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Suppressed undercooling

Nucleation mechanism

Grain refinement

Mechanisms of beta-Sn nucleation and microstructure evolution in Sn-Ag-Cu solders containing titanium

Z.L. Ma^{1#*}, H. Shang^{1#*}, A. A. Daszki¹, S.A. Belyakov¹, C.M. Gourlay¹

¹ Department of Materials, Imperial College London, London. SW7 2AZ. UK

ZLM and HS contributed equally

*z.ma13@imperial.ac.uk; +86 15801018340

*h.shang@hw.ac.uk; +44 (0)7540437329

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Abstract:

The mechanisms by which Ti additions catalyse the nucleation of β -Sn are studied in 550 μm Sn-3Ag-0.5Cu (wt%) solder balls and joints on Cu and Ni substrates. It is shown that at least two new intermetallic compounds (IMCs), Ti_2Sn_3 and $(\text{Ti,Fe,Cu})\text{Sn}_2$, form as a result of a 0.2wt% Ti addition. The nucleation potential of each IMC was studied by electron backscatter diffraction (EBSD) of tin droplets solidified on the cross sectioned facets of each IMC. It is found that reproducible orientation relationships (ORs) form only between β -Sn and Ti_2Sn_3 and that the two ORs generate good atomic matching between the Sn atoms in Ti_2Sn_3 and the closest packed plane in β -Sn, $\{100\}$. β -Sn cyclic twinning occurred in droplets on Ti_2Sn_3 where the twinning axis $\langle 100 \rangle_{\text{Sn}}$ was always parallel with the lowest disregistry direction in the ORs. In solder balls and joints, the Ti_2Sn_3 addition triggered up to 12 independent β -Sn grains, whereas Ti-free SAC305 always solidified with one independent grain.

1. Introduction:

Sn-Ag-Cu (SAC) solders are common alternatives to eutectic Sn-Pb solders and have been intensively studied in recent decades [1-5]. A concern of SAC solders is the large melt undercooling prior to β -Sn nucleation (~ 10 -40 K), which induces large primary Cu_6Sn_5 rods [6] and Ag_3Sn plates [7], that can lead to poor mechanical behaviour of solder joints [8-10]. A further problem related with a large nucleation undercooling is that SAC solder joints usually solidify with a single β -Sn nucleation event and develop only 1-3 β -Sn orientations. These oligocrystal solder joints are anisotropic in thermal expansion and mechanical properties due to the anisotropy of β -Sn [4, 11-16], and each joint is unique since the β -Sn grains are oriented differently in each joint [17].

Microalloying has been extensively studied to suppress nucleation undercooling in SAC solders and joints. It has been shown that Co [3, 18-22], Zn [19, 22-24], Ti [24-28], Al [18, 29], Pt [17, 24, 30], Pd [17, 24, 30], and Ir [17, 24], all effectively suppress nucleation undercooling of SAC solders and joints. Among these, the underlying nucleation mechanisms of Co, Pt, Pd, and Ir additions have been identified in previous studies [3, 17, 30]. Although it has been shown that titanium additions can be as potent as Co, Pt, Pd, and Ir additions [24] [25-28] as indicated by the nucleation undercoolings in Table 1 and reports of grain refinement in reference [31], the mechanisms by which Ti has these effects are currently unclear. Past research has suggested that Ti_2Sn_3 may be a nucleant [24, 26] but this idea has not been tested.

In this study, we prove the nucleant phase in Ti-microalloyed SAC solders, investigate the β -Sn nucleation mechanisms, and explore the influence of Ti on the β -Sn microstructure in

solder joints. We then consider the potential of using Ti-microalloying to control β -Sn nucleation and microstructure in SAC solder joints.

2. Methods

Sn-3Ag-0.5Cu-0.2Ti (wt%) samples were made by arc melting commercial Sn-3Ag-0.5Cu (SAC305) ingot and 99.9% Ti foil. Arc melting was conducted in vacuum, back-filled with Ar on a water-cooled Cu plate. The alloy was melted, flipped, remelted and then cast into a rectangular copper mould. The composition was then measured by XRF spectroscopy giving the results in Table 2.

Ball grid array (BGA) scale solder balls were made by rolling the ingots to foil of 0.05 mm thickness, punching to $\varnothing$ 1.6 mm discs and, finally, reflowing on a hot plate with a ROL1 tacky flux (Nihon Superior Co., Ltd) to make 550 ± 25 μ m diameter solder balls due to surface tension. For solder joints, 500 μ m thick Cu and Ni sheets were masked with resist to produce 500 μ m pads which were coated with a ROL1 tacky flux. SAC305 and SAC305-0.2Ti balls were then soldered to the Cu and Ni pads on a hotplate at 240 °C. Solder balls and joints 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/joint was given two and/or multiple cycles and at least 10 balls/joints of each solder/substrate combination were measured.

To determine the liquidus temperature of β -Sn in each solder/substrate combination, a similar cyclic method to Ref. [32] was used which is overviewed in Figure 1 (C). In the first cycle in the DSC, the sample was held at the melting onset temperature (as shown in DSC curves in Figure 1 (A) and (B)) for 30 min before being heated up to 250 °C, and cooled down

to 180 °C. In the second and following cycles, 30 min isothermal holding was performed at a temperature 0.5 K higher than the previous cycle. The liquidus temperature was then defined to be between the holding temperatures that exhibit an endothermic peak and no endothermic peak on heating (e.g. between 5 and 6), and is taken as the average between these two temperature [32]. The β -Sn nucleation undercooling was defined as the β -Sn liquidus temperature minus the solidification onset on cooling, as shown in Figure 1.

Cross-sections of solder joints were prepared by mounting in Struers VersoCit cold mounting acrylic resin, wet grinding to 4000 grit SiC paper, and carefully polishing with colloidal silica suspension. 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 (EDX) detector and a BRUKER e-FlashHR electron backscatter diffraction (EBSD) detector. BRUKER ESPRIT 2.1 was used to index EBSD patterns via the Hough transform and analyse orientation data. BRUKER DynamicS was used to generate dynamical simulations of EBSD patterns and perform cross-correlation analyses to quantitatively compare experimental and calculated EBSD patterns.

The new intermetallic compounds (IMCs) introduced by the Ti addition were extracted using a solution of 5% NaOH and 3.5% ortho-nitrophenol in distilled water. To identify the heterogeneous nucleant responsible for undercooling suppression, Sn droplets were solidified on these new IMCs. Different from our previous studies [3, 17, 33, 34], in which the natural growth facets of the extracted IMCs were used, in this study, the cross-sectioned facets of the Ti IMCs were used since their natural facets were heavily oxidized during etching and were poorly wet by Sn droplets. Droplets of 99.9% Sn with size $< \sim 5 \mu\text{m}$ were placed on cross-sectioned IMC facets covered with a $\text{ZnCl}_2\text{-NH}_4\text{Cl}$ based flux (Stay-Clean®

liquid flux, HARRIS), and reflowed in a forced air convection Tornado LFR400 reflow oven with thermal profile of heating rate 1K/s, peak temperature 240°C, time above the eutectic temperature 80s, and cooling rate ~3K/s. Flux residues were removed in ethanol in an ultrasonic bath. The microstructures and orientation relationships (ORs) between the β -Sn droplets and IMC facets were then measured by EBSD directly without further sample preparation.

3. Results and Discussion

3.1 Nucleation undercooling

Figure 2 shows the nucleation undercooling of 550 μm freestanding balls and joints of SAC305 and SAC305-0.2Ti. It is clear that, in both balls and joints, $\beta\text{-Sn}$ nucleation undercooling was substantially suppressed when 0.2wt% Ti was added, consistent with the past work summarised in Table 1. Nucleation undercoolings of freestanding balls and joints under multiple-cycling were also studied. Figure 3 (A)-(F) shows typical 100-cycled DSC curves, it can be seen that the melting peak in each case is highly reproducible. The solidification onset varies from cycle to cycle for SAC305 solder balls and joints (Figure 3 (A)-(C)), and this induces the widely varied nucleation undercoolings shown in Figure 3 (G)-(I). It can also be seen that SAC305 solder joints on Cu and Ni show smaller and less scattered nucleation undercoolings compared with the freestanding ball (Figure 3 (G)-(I)). For Cu substrates, this has been attributed to the catalytic effect of interfacial Cu_6Sn_5 layers [33]. For Ni substrates, nucleation catalysis has also been attributed to the Ni_3Sn_4 interfacial layer [30, 34-36], but the decreased nucleation undercooling ($\sim 5\text{-}12\text{K}$) in the range 30-70 cycles (Figure 3 (I)) indicates that the nucleation mechanisms may be changing during cyclic testing which needs to be studied further in the future.

In contrast, SAC305-0.2Ti solder balls and joints show relatively reproducible melting and solidification onsets (Figure 3 (D)-(F)) and, therefore, more constant and significantly lower nucleation undercoolings of $\leq 6\text{ K}$ in Figure 3 (J)-(L). It can also be seen that the undercooling is even lower for joints than for freestanding balls when Ti is present.

The nucleation undercooling results in Figure 2 and 3 indicate that Ti additions are effective at catalysing β -Sn nucleation, and multiple cycling which can cause increasing oxidation, does not influence the catalytic effect.

3.2 Nucleant phase identification

Microstructural analysis revealed that SAC305-0.2Ti solder balls and joints contained extra phases that have EDX-measured compositions close to Ti_2Sn_3 and $(Ti,Fe,Cu)Sn_2$ stoichiometry (Table 3), where Fe is an impurity in the base SAC305 alloy (Table 2). Figure 4 shows typical examples of these phases in the microstructure of freestanding SAC305-0.2Ti solder balls. The same phases were found in single-cycled balls, multiple-cycled balls and solder joints with 0.2Ti addition. The phases were identified by quantitatively comparing experimental EBSD patterns with both kinematic and dynamical simulations of the Kikuchi patterns for known structure types [37-47] (as shown in S.I. Table 1) with stoichiometry close to that measured by EDX. The approach is overviewed in Figure 5. The phase with composition close to Ti_2Sn_3 is shown in Figure 5(A). The experimental pattern is given on the left; this pattern is indexed to the σ S40-GaSn₂V₂ structure type [37] in the centre image based on the Hough transform within Bruker Esprit 2.1. The mean angular deviation (MAD) of 0.46 is suitably low. The right-hand image is a dynamical simulation of the EBSD pattern conducted within Bruker DynamicS, initially using the Euler angles from the Hough-transform indexing. The cross-correlation coefficient (CCC) between the experimental and simulated patterns is 0.66, indicating a good fit, and this can be confirmed by visual band-by-band comparison. From this and the EDX composition, it is confirmed that the phase is Ti_2Sn_3 with σ S40-GaSn₂V₂ structure type, which is an expected phase as the most Sn-rich IMC in the Sn-Ti phase diagram [48].

EBSD pattern analysis of a typical (Ti,Fe,Cu)Sn₂ phase is shown in Figure 5(B) using the same format as Figure 5(A). The measured pattern was compared with the structure types of known transition metal distannides (MSn₂) of *oF*48-Mg₂Cu [38-40], *oF*24-TiSi₂ [41], *oS*12-ZrSi₂ [42], *hP*18-Mg₂Ni [43, 44], *tI*12-Al₂Cu [45, 46], and *hP*9-CrSi₂ [47], as shown in S.I. Table 1. Note that TiSn₂ is not a stable phase in the binary Ti-Sn system [48]. It was found that (Ti,Fe,Cu)Sn₂ could be well-fit by the Mg₂Ni structure-type which had the lowest mean angular deviation MAD (0.62), the highest cross-correlation coefficient CCC (0.69) and a good visual fit between the dynamical-simulated and experimental EBSD patterns, as shown in Figure 5(B). Specifically, there is a good quantitative and visual match between the band positions, the relative band intensities and the pole positions. Further details of the relatively poor fits between the experimental EBSD patterns and the other MSn₂ structure types are given in the Supplementary Information. Thus, it seems that the combination of Ti, Fe and/or Cu has stabilised an IMC with Mg₂Ni structure-type in this system. Note that it is not uncommon for a structure-type that is not an equilibrium phase in the binary systems to become an equilibrium phase in a ternary or higher order system. An example is the (Ni,Co)Sn₄ phase with *oS*20-PtSn₄ structure-type in the Sn-Co-Ni system [49] which is not an equilibrium phase in the Ni-Sn or Co-Sn binary systems [50-53].

3.3 Nucleation mechanisms

To identify whether Ti₂Sn₃ and/or (Ti,Fe,Cu)Sn₂ are active nucleants and investigate the underlying nucleation mechanisms, the droplet solidification technique developed in our previous research [3, 17, 33, 34] was applied. Figure 6(A) shows the typical result of solidifying Sn droplets on a cross-sectioned (010) facet of Ti₂Sn₃. The corresponding EBSD inverse pole figure maps in the Y direction (IPF-Y) of β -Sn and Ti₂Sn₃ are shown in Figure 6(B)

and (C) respectively. It is clear that the numerous solidified β -Sn droplets only exhibit three main orientations as indicated by purple, yellow, and blue in Figure 6(B). The three β -Sn orientations and the Ti_2Sn_3 orientation are shown by pole figures in Figure 6(F). Comparing pole figures of “yellow” β -Sn with those of Ti_2Sn_3 , it can be clearly seen that there is a preferred OR (OR1) as indicated by the common circles, triangles, and squares.

$$(010)\text{Sn} \parallel (010)\text{Ti}_2\text{Sn}_3 \text{ and } [001]\text{Sn} \parallel [001]\text{Ti}_2\text{Sn}_3 \quad \text{OR1}$$

Similarly, there is a preferred OR (OR2) between “blue” and “purple” β -Sn and the Ti_2Sn_3 , as shown in Figure 6(F).

$$(011)\text{Sn} \parallel (010)\text{Ti}_2\text{Sn}_3 \text{ and } [0\bar{1}1]\text{Sn} \parallel [001]\text{Ti}_2\text{Sn}_3 \quad \text{OR2}$$

In Figure 6(G), unit cell wireframes have been plotted using the measured Euler angles of the three β -Sn orientations and the single Ti_2Sn_3 orientation in Figure 6(B) and (C). Although there are three β -Sn orientations in Figure 6(B), they are copied and arranged to form a six-fold cyclic ring to demonstrate the nature of cyclic twinning. Note that all unit cells have been rotated together (compare the coordinate systems in Figure 6(A) and (G)) to aid visualisation of OR1 and OR2. Planes parallel to the polished (010) of Ti_2Sn_3 have been cross-hatched. The unit cell wireframes are plotted using the same colours as the EBSD IPF-Y maps in Figure 6(B) and (C). As shown in Figure 6(G), the three β -Sn orientations exhibit a common $\langle 100 \rangle$ axis and are rotated $\sim 60^\circ$ around this axis which causes the three orientations to form a cyclic ring. The common $\langle 100 \rangle$ and $\{100\}$ in the three β -Sn orientations can also be seen by the yellow circle in the pole figures in Figure 6(F). Thus, the three β -Sn grains are cyclic twinned, corresponding to either $\{101\}$ or $\{301\}$ type twins with 57.2° and 62.8°

rotations around $\langle 100 \rangle_{\text{Sn}}$ respectively [1], which is very common in Sn-Ag-Cu-based solders [1, 54-56].

It is found that individual tin droplets sometimes contained twinned β -Sn grains and sometimes contained a single β -Sn orientation, as shown in Figure 6(D) and (E). The single-grain droplets featured either $\{010\}_{\text{Sn}} \parallel \{010\}_{\text{Ti}_2\text{Sn}_3}$ or $\{011\}_{\text{Sn}} \parallel \{010\}_{\text{Ti}_2\text{Sn}_3}$, both with $\langle 100 \rangle_{\text{Sn}} \parallel \langle 100 \rangle_{\text{Ti}_2\text{Sn}_3}$ (i.e. either OR1 or OR2 formed for droplets with a single β -Sn orientation). In twinned droplets, it was found that the $\langle 100 \rangle_{\text{Sn}}$ twinning axis (e.g. the red axis in Figure 6(D)) was always parallel with the $\langle 100 \rangle_{\text{Ti}_2\text{Sn}_3}$.

Lattice matching based on OR1 and OR2 are overviewed in Figure 7. Interfaces are indicated by “red” planes and all near-interface atoms have been projected into the plane as semi-transparent atoms. It can be clearly seen that, in both OR1 and OR2, there is a relative low ($\sim 2\%$) and constant disregistry along $\langle 100 \rangle_{\text{Sn}} \parallel \langle 100 \rangle_{\text{Ti}_2\text{Sn}_3}$. However, the other directions show substantial larger disregistry (i.e. $\sim 9\%$ along $\langle 001 \rangle_{\text{Sn}} \parallel \langle 001 \rangle_{\text{Ti}_2\text{Sn}_3}$ in OR1, $\sim 5\%$ along $\langle 011 \rangle_{\text{Sn}} \parallel \langle 001 \rangle_{\text{Ti}_2\text{Sn}_3}$ in OR2), though both are $< 10\%$, which is considered as a critical value for effective nucleation catalysts [57-59]. Although the disregistries in OR1 and OR2 are different, considering that either OR1 or OR2 can appear in single grain droplets, there may be similar interfacial energies in these two nucleation states.

Sn droplets were also solidified on $(\text{Ti,Fe,Cu})\text{Sn}_2$ single crystals as shown in Figure 8. The EBSD maps and pole figures show a wide range of β -Sn orientations with no preferred ORs, indicating that β -Sn did not nucleate crystallographically on $(\text{Ti,Fe,Cu})\text{Sn}_2$. This is in contrast with the consistent and simple ORs between β -Sn and Ti_2Sn_3 .

Combining the significantly suppressed β -Sn nucleation undercooling (Figure 1, 2, and 3) with the reproducible OR1 and OR2 (Figure 6 and 7), it can be concluded that Ti_2Sn_3 is the catalyst for β -Sn nucleation in solder balls and joints with Ti additions.

Ti_2Sn_3 is as potent as βIrSn_4 , αCoSn_3 and PtSn_4 , since similar nucleation undercoolings have been measured in 550 μm SAC305 freestanding solder balls with corresponding additions [24]. However, there are some interesting differences between the ORs involving Ti_2Sn_3 and the other nucleant IMCs. First, in the β -Sn- Ti_2Sn_3 ORs, some atoms are out-of-plane (semi-transparent atoms in Figure 7) whereas all atoms are in-plane in the ORs between β -Sn and βIrSn_4 , αCoSn_3 , PdSn_4 and PtSn_4 [3, 17, 30]. Second, in Ref. [34], we found only a single β -Sn orientation in Sn droplets on βIrSn_4 , αCoSn_3 and PtSn_4 , but both single-grain and twinned structures were found in droplets on Ti_2Sn_3 here. This obvious distinction may be related to the disregistry along the $\langle 100 \rangle_{\text{Sn}}$ twinning direction for the ORs of each nucleant: for Sn/ Ti_2Sn_3 , the disregistry along the $\langle 100 \rangle_{\text{Sn}}$ twinning direction is $\sim 2\%$ which is much smaller than along the other directions in the interface plane (Figure 7), and implies that twinning along this low disregistry axis would not cause much interfacial energy variation according to the Edge-to-Edge theory [59, 60]. In contrast, this is not the case for βIrSn_4 , αCoSn_3 and PtSn_4 , where disregistries along $\langle 100 \rangle_{\text{Sn}}$ are the largest among the parallel directions in the interface plane (8.2% for βIrSn_4 , 7.5% for αCoSn_3 , and 9.5% for PtSn_4 [17]) and, therefore, twinning is not energetically favourable on those nucleants. In our previous study solidifying tin droplets on Cu_6Sn_5 , Ag_3Sn , and Ni_3Sn_4 [34], we also found that twinning occurred along the lowest disregistry $\langle 100 \rangle_{\text{Sn}}$ but, in that study, the IMCs were of low potency. This study shows that the β -Sn twinning axis parallel to the lowest disregistry direction on the nucleant can occur for both potent and low potency nucleants.

3.4 Microstructures in 550 μ m solder balls and joints

To investigate the influence of heterogeneous nucleant Ti_2Sn_3 on the β -Sn microstructure, solder balls and joints with and without Ti additions were cross-sectioned and measured by EBSD. Typical SAC305 solder balls had single-grain or cyclic-twinned β -Sn structures of either 'beachball' or interlaced form, as shown in Figure 9 (A) and (B) similar to past work [1, 54]. In both beachball and interlaced microstructures, the twinning axis was $\langle 100 \rangle_{\text{Sn}}$ and the twinning angle is $\sim 60^\circ$, as can be seen from the misorientation histograms and pole figures. 33 SAC305 balls with 0.33K/s cooling rate were examined; 5 out of 33 had single-grain structures and the remaining 28 had cyclic twinned structures (Table 4). For higher cooling rates (17K/s), 16 out of 16 SAC305 balls had cyclic twinned structures. All single-grain and twinned-grain samples only had one independent grain in each case and, therefore, these two types of microstructure are consistent with one β -Sn nucleation event in each ball (Table 4).

SAC305-0.2Ti solder balls and joints with lower cooling rate (0.0033K/s and 0.33K/s) solidified with single-grain β -Sn structures (Table 4), such as the typical example shown in Figure 9(C). At higher cooling rates (2K/s and 17K/s), many SAC305-0.2Ti balls exhibited multiple independent β -Sn grains (Table 4). For example, the solder ball in Figure 9(D) has 4 independent grains, as can be seen from the range of different misorientation angles, the presence of twice as many spots in the $\langle 100 \rangle$ pole figure as in the $\langle 001 \rangle$ pole figure, and the lack of common poles in the $\langle 100 \rangle$ pole figure (the lack of other common directions/planes was also checked). Up to 12 independent β -Sn grains were found in SAC305-0.2Ti solder balls and/or joints (See the example in the Supplementary Information). Multiple independent grains correspond to multiple nucleation events, which indicates that

Ti_2Sn_3 particles triggered multiple nucleation during fast cooling. The mechanisms of grain refinement in SAC305 microalloyed with catalysts such as Ti, and the need for a high cooling rate, are discussed in more detail in references [3, 24].

An obvious distinction between SAC305 with and without Ti, is that 550 μm SAC305-0.2Ti solder balls and joints never solidified with cyclic twinned β -Sn in this work, whereas SAC305 was often cyclic twinned (Table 4). Besides the influence of nucleation phases and Ti solute atoms, the effect of the nucleation undercooling should also be considered. Figure 10 plots the nucleation undercooling versus the β -Sn microstructure (classified into twinned and not twinned) in solder balls and joints of SAC305 compared with SAC305-0.05Ti. It can be clearly seen that, for SAC305, balls and joints with no cyclic twinning form at relatively smaller average nucleation undercooling (the grey bars) compared with cyclic twinned samples, though there is overlap over a wide range of undercooling values. This indicates that lower nucleation undercooling is more likely to promote the formation of a single-grain structure in SAC305 balls and joints. Therefore, the lack of twinning in SAC305-0.2Ti solder balls and joints seems to be mostly due to their low nucleation undercooling (Figure 10).

It is also notable that 550 μm SAC305-0.2Ti solder balls and joints never solidified with cyclic twinned β -Sn in this work (Table 4), whereas cyclic-twinning commonly occurred in tin droplets that solidified on Ti_2Sn_3 (Figure 6). This difference is probably due to the very small droplet size (i.e. $<5\mu\text{m}$ compared with $\sim 550\mu\text{m}$ for solder balls and joints) which most likely gave a larger nucleation undercooling in small droplets.

4. Conclusions

The mechanisms of β -Sn nucleation have been studied in titanium-microalloyed Sn-3Ag-0.5Cu (wt%) solder. The following conclusions can be drawn:

- (1) A 0.2wt%Ti addition substantially reduced the nucleation undercooling for β -Sn in both freestanding solder balls and in joints on Cu and Ni substrates.
- (2) The titanium addition continued to catalyse β -Sn nucleation after 100 thermal cycles of freestanding balls and joints on Cu and Ni.
- (3) At least two primary intermetallic compounds (IMCs) were introduced by the Ti addition. These were identified by EDS and EBSD to be Ti_2Sn_3 (*o*S40-GaSn₂V₂ type) and (Ti,Cu,Fe)Sn₂ (*h*P18-Mg₂Ni type) where the Fe was present as an impurity in the commercial-purity solder.
- (4) To identify which IMC is the heterogeneous nucleant, Sn droplets were solidified on the cross sectioned facets of each IMC. β -Sn solidified with reproducible orientation relationships (ORs) on Ti_2Sn_3 and not on (Ti,Cu,Fe)Sn₂, indicating that Ti_2Sn_3 is the active nucleant. Two ORs were identified in this work:

$$(010)\text{Sn} \parallel (010)\text{Ti}_2\text{Sn}_3 \text{ and } [001]\text{Sn} \parallel [001]\text{Ti}_2\text{Sn}_3$$

$$(011)\text{Sn} \parallel (010)\text{Ti}_2\text{Sn}_3 \text{ and } [0\bar{1}1]\text{Sn} \parallel [001]\text{Ti}_2\text{Sn}_3$$

- (5) The lowest disregistry direction in both ORs, $\langle 100 \rangle \text{Sn} \parallel \langle 100 \rangle \text{Ti}_2\text{Sn}_3$, was always parallel with the twinning axis $\langle 100 \rangle \text{Sn}$ in twinned tin droplets on Ti_2Sn_3 . This is similar to past work on low potency nucleants, Cu_6Sn_5 , Ag_3Sn , and Ni_3Sn_4 , and shows that the twinning axis $\parallel$ the lowest disregistry direction can occur for both potent and low potency nucleants.

- (6) The 0.2Ti addition to 550 μ m solder balls and joints generated some grain refinement, with up to 12 independent β -Sn grains nucleating at high cooling rates of 2 K/s and 17 K/s. No cyclic twinned microstructures formed in 550 μ m Ti microalloyed balls and joints, which is likely to be due to the low undercooling in balls and joints of this size.

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Figure titles:

Figure 1 Typical DSC profiles of (A) SAC 305 and (B) SAC305-0.2Ti freestanding solder balls. (C) Multiple-cycling method to determine the liquidus temperature of β -Sn, here, a SAC305+0.5Ti/Cu solder joint is used as an example. The Isothermal holding temperature step is 0.5 K.

Figure 2 Nucleation undercooling of 550 μ m freestanding balls and joints on Cu and Ni substrates. In each case, mean value and standard deviation are from at least 20 measurements.

Figure 3 Multiple cycling DSC results. (A)-(F) Typical 100 times cycled DSC profiles of SAC305 and SAC305-0.2Ti solder balls and joints. (G)-(L) Corresponding nucleation undercoolings versus the cycling number. Circle and triangle datapoints in (G)-(I) represent two different samples in each.

Figure 4 SEM images of SAC305-0.2Ti freestanding solder balls. (A) A typical ball with 0.33K/s cooling rate. (B) The enlarged area in (A) shown Ti_2Sn_3 , Cu_6Sn_5 , and Ag_3Sn IMCs. (C) A typical ball with 0.0033K/s cooling rate. (D) and (E) Enlarged areas in (C) showing MSn_2 and Ti_2Sn_3 phases.

Figure 5 Phase identification by EBSD. From left to right: detected EBSD pattern, indexed EBSD pattern, and dynamic simulated EBSD pattern. (A) Ti_2Sn_3 indexed as $\text{oS40-GaSn}_2\text{V}_2$ structure. (B) $(\text{Ti,Cu,Fe})\text{Sn}_2$ indexed as $\text{hP18-Mg}_2\text{Ni}$ structure. MAD = Mean angular deviation; CCC = Cross correlation coefficient.

Figure 6 (A) SEM image of numerous Sn droplets solidified on a cross sectioned (010) facet of Ti_2Sn_3 . (B) EBSD IPF-Y map of β -Sn. (C) EBSD IPF-Y map of Ti_2Sn_3 . (D) A typical single droplet with a cyclic twinned β -Sn structure. The twinning axis is labelled red. (E) A typical single droplet with a single-grain β -Sn structure. (F) EBSD pole figures of β -Sn and Ti_2Sn_3 in (B) and (C). (G) Plot of the ORs between three cyclic twinned β -Sn orientations and the Ti_2Sn_3 crystal, plotted using the EBSD-measured Euler angles. Note that each β -Sn orientation is shown twice to make clear the pseudo-hexagonal arrangement in the cyclic twin. Common $\{100\}_{\text{Sn}}$ are shaded grey.

Figure 7 Interfacial planes and lattice match based on OR1 and OR2.

Figure 8 (A) SEM image showing numerous Sn droplets solidified on a cross sectioned facet of $(\text{Ti,Cu,Fe})\text{Sn}_2$. (B) EBSD IPF-Z map of β -Sn. (C) EBSD IPF-Z map of $(\text{Ti,Cu,Fe})\text{Sn}_2$ indexed by $\text{hP18-Mg}_2\text{Ni}$ structure-type. (D) Corresponding pole figures of β -Sn and $(\text{Ti,Cu,Fe})\text{Sn}_2$ in (B) and (C).

Figure 9 A representative range of β -Sn grain structures in balls and joints cooled at 0.0033-17 K/s. From left to right: Optical images, EBSD IPF-X maps, misorientation angle distributions, and pole figures. (A) A typical freestanding SAC305 solder ball under 0.33 K/s cooling rate. (B) A typical freestanding SAC305 solder ball under 17 K/s cooling rate. (C) A typical freestanding SAC305-0.2Ti solder ball under 0.33K/s cooling rate. (D) A typical freestanding SAC305-0.2Ti solder ball under 17 K/s cooling rate. TA = twinning axis.

Figure 10 Nucleation undercooling versus β -Sn structures in 550 μ m solder balls and joints. Each data point represents a ball/joint and the grey bar indicates the average nucleation undercooling from balls or joints of the same β -Sn structure.

Tables:

Table 1 Summary of past literature on the influence of Ti additions on nucleation undercooling Sn and Sn-based solders. All studies used DSC. ESD = Equivalent sphere diameter.

Base alloy [wt%]	Ti addition [wt%]	ESD [μm]	Cooling rate [K/s]	ΔT_{nuc} [K]		Ref.
				Without Ti	With Ti	
Sn(99.99%)	0.2	1080	0.1	31.2	5.4	[27]
Sn-0.7Cu	0.2	1095	0.1	34.5	3.9	[28]
Sn-0.7Cu	0.6	1095	0.1	34.5	3.6	[28]
Sn-1.0Ag	0.2	1095	0.1	39.5	3.1	[28]
Sn-1.0Ag	0.6	1095	0.1	39.5	2.7	[28]
Sn-1.0Ag-0.5Cu	0.15	--	0.033	24.0	8	[26]
Sn-1.0Ag-0.5Cu	0.5	--	0.033	24.0	4	[26]
Sn-1.0Ag-0.5Cu	0.02	807	0.167	64.47	3.2	[25]
Sn-2.5Ag-0.5Cu	0.02	807	0.167	58.92	11.11	[25]
Sn-3.0Ag-0.5Cu	0.2	500	0.33	27.5	7.65	[24]

Table 2 Compositions of all alloys as measured by X-ray fluorescence spectroscopy (XRF). ND = <0.001wt%.

Nominal Composition	Zn (wt%)	Bi (wt%)	Ag (wt%)	Cu (wt%)	Pb (wt%)	Co (wt%)	Mn (wt%)	Ti (wt%)	Pt (wt%)	Fe (wt%)
SAC 305	ND	0.014	2.930	0.588	0.025	ND	ND	ND	ND	0.004
SAC305-0.2Ti	ND	0.003	3.000	0.580	0.034	ND	ND	0.168	ND	0.005

Table 3 Compositions of Ti_2Sn_3 and $(\text{Ti,Cu,Fe})\text{Sn}_2$ phases measured by EDX.

Particle	Ti (at%)	Fe (at%)	Cu (at%)	Sn (at%)
Ti_2Sn_3	39.8 (0.7)	--	--	60.2 (0.6)
$(\text{Ti,Cu,Fe})\text{Sn}_2$	16.9 (1.1)	8.6 (2.1)	7.1 (1.2)	67.4 (2.9)

Table 4 Summary of β -Sn microstructures in 550 μm freestanding solder balls and joints on Cu and Ni substrates. IG = independent grains.

Alloy	Cooling Rate (K/s)	Substrate	No. of samples	Microstructure and frequency of occurrence			
				Single grain	Twinned grain	One IG	Multiple IGs
SAC305	0.33	--	33	5	28	33	0
SAC305	17	--	16	0	16	16	0
SAC305-0.2Ti	0.0033	--	6	6	0	6	0
SAC305-0.2Ti	0.33	--	15	15	0	15	0
SAC305-0.2Ti	2	--	14	4	0	4	10
SAC305-0.2Ti	17	--	5	1	0	1	4
SAC305-0.2Ti	0.33	Cu	10	10	0	10	0
SAC305-0.2Ti	0.33	Ni	10	10	0	10	0

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Figure 1 Typical DSC profiles of (A) SAC 305 and (B) SAC305-0.2Ti freestanding solder balls. (C) Multiple-cycling method to determine the liquidus temperature of β -Sn, here, a SAC305+0.5Ti/Cu solder joint is used as an example. The Isothermal holding temperature step is 0.5 K.

Figure 2 Nucleation undercooling of 550 μm freestanding balls and joints on Cu and Ni substrates. In each case, mean value and standard deviation are from at least 20 measurements.

Figure 3 Multiple cycling DSC results. (A)-(F) Typical 100 times cycled DSC profiles of SAC305 and SAC305-0.2Ti solder balls and joints. (G)-(L) Corresponding nucleation undercoolings versus the cycling number. Circle and triangle datapoints in (G)-(I) represent two different samples in each.

Figure 4 SEM images of SAC305-0.2Ti freestanding solder balls. (A) A typical ball with 0.33K/s cooling rate. (B) The enlarged area in (A) shown Ti_2Sn_3 , Cu_6Sn_5 , and Ag_3Sn IMCs. (C) A typical ball with 0.0033K/s cooling rate. (D) and (E) Enlarged areas in (C) showing MSn_2 and Ti_2Sn_3 phases.

Figure 5 Phase identification by EBSD. From left to right: detected EBSD pattern, indexed EBSD pattern, and dynamic simulated EBSD pattern. (A) Ti_2Sn_3 indexed as $oS40\text{-GaSn}_2\text{V}_2$ structure. (B) $(\text{Ti,Cu,Fe})\text{Sn}_2$ indexed as $hP18\text{-Mg}_2\text{Ni}$ structure. MAD = Mean angular deviation; CCC = Cross correlation coefficient.

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- Two new stannides are introduced by microalloying Sn-Ag-Cu solders with Ti
- Ti_2Sn_3 is proved to be a potent nucleant for β -Sn nucleation
- β -Sn twinning axis is parallel to the lowest disregistry direction on the nucleant
- Ti additions can trigger up to 12 independent grains in Sn-Ag-Cu solders and joints