

Grain refinement of electronic solders: the potential of combining solute with nucleant particles

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Abstract

Sn-Ag-Cu electronic solder joints typically solidify from a single nucleation event producing either a single β Sn grain or twinned grains. With so few and variable β Sn orientations, each joint is mechanically unique due to the anisotropy of tetragonal β Sn. Here we explore the potential of increasing the number of β Sn orientations in solder joints by promoting heterogeneous nucleation during solidification. It is shown that large (60 g) samples can be grain refined effectively by combining growth restricting solute with potent heterogeneous nucleant particles introduced by alloying additions of Zn, Ti, Co, Ir, Pd, or Pt. These mechanisms are discussed with reference to the grain refinement of structural casting alloys. In 500 μ m solder balls, these grain refinement approaches were less effective and a relatively high cooling rate of 17 K/s combined with solute and nucleant particles were required to trigger multiple nucleation events. With this approach, up to 12 independent grains formed in 500 μ m balls of Sn-3Ag-0.5Cu alloyed with Pt, Co, or Ti, compared with one independent grain in balls without nucleant particle additions.

Keywords: Solidification; Nucleation; Pb-free soldering; EBSD

1. Introduction

Electronic solder balls and joints such as Sn-Ag-Cu (SAC) and Sn-Ag typically solidify with a large and variable nucleation undercooling for β Sn [1-3] and usually contain either a single β Sn grain or two/three β Sn orientations related by cyclic twinning [4, 5]. The large undercooling can lead to excessive dissolution of the substrate [6] and large primary intermetallic compounds (IMCs) such as Ag_3Sn blades, which can result in poor mechanical performance [3-5, 7-11]. The variable undercooling causes the microstructure to vary from joint to joint [12] and the small number of grains per joint is a concern because β Sn is tetragonal and has highly anisotropic properties such as thermal expansion [13] stiffness [14], and the diffusion of Ni and Cu [15, 16]. The orientation of the β Sn grain(s) plays an important role in electromigration resistance [17-21] and in the lifetime of a joint during thermal cycling [22, 23]. The presence of few β Sn grains that are oriented differently in each joint makes every joint unique which is a problem for predicting reliability. One potential solution would be to increase the number of β Sn orientations per joint through grain refinement during solidification. This paper explores the potential of grain refining solders.

Most electronic solders based on the Sn-Ag-Cu, Sn-Ag, or Sn-Cu systems have near-eutectic compositions and, after Cu substrate dissolution, the new liquid composition lies in the Cu_6Sn_5 primary phase field. While equilibrium solidification of this liquid would result in primary Cu_6Sn_5 and eutectic, the nucleation undercooling for β Sn and the growth kinetics favour β Sn dendrite growth. Therefore, the focus of this paper is on refining the size of β Sn dendrites (i.e. maximising the number of dendrites per unit volume).

A large body of work has explored the effect of dilute element additions on the nucleation undercooling for β Sn. This has found that the undercooling can be suppressed significantly by additions including: Zn [1-3, 11, 24-34], Al [2, 24, 30, 34-36], Co [2, 32-34, 37, 38], Mn [2, 30, 33, 39], Pt [40], Ti [33, 39, 41], and Pd [40]. Of these, Co [38], Pt [40], and

Pd [40] have been deduced to suppress undercooling by introducing heterogeneous nucleant particles of αCoSn_3 , PtSn_4 , and PdSn_4 , each of which has been shown to be a relatively good lattice match to βSn and to form a reproducible crystallographic orientation relationship [38, 40]. For most of the other additions, the mechanisms of undercooling suppression have not been explored in detail. Furthermore, it is not clear to what extent these additions cause grain refinement of βSn . Chung et al. [42] found that adding 0.2 wt% Mn or 0.4 wt% Zn to 600 μm diameter Sn-2.4Ag solder balls caused no grain refinement whereas adding 0.2 wt% Ti resulted in a fine grained microstructure. However, it is not clear from their micrographs whether there are (i) numerous independent grains or (ii) interlaced twinned dendrites growing from a single nucleation event with only three βSn orientations similar to the work in [4, 5, 43]. Ma et al. [38] found that adding 0.05 wt% Co to 550 μm Sn-3Ag-0.5Cu solder balls caused strong undercooling suppression but no grain refinement when the cooling rate was 0.33 K/s but resulted in up to three independent βSn nucleation events at cooling rates ≥ 5 K/s

In Al, Mg and Ti alloys [44-47], it has been shown that potent nucleant particles are much more effective at generating grain refinement when combined with solute [48, 49]. Solute restricts crystal growth by requiring an interface to cool as it grows [50]. It also causes a region of constitutional supercooling to develop in the liquid ahead of growing crystals in which further nucleation events can be triggered [51, 52]. A measure of how rapidly constitutional supercooling develops in the early stages of growth is Q , the “growth restriction factor”, which is defined in Eq. 1 and Eq. 2. m is the liquidus slope; k is the partition coefficient; C_0 is the bulk alloy composition; ΔT_s is the solute undercooling; T is the interface temperature; and f_s is the mass fraction of solid. Note that Eq. 1 and 2 are equal for binary alloys with constant m and k . Eq. 2 is more general and can be calculated for any alloy using a CALPHAD approach [53, 54]

$$Q = m(k - 1)C_0 \quad \text{Eq. 1}$$

$$Q = \left(\frac{\partial \Delta T_s}{\partial f_s} \right)_{f_s \rightarrow 0} = - \left(\frac{\partial T}{\partial f_s} \right)_{f_s \rightarrow 0} \quad \text{Eq. 2}$$

In Al, Mg, and Ti-based alloys [47, 55-57], it has been shown that the grain size is often inversely proportional to Q as in Eq.3, provided the solute addition does not significantly influence the nucleant particles (e.g. by reacting with them or changing their morphology or size distribution etc.):

$$d = a + b/Q \quad \text{Eq. 3}$$

Where d is the grain size and a and b are empirical constants to be determined from experimental measurements. Recent theoretical treatments give a similar expression [51, 58]. The role of Q on the grain refinement of solders has not been explored in detail previously. Figure 1(A) is a plot of growth restriction factor, Q , versus solute content for binary Sn-X systems relevant to electronic soldering, based on phase diagram data from the TCSD3 database of Thermo-Calc [59]. It can be seen that, for the maximum addition levels where β Sn is still the primary phase for equilibrium solidification, Bi, Pb, Cd, and Zn give the highest Q -values; Au, Ag, In, and Cu give moderately high Q -value; and Mn, Fe, Co, Ni, Pd, and Pt have a negligible Q -value. Note that Figure 1(A) is valid only for binary Sn-X alloys and that the Q -value of multicomponent alloys should be calculated using Eq. 2 and a thermodynamic database [53, 54] as shown for Sn-3Ag-0.5Cu in Figure 1(B).

This paper presents a systematic study of the effects of solute and heterogeneous nucleant particles on the grain refinement of β Sn in solder alloys. Since the effects of solute and nucleant particles are interdependent [51, 52, 60], we separate these factors (as far as is possible) by studying (i) the influence of solute at a near-constant value of nucleation undercooling and with similar nucleant and (ii) the influence of different nucleant particles at a near-constant value of Q .

To study the influence of solute, we study Sn- x Zn and Sn- y Bi- x Zn alloys where $x = 1$ -6 wt% Zn and $y = 0$ -35 wt% Bi We also study Sn- x Ag-0.5Cu-0.07Pt where $x = 0.05$ -3 wt%

Ag to understand how Ag solute affects grain refinement in the presence of potent PtSn_4 nucleant particles.

To study the influence of different nucleant particles, we study ‘alloying’ additions to Sn-3Ag-0.5Cu (wt%) solder that (i) do not significantly affect the Q-value of Sn-3Ag-0.5Cu (calculated using [59]) and (ii) strongly reduce the nucleation undercooling, based on a review of the literature [1-3, 11, 24-40, 61]. We selected seven additions at the level given in S.I.-Table 1: Pd, Pt, Co, Mn, Ti, and Zn. We also selected 0.07 wt% Ir because we expect IrSn_4 to be a heterogeneous nucleant similar to αCoSn_3 [38], PtSn_4 [40], and PdSn_4 [40] based on a lattice matching analysis.

We first study volumes comparable to previous studies on the grain refinement of Al-, Mg-, and Ti-based alloys [47, 62, 63] to extract information on the heterogeneous nucleation and grain refinement mechanisms of solder alloys. We then study volumes relevant to electronic soldering to explore the extent to which solder joints can be grain refined.

Note that in solder joints, the liquid solder is in contact with a rough intermetallic reaction layer that significantly affects βSn nucleation [12, 64, 65]. For example, βSn usually nucleates on the Cu_6Sn_5 layer in joints on Cu substrates unless heterogeneous nucleants are added [65]. In this paper, we restrict ourselves only to freestanding balls and bulk alloys (i.e. without a reactive substrate) to focus on the role of alloy compositions and nucleant particles.

2. Materials and Methods

Alloys were prepared from 99.9% purity materials. For most alloys, 366±3 g was made by mixing the required amounts of Sn, Zn, Bi, Ag, and/or master alloys of Sn-10Cu, Sn-10Mn, Sn-10Co, Sn-2Pd, and/or Sn-1Pt in graphite crucibles. The mixtures were held at 400 °C in a forced-air convection resistance oven (Lenton, UK) for 1-h and were then stirred with a graphite rod to ensure complete dissolution and a uniform mixture. SAC305-0.2Ti samples were made by arc melting SAC305 and Ti directly. A portion of each melt was then cast into a chemical analysis mould, producing 30 g button-like samples. These were measured by X-ray fluorescence (XRF) spectroscopy and the measured compositions are shown in SI-Table 1.

Cylindrical graphite moulds with 10 mm wall thickness, 19.5 mm inner diameter, and 39.5 mm inner height were heated to the same temperature as the crucible and melt by heating them together. The following procedure was then used for each experiment: a mould was removed from the oven and placed on an insulating Fibrefrax® board, liquid was poured into the preheated mould, a thermocouple was placed in the centre of the melt and a second insulating Fibrefrax® board was placed on top of the mould. The thermocouple was a 1.5mm K-type held within a 1.5 mm inner diameter quartz tube containing silicone oil to improve the response time. The temperature was recorded by a datalogger (TC-08(USB), Picolog) every 100 ms during cooling. An important feature of this experiment is that the mould and liquid metal are initially at the same temperature above the liquidus temperature to minimise temperature gradients and conduct solidification in a near-uniform thermal field (Biot number ~0.1), and to prevent the formation of a chill zone. The relatively large samples (60 g, ~8370 mm³) are comparable to grain refinement studies on other alloy systems [34] and allow an immersed thermocouple for cooling curve analysis.

Figure 2(A) shows a typical example of a Sn-3Ag-0.5Cu cooling curve and its first derivative. The cooling rate was defined as the mean value in the range of 250 – 235 °C and

was ~ 1.1 K/s for all alloys. Figure 2(B) defines four temperatures in the early stages of solidification. T_{eq} is the equilibrium liquidus temperature; T_{nuc} is the nucleation temperature defined as the temperature at which latent heat is first detected in the derivative curve; T_{min} is the minimum temperature reached prior to recalescence; and T_{max} is the maximum temperature reached after recalescence. These temperatures can be combined to give the following definitions.

True nucleation undercooling: $\Delta T_{true} = T_{eq} - T_{nuc}$

Recalescence: $\Delta T_{rec} = T_{max} - T_{min}$

Measured nucleation undercooling: $\Delta T_n = T_{max} - T_{nuc}$

Note that the nucleation undercooling was defined here as $T_{max} - T_{nuc}$, as is common in cooling curve analysis by the immersed thermocouple technique [66], because T_{eq} is not accurately known. In each cooling curve, T_{nuc} , T_{min} , T_{max} and dT/dt were measured.

Past studies on the grain size of tin alloys found that recrystallization can occur during sample preparation, precluding the measurement of the solidification microstructure [34]. Therefore, trials were performed to develop a suitable sample preparation technique. It was found to be necessary to avoid using a saw, to mount samples in cold mounting resin and to carefully wet-grind to the mid-section of the sample with SiC paper (ending with 2500 grit). Samples were then carefully polished with either colloidal silica suspension or, in the case of high Bi and Zn containing alloys, with neutral alumina suspension.

To reveal the grain size in large samples, cross-sections were etched with 4.3% HCl + 8.7% FeCl₃ in distilled water for 15-30 s depending on the composition. The whole $\sim 26000 \times 22000$ μm cross-section of etched samples were photographed with an Olympus E-PM1 camera. To confirm that the sample preparation and imaging method revealed the as-solidified βSn grains, the etched macrographs were compared with polarised light micrographs from before etching. It was confirmed that the grain boundaries in the macrographs of etched samples

correlated with the grain boundaries under polarised light microscopy of the unetched structures, and that most grains in the polarised light micrographs corresponded to an obvious dendrite. Typical examples are shown in (S.I. Figure 1).

β Sn grain size was defined and measured using the linear intercept method [67]. Four samples at each composition were used for grain size measurements. 6 horizontal and 11 vertical lines were drawn across each full cross-section as shown in (S.I. Figure 2). This resulted in 97- 403 intercepts per sample depending on the grain size. The mean grain size was found for each cross-section and the standard deviation was calculated from the means of the four samples.

Ball grid array (BGA) scale solder balls were made from the same compositions as the 60 g samples. Ingots were first rolled to foils of 0.03 mm thickness, then punched to $\varnothing$ 1.6 mm solder discs and, finally, 525 ± 25 μ m diameter solder balls were formed by reflow on a hot plate with a ROL1 tacky flux (IPC J-STD-004) due to surface tension. Solder balls were then reflowed in a Mettler Toledo DSC in aluminium crucibles under a nitrogen atmosphere. The heating rate was 0.17 K/s, the peak temperature was 240 °C and the cooling rate was 0.33 K/s. Every solder ball was given two cycles and at least 10 balls of each composition were measured. To explore the effects of nucleant particles and solute at higher cooling rate, some solder balls were heated to 240 °C on a STUART digital hotplate and were then cooled by forced convection giving a cooling rate of $\sim$ 17 K/s. At least 5 samples were tested per composition at high cooling rate for chosen compositions.

Solder ball microstructures were studied using a Zeiss AURIGA field emission gun SEM (FEG-SEM) equipped with an Oxford Instruments INCA x-sight energy dispersive X-ray detector (EDX) and a BRUKER e-FlashHR electron backscatter diffraction (EBSD) detector. BRUKER ESPRIT 2.0 software was used to analyse the obtained EBSD patterns and

BRUKER ESPRIT DynamicS software was used for comparison of the experimental and dynamical simulated EBSD patterns.

3. Results and Discussion

3.1 *The influence of solute on the grain refinement of 60 g samples*

The cooling curve and microstructure of a typical 60 g sample of commercial purity (99.9%) Sn is shown in Figure 3. In Figure 3C, ΔT_n is ~ 12 K. Figure 3A and B show that there is a single dendrite in the whole 60 g sample. This can be seen from the single orientation of the dendrite arms throughout the cross section (Figure 3A) and from the top surface (Figure 3B) where liquid has flowed down through the dendrite network due to shrinkage and revealed dendrite arms with a single orientation. For a 12K undercooling to generate a single dendrite in a 60 g sample cooled in a near-uniform thermal field, it can be inferred that the naturally occurring heterogeneous nucleation sites in CP-Sn are both of low potency and of small number per unit volume, and also possibly have a wide distribution of low potencies. Under these conditions, nucleation occurs at relatively large undercooling (for a 60 g sample) which leads to rapid growth and latent heat release, and no further nucleation events occur because there is a lack of other nucleation sites requiring similar undercooling which allows latent heat release to stifle nucleation on all other sites. Furthermore, the very low solute content in CP-Sn cannot develop sufficient constitutional supercooling in the liquid to trigger further nucleation events. All other alloys in this work exhibited multiple β Sn grains in 60 g samples, even alloys with ΔT_n exceeding that of CP-Sn.

Figure 4 and Table 1 shows the ΔT_n and grain size data for Sn-xZn alloys along with the relevant part of the Sn-Zn phase diagram. In Figure 4B, it can be seen that ΔT_n decreases sharply with Zn additions, from 10.9 ± 2.1 K without Zn to 0.9 ± 0.2 K with 1wt% Zn. With Zn additions in the range 1-7.5 wt%, the undercooling remains at 0.7 ± 0.1 K. Figure 4C is a plot of the β Sn grain size versus Zn content for the range of Zn contents where the ΔT_n is near-constant. It can be seen that the mean grain size decreases substantially with increasing Zn addition from 3180 to 1050 μm . Typical etched cross-sections are shown in Figure 5 where the

decreasing grain size with increasing Zn content can be seen clearly. Note that there is no chill zone and that the microstructure is equiaxed throughout the cross-sections.

Figure 6 and Table 1 show the ΔT_n and grain size for Sn-xBi-2Zn ternary alloys along with the relevant part of the Sn-Zn-Bi liquidus projection with the four measured compositions superimposed as red crosses. In Figure 6A, it can be seen that all four compositions are in the β Sn primary phase field. Figure 6B shows that these compositions each had a near-constant ΔT_n of 0.7 ± 0.3 K, which is similar to the Sn-Zn alloys used for grain size measurement (Figure 4B). The β Sn grain size decreased with increasing Bi content and reached a smallest mean grain size of 829 μm at Sn-35Bi-2Zn (Figure 6C).

Figure 7 shows the ΔT_n and grain size for Sn-xAg-0.5Cu-0.07Pt alloys along with the relevant part of the Sn-Ag-Cu liquidus projection with the four measured compositions superimposed. Note that the nucleant particles introduced by the Pt addition were required to ensure that the grain size was not too large; without the Pt addition, the Sn-3Ag-0.5Cu grain size was ~ 3724 μm which is off the grain size scale in Figure 7C. The 0.07Pt addition had a negligible effect on the Q-value and resulted in a near constant value of ΔT_n of 0.4 ± 0.2 K as shown in Figure 7B and Table 1. The β Sn grain size decreased with increasing Ag content and reached a smallest mean grain size of 817 μm at Sn-3Ag-0.5Cu-0.07Pt (Figure 7C). Typical etched cross-sections are shown in S.I. Figure 3 where the decreasing grain size with increasing Ag content can be seen clearly.

Figure 8 is a plot of the grain size versus $1/Q$ for the Sn-xZn, Sn-2Zn-xBi and Sn-xAg-0.5Cu-0.07Pt alloys. In all three alloy systems, the data can be fit reasonably well by a linear curves of the form in Eq.3 [68] as shown by the lines of best fit on Figure 8 and Table 2. The linear fits to the d - $1/Q$ plots in Figure 8 reveal information on the mechanisms of heterogeneous nucleation and grain refinement in these solder alloys.

The intercept value of $a = 750 \pm 65 \mu\text{m}$ in Sn-Zn and Sn-Bi-Zn alloys (Figure 8) is high compared with past work on other alloy systems. For example, the intercept is $< 200 \mu\text{m}$ for Al [69], Mg [47], and Ti [70] alloys for a similar cooling rate, ΔT_n and Biot number to this study. The intercept of $d-1/Q$ plots is associated with the mean spacing between nucleant particles [51] and so the number of nucleant particles per unit volume [56]. Thus, the high intercept value of $a \sim 750 \mu\text{m}$ in Sn-Zn and Sn-Bi-Zn alloys indicates that, while the Zn addition strongly reduces the undercooling for βSn nucleation, there are relatively few nucleant particles in the liquid. This might be because the Zn addition did not introduce a high number density of nucleant particles or, perhaps, they were not well dispersed throughout the liquid. The similar undercoolings and intercepts in the Sn-Zn and Sn-Bi-Zn alloys suggests that the nucleant particles and their distribution were similar in both systems. The intercept value of $a \sim -50 \mu\text{m}$ in Sn-xAg-0.5Cu-0.07Pt alloys (Figure 8) is much lower than in the Sn-Zn and Sn-Bi-Zn alloys, indicating that the Pt addition introduced more closely spaced nucleant particles (PtSn_4). The negative intercept value of $a \sim -50 \mu\text{m}$ in Sn-xAg-0.5Cu-0.07Pt alloys (Figure 8) is similar to negative values reported for other alloy systems [68]. This is most likely due to errors arising from finding a best fit line from four data points with significant scatter.

The slopes of the $d-1/Q$ plots in Figure 8 are also high compared with other systems. The slope is related to the constitutional supercooling profile ahead of a growing dendrite and to the potency of the nucleant particles, and has been approximated with Eq. 4 by StJohn et al. for Al, Mg, and Ti alloys [58].

$$d = a + \left(\frac{5.6D_L z \Delta T_n}{v} \right) \frac{1}{Q} \quad \text{Eq. 4}$$

Where D_L is the diffusivity of the solute in liquid Sn; ΔT_n is the undercooling required for nucleation of βSn on a nucleant particle; z is the fraction of the ΔT_n that is required to re-establish the necessary constitutional supercooling for another nucleation event after a grain nucleates in constitutionally supercooled liquid; and v is the interface velocity which is

assumed constant in [51, 58]. A practical problem with Eq. 4 (and its other variants) is that v and z are unknown and there is a large uncertainty in the value of D_L due to measurement difficulties (e.g. [71]). In their work on Al and Mg alloys, StJohn et al. [51] found a reasonable fit to their data when taking $v = 2 \mu\text{m/s}$ and $z = 0.1$. Assuming these v and z values, a value of D_L for Zn in liquid Sn of $(6.00 \pm 2.00) \times 10^{-9} \text{ m}^2/\text{s}$ [71] and the measured value of $\Delta T_n = 0.7 \pm 0.2 \text{ K}$ (Figure 4), gives a slope of $1064 \pm 504 \mu\text{m/K}$ compared with the best fit slope to the Sn - xZn experimental data of $9890 \mu\text{m/K}$ in Table 2. Thus, it has been found in this work that solders approximately follow the d vs. $1/Q$ relationship in Eq. 3, similar to Mg-, Al-, and Ti-based casting alloys. However, further work is required to quantitatively link the slopes of the d vs. $1/Q$ data with these other alloy systems.

3.2 The influence of nucleant particles at near-constant Q

The growth restriction factors, Q , of Sn-3Ag-0.5Cu with the different alloying additions are shown in Table 3. It can be seen that all Q -values are similar to each other and that all $1/Q$ values are in the range 0.08 - 0.09 which is very narrow compared with Figure 8. Thus, the additions are suitable for studying the effect of nucleant particles at near-constant Q .

Figure 9 shows typical etched cross-sections of 60 g SAC305 samples with and without alloying additions. It is clear that alloying with Zn, Ti, Ir, Co, Pd, and Pt caused significant grain refinement (i.e. more β Sn grains) and that the 0.2 Mn addition had little grain refining effect. The grain size data are summarised in Figure 10(A) where the alloys are ranked in order of the mean grain size. The most effective grain refiner was the 0.07 Pt addition which reduced the grain size from 3747 to 817 μm . The ΔT_n data are summarised in Figure 10(B) and are arranged in the same order as in Figure 10(A). Note that the undercooling axis (y-axis) is broken and that SAC305 had a mean undercooling of ~ 15 K whereas all alloying additions resulted in a mean undercooling of less than 2 K. The smallest ΔT_n of less than 0.5 K occurred with Ti, Co, and Pt additions. This strongly reduced ΔT_n with these 7 additions is consistent with past work [38, 40, 72] and indicates that the addition levels were suitable. By comparing Figure 10(A) and (B) it can be seen that there is no simple correlation between undercooling and grain size. For example, the 0.2 Ti addition gave a smaller undercooling but larger grain size than the 0.2 Pd addition. This is most likely because, for the same solidification conditions and Q -value, the grain size will depend on the size, shape, size distribution, and number density of the nucleant particles and not just on the nucleant potency. We did not attempt to optimise the size/shape properties of each nucleant in this work.

SEM analysis was performed to identify the nucleant particles. It was found that an additional IMC phase (in addition to Cu_6Sn_5 and Ag_3Sn) was present in samples alloyed with Mn, Ti, Ir, Co, Pd, and Pt. These had a morphology consistent with primary phases and,

therefore, are likely to have been present prior to β Sn nucleation. Figure 11 gives typical examples of the particles in Sn-3Ag-0.5Cu + Mn, Ti, and Pt, many of which are in the interdendritic eutectic and some of which are within the β Sn dendrites. The IMC phases were identified by combining EDS with EBSD as MnSn_2 , Ti_2Sn_3 , βIrSn_4 , αCoSn_3 , PdSn_4 , and PtSn_4 , as summarised in Table 4 (where the phases used for indexing are from references [73-78]) and Supplementary Information Figure 4. The EBSD analysis was limited to identifying the best-fit known phase with stoichiometry close to that measured by EDS. This involved finding the phase with the lowest “mean angular deviation” (MAD) coupled with visual inspection of the experimental and dynamical-simulated Kikuchi patterns. A low MAD of <0.68 was found for each of the identified phases using the eight bands of highest intensity. In the case of these IMC phases, this simple MAD approach was sufficient for phase discrimination and more complex methods such as cross-correlation between experimental and simulated Kikuchi patterns were not required. In contrast to Mn, Ti, Ir, Co, Pd, and Pt, alloying with 0.5wt% Zn did not appear to introduce a new primary phase, consistent with Thermo-Calc predictions [59].

In past work, we have shown that the main facets of PtSn_4 [40], PdSn_4 [40], and αCoSn_3 [38] are nucleation sites for β Sn and it is likely that βIrSn_4 operates by a similar mechanism due to the crystallographic similarities between βIrSn_4 and PtSn_4 [74]. Further work is required to confirm the heterogeneous nucleation mechanisms with Zn, Ti, and Mn additions. It may be that Ti_2Sn_3 and MnSn_2 are heterogeneous nucleants for β Sn [72] although this has not been proved yet and the fact that Mn additions did not result in significant grain refinement (Figure 9 and Figure 10) but did contain numerous MnSn_2 particles (Figure 11) suggests that a detailed study on the influence of Mn is required. Similarly, a detailed study is required to identify the heterogeneous nucleants introduced by Zn additions.

Further evidence for β Sn nucleation on the introduced IMCs can be gained from examination of the distribution of β Sn grains in Figure 9. In SAC305-0.07Pt, the grain size was smaller near

the bottom of the sample (Figure 9) and it was observed that there was a higher number of PtSn_4 particles near the sample bottom, due to their higher mass density relative to liquid Sn. Conversely, in SAC305-0.2Ti, it can be seen that the grain size was smaller near the top of samples (Figure 9) and it was observed that there was a higher number of Ti_2Sn_3 particles near the top of the sample, presumably due to the similar mass density of Ti_2Sn_3 ($\sim 7.2 \text{ g/cm}^3$ [75]) and liquid Sn ($\sim 6.9 \text{ g/cm}^3$ [79]).

Combining Figure 7, Figure 10, and Table 1, it can be seen that PtSn_4 particles caused a low undercooling of $0.4 \pm 0.2 \text{ K}$ at any Ag level but the effectiveness of PtSn_4 as a grain refiner depended on the Ag solute content via the Q-value, such that the grain size decreased from $2392 \mu\text{m}$ at 0.5 wt% Ag to $817 \mu\text{m}$ at 3 wt% Ag. This clearly shows that nucleant particles need to be combined with growth restricting solute to most effectively grain refine 60 g samples of solders.

A striking feature of all 60 g sample microstructures in this work is that, although the grain size was significantly reduced by combining solute with nucleant particles, the βSn grain size was relatively large in all cases. Indeed the smallest grain sizes ($\sim 817 - 830 \mu\text{m}$ in SAC305-0.07Pt and Sn-2Zn-35Bi) were larger than a typical BGA ball used in electronic packaging. One reason for this may be the relatively large size of the IMC nucleant particles. For example, TiB_2 particles in Al grain refinement tend to be numerous $0.5 - 3 \mu\text{m}$ wide platelets that are well-dispersed throughout the melt. In contrast, the primary IMCs introduced by alloying and slow cooling in this work (overviewed in Table 4) were typically $20 - 200 \mu\text{m}$ wide at which size there will be a relatively low number density of nucleant particles.

3.3 Grain refinement of 500 μm BGA solder balls

Figure 12(A)-(C) overviews the typical microstructure of 500 μm solder balls cooled at 0.33 K/s from 240°C in a DSC. From the optical micrographs in Figure 12 (A)-(C), it can be seen that, as the Zn content increased, the βSn dendrite morphology became more intricate and the volume fraction of eutectic increased as expected. The EBSD IPF-x and IPF-y maps show that the Sn-1Zn ball contains three βSn orientations that appear to form multiple ‘grains’ in this 2D section, that the Sn-3Zn ball contains two dendritic ‘grains’ and that the Sn-6Zn ball contains a single dendrite. This might appear to imply that increasing the Zn content decreased the number of nucleation events but, examination of the pole figures and misorientation histograms in Figure 12 (A)-(C) shows that the different βSn orientations are all related by $\sim 60^\circ$ rotations around a common $\langle 100 \rangle$ axis (the common $\{100\}$ plane is marked ‘CP’ in the pole figures). This is the widely reported phenomenon of $57.2^\circ \{101\}$ or $62.8^\circ \{301\}$ solidification twinning in solder balls [4, 5, 80]. Since all the grains in one solder ball are related by a twin OR, it can be concluded that they grew from a single nucleation event in each ball. That is to say, all balls solidified with a single βSn nucleation event and the increasing Zn content did not affect the number of βSn nucleation events in 500 μm solder balls cooled at 0.33 K/s. It was found that solidification twinning could occur in all Sn-xZn compositions ($x=1-6$ wt% Zn) but was variable from ball to ball, occurring in some samples (e.g. Figure 12((A) and (B)) and not in others (e.g. Figure 12(C)).

Figure 12(D)-(E) are typical examples of microstructures in 500 μm Sn-3Ag-0.5Cu-X solder balls cooled at 0.33 K/s in a DSC. The optical micrographs show the typical βSn dendrite morphology in slow cooled SAC305-X balls. Figure 12(D) is a Sn-3Ag-0.5Cu-0.5Zn ball consisting of three βSn orientations related by $\sim 60^\circ$ rotations around a common $\langle 100 \rangle$ axis, indicating solidification twinning similar to that in Figure 12(A)-(B). Figure 12(E) is a Sn-3Ag-0.5Cu-0.2Mn ball consisting of a single βSn orientation. At least 5 balls from each Sn-

3Ag-0.5Cu-X composition were studied by EBSD mapping similar to Figure 12(D)-(E). Table 5 summarises the results for each alloy. Table 5 shows the number of balls with a single β Sn orientation, the number with two/three orientations related by solidification twinning, and the number of balls with multiple independent grains. Here, independent grains are defined as those not related by a common $\langle 100 \rangle$, $\langle 001 \rangle$, or $\langle 110 \rangle$ axis. It can be seen in Table 5 that all Sn-3Ag-0.5Cu-X solder balls cooled at 0.33 K/s solidified to contain either a single orientation or two/three orientations related by cyclic twinning, and all balls contained only one independent orientation. Thus, it can be concluded that all SAC305-X solder balls solidified with a single β Sn nucleation event and the alloying additions did not increase the number of nucleation events in solder balls cooled at 0.33 K/s.

The ΔT_n for β Sn in alloyed solder balls cooled in the DSC are shown in Figure 13. The ΔT_n was substantially smaller than in unalloyed Sn-3Ag-0.5Cu but was somewhat larger than in the 60 g samples. Microstructural analysis confirmed that the same primary IMC particles were present in solder balls as in 60 g samples (given in Table 4). These particles had fairly uniform distribution with multiple particles in each cross-section of 500 μ m solder balls.

Clearly, the lack of grain refinement in DSC cooled solder balls cooled at 0.33 K/s is partially related with the small size of solder balls since, in 60 g samples cooled at 1 K/s in a near-uniform thermal field, the grain size is larger than the solder ball diameter even for the most grain refined composition (Sn-3Ag-0.5Cu-0.07Pt) (as shown in Figure 10). The small solder ball size will also promote thermal mixing which causes the whole ball to heat up rapidly during latent heat release, and solutal mixing in the liquid which will reduce the degree of constitutional supercooling (CS) that can develop and, therefore, impede CS-driven grain refinement.

In an attempt to trigger more nucleation events, solder balls were next cooled at the higher cooling rate of 17 K/s. Figure 14(A) and (C) are typical EBSD maps of CP-Sn and

SAC305 after cooling at 17 K/s which have a single orientation and cyclically-twinned β Sn grains respectively, indicating that there was only one nucleation event in each case. Similarly, all CP-Sn and SAC305 balls cooled at 17 K/s contained only one independent grain per ball (as summarised in Table 6). In contrast, fast cooled solder balls of compositions with added nucleant particles usually solidified to give multiple independent grain structures as summarised in Table 6 based on at least 5 samples for each tested composition. Typical examples are given in Figure 14(B) and (D) for Sn-0.07Pt and SAC-0.2Ti. The presence of independent grains can be seen by noting that pole figures with independent grains of tetragonal β Sn have twice as many $\{100\}$ planes as $\{001\}$ planes. As an example, the Sn-0.07Pt sample in Figure 14(B) and the SAC305-0.2Ti sample in Figure 14(D) both have 3 spots in the $\{001\}$ pole figure and 6 spots in the $\{100\}$ pole figure, indicating 3 independent grains in each case. Similar results were found with Co, Zn, Ir, Pd, and Pt additions as summarised in Table 6. Thus, it can be concluded that the nucleant particles successfully triggered additional nucleation events in 500 μ m BGA balls when the cooling rate was 17 K/s.

In some SAC-X samples cooled at 17 K/s, the eutectic β Sn had a different orientation to the surrounding β Sn dendrite. An example is given in Figure 14(E), where it can be seen that most pink, purple and blue oriented dendrites have a green β Sn orientation between the dendrite arms, and the green dendrite has blue β Sn orientation between its dendrite arms. This is a potentially useful microstructure as it creates a large interfacial area of high angle grain boundaries combined with a significantly increased number of orientations compared with SAC305 (Figure 14(C)). However, unfortunately, this phenomenon was not reproducible and occurred in some samples but not others and further work is required to identify a method to reproducibly generate this microstructure.

To test whether the number of nucleation events in BGA balls could be increased further by combining solute with nucleant particles, studies were performed on SAC305-

0.07Pt-5Bi. Note that the Bi content (and therefore Q-value) that can be added to SAC305 whilst remaining in the β Sn primary phase field is limited [59] and, therefore, SAC305-0.07Pt-5Bi with $Q = 25.5$ K [59] was selected in this work. An example of a SAC305-0.07Pt-5Bi ball cooled at 17 K/s is shown in Figure 14(F), where the presence of twelve independent grains can be seen from the 12 spots in the $\{001\}$ pole figure and 24 spots in the $\{100\}$ pole figure. Results of multiple balls are summarised in Table 6 where a Q-value effect can be seen by comparing fast cooled Sn-0.07Pt ($Q \sim 0$), SAC305-0.07Pt ($Q = 11.2$ K), and SAC305-0.07Pt-5Bi ($Q = 25.5$ K) samples and noting that the percentage of samples with multiple independent grains was 50% for Sn-0.07Pt, 80% for SAC305-0.07Pt, and 100% for SAC305-0.07Pt-5Bi based on 5 or 6 samples of each. Additionally, for the samples that contained independent grains, the mean number of independent grains was 2 for Sn-0.07Pt, 3 for SAC305-0.07Pt, and 7 for SAC305-0.07Pt-5Bi. These results show that combining solute with nucleant particles in 500 μ m balls does increase the number of nucleation events at high cooling rate, but this effect is more subtle than in large (60 g) samples (e.g. Figure 8 and Table 1).

Combining the findings on the grain refinement of BGA balls in Figure 14 and Table 5, it can be concluded that the combination of solute, nucleant particles and high cooling rate significantly increased the number of nucleation events in BGA-scale balls from 1 to up to ~ 12 (Figure 14 and Table 5). However, even with 12 independent β Sn orientations, solder balls would still be expected exhibit anisotropic behaviour and large joint-to-joint variability in their thermo-mechanical response.

3.4 Outlook for the grain refinement of solder joints:

The approach to grain refinement in this paper has been to increase the number of independent β Sn grains by increasing the number of β Sn nucleation events through a combination of nucleant particles, solute, and high cooling rate. However, even if this approach is further optimised and better nucleants are developed, it is unlikely to be able to generate tens or hundreds of different orientations in a BGA solder ball.

Another approach to achieving a fine-grained microstructure is to encourage the interlaced twinned microstructure that can occur in Sn-Ag and Sn-Ag-Cu solders [80] [5]. Figure 15 gives a typical example. The EBSD IPF-y map shows numerous regions of blue, purple and salmon-coloured orientations. From the pole figures, it can be seen that there are only three β Sn orientations that all share a common $\{100\}$ plane. Thus, the interlaced twinned SAC305 microstructure comes from a single nucleation event, similar to the twinned Sn-Zn and SAC305 microstructures in Figure 12 (A,B,D) and Figure 14 (C). If we define the ‘grain size’ in interlaced twinned microstructures as the linear distance between the high angle boundaries using the linear intercept method on EBSD orientation maps, then the mean ‘grain size’ in Figure 15 is $\sim 7\ \mu\text{m}$. This could be said to be considerable refinement but there are only three orientations which all share a common $\langle 100 \rangle$ axis and, therefore, this approach does not solve the problem of each joint being an oligo-crystal with highly anisotropic properties and stochastic differences in orientations from joint to joint. Furthermore, fully-interlaced microstructures in Sn-Ag-Cu solders usually require a relatively deep undercooling [5] which is difficult to control reproducibly.

A further approach to the grain refinement of solder joints is the application of ultrasonic vibration during solidification. This approach is already showing promise [81] [82] and it is likely to be more effective when combined with solute and nucleant particles.

In this paper, we have focussed on freestanding solder balls. In joints, β Sn nucleates in a liquid contacting rough IMC reaction layers that can affect nucleation significantly [64, 65, 83, 84]. For example, we have shown previously that different metallic substrates can catalyse β Sn nucleation to different degrees [12] and that certain solder-substrate combinations (e.g. Sn-0.7Cu/Cu and Sn-0.7Cu-0.05Ni/Cu) result in multiple independent grains growing from the IMC layer [65, 85]. Therefore, there may be opportunities to engineer the substrate to control the number of β Sn nucleation events and this approach is likely to be most effective when solute and nucleation sites are combined.

4. Conclusions

The potential of grain refining solder alloys by combining nucleant particles with solute has been explored.

Large (60 g) samples of Sn-based solders were grain refined effectively by combining growth restricting solute with potent heterogeneous nucleant particles. Solute played a strong role in grain refinement and the solders approximately followed the d vs. $1/Q$ relationship shown previously for casting alloys (Mg-, Al-, and Ti-based alloys). Bi and Zn were effective growth restricting solutes when added at high concentration and Ag was also effective when potent nucleant particles were present.

Six alloying additions that are known to suppress undercooling (Zn, Ti, Co, Ir, Pd, and Pt) were shown to cause significant grain refinement of Sn-3Ag-0.5Cu. The smallest grain size formed with Pt, Pd, and Co micro-alloying due to heterogeneous nucleation on PtSn_4 , PdSn_4 , and αCoSn_3 particles. Further work is required to confirm the heterogeneous nucleation mechanisms with dilute Zn and Ti additions.

In 500 μm BGA balls, the key factors affecting the number of nucleation events during solidification have been shown to be:

- 1- The addition of nucleant particles such as PtSn_4 or αCoSn_3
- 2- The addition of solute that generates a high growth restriction factor
- 3- A high cooling rate

CP-Sn and SAC305 BGA balls solidified with a single nucleation event under all conditions in this work and any of (1), (2), or (3) applied alone did not trigger additional nucleation events. Combining (1) and (3) triggered additional nucleation events (e.g. Sn-0.07Pt) but the most nucleation events were triggered when combining (1), (2), and (3) (e.g. SAC305-5Bi-0.07Pt).

The addition of nucleant particles, solute and high cooling rate successfully generated up to ~12 independent β Sn orientations in 500 μ m BGA balls compared with 1 independent grain in SAC305. However, even if this approach is further optimised and better nucleants are developed, it is unlikely to be able to generate the hundreds of different β Sn orientations in a BGA solder ball that would be required to give a near-isotropic joint, unless it is combined with other approaches.

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References

- [1] I. de Sousa, D.W. Henderson, L. Patry, S.K. Kang, D.Y. Shih, The influence of low level doping on the thermal evolution of SAC alloy solder joints with Cu pad structures, in: 56th IEEE Electronic Components & Technology Conference (ECTC) 2006,, 2006, pp. 1454-1461.
- [2] I.E. Anderson, J.W. Walliser, J.L. Harringa, F. Laabs, A. Kracher, Nucleation Control and Thermal Aging Resistance of Near-Eutectic Sn-Ag-Cu-X Solder Joints by Alloy Design, *J. Electron. Mater.*, 38 (2009) 2770-2779.
- [3] D. Swenson, The effects of suppressed beta tin nucleation on the microstructural evolution of lead-free solder joints, *J. Mater. Sci.-Mater. Electron.*, 18 (2007) 39-54.
- [4] L.P. Lehman, Y. Xing, T.R. Bieler, E.J. Cotts, Cyclic twin nucleation in tin-based solder alloys, *Acta Mater.*, 58 (2010) 3546-3556.
- [5] B. Arfaei, N. Kim, E.J. Cotts, Dependence of Sn Grain Morphology of Sn-Ag-Cu Solder on Solidification Temperature, *J. Electron. Mater.*, 41 (2012) 362-374.
- [6] S. Chada, R.A. Fournelle, W. Laub, D. Shangguan, Copper substrate dissolution in eutectic Sn-Ag solder and its effect on microstructure, *J. Electron. Mater.*, 29 (2000) 1214-1221.
- [7] T.-K. Lee, B. Zhou, L. Blair, K.-C. Liu, T.R. Bieler, Sn-Ag-Cu Solder Joint Microstructure and Orientation Evolution as a Function of Position and Thermal Cycles in Ball Grid Arrays Using Orientation Imaging Microscopy, *J. Electron. Mater.*, 39 (2010) 2588-2597.
- [8] J.-M. Song, J.-J. Lin, C.-F. Huang, H.-Y. Chuang, Crystallization, morphology and distribution of Ag₃Sn in Sn-Ag-Cu alloys and their influence on the vibration fracture properties, *Materials Science and Engineering: A*, 466 (2007) 9-17.
- [9] R. Kinyanjui, L.P. Lehman, L. Zavalij, E. Cotts, Effect of Sample Size on the Solidification Temperature and Microstructure of SnAgCu Near Eutectic Alloys, *Journal of Materials Research*, 20 (2005) 2914-2918.
- [10] Y. Takamatsu, H. Esaka, K. Shinozuka, Formation Mechanism of Eutectic Cu₆Sn₅ and Ag₃Sn after Growth of Primary beta-Sn in Sn-Ag-Cu Alloy, *Materials Transactions*, 52 (2011) 189-195.
- [11] S.K. Kang, D.Y. Shih, D. Leonard, D.W. Henderson, T. Gosselin, S.I. Cho, J. Yu, W.K. Choi, Controlling Ag₃Sn plate formation, in near-ternary-eutectic Sn-Ag-Cu solder by minor Zn alloying, *Jom*, 56 (2004) 34-38.
- [12] C.M. Gourlay, S.A. Belyakov, Z.L. Ma, J.W. Xian, Nucleation and Growth of Tin in Pb-Free Solder Joints, *Jom*, 67 (2015) 2383-2393.
- [13] B.G. Childs, The Thermal Expansion of Anisotropic Metals, *Reviews of Modern Physics*, 25 (1953) 665-670.
- [14] E.W. Kammer, L.C. Cardinal, C.L. Vold, M.E. Glicksman, The elastic constants for single-crystal bismuth and tin from room temperature to the melting point, *Journal of Physics and Chemistry of Solids*, 33 (1972) 1891-1898.
- [15] B.F. Dyson, T.R. Anthony, D. Turnbull, Interstitial Diffusion of Copper in Tin, *Journal of Applied Physics*, 38 (1967) 3408-3408.
- [16] D.C. Yeh, H.B. Huntington, Extreme Fast-Diffusion System: Nickel in Single-Crystal Tin, *Physical Review Letters*, 53 (1984) 1469-1472.
- [17] M. Lu, D.-Y. Shih, P. Lauro, C. Goldsmith, D.W. Henderson, Effect of Sn grain orientation on electromigration degradation mechanism in high Sn-based Pb-free solders, *Applied Physics Letters*, 92 (2008) 211909.
- [18] T.L. Yang, J.J. Yu, C.C. Li, Y.F. Lin, C.R. Kao, Dominant effects of Sn orientation on serrated cathode dissolution and resulting failure in actual solder joints under electromigration, *Journal of Alloys and Compounds*, 627 (2015) 281-286.
- [19] C. Kinney, X. Linares, K.-O. Lee, J.W. Morris, The Effect of Sn Orientation on Intermetallic Compound Growth in Idealized Sn-Cu-Ag Interconnects, *J. Electron. Mater.*, 42 (2013) 607-615.
- [20] C.E. Ho, C.H. Yang, L.H. Hsu, Electromigration in thin-film solder joints, *Surface and Coatings Technology*, 259, Part B (2014) 257-261.

- [21] J.-Q. Chen, J.-D. Guo, K.-L. Liu, J.-K. Shang, Dependence of electromigration damage on Sn grain orientation in Sn–Ag–Cu solder joints, *Journal of Applied Physics*, 114 (2013) 153509.
- [22] B. Arfaei, Y. Xing, J. Woods, J. Wolcott, P. Tumne, P. Borgesen, E. Cotts, The effect of Sn grain number and orientation on the shear fatigue life of SnAgCu solder joints, in: 2008 58th Electronic Components and Technology Conference (ECTC), IEEE, 2008, pp. 459-465.
- [23] T.R. Bieler, H. Jiang, L.P. Lehman, T. Kirkpatrick, E.J. Cotts, B. Nandagopal, Influence of Sn Grain Size and Orientation on the Thermomechanical Response and Reliability of Pb-free Solder Joints, *IEEE Transactions on Components and Packaging Technologies*, 31 (2008) 370-381.
- [24] A. Ohno, T. Motegi, The Effect of Small Additives on the Undercooling of Pure Tin, *J. Japan Inst. Metals*, 37 (1973) 777-780.
- [25] H.R. Kotadia, O. Mokhtari, M.P. Clode, M.A. Green, S.H. Mannan, Intermetallic compound growth suppression at high temperature in SAC solders with Zn addition on Cu and Ni-P substrates, *Journal of Alloys and Compounds*, 511 (2012) 176-188.
- [26] J.-M. Song, C.-F. Huang, H.-Y. Chuang, Microstructural characteristics and vibration fracture properties of Sn-Ag-Cu-TM (TM = Co, Ni, and Zn) alloys, *J. Electron. Mater.*, 35 (2006) 2154-2163.
- [27] I.E. Anderson, J. Walleiser, J.L. Harringa, Observations of nucleation catalysis effects during solidification of SnAgCuX solder joints, *Jom*, 59 (2007) 38-43.
- [28] A.A. El-Daly, A.M. El-Taher, Evolution of thermal property and creep resistance of Ni and Zn-doped Sn-2.0Ag-0.5Cu lead-free solders, *Materials & Design*, 51 (2013) 789-796.
- [29] A.A. El-Daly, A.E. Hammad, G.S. Al-Ganainy, M. Ragab, Influence of Zn addition on the microstructure, melt properties and creep behavior of low Ag-content Sn–Ag–Cu lead-free solders, *Materials Science and Engineering: A*, 608 (2014) 130-138.
- [30] A.J. Boesenberg, Development of Al, Mn, & Zn doped Sn-Ag-Cu-X solders for electronic assembly, in, Iowa State University, MSc Thesis, 2011.
- [31] Y.S. Kim, K.S. Kim, C.W. Hwang, K. Suganuma, Effect of composition and cooling rate on microstructure and tensile properties of Sn-Zn-Bi alloys, *Journal of Alloys and Compounds*, 352 (2003) 237-245.
- [32] S.K. Kang, M.G. Cho, P. Lauro, D.-Y. Shih, Critical factors affecting the undercooling of Pb-free, flip-chip solder bumps and in-situ observation of solidification process, in: 57th IEEE Electronic Components & Technology Conference (ECTC), 2007 Proceedings, 2007, pp. 1597-1603.
- [33] M.G. Cho, H.Y. Kim, S.K. Seo, H.M. Lee, Enhancement of heterogeneous nucleation of beta-Sn phases in Sn-rich solders by adding minor alloying elements with hexagonal closed packed structures, *Applied Physics Letters*, 95 (2009).
- [34] K. Sweatman, S.D. McDonald, M. Whitewick, T. Nishimura, K. Nogita, Grain Refinement for Improved Lead-Free Solder Joint Reliability, in: IPC APEX EXPO, San Diego Conference Centre, USA, 2013.
- [35] A.J. Boesenberg, I.E. Anderson, J.L. Harringa, Development of Sn-Ag-Cu-X Solders for Electronic Assembly by Micro-Alloying with Al, *J. Electron. Mater.*, 41 (2012) 1868-1881.
- [36] H.R. Kotadia, O. Mokhtari, M. Bottrill, M.P. Clode, M.A. Green, S.H. Mannan, Reactions of Sn-3.5Ag-Based Solders Containing Zn and Al Additions on Cu and Ni(P) Substrates, *J. Electron. Mater.*, 39 (2010) 2720-2731.
- [37] D.H. Kim, M.G. Cho, S.-K. Seo, H.M. Lee, Effects of Co Addition on Bulk Properties of Sn-3.5Ag Solder and Interfacial Reactions with Ni-P UBM, *J. Electron. Mater.*, 38 (2009) 39-45.
- [38] Z.L. Ma, S.A. Belyakov, C.M. Gourlay, Effects of cobalt on the nucleation and grain refinement of Sn-3Ag-0.5Cu solders, *Journal of Alloys and Compounds*, 682 (2016) 326-337.
- [39] W. Liu, P. Bachorik, N. Lee, The superior drop test performance of SAC-Ti solders and its mechanism, in: 2008 58th IEEE Electronic Components and Technology Conference (ECTC), 2008, pp. 452-458.
- [40] S.A. Belyakov, C.M. Gourlay, Heterogeneous nucleation of β Sn on NiSn₄, PdSn₄ and PtSn₄, *Acta Mater.*, 71 (2014) 56-68.

- [41] W.M. Chen, S.K. Kang, C.R. Kao, Effects of Ti addition to Sn-Ag and Sn-Cu solders, *Journal of Alloys and Compounds*, 520 (2012) 244-249.
- [42] C. Chung, J. Yu, T. Yang, C. Kao, Grain refinement of solder materials by minor element addition, in: 2013 8th International Microsystems, Packaging, Assembly and Circuits Technology Conference (IMPACT), IEEE, 2013, pp. 124-127.
- [43] Y. Wang, K.H. Lu, V. Gupta, L. Stiborek, D. Shirley, S.-H. Chae, J. Im, P.S. Ho, Effects of Sn grain structure on the electromigration of Sn-Ag solder joints, *Journal of Materials Research*, 27 (2012) 1131-1141.
- [44] M. Easton, D. StJohn, Grain refinement of aluminum alloys: Part I. the nucleant and solute paradigms—a review of the literature, *Metallurgical and Materials Transactions A*, 30 (1999) 1613-1623.
- [45] A.L. Greer, P.S. Cooper, M.W. Meredith, W. Schneider, P. Schumacher, J.A. Spittle, A. Tronche, Grain refinement of aluminium alloys by inoculation, *Adv. Eng. Mater.*, 5 (2003) 81-91.
- [46] B.S. Murty, S.A. Kori, M. Chakraborty, Grain refinement of aluminium and its alloys by heterogeneous nucleation and alloying, *International Materials Reviews*, 47 (2002) 3-29.
- [47] D.H. StJohn, M. Qian, M.A. Easton, P. Cao, Z. Hildebrand, Grain refinement of magnesium alloys, *Metallurgical and Materials Transactions A*, 36 (2005) 1669-1679.
- [48] J. Spittle, S. Sadli, Effect of alloy variables on grain refinement of binary aluminium alloys with Al-Ti-B, *Materials Science and Technology*, 11 (1995) 533-537.
- [49] M. Easton, D. StJohn, Grain refinement of aluminum alloys: Part II. Confirmation of, and a mechanism for, the solute paradigm, *Metallurgical and Materials Transactions A*, 30 (1999) 1625-1633.
- [50] I. Maxwell, A. Hellawell, A simple model for grain refinement during solidification, *Acta Metallurgica*, 23 (1975) 229-237.
- [51] D.H. StJohn, M. Qian, M.A. Easton, P. Cao, The Interdependence Theory: The relationship between grain formation and nucleant selection, *Acta Mater.*, 59 (2011) 4907-4921.
- [52] D. Shu, B. Sun, J. Mi, P.S. Grant, A quantitative study of solute diffusion field effects on heterogeneous nucleation and the grain size of alloys, *Acta Mater.*, 59 (2011) 2135-2144.
- [53] T.E. Quested, A.T. Dinsdale, A.L. Greer, Thermodynamic modelling of growth-restriction effects in aluminium alloys, *Acta Mater.*, 53 (2005) 1323-1334.
- [54] R. Schmid-Fetzer, A. Kozlov, Thermodynamic aspects of grain growth restriction in multicomponent alloy solidification, *Acta Mater.*, 59 (2011) 6133-6144.
- [55] G. Chai, L. Bäckerud, L. Arnberg, Relation between grain size and coherency parameters in aluminium alloys, *Materials science and technology*, 11 (1995) 1099-1103.
- [56] M. Easton, D. StJohn, An analysis of the relationship between grain size, solute content, and the potency and number density of nucleant particles, *Metallurgical and Materials Transactions A*, 36 (2005) 1911-1920.
- [57] M. Bermingham, S. McDonald, D. StJohn, M. Dargusch, Beryllium as a grain refiner in titanium alloys, *Journal of Alloys and Compounds*, 481 (2009) L20-L23.
- [58] D. StJohn, M. Easton, M. Qian, J. Taylor, Grain refinement of magnesium alloys: a review of recent research, theoretical developments, and their application, *Metallurgical and materials transactions A*, 44 (2013) 2935-2949.
- [59] TCSLD Database version 3.0, in, *Thermal Calc* 2015.
- [60] Q. Du, Y. Li, An extension of the Kampmann-Wagner numerical model towards as-cast grain size prediction of multicomponent aluminum alloys, *Acta Mater.*, 71 (2014) 380-389.
- [61] K.N. Subramanian, *Lead-Free Electronic Solders*, Springer US, 2007.
- [62] Standard Test Procedure for Aluminium Alloy Grain Refiners: TP-1, 3rd Edition, January 1, 2012 ed., Aluminum Association (AA), 2012.
- [63] M.J. Bermingham, S.D. McDonald, K. Nogita, D.H. St. John, M.S. Dargusch, Effects of boron on microstructure in cast titanium alloys, *Scripta Materialia*, 59 (2008) 538-541.
- [64] Y.C. Huang, S.W. Chen, K.S. Wu, Size and Substrate Effects upon Undercooling of Pb-Free Solders, *J. Electron. Mater.*, 39 (2010) 109-114.

- [65] J.W. Xian, Z.L. Ma, S.A. Belyakov, M. Ollivier, C.M. Gourlay, Nucleation of tin on the Cu₆Sn₅ layer in electronic interconnections, *Acta Mater.*, 123 (2017) 404-415.
- [66] J. Tamminen, Thermal analysis for investigation of solidification mechanisms in metals and alloys, in, University of Stockholm Sweden, 1988.
- [67] Standard Test Methods for Determining Average Grain Size, in, ASTM International, 2013.
- [68] D.H. StJohn, P. Cao, M. Qian, M.A. Easton, A New Analytical Approach to Reveal the Mechanisms of Grain Refinement, *Adv. Eng. Mater.*, 9 (2007) 739-746.
- [69] A.L. Greer, A.M. Bunn, A. Tronche, P.V. Evans, D.J. Bristow, Modelling of inoculation of metallic melts: Application to grain refinement of aluminium by Al-Ti-B, *Acta Mater.*, 48 (2000) 2823-2835.
- [70] M.J. Bermingham, S.D. McDonald, M.S. Dargusch, D.H. StJohn, The mechanism of grain refinement of titanium by silicon, *Scripta Materialia*, 58 (2008) 1050-1053.
- [71] J. Cahoon, Y. Jiao, K. Tandon, M. Chaturvedi, Interdiffusion in liquid tin, *Journal of Phase Equilibria and Diffusion*, 27 (2006) 325-332.
- [72] L.-W. Lin, J.-M. Song, Y.-S. Lai, Y.-T. Chiu, N.-C. Lee, J.-Y. Uan, Alloying modification of Sn–Ag–Cu solders by manganese and titanium, *Microelectronics Reliability*, 49 (2009) 235-241.
- [73] M. Armbrüster, W. Schnelle, R. Cardoso-Gil, Y. Grin, Chemical Bonding in Compounds of the CuAl₂ Family: MnSn₂, FeSn₂ and CoSn₂, *Chemistry – A European Journal*, 16 (2010) 10357-10365.
- [74] E.-L. Nordmark, O. Wallner, U. Häussermann, Polymorphism of IrSn₄, *Journal of Solid State Chemistry*, 168 (2002) 34-40.
- [75] B. Künnen, W. Jeitschko, G. Kotzyba, B. Mosel, Crystal structure and properties of the titanium stannide Ti₂Sn₃, *Zeitschrift für Naturforschung B*, 55 (2000) 425-430.
- [76] A. Lang, W. Jeitschko, Two new phases in the system cobalt-tin: the crystal structures of α - and β -CoSn₃, *Z. Metallk.*, 87 (1996) 759-764.
- [77] J. Nylén, F.G.a. García, B. Mosel, R. Pöttgen, U. Häussermann, Structural relationships, phase stability and bonding of compounds PdSn_n (n = 2, 3, 4), *Solid state sciences*, 6 (2004) 147-155.
- [78] B. Künnen, D. Niepmann, W. Jeitschko, Structure refinements and some properties of the transition metal stannides Os₃Sn₇, Ir₅Sn₇, Ni_{0.402}(4)Pd_{0.598}Sn₄, α -PdSn₂ and PtSn₄, *Journal of Alloys and Compounds*, 309 (2000) 1-9.
- [79] M.J. Assael, A.E. Kalyva, K.D. Antoniadis, R.M. Banish, I. Egry, J. Wu, E. Kaschnitz, W.A. Wakeham, Reference Data for the Density and Viscosity of Liquid Copper and Liquid Tin, *Journal of Physical and Chemical Reference Data*, 39 (2010) 033105.
- [80] M. Mueller, S. Wiese, K.J. Wolter, The twinning phenomenon in SnAgCu solder balls, in: 2009 59th Electronic Components and Technology Conference, 2009, pp. 1027-1036.
- [81] H. Ji, Q. Wang, M. Li, C. Wang, Ultrafine-Grain and Isotropic Cu/SAC305/Cu Solder Interconnects Fabricated by High-Intensity Ultrasound-Assisted Solidification, *J. Electron. Mater.*, 43 (2014) 2467-2478.
- [82] H. Ji, Q. Wang, M. Li, C. Wang, Effects of ultrasonic irradiation and cooling rate on the solidification microstructure of Sn–3.0Ag–0.5Cu alloy, *Journal of Materials Processing Technology*, 214 (2014) 13-20.
- [83] M.G. Cho, S.K. Kang, H.M. Lee, Undercooling and microhardness of Pb-free solders on various under bump metallurgies, *Journal of Materials Research*, 23 (2008) 1147-1154.
- [84] J.W. Elmer, E.D. Specht, M. Kumar, Microstructure and In Situ Observations of Undercooling for Nucleation of β -Sn Relevant to Lead-Free Solder Alloys, *J. Electron. Mater.*, 39 (2010) 273-282.
- [85] S.A. Belyakov, J.W. Xian, K. Sweatman, T. Nishimura, T. Akaiwa, C.M. Gourlay, Influence of bismuth on the solidification of Sn-0.7Cu-0.05Ni-xBi/Cu joints, *Journal of Alloys and Compounds*, 701 (2017) 321-334.

Table 1. Summary of the nucleation undercooling and grain size for all alloys in the 60g samples study. Mean values with standard deviations in brackets are given based on 4 samples for each alloy for grain size, 6 samples for thermal test data. The cooling rate of all experiments are $1.1 \pm 0.1 \text{ K/s}$. 'NM' = not measured

Alloys	$T_{\min}$ (°C)	$T_{\max}$ (°C)	ΔT (°C)	Grain Size (μm)
CP-Sn	220.3(1.8)	231.7(2.0)	11.4(2.1)	NM
Sn-0.01Zn	223.2(0.6)	231.0(0.7)	7.8(0.8)	NM
Sn-0.03Zn	224.8(0.8)	231.9(0.1)	7.1(0.7)	NM
Sn-0.1Zn	228.2(1.2)	231.4(0.1)	3.2(1.1)	NM
Sn-0.2Zn	227.7(0.9)	230.1(0.6)	2.4(0.6)	NM
Sn-1Zn	225.0 (0.3)	225.9 (0.2)	0.9 (0.2)	3178 (143)
Sn-1.5Zn	222.1 (0.3)	222.6 (0.2)	0.5 (0.1)	2218 (132)
Sn-3Zn	214.9 (0.9)	215.7 (1.2)	0.8 (0.4)	1630 (47)
Sn-6Zn	201.8 (0.3)	202.4 (0.2)	0.7 (0.1)	1055 (20)
Sn-2Zn-1Bi	218.6 (0.2)	219.5 (0.2)	1.0 (0.1)	2161 (34)
Sn-2Zn-5Bi	213.0 (0.2)	213.7 (0.1)	0.6 (0.1)	1936 (15)
Sn-2Zn-15Bi	198.0 (0.1)	198.6 (0.1)	0.6 (0.2)	1393 (10)
Sn-2Zn-35Bi	164.7 (0.2)	165.2 (0.3)	0.5 (0.3)	829 (9)
SAC305	202.7 (1.0)	217.6 (0.2)	14.9 (0.9)	3724 (304)
SAC305-0.2Mn	216.1 (0.3)	217.7 (0.3)	1.5 (0.4)	3562 (85)
SAC305-0.5Zn	215.5 (0.1)	216.7 (0.2)	1.1 (0.1)	1449 (135)
SAC305-0.07Ir	217.7 (0.1)	218.7 (0.3)	1.0 (0.3)	1347 (24)
SAC305-0.2Ti	218.7 (0.1)	219.0 (0.1)	0.3 (0.1)	1336 (48)
SAC305-0.05Co	218.1 (0.5)	218.3 (0.5)	0.2 (0.1)	1174 (44)
SAC305-0.2Pd	218.0 (0.1)	218.5 (0.3)	0.6 (0.2)	961 (9)
SAC305-0.07Pt	219.5 (0.1)	219.8 (0.0)	0.2 (0.1)	817 (14)
SAC205-0.07Pt	221.8 (0.3)	222.3 (0.2)	0.3 (0.1)	1338 (24)
SAC105-0.07Pt	225.3 (0.1)	225.7 (0.0)	0.4 (0.1)	1711 (22)
SAC0505-0.07Pt	226.8 (0.1)	227.4 (0.1)	0.6 (0.0)	2392 (64)

Table 2. The parameters a and b for lines of best fit in Figure 10.

	b	a	R^2
L_{Zn}	9886	684	0.992
L_{Bi}	12532	810	1.009
L_{Ag}	10848	-50	0.969

Table 3. Growth Restriction factors of SAC305 with the seven additions

Alloys	Q	1/Q
SAC 305	11.19	0.09
SAC305-0.2Mn	11.37	0.09
SAC305-0.5Zn	12.35	0.08
SAC305-0.5Ti	11.19	0.09
SAC305-0.07Ir	?	?
SAC305-0.05Co	11.24	0.09
SAC305-0.2Pd	10.76	0.09
SAC305-0.07Pt	11.21	0.09

Table 4. Primary IMC phases in the SAC305-X alloys as determined by combining EDS and EBSD. TM = transition metal addition (e.g. Mn, Pt etc.). References are to the best-fit structures/phases used for EBSD indexing.

Alloy	phase	Composition by EDS			Crystal structure by EBSD		Ref
		TM [at%]	Cu [at%]	Sn [at%]	Pearson symbol	Structure type	
SAC305-0.2Mn	MnSn ₂	29.3	-	70.7	tI12	CuAl ₂	[73]
SAC305-0.5Zn	-	-	-	-	-	-	-
SAC305-0.07Ir	IrSn ₄	20.5	-	79.5	tI40	βIrSn ₄	[74]
SAC305-0.2Ti	Ti ₂ Sn ₃	40.1	-	59.9	oS40	GaSn ₂ V ₂	[75]
SAC305-0.05Co	αCoSn ₃	16.6	7.5	75.9	oS32	PdSn ₃	[76]
SAC305-0.2Pd	PdSn ₄	17.6	1.9	80.5	oS20	PtSn ₄	[77]
SAC305-0.07Pt	PtSn ₄	18.1	-	81.9	oS20	PtSn ₄	[78]

Table 5. EBSD summary of 0.33K/s cooled freestanding solder balls (IG: Independent grain)

Alloy	No. of sample	Single orientation	Twinned	One IG	Multiple IGs
CP-Sn	6	6	0	6	0
Sn-0.07Pt	6	6	0	6	0
SAC305	33	5	28	33	0
SAC305-0.2Mn	8	6	2	8	0
SAC305-0.5Zn	10	4	6	10	0
SAC305-0.07Ir	5	2	3	5	0
SAC305-0.2Ti	5	5	0	5	0
SAC305-0.05Co	17	12	5	17	0
SAC305-0.2Pd	7	4	3	7	0
SAC305-0.07Pt	5	5	0	5	0
SAC305-5Bi-0.07Pt	6	6	0	6	0

Table 6. EBSD summary of 17K/s cooled freestanding solder balls (IG: Independent grain)

Alloy	No. of sample	Single orientation	Twinned	One IG	Multiple IGs
CP-Sn	6	6	0	6	0
Sn-0.07Pt	6	3	0	3	3
SAC305	16	0	16	16	0
SAC305-0.05Co	9	2	2	4	5
SAC305-0.2Mn	0	0	0	0	0
SAC305-0.5Zn	5	0	1	1	4
SAC305-0.2Ti	5	1	0	1	4
SAC305-0.07Pt	5	1	0	1	4
SAC305-0.2Pd	6	2	0	2	4
SAC305-0.07Ir	7	2	2	4	3
SAC305-5Bi-0.07Pt	5	0	0	0	5

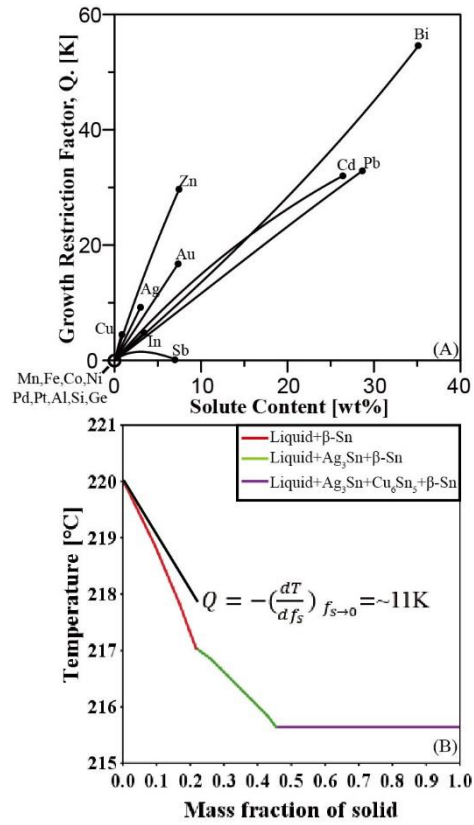


Figure 1. (A) The growth restriction factor, Q , as a function of solute content for binary Sn-X alloys relevant to soldering. (B) The definition of Q in multicomponent alloys using Sn-3Ag-0.5Cu as an example. Data is from ref [59]

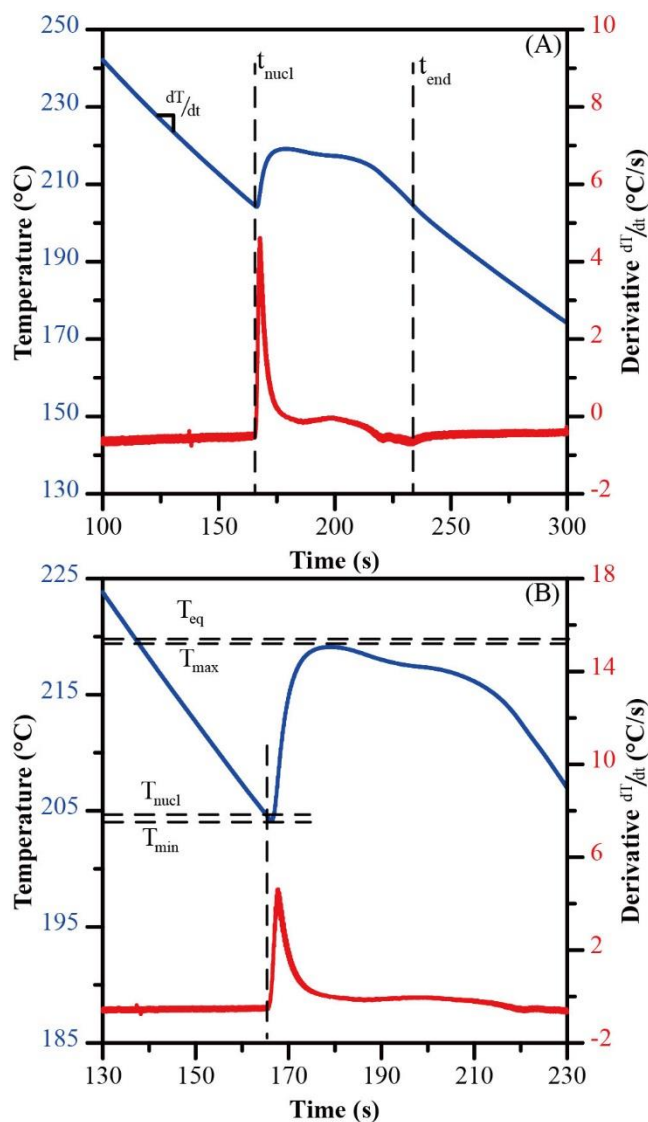


Figure 2. Cooling curve analysis of 60g samples with the immersed thermocouple method using Sn-3Ag-0.5Cu as an example. (A) Complete experiment. (B) Focus on the region of supercooling, β Sn nucleation and recalescence. The terms are defined in the text.

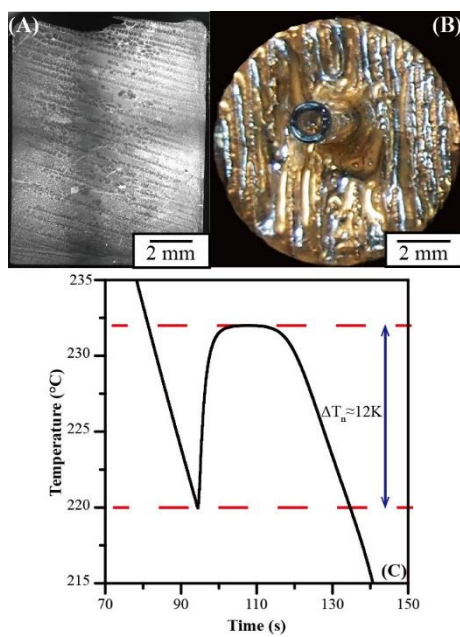


Figure 3. Typical microstructure and cooling curve of a 60g CP-Sn sample. (A) vertical section and (B) the top of a sample viewed from above, showing the presence of a single dendrite. (C) Cooling curve.

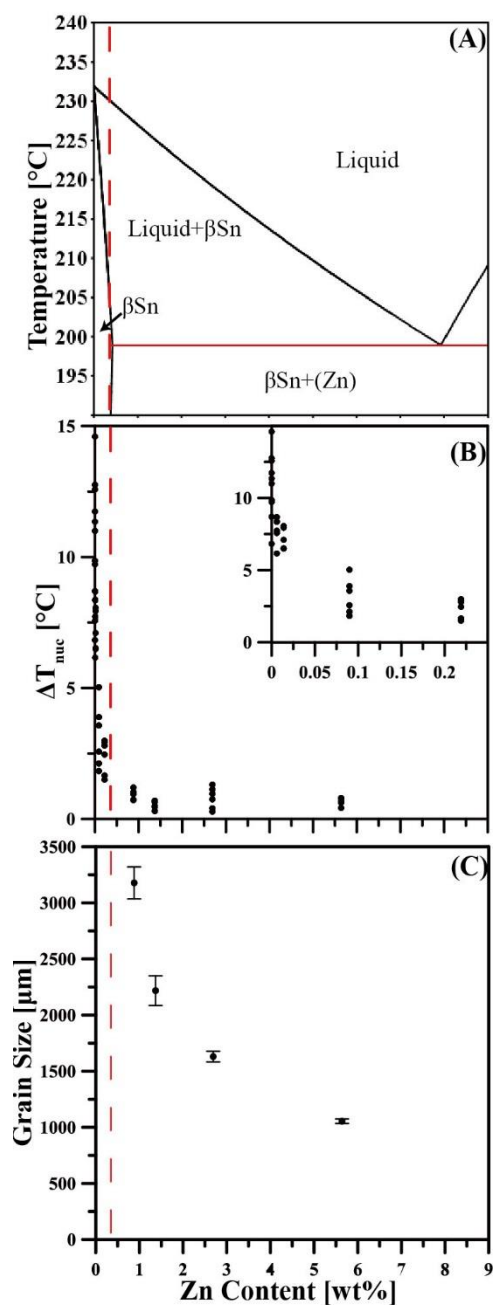


Figure 4. Influence of Zn on the grain refinement of 60g Sn-xZn samples. (A) Sn-Zn phase diagram from [59]. (B) Measured undercooling versus Zn content. (C) Measured βSn grain size versus Zn content.

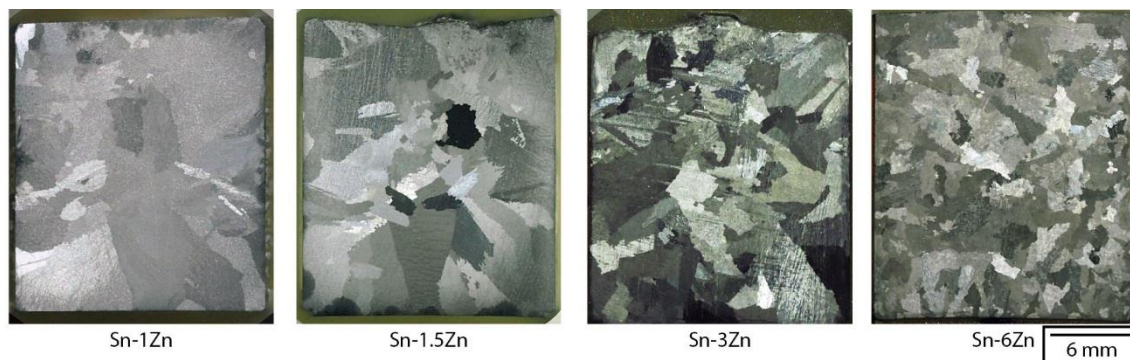


Figure 5. Typical etched cross-sections of 60g Sn-xZn samples containing 1 - 6 wt% Zn.

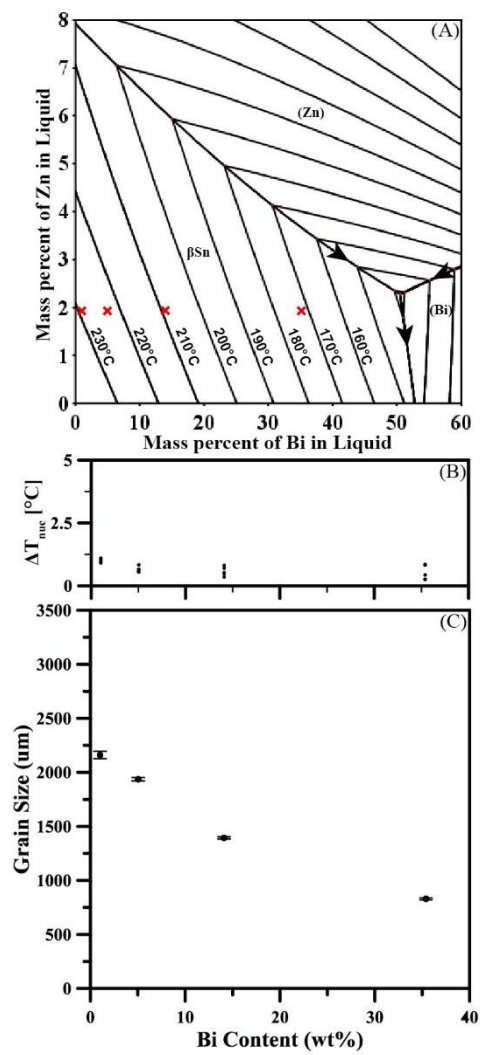


Figure 6. Influence of Bi and Zn on the grain refinement of 60g Sn-xBi-2Zn samples. (A) Sn-Zn-Bi liquidus projection from [59]. (B) Measured undercooling versus Bi content. (C) Measured βSn grain size versus Bi content.

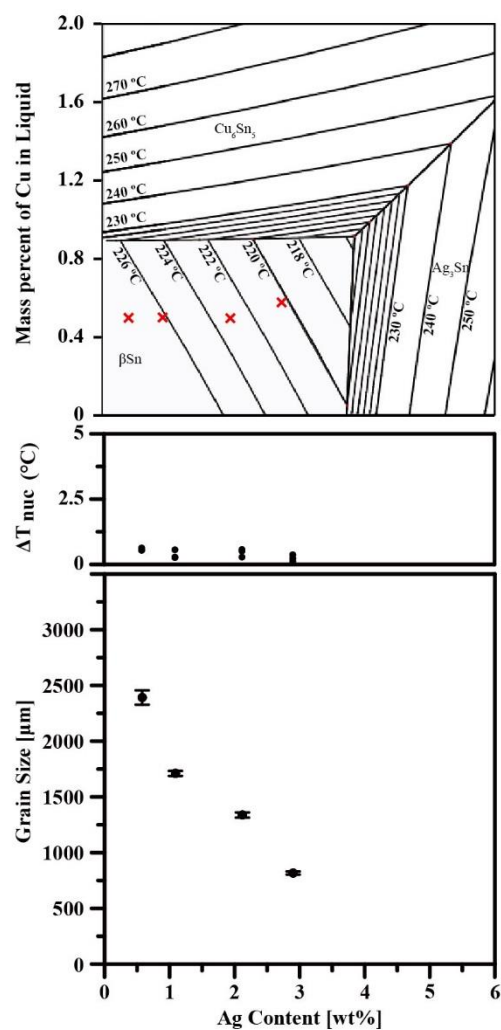


Figure 7. Influence of Ag on the grain refinement of 60g Sn-xAg-0.5Cu-0.07Pt samples. (A) Sn-Ag-Cu liquidus projection from [59] (B) Measured undercooling versus Ag content. (C) Measured β Sn grain size versus Ag content.

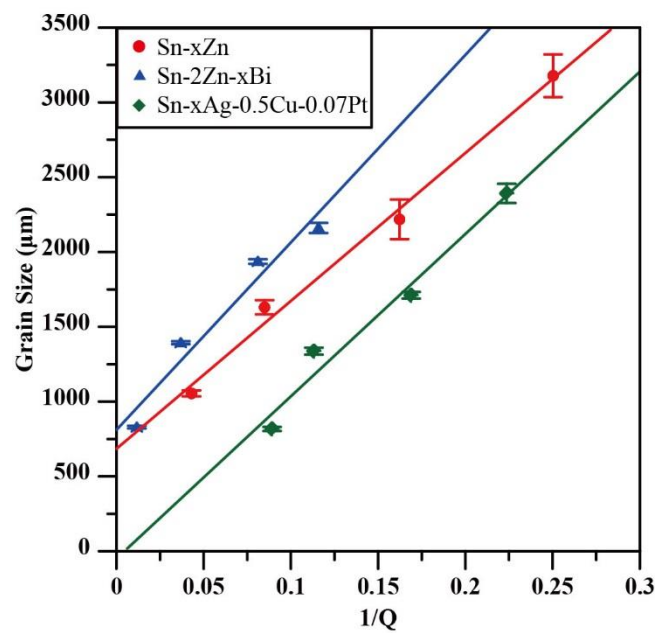


Figure 8. β Sn grain size vs $1/Q$ for 60g Sn-xZn, Sn-2Zn-xBi and Sn-xAg-0.5Cu-0.07Pt alloys.

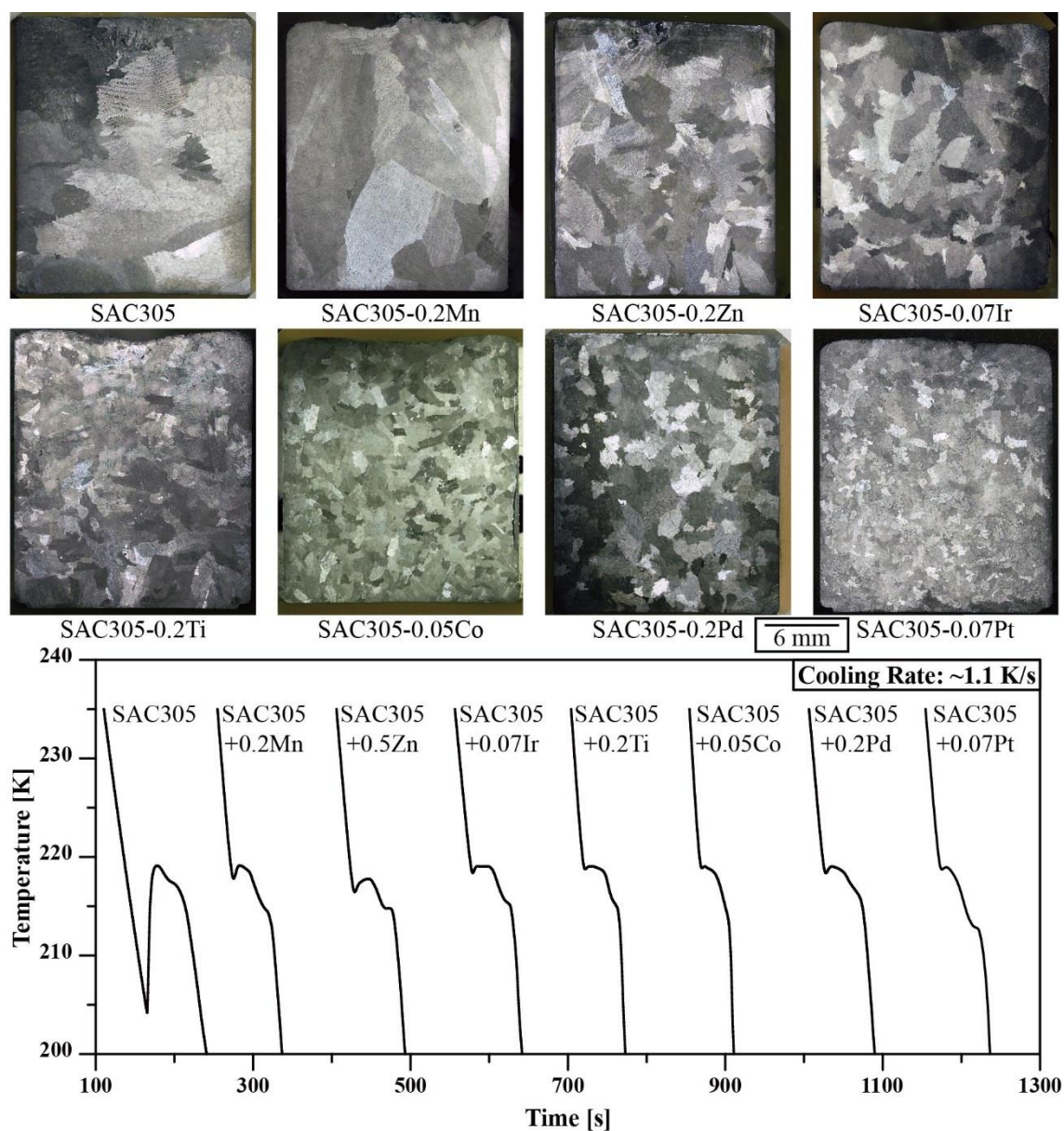


Figure 9. Typical etched cross-sections and cooling curves of 60g SAC305-X samples with 7 alloying additions.

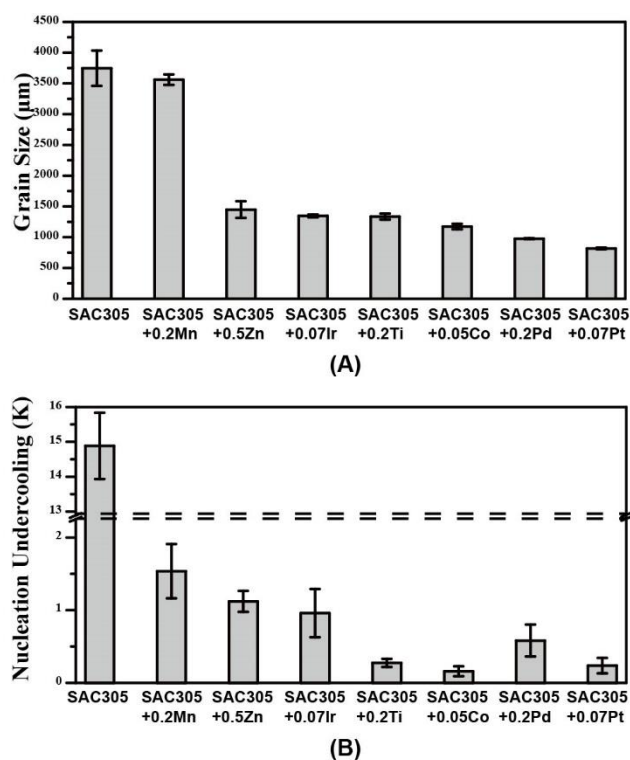


Figure 10: Grain size and nucleation undercooling data for the 60g SAC305-X alloys. Error bars are standard deviations from at least 4 samples for grain size and 6 samples for undercooling. Note the broken undercooling axis in (B).

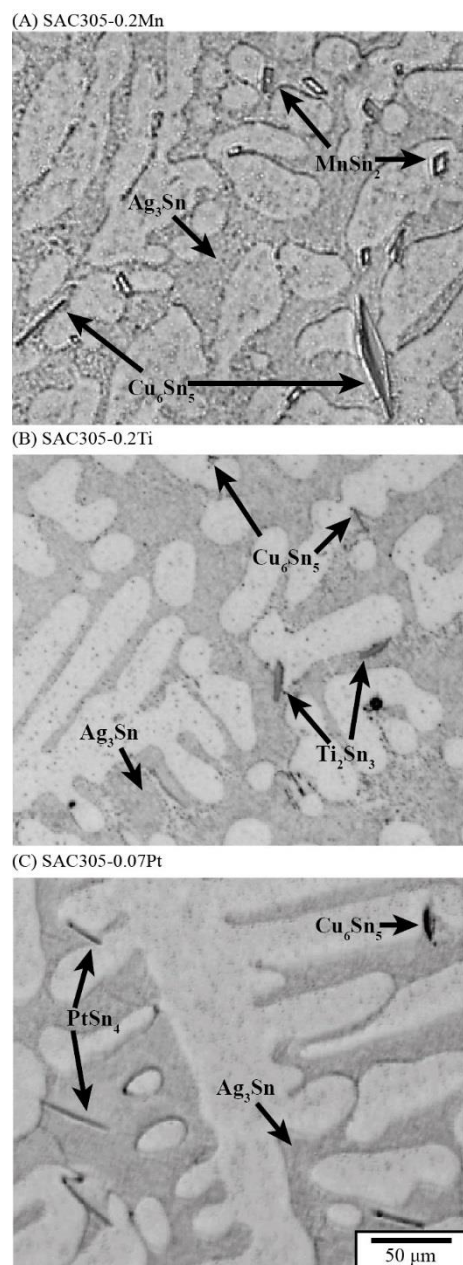


Figure 11. Intermetallics present in 60g sample cooled at 1K/s. (A) Ti_2Sn_3 in SAC305-0.2Ti and (B) PtSn_4 in SAC305-0.07Pt (C) MnSn_2 in SAC305-0.2Mn, in addition to Ag_3Sn and Cu_6Sn_5 . See Table 4 for further details.

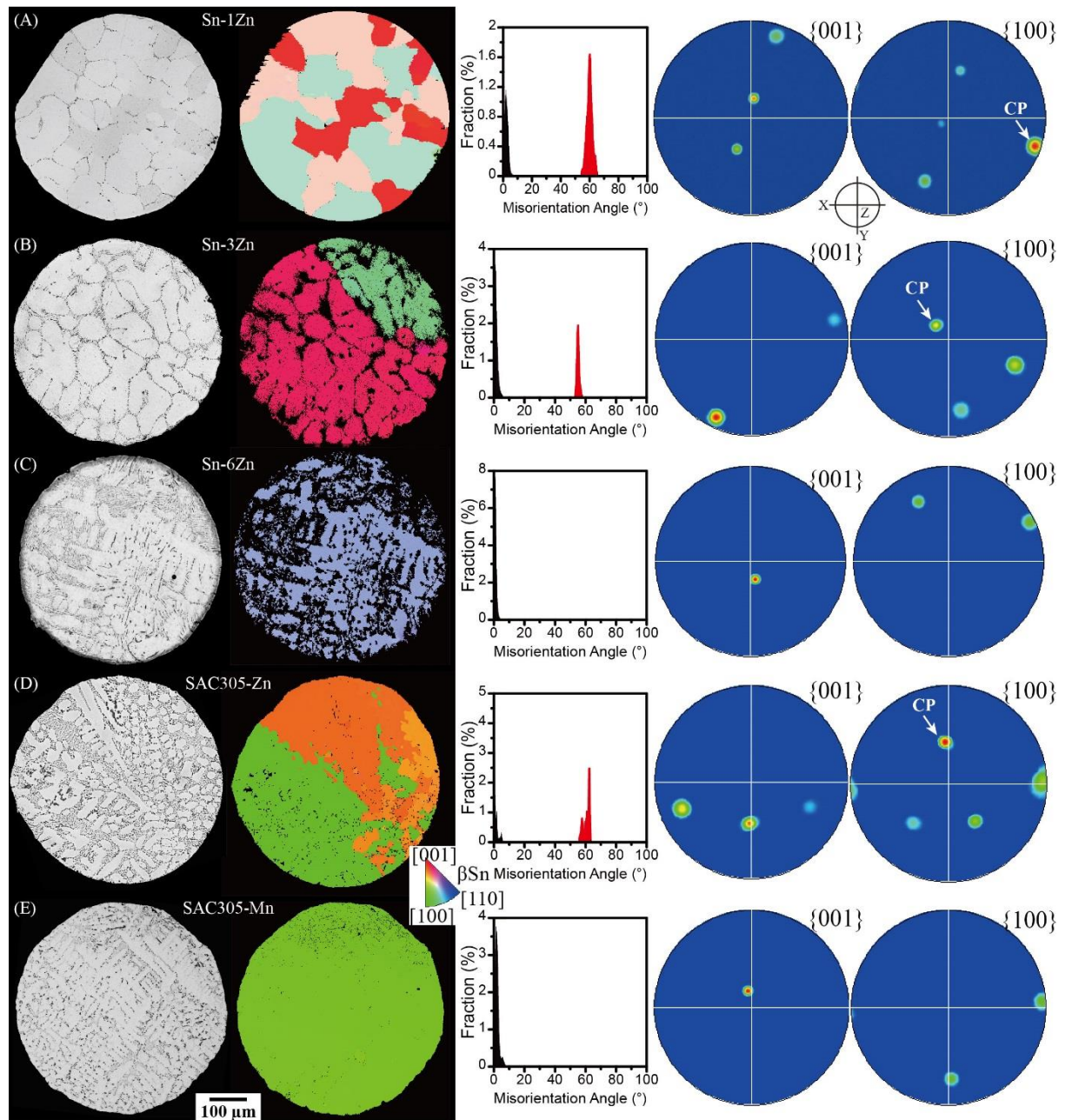


Figure 12. Typical microstructures of 500 μ m solder balls cooled at 0.33 K/s. The left columns are optical micrographs of the dendrite structure and EBSD maps of the β Sn orientations (IPF-x for A,B,C and IPF-y for D, E). The middle columns are misorientation histograms with 55-65 $^\circ$ highlighted red. The right columns are {001} and {100} pole figures of tetragonal β Sn where the white arrows point to the common plane of twinned grains.

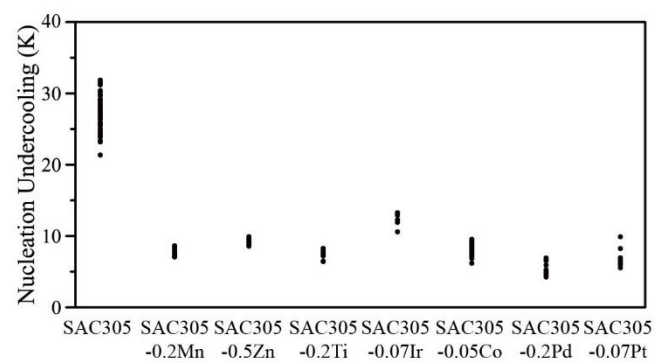


Figure 13. Nucleation undercooling for β Sn in 500 μ m SAC305-X solder balls cooled at 0.33 K/s. At least 12 samples were tested for each composition.

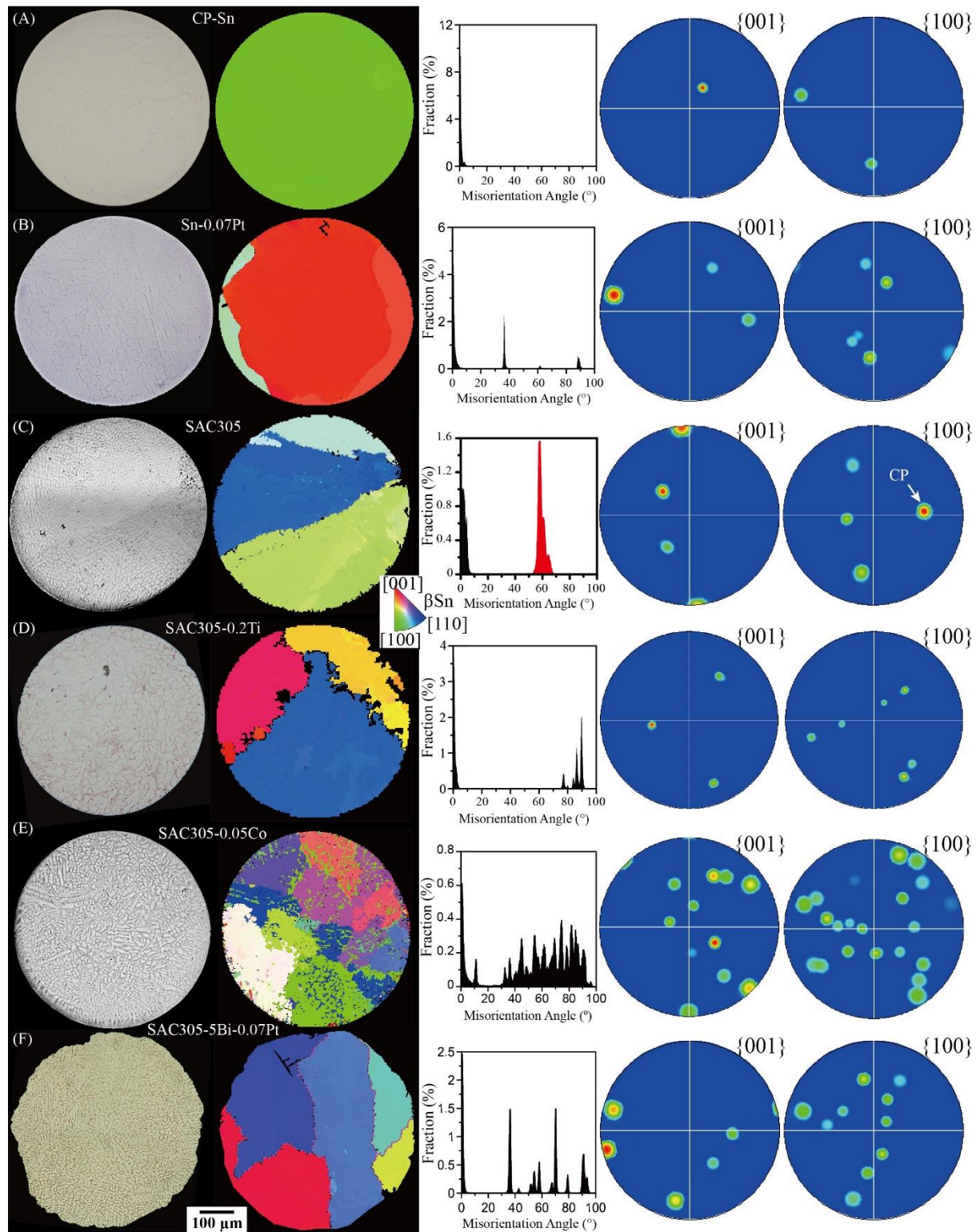


Figure 14. EBSD of solder balls cooled at 17 K/s. (A) CP-Sn, (B) Sn-0.07Pt, (C) SAC305, (D) SAC305-0.2Ti, (E) SAC305-0.05Co (F) SAC305-5Bi-0.07Pt (IPF-x for A,B,C, E; IPF-y for D and IPF-z for F) White arrows point to the common plane of twinned grains.

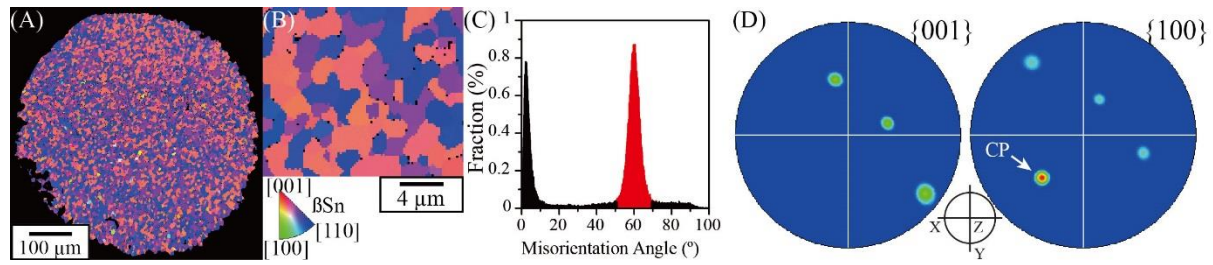
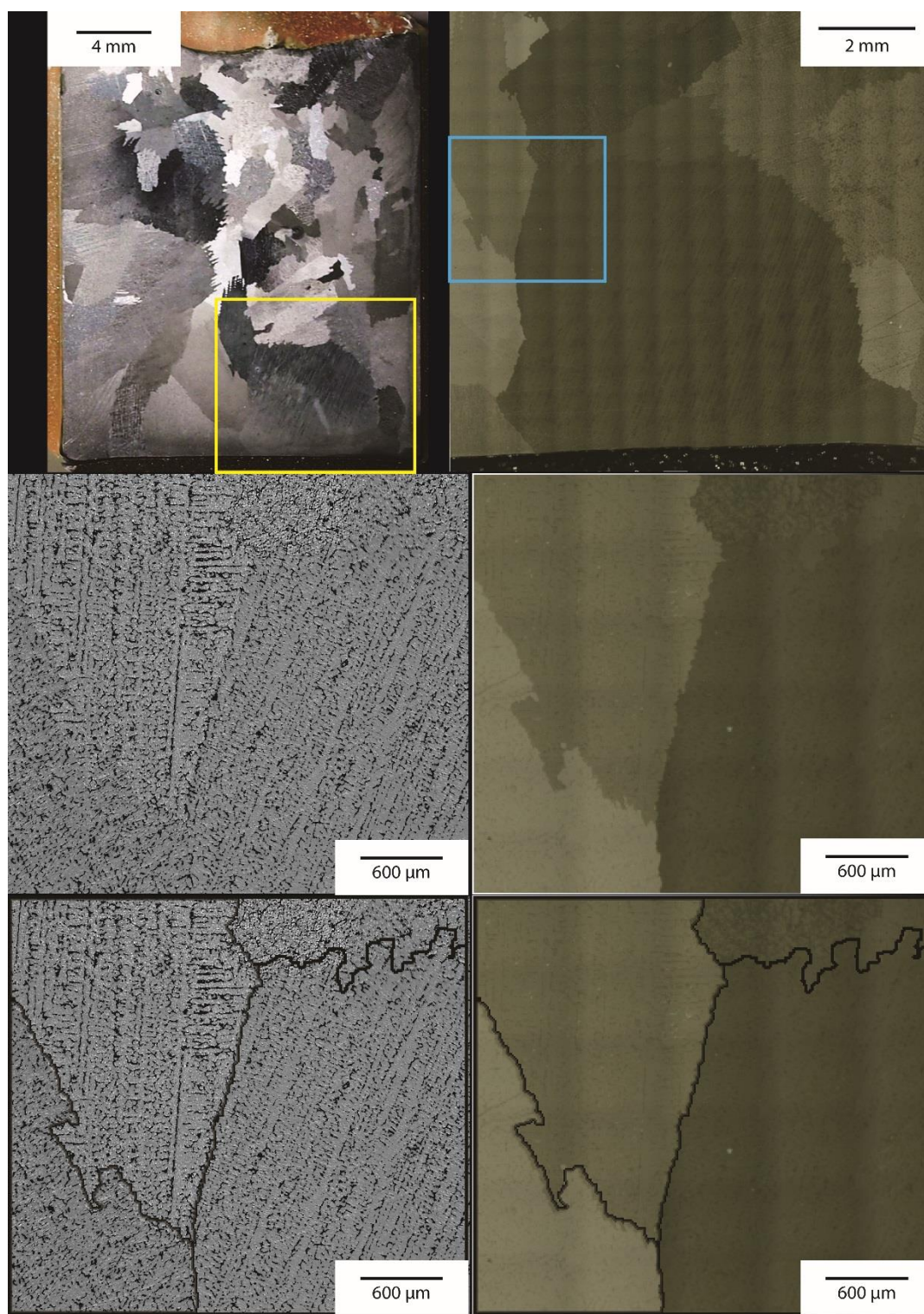


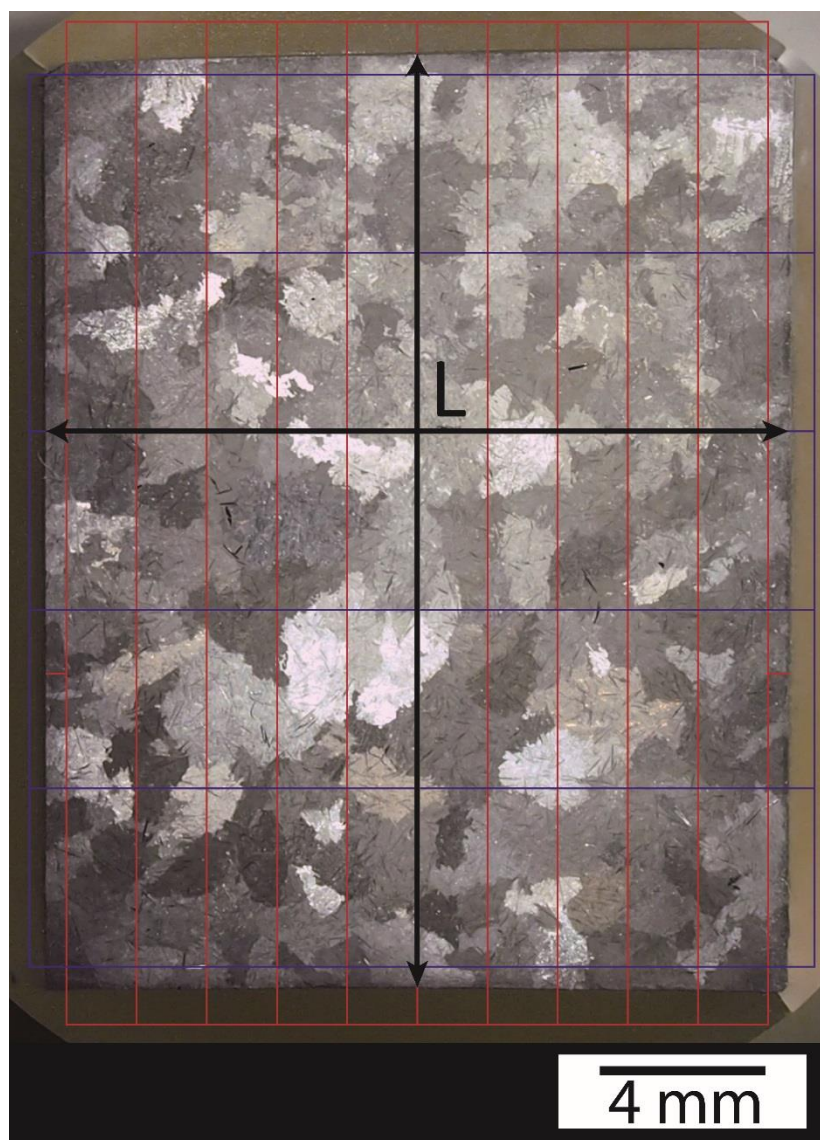
Figure 15. SAC305 with a fully-interlaced twinned β Sn structure. (A) EBSD IPF-y Map. (B) higher magnification region from (A). (C) misorientation histogram from (A) where all orientations are $<15^\circ$ or $\sim 60^\circ$. (D) pole figures from the map in (A) where the white arrow points to the common $\{100\}$ plane of all three orientations.

S.I. Table 7. Compositions of all alloys as measured by X-ray fluorescence spectroscopy (XRF). The Fe content of all compositions is lower than 0.005wt%, ND = <0.001 wt%.

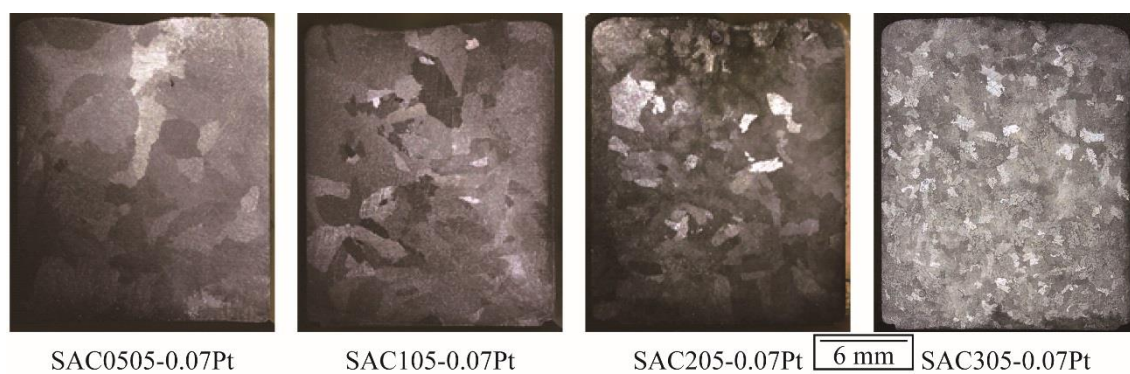
Nominal Composition	Zn	Bi	Ag	Cu	Pb	Co	Mn	Ti	Pt
	%	%	%	%	%	%	%	%	%
CP-Sn	ND	ND	ND	0.003	0.011	ND	ND	ND	ND
Sn-0.01Zn	0.007	ND	0.001	0.005	0.012	ND	ND	ND	ND
Sn-0.03Zn	0.014	ND	ND	0.005	0.013	ND	ND	ND	ND
Sn-0.1Zn	0.090	ND	0.001	0.005	0.013	ND	ND	ND	ND
Sn-0.2Zn	0.220	ND	ND	0.004	0.011	ND	ND	ND	ND
Sn-1Zn	0.880	ND	0.004	0.007	0.013	ND	ND	ND	ND
Sn-1.5Zn	1.370	ND	0.003	0.007	0.013	ND	ND	ND	ND
Sn-3Zn	2.690	ND	0.001	0.008	0.013	ND	ND	ND	ND
Sn-6Zn	5.640	ND	ND	0.010	0.009	ND	ND	ND	ND
Sn-2Zn-1Bi	1.810	1.020	0.013	0.020	ND	ND	ND	ND	ND
Sn-2Zn-5Bi	1.800	5.040	0.008	0.007	0.014	ND	ND	ND	ND
Sn-2Zn-15Bi	1.880	14.10	ND	0.012	ND	ND	ND	ND	ND
Sn-2Zn-35Bi	1.820	35.40	ND	0.020	ND	ND	ND	ND	ND
SAC 305	ND	0.014	2.930	0.588	0.025	ND	ND	ND	ND
SAC305-0.05Co	ND	0.004	2.990	0.577	0.027	0.046	ND	ND	ND
SAC305-0.5Zn	0.550	0.004	2.980	0.574	0.028	ND	ND	ND	ND
SAC305-0.2Mn	ND	ND	2.980	0.570	0.034	ND	0.145	ND	ND
SAC305- 0.2Ti	ND	0.003	3.000	0.580	0.034	ND	ND	0.168	ND
SAC305-0.07Pt	ND	0.002	2.900	0.580	0.013	ND	ND	ND	0.073
SAC205-0.07Pt	ND	ND	2.120	0.497	0.004	ND	ND	ND	0.074
SAC105-0.07Pt	ND	ND	1.090	0.501	0.005	ND	ND	ND	0.078
SAC0505-0.07Pt	ND	ND	0.579	0.502	0.003	ND	ND	ND	0.076



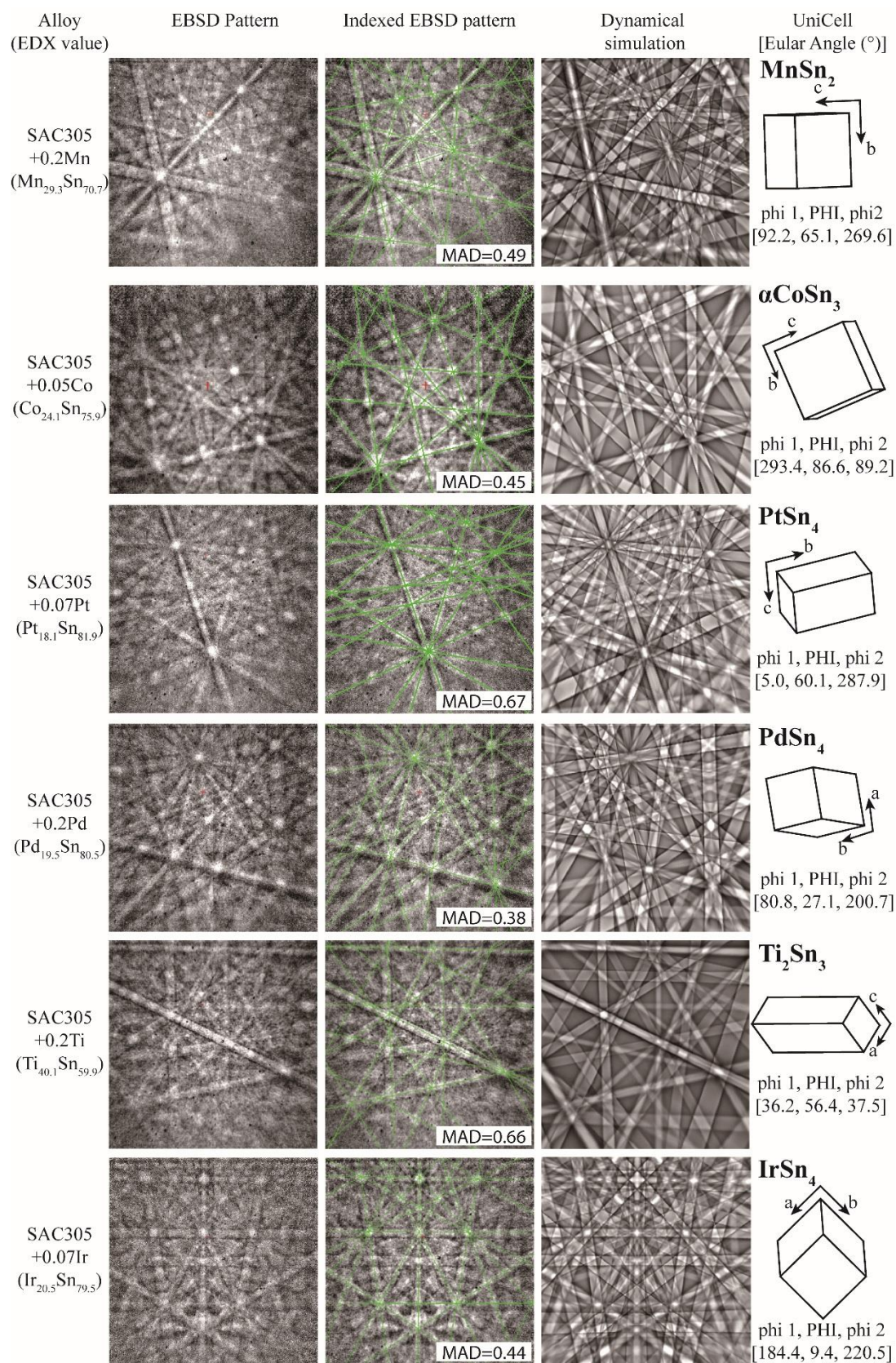
S.I. Figure 1. Proof of photograph methods



S.I. Figure 2. Grain Size measurement method (example: SAC305-0.2Pd)



S.I. Figure 3. Typical Etched cross-sections of Sn-xAg-0.5Cu-0.07Pt samples



S.I. Figure 4. EBSD pattern and simulation bands of particles in SAC305+X alloys.