pm 3.9 \mu\text{m/s}$. Fig. 12B shows the same dendrite with faceting (red tips) that developed at a later stage (~50-150s) near the tips of the dendrite. Fig. 12C gives another example of facet development during growth, where blue regions at the early stage show no discriminable faceting and obvious faceting (red regions) occurs later. Note that for each dendrite, all red regions share a common alignment which is very likely to be [0001]. The phenomenon of faceting during coarsening adds significant complexity to the study of the faceted-to-nonfaceted growth transition in Cu_6Sn_5 . For example, this transition occurs at lower interface velocity ($\sim 11.1 \mu\text{m/s}$) and cooling rate than would be suggested from the *post mortem* characterisation.

3.5 Cu₆Sn₅ formation in Sn0.7Cu/Cu solder joints

Fig. 13 shows typical microstructures of Sn-0.7Cu/Cu joints produced with 500 μm diameter solder balls at a range of peak temperatures and cooling rates. Samples in Fig. 13A were held for 5 mins at peak temperatures in the range 240°C to 390°C and cooled at 0.66 K/s. It can be seen that the area fraction of primary Cu₆Sn₅ increases with increasing holding temperature and there is a morphological transition as the peak temperature increased, from hexagonal rods when $T^{\text{peak}}=240\text{--}300^\circ\text{C}$ to grooved rods at $T^{\text{peak}}=350^\circ\text{C}$ and grooved and in-plane branched-faceted crystals at $T^{\text{peak}}=390^\circ\text{C}$, similar to Fig. 1A, B and C respectively.

Samples in Fig. 13B were held for the same time at the same peak temperatures and were then cooled at ~ 30 K/s. At $T^{\text{peak}}=240^\circ\text{C}$, no primary Cu₆Sn₅ formed. At $T^{\text{peak}}=270^\circ\text{C}$, there is a mixed branched-faceted and dendritic microstructure, and at $T^{\text{peak}}\geq 300^\circ\text{C}$, primary Cu₆Sn₅ grew as dendrites. For example, note the similarities between the triangular arrays at $T^{\text{peak}}=300^\circ\text{C}$ in Fig. 13B and in Fig. 1D.

Fig. 14A is an EBSD IPF-x map of the Cu₆Sn₅ dendrites in a Sn-0.7Cu/Cu joint with $T^{\text{peak}}=390^\circ\text{C}$ cooled at ~ 30 K/s. The approximate primary arm (circles) and secondary arm (squares) growth directions are marked on the 2D section sections in Fig. 14A with arrows and the orientation of each dendrite is summarised in the corresponding $\langle 405 \rangle$ pole figures in Fig. 14B. Note that the $\{1\bar{2}14\}$ plane normal or the $\langle 101 \rangle$ pole figures give very similar results. Comparing Fig. 14A-B shows that both primary and secondary arms grew close to $\langle 405 \rangle$. However, the marked arrows on the EBSD maps are unlikely to be perfectly parallel with the 3D growth directions, so the interpretation of the growth direction based on EBSD of random 2D sections is less accurate than the EBSD+FIB-tomography in Fig. 8 where the desired crystallographic plane can be digitally sectioned. Nevertheless, there is little doubt

that the preferred directions are close to $\langle 405 \rangle$ (and between $\{11\bar{2}4\}$ plane normal and $\langle 101 \rangle$), which is consistent with Fig. 8G for bulk alloys.

Comparing the joint microstructures in Fig. 13 with the bulk alloy microstructures in Fig. 1 and the microstructure map in Fig. 2A, it can be seen that the full range of primary Cu_6Sn_5 morphologies (including no primary Cu_6Sn_5) that grow for different composition and cooling rate combinations in the bulk alloys can be engineered to grow in solder joints made with a single composition (Sn-0.7Cu) by altering the peak temperature and the cooling rate. This can be understood from the influence of the peak temperature on the change in liquid composition due to the dissolution of the Cu substrate into the liquid solder. The peak temperature determines the liquid composition at the edge of the Cu_6Sn_5 reaction layer (via the phase diagram in Fig. 2C) and the diffusion profile in the liquid ahead of the Cu_6Sn_5 layer depends on factors including the volume of solder and the time at the peak temperature (e.g. [44]).

A microstructure map of primary Cu_6Sn_5 in Sn-0.7Cu/Cu joints are shown by symbols in Fig. 15, where the lower x-axis shows the peak temperature and the upper x-axis is the corresponding liquid composition assuming uniform saturation at the peak temperatures. Comparing with Fig. 2A for bulk alloys, it can be seen that the symbols for joints are generally shifted to the right (higher apparent Cu content). This suggests that the joints are not uniformly saturated in Cu and the actual mean liquid composition is lower than (to the left of) the displayed symbols. This is probably partially because the IMC layer consumes Cu as it thickens and the layer itself acts as a barrier for Cu diffusion, and there was insufficient time to uniformly saturate the liquid.

A significant difference between primary Cu_6Sn_5 formation in the bulk alloys (e.g. Figs. 1-12) and in solder joints on Cu substrates is that, in the latter case, there is a pre-existing Cu_6Sn_5 reaction layer in contact with the liquid at the peak temperature. Therefore, during cooling from the peak temperature, there is the possibility of growth of the pre-existing Cu_6Sn_5 layer into the liquid and/or the nucleation of new Cu_6Sn_5 grains in the liquid above the layer. Both phenomena occurred in this work. For example, the hexagonal rods near the top of the joints with $T^{\text{peak}}=240\text{-}300^\circ\text{C}$ in Fig. 13A formed far from the IMC layer, which is consistent with a recent study that directly observed the nucleation of primary Cu_6Sn_5 in the liquid away from the IMC layer in Sn-0.7Cu/Cu using in situ synchrotron imaging [23]. On the other hand, in the sample held at 390°C in Fig. 14A, the dendrites labelled “i, ii” grew from the Cu_6Sn_5 layer while the dendrite labelled “iii” seems to have nucleated in the bulk liquid or on the free surface.

The different morphologies of Cu_6Sn_5 observed in Sn-0.7Cu/Cu solder joints in this work (Fig. 13A-B) span the wide range of morphologies reported in the literature and the Cu_6Sn_5 microstructure maps in Fig. 2A and Fig. 15 allow this to be understood within a single framework. Hexagonal Cu_6Sn_5 rods are common in Sn-rich solders on polycrystalline Cu substrates where the peak temperature is typically $240\text{-}250^\circ\text{C}$ and the cooling rate is $\sim <3$ K/s [13, 15, 22, 23]. Gagliano et al. [45] showed that Cu_6Sn_5 hexagonal rods transformed to grooved rods when held at 275°C for different holding time (1-1000mins) in Sn/Cu joints. Chada et al. [14] reported the morphologies of primary Cu_6Sn_5 in Sn-3.5Ag/Cu solder joints change from grooved to branched as the peak temperature increased from 236°C to 292°C before cooling at 25 K/s. Hwang et al. [18] observed dendritic Cu_6Sn_5 in Sn-6.9Cu-2.9Ag alloy cooled at $\sim 17\text{-}500$ K/s. Liu et al. [6] reported Cu_6Sn_5 dendrites in Sn/Cu joints held at 426°C

for 80ms and 120ms before cooling at >800 K/s. For synchrotron radiography studies, direct observations showed that rod-like Cu_6Sn_5 formed in Sn-4Ag-0.5Cu cooled at 1 K/s [46] and Sn-0.7Cu/Cu cooled at ~ 0.33 K/s [22, 23], and branched Cu_6Sn_5 formed in Sn-4Cu [7] and Sn-6.5Cu cooled at 0.05 K/s [9, 47]. While these studies can seem a complex array of results, all are consistent with each other when interpreted with the microstructure map in Fig. 2A and the transitions and mechanisms found in this study.

Furthermore, the primary Cu_6Sn_5 microstructure maps in Fig. 2A and Fig. 15 provide a useful framework to control and engineer the primary Cu_6Sn_5 microstructure in electronic interconnections. For example, they show that primary Cu_6Sn_5 can be prevented from forming by using a low peak temperature and high cooling rate in ball grid array (BGA) joints. On the other hand, the high Cu_6Sn_5 -L interfacial area created by dendrite growth at high peak temperature and cooling rate may offer an approach to minimise the time required to create fully intermetallic joints by transient liquid phase bonding (TLPB).

4 Conclusions

The crystal growth mechanisms of primary Cu_6Sn_5 have been studied in bulk Sn-Cu alloys and in Sn-0.7wt%Cu/Cu BGA-scale solder joints by combining EBSD, FIB-tomography and synchrotron radiography. The following conclusions can be drawn:

- Primary Cu_6Sn_5 morphologies ranging from faceted rods to nonfaceted dendrites can be controlled by increasing the cooling rate in the range 0.03-100 K/s and Cu content in the range 0.7-4.2 wt%. This is related to the Jackson alpha factor of Cu_6Sn_5 being close to 2 so that a relatively small driving force can trigger a transition from an atomically smooth to atomically rough interface, leading to a faceted to nonfaceted growth transition.
- The preferred growth direction of faceted Cu_6Sn_5 was $\langle 0001 \rangle$ and the growth facets were $\{10\bar{1}0\}$. Hollow faceted hexagonal rods formed by remelting of the rod core during crystal growth and there was some evidence of spiral growth along the axial $[0001]$ direction.
- For dendritic Cu_6Sn_5 , the primary, secondary and tertiary arms grew along the $12 \langle 405 \rangle$ directions (which are close to $\langle 101 \rangle$ and the $\{1\bar{2}14\}$ plane normals). The complex dendrite shapes observed in 2D sections were correlated with sections through this 3D dendrite morphology.
- The full range of primary Cu_6Sn_5 morphologies (including no primary Cu_6Sn_5) that grew for different composition and cooling rate combinations in bulk Sn-xCu alloys can be engineered to grow in solder joints made with a single composition (Sn-0.7Cu/Cu) by altering the peak temperature and the cooling rate.

- The range of Cu_6Sn_5 morphologies that form in bulk alloys and joints has been rationalised into a kinetic microstructure map which can be used to select solder process parameters to generate desired Cu_6Sn_5 microstructures in solder joints.

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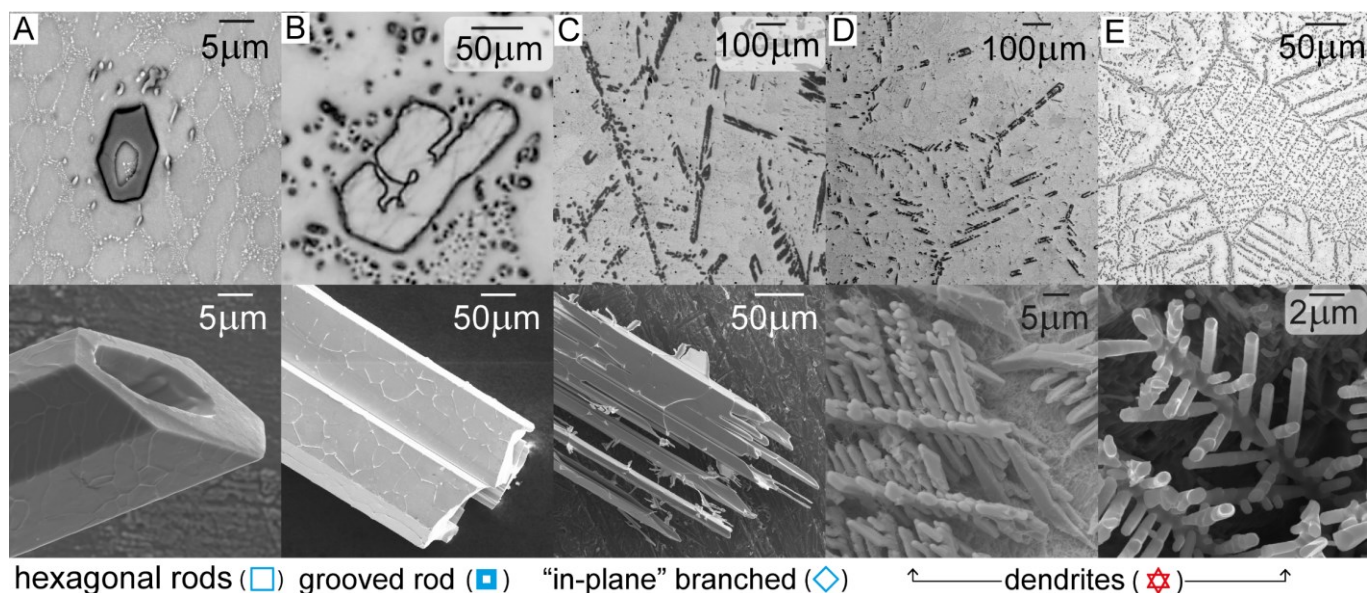


Fig. 1. Typical 2D and 3D shapes of primary Cu_6Sn_5 in Sn-Cu samples under different conditions. A) Sn-0.7Cu cooled at $\sim 0.03\text{K/s}$, B) Sn-1.1Cu cooled at $\sim 0.03\text{K/s}$, C) Sn-2.3Cu cooled at $\sim 1.7\text{K/s}$, D) Sn-2.3Cu cooled at $\sim 30\text{K/s}$, E) Sn-4.2Cu cooled at $\sim 100\text{K/s}$. Symbols in brackets correspond to the legends in Fig. 2A.

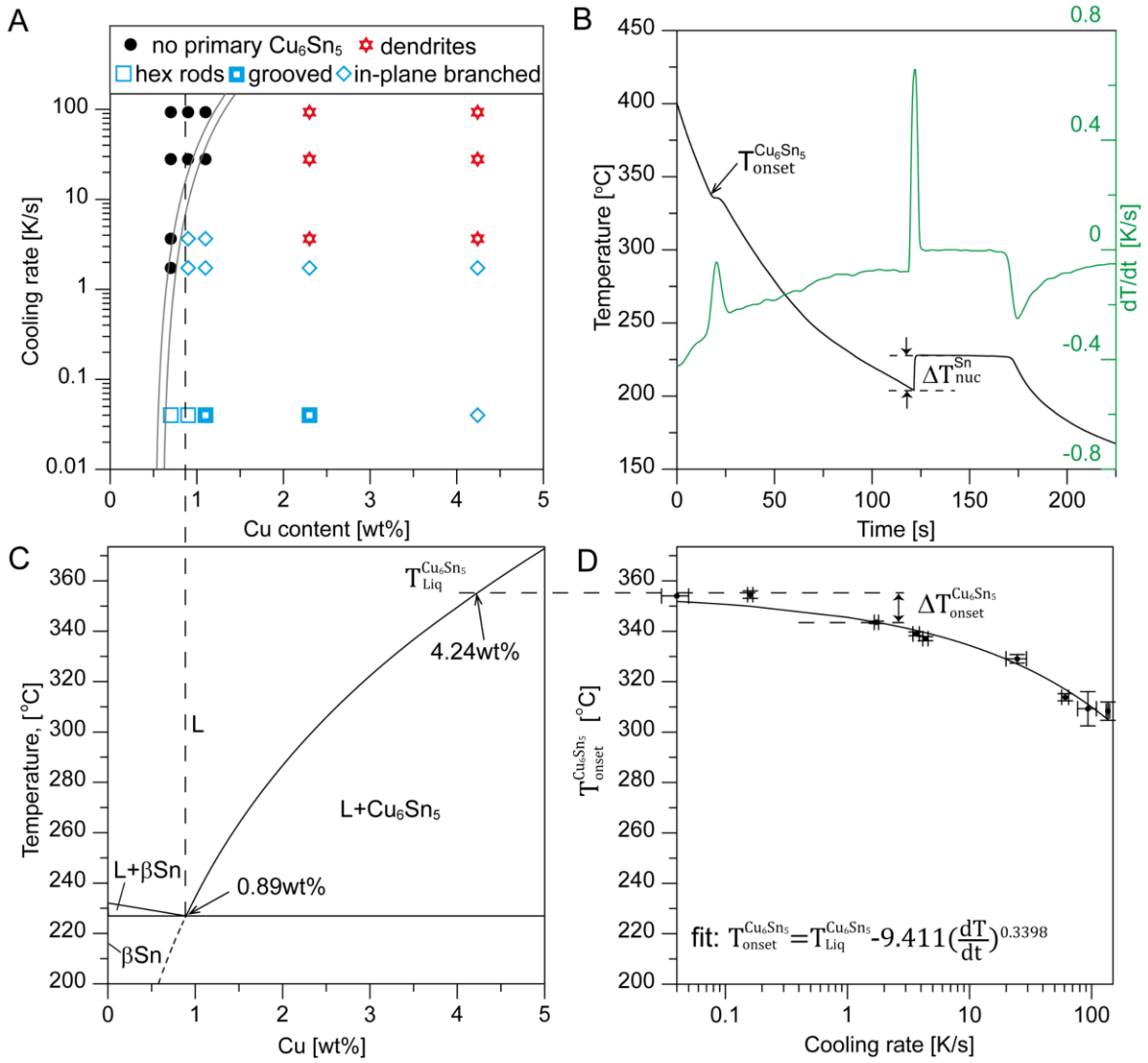


Fig. 2. A) A solidification microstructure map for primary Cu_6Sn_5 as a function of cooling rate and composition, B) a typical cooling curve and its first derivative for a Sn-4.2Cu sample, C) The Sn-rich end of the Sn-Cu phase diagram from [24], D) T_{onset} of Cu_6Sn_5 at different cooling rates and an exponential fit line.

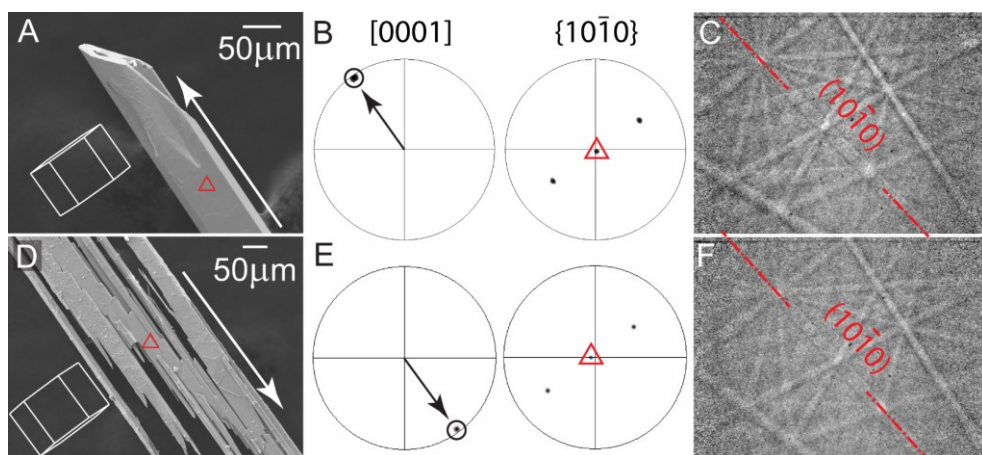


Fig. 3. Typical faceted Cu_6Sn_5 single crystals (viewed normal to the SEM stub). A) hexagonal rod and D) in-plane branched faceted crystal. B-C) Pole figures and EBSD pattern of A), and E-F) show those of D). Red triangles mark the facet planes. Arrows and circles mark the growth directions.

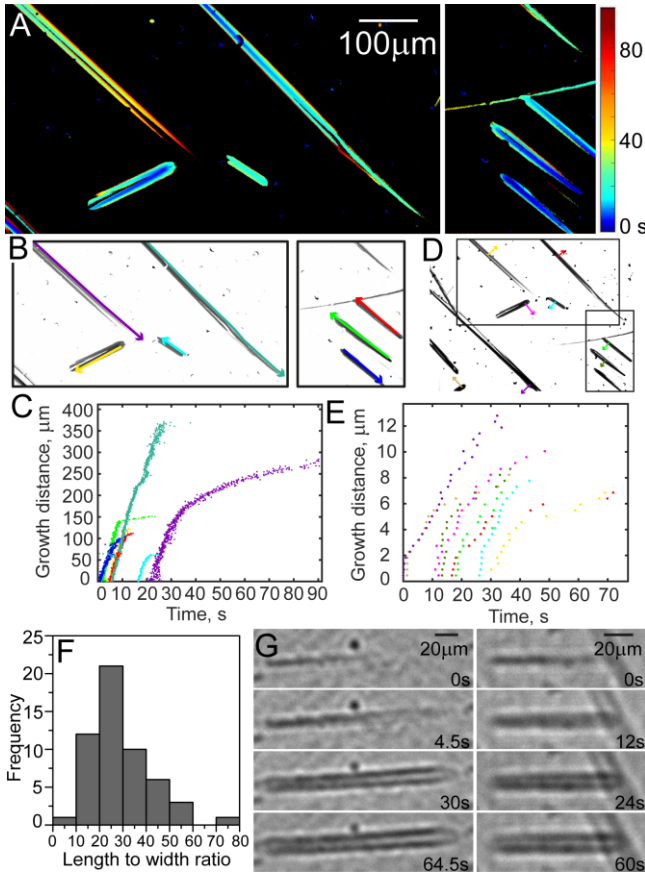


Fig. 4. Synchrotron radiography of the growth kinetics of rod-like Cu_6Sn_5 in Sn-1.1Cu . A) maps coloured by the time when liquid becomes solid based on image processing of raw radiograph sequences, B) a grey version of A) with coloured arrows marking the $[0001]$ growth paths, C) $[0001]$ growth distance (length) vs time for the coloured paths in B). D) A grey version of the whole sample with arrows marking the transverse growth directions, E) growth distance (width) vs time for the directions in D). F) The distribution of length to width ratio among 53 Cu_6Sn_5 rods extracted by deep etching. G) Raw radiographic images showing the development of hollowness during Cu_6Sn_5 rod growth.

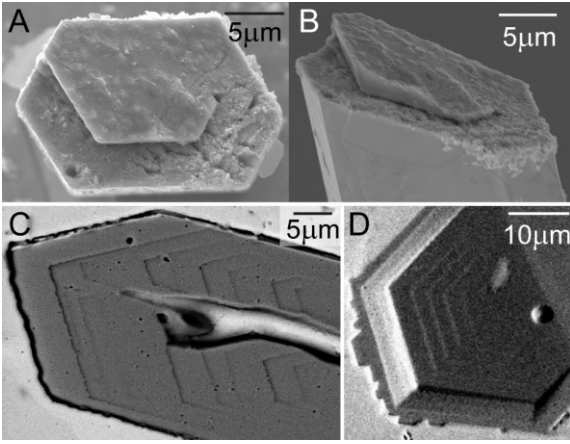


Fig. 5. Faceted ledges observed on Cu_6Sn_5 in A-B) Sn-0.7Cu/Cu joints cooled at 0.33K/s with Cu_6Sn_5 growing along $[0001]$ and C-D) constrained $\sim 50\mu\text{m}$ thick Sn-1.1Cu samples with Cu_6Sn_5 growing in the (0001) plane.

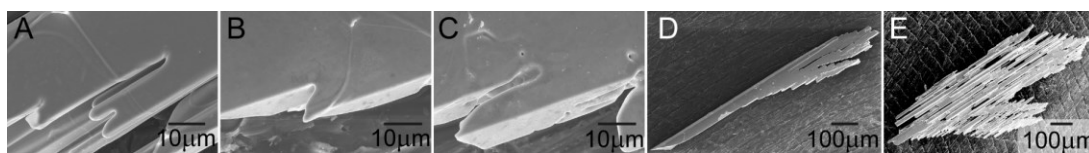


Fig. 6. The development of in-plane branched faceted crystals of Cu_6Sn_5 in Sn-4.2Cu cooled at $\sim 1.7\text{K/s}$. Note the different magnifications.

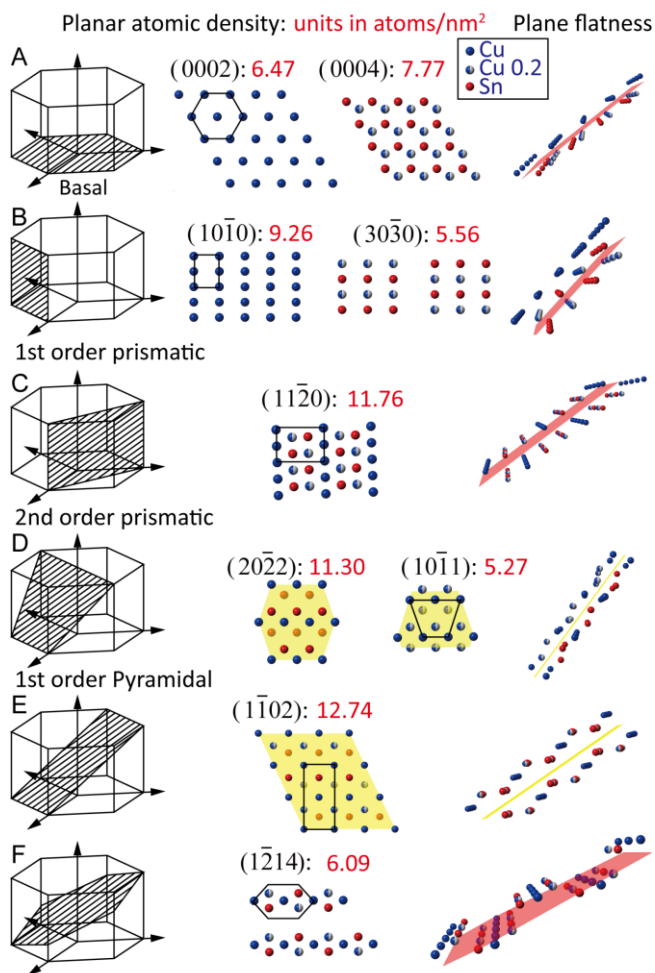


Fig. 7. Atomic densities of planes in hexagonal η -Cu₆Sn₅ based on the structure in [25-27]. Black shapes superimposed on the atomic planes correspond to the shaded planes in the unit cells. Zig-zag planes are highlighted in yellow.

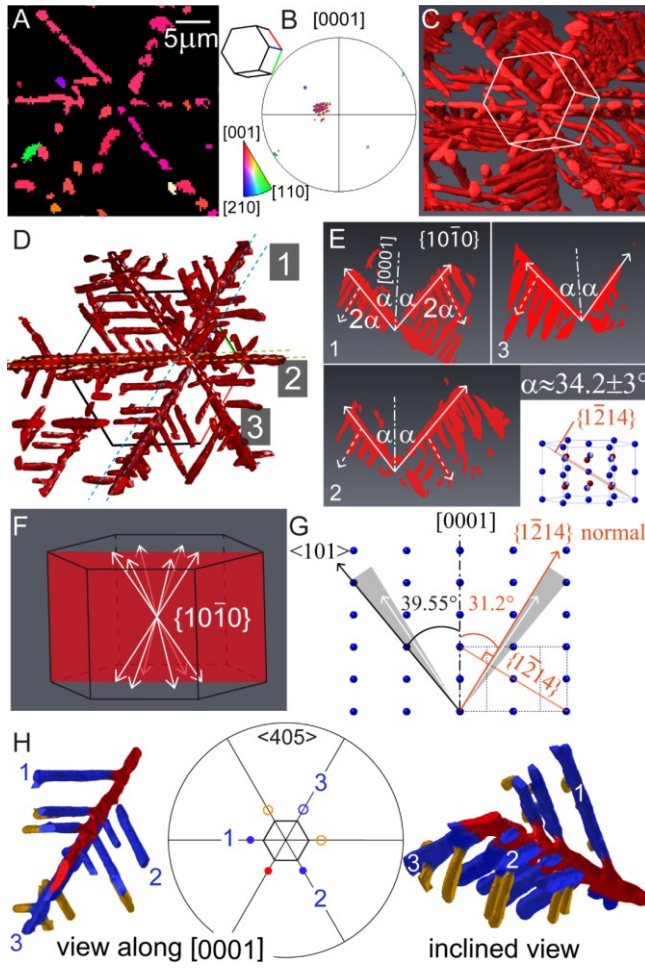


Fig. 8. A) IPF-z map of a Cu_6Sn_5 dendrite in Sn-4Cu cooled at $\sim 100\text{K/s}$, B) $[0001]$ pole figure of Cu_6Sn_5 in A), C) 3D structure of the Cu_6Sn_5 dendrite based on a reconstruction of FIB slices, and a superimposed unit cell, D) Cu_6Sn_5 dendrite viewed along $[0001]$ where dashed lines show primary arms in the $\{10\bar{1}0\}$ planes, E) slices in the $\{10\bar{1}0\}$ planes in D) with white solid arrows showing primary arms and dashed arrows showing some secondary arms in-plane of their parent primary arm. The average angle α between $[0001]$ and the arms is $\sim 34.2^\circ$, F) all 12 symmetrically equivalent branching directions within one Cu_6Sn_5 unit cell, G) atomic arrangement in $\{10\bar{1}0\}$ and a grey wedge of possible branching directions: white vectors = $\langle 405 \rangle$, black vectors = $\langle 101 \rangle$ and orange vectors = $\{1\bar{2}14\}$ plane normal. H) Primary (red), secondary (blue) and tertiary (yellow) arms from a typical region of D). The $\langle 405 \rangle$ pole figure shows the branching directions in the $\{10\bar{1}0\}$ planes.

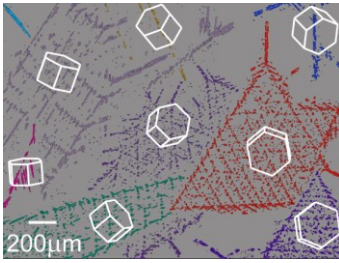


Fig. 9. 2D section through randomly orientated Cu_6Sn_5 dendrites in Sn-2.3Cu alloy cooled at $\sim 3.7\text{K/s}$.

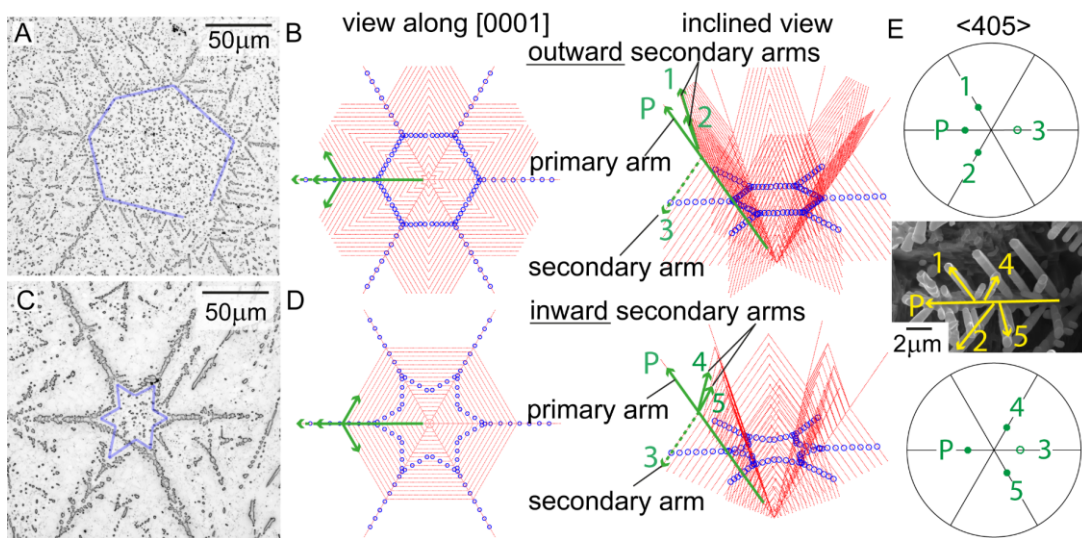


Fig. 10. Interpretation of 2D sections of Cu_6Sn_5 dendrites sectioned in $\{0001\}$. A) a hexagon 2D section in Sn-4.2Cu cooled at $\sim 100\text{K/s}$, B) 3D geometrically models of dendritic Cu_6Sn_5 growth where secondary dendrite arms “1 and 2” grew “outwards” and form a hexagon in a (0001) slice marked by blue circles, C) a hexagram 2D section in Sn-2.3Cu cooled at $\sim 100\text{K/s}$, D) similar to B) but secondary dendrite arms “4 and 5” grew “inwards” and form a hexagram, E) theoretical dendrite pole figures for B) and D) respectively and a SEM image showing all “1,2,4,5” dendrite arms can coexist on one primary dendrite arm “P”. Note that in both cases, common secondary arm “3” (dashed green arrow) grew with a component into the page and is denoted by open circles in the pole figures.

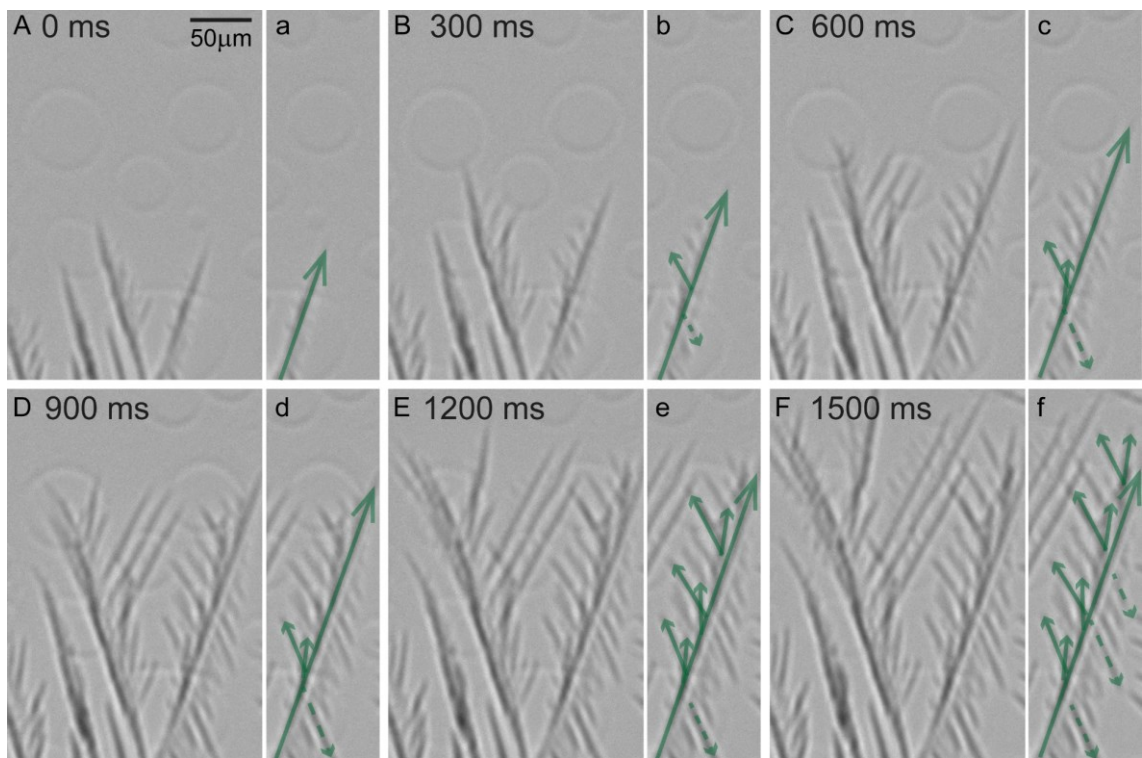


Fig. 11. Synchrotron radiograph sequences of a growing Cu_6Sn_5 dendrite in Sn-4.2Cu showing three secondary branching directions from one main dendrite trunk.

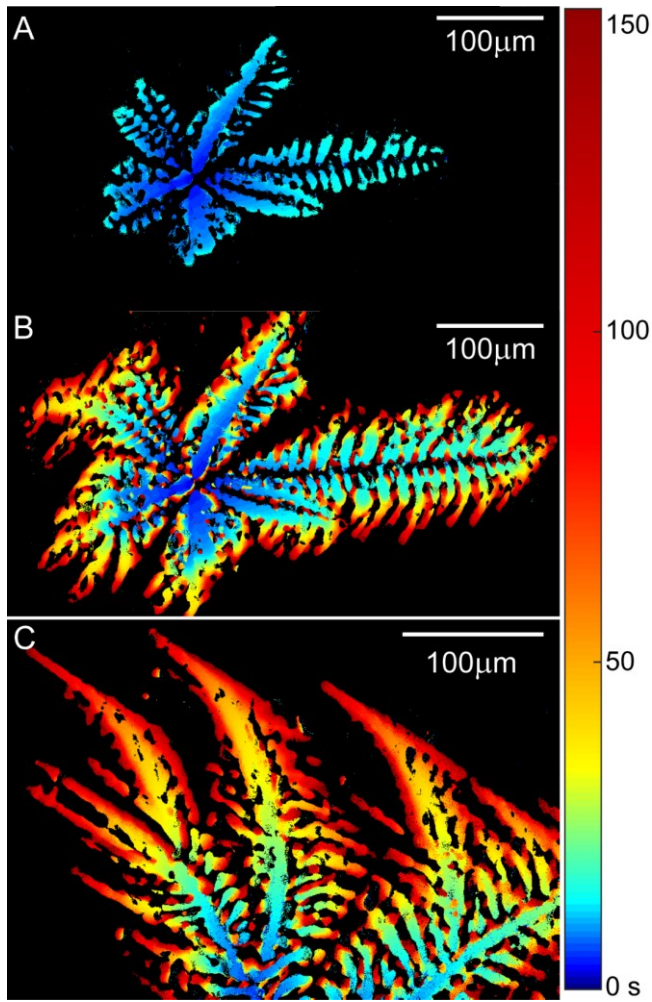


Fig. 12. Synchrotron radiography of equiaxed Cu_6Sn_5 dendrite growth in Sn-10Cu . Images are coloured by the time each pixel becomes solid based on image processing of raw radiograph sequences. A) A non-faceted dendrite at 15s since nucleation. B) The same crystal as A) at 150s after further growth and coarsening. C) shows obvious faceting at dendritic tips that developed during coarsening towards the end of solidification.

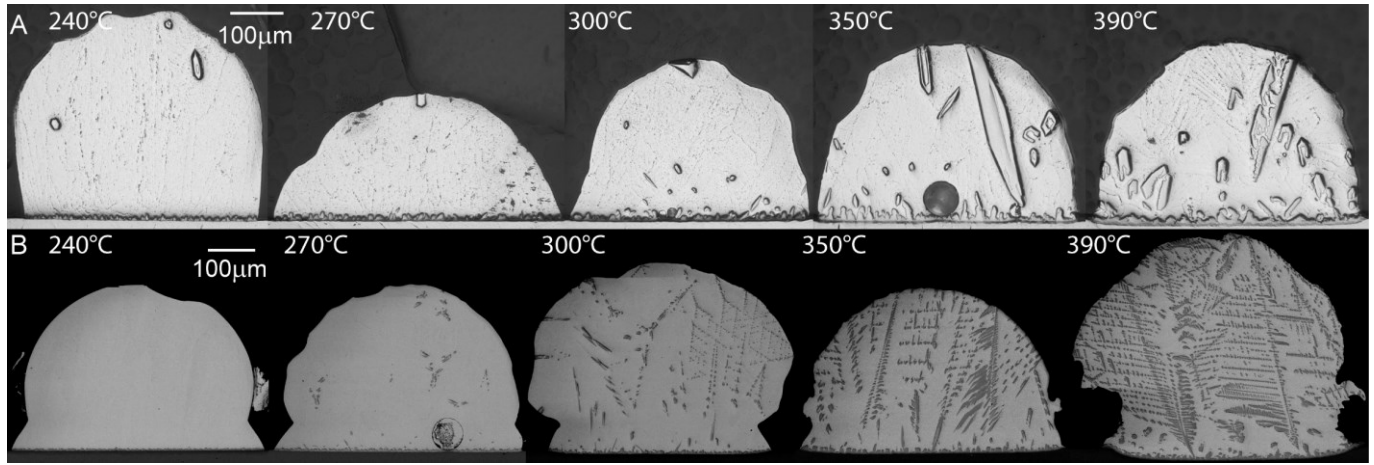


Fig. 13. The morphologies of primary Cu_6Sn_5 in Sn-0.7Cu/Cu joints held for 5 mins at the five peak temperatures shown and then cooled at either A) 0.67K/s or B) $\sim 30\text{K/s}$.

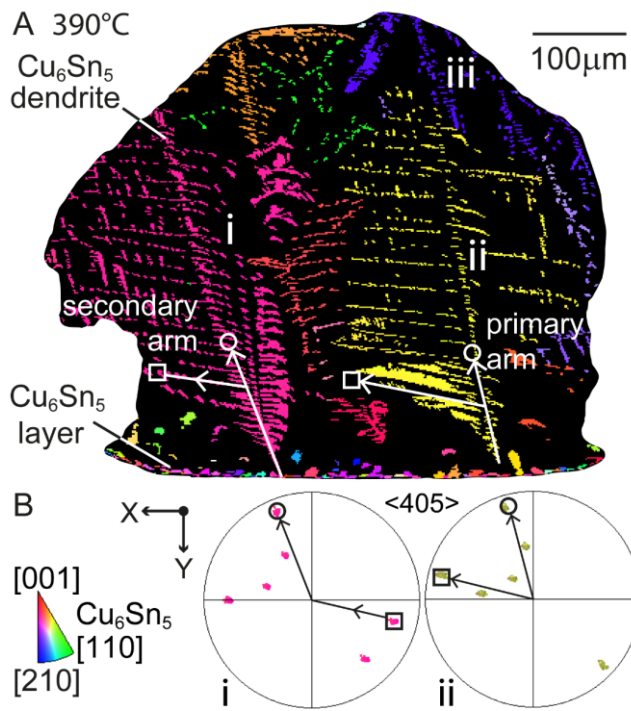


Fig. 14. A) IPF-x map of Sn-0.7Cu/Cu joints held at 390 °C then cooled at ~30K/s. Arrows mark the growth directions of primary (circle) and secondary (square) arms in grains labelled by “i, ii”. B) <405> pole figures with branching directions marked in grains “i, ii” respectively. The black arrows in B) correspond to arrows in A).

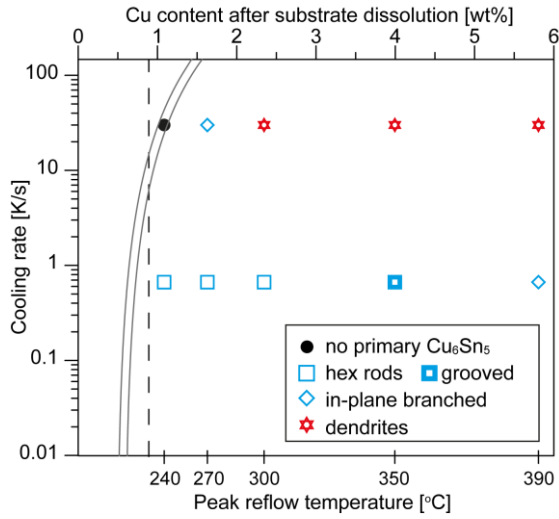


Fig. 15. Microstructure map for primary Cu_6Sn_5 in Sn-0.7Cu/Cu joints. The peak temperature is shown in the lower x-axis and the equilibrium liquid composition assuming uniform saturation is shown in the upper x-axis. The limit of no primary Cu_6Sn_5 is plotted as a grey line from Fig. 2A.