

Competition between stable and metastable eutectic growth in Sn-Ni alloys

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Abstract

Metastable Sn-NiSn₄ eutectic can form in electronic solder joints and is a reliability concern. Here the competition between stable Sn-Ni₃Sn₄ and metastable Sn-NiSn₄ eutectic growth is studied during unidirectional solidification. The stable and metastable eutectic points are measured, the dynamics of eutectic growth and the transition between the two eutectics is investigated by synchrotron radiography, and the crystallography of eutectic growth is measured by EBSD. It is shown that the Sn-Ni₃Sn₄ eutectic has a highly irregular morphology with diverging and converging rods because monoclinic Ni₃Sn₄ grows only along [010] without a reproducible orientation relationship (OR) with Sn. The metastable Sn-NiSn₄ eutectic has a more regular broken-lamellar morphology and a reproducible OR with Sn. The critical velocity between the two eutectics is less than 1 $\mu\text{m/s}$ which is discussed in terms of the small temperature difference between the two eutectic points and the kinetic growth advantages of the metastable eutectic.

Key words

Directional Solidification;

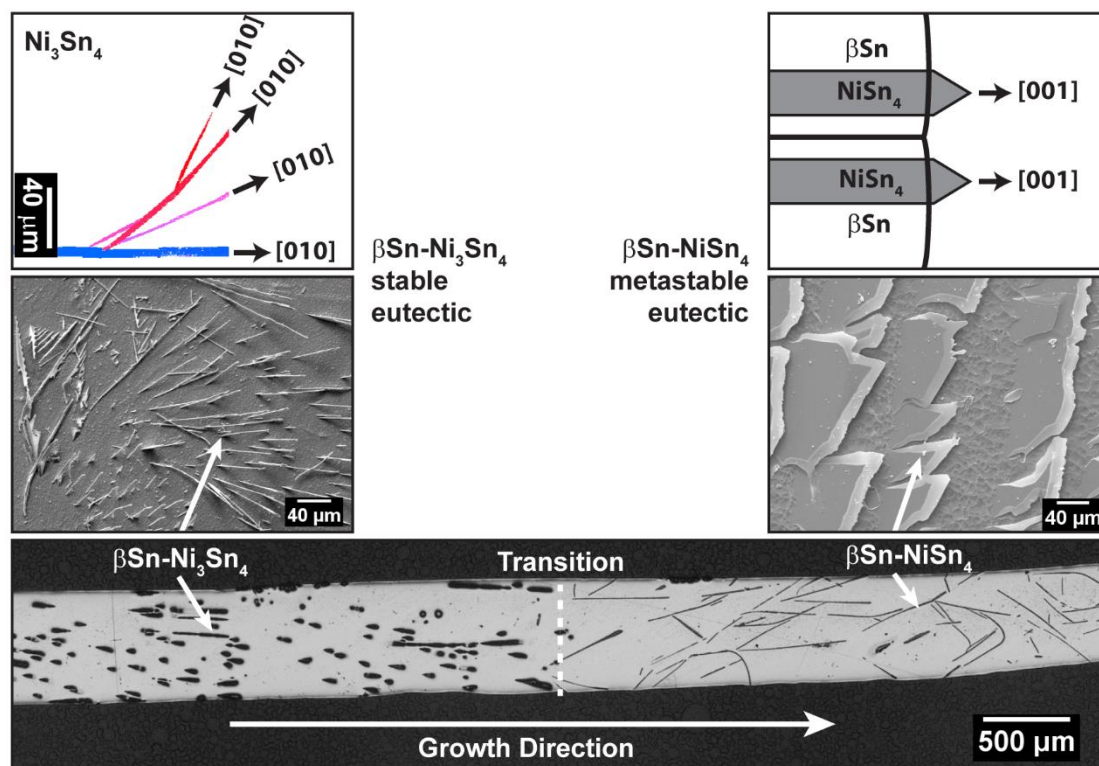
Eutectic;

Phase diagram;

Alloys;

X-ray radiography.

Graphical abstract



1. Introduction

In many alloy systems containing a eutectic point, there can be competition between a stable and metastable eutectic reaction. Examples include $\gamma\text{Fe-C}$ versus $\gamma\text{Fe-Fe}_3\text{C}$ in cast irons [1], $\text{Al-Al}_3\text{Fe}$ versus $\text{Al-Al}_6\text{Fe}$ in wrought Al alloys [2, 3], and $\text{Al}_2\text{O}_3\text{-YAG}$ versus $\text{Al}_2\text{O}_3\text{-YAP}$ scintillator materials [4]. In each case, the selected eutectic usually has a significant influence on the properties of the solidified alloy (mechanical, corrosion, electrical etc.) and, therefore, it is important to be able to predict and control which eutectic forms.

Recently, it has been shown that a metastable eutectic can also form in Sn-rich Sn-Ni alloys [5-7]. In this case, the stable eutectic is $\beta\text{Sn-Ni}_3\text{Sn}_4$ and the metastable eutectic is $\beta\text{Sn-NiSn}_4$. A similar metastable eutectic also forms in electronic solder joints when joining Ni-based substrates with Sn-3.5Ag solder [8], where the metastable ternary eutectic $\text{L} \rightarrow \beta\text{Sn} + \text{Ag}_3\text{Sn} + \text{NiSn}_4$ forms preferentially over the stable $\text{L} \rightarrow \beta\text{Sn} + \text{Ag}_3\text{Sn} + \text{Ni}_3\text{Sn}_4$ eutectic for solidification conditions typical of industrial soldering. The presence of metastable NiSn_4 is a potential reliability concern in solder joints and a deeper understanding of its formation is required. At present, there is little known of the competition between the stable and metastable eutectics in the Sn-Ni system. For example, while much of the Sn-Ni phase diagram has been accurately determined recently [9-11], the least researched region is the Sn-rich end where the stable and metastable eutectic points exist [12-14]. Furthermore, while the crystal structure of metastable NiSn_4 has been investigated [15-17], and the presence of eutectic NiSn_4 has been confirmed after solidification [18-20], the conditions for the transition from stable to metastable eutectic growth have not been investigated.

In this paper, we first measure the stable and metastable Sn-Ni phase diagrams at Sn-rich compositions near the stable and metastable eutectic points. We then use Bridgman growth to study the influence of interface velocity on the competition between stable and metastable eutectic growth where the dynamics of eutectic growth are investigated by synchrotron radiography and the crystallography of eutectic growth are studied by EBSD.

2 Methods

2.1 Materials

A Sn-10 wt% Ni master alloy was first produced by encapsulating 99.999% Sn and 99.99% Ni in an evacuated quartz ampoule and holding at 1200 °C for one week. Sn-x Ni alloys with x=0.04, 0.09, 0.1, 0.14, 0.19 and 0.26 wt% were prepared by mixing 99.999% Sn and the master alloy, melting in a high-purity graphite crucible and holding at 450 °C for 1 hour. Some liquid was drawn into 4 mm diameter quartz tubes under vacuum. These rods were used for composition measurement by ICP-AES and for isothermal holding experiments to measure the Ni₃Sn₄ liquidus temperatures. The remaining liquid was cast into a steel chill mould to produce samples for unidirectional solidification and DSC.

2.2 Phase diagram determination

In our past work, we found that the temperature difference between the two eutectic temperatures is less than 0.4 K.[18] To enable the two peaks to be separated and accurately determine their onset temperature, a slow heating rate of 0.02 K/min and a small sample mass 15±4 mg were used. Sn-0.19Ni alloys were tested in Al pans under N₂ in a Mettler Toledo DSC1. The first cycle, with a 20 K/min heating/cooling rate from 35 °C - 350 °C – 35 °C, was applied to generate the same initial microstructures for all samples. Next a sample was heated to 230 °C at 20 K/min and isothermally held for 0, 1, 6 or 10 hours. Then the sample was heated at 0.02 K/min from 230 °C to 233 °C to melt the eutectic(s). Finally, the sample was cooled at 20 K/min to 35 °C. To perform 2 months holding at 230 °C, samples were given the same first DSC cycle and were then held for 2 months at 230 °C in a separate oven before being reheated to 230 °C in the DSC and being heated at 0.02 K/min from 230 °C to 233 °C similar to all other samples. To interpret the DSC curves, some samples were cooled at the end of isothermal holding at 230 °C (without the being melted) and their microstructures were characterised. It was found that the cyclic DSC method described in [21-23] was not suitable for measuring the Ni₃Sn₄ liquidus temperatures, due to the formation of a small mass fraction of primary Ni₃Sn₄ (only 0.92

mass% Ni_3Sn_4 for Sn-0.26 wt% Ni) and steep Ni_3Sn_4 liquidus line (~ 1800 K/wt% Ni in the range 0.09 – 0.26 wt% Ni according to [24]). Therefore, the following method was used to identify the Ni_3Sn_4 liquidus temperatures. A 500 mg sample was held isothermally above the stable eutectic temperature in evacuated 4 mm diameter quartz tubes for two days and was then quenched in water. The presence or absence of settled Ni_3Sn_4 particles was then confirmed by optical microscopy and SEM. The initial holding temperatures were set to be 35 K above and below the liquidus temperature reported in [24]. If one temperature contained settled Ni_3Sn_4 particles and the other did not, the next holding temperature was set as the median of the two temperatures. Repeating this procedure enabled the Ni_3Sn_4 liquidus temperatures to be confirmed to within ± 1 K. The furnace temperature was calibrated by a thermocouple calibrated against 99.99Sn.

Alloy compositions were determined by ICP-AES measurements of samples cut from the rods used for liquidus temperature measurements. Two samples were tested for each composition, one from either side of the material used for liquidus temperature measurements. Table 1 provides the measured compositions.

2.3 Bridgman growth experiments

Thin sample unidirectional solidification was performed on the alloys by horizontal unidirectional solidification in our laboratory and vertical unidirectional solidification at the SPring-8 synchrotron. Horizontal unidirectional solidification was conducted on $60 \text{ mm} \times 10 \text{ mm} \times 500 \text{ }\mu\text{m}$ samples using a modified tensile testing hot stage. The hot zone temperature was $350 \text{ }^\circ\text{C}$, the cold zone was $20.5 \pm 1 \text{ }^\circ\text{C}$, and the temperature gradient in the liquid near the S-L interface was 12 K/mm as measured with a $\varnothing=0.25 \text{ mm}$ K-type thermocouple. Initially, samples were partially remelted to have a stationary βSn -L interface and some Ni_3Sn_4 particles at the growth front. Samples were then grown to a distance of 21 mm at a pulling rate in the range $0.5 - 500 \text{ }\mu\text{m/s}$ and the interface was then quenched with high pressure room temperature Ar.

Synchrotron radiography of vertical unidirectional solidification was performed on BL20XU at SPring8, using an X-ray energy of 16 keV and the apparatus developed by Yasuda et al.[25]. 20 μ m thick samples were used, confined within a 20 μ m thick PTFE spacer cavity between SiO₂ sheets similar to (but thinner than) ref.[26] The field of view was $\sim 1 \times 1$ mm recorded with 0.502 μ m per pixel at 1 frame per second with a 0.5s exposure time using a CMOS camera. The hot zone was set to 400 °C and Bridgman growth was imposed by pulling the sample downwards away from the hot zone. To study transitions between stable and metastable eutectic growth, samples were initially pulled at 1 μ m/s, were then increased to 5 or 10 μ m/s and finally reduced back to 1 μ m/s. Actual interface velocities were tracked in the images. The temperature gradient in the liquid near the S-L interface was ~ 5 K/mm as measured with a $\varnothing=0.1$ mm B-type thermocouple in a separate experiment.

2.4 Analytical scanning electron microscopy (SEM)

Laboratory samples were mounted in Struers VersoCit acrylic cold mounting resin, ground with SiC paper to 2000 grit, and were then polished with colloidal silica. Microstructures were investigated using an Olympus BX51 optical microscope and a Zeiss Auriga field emission gun scanning electron microscope (FEG-SEM). The latter was equipped with an Oxford Instruments INCA x-sight energy dispersive X-ray (EDX) detector and a BRUKER e-FlashHR electron backscatter diffraction (EBSD) detector. Phases were identified by combining EBSD and EDX. The crystal facets, growth directions and orientation relationships (ORs) between phases were analysed by EBSD using Bruker Esprit 2.0 and HKL Flamenco acquisition software was used for indexing of Kikuchi patterns. [18]

The thin synchrotron samples were carefully separated from the SiO₂ sheets and examined directly, without further preparation, by analytical SEM. It was found that these unpolished surfaces were suitable for EBSD and EDS analyses and, for many regions, the *post mortem* surface microstructure could be correlated with the through-thickness integrated radiographs from the *in situ* image sequences.

3 Results and Discussion

3.1 Stable and metastable Sn-Ni phase diagram (Sn-rich end)

Figure 1(a) shows typical DSC heating curves from Sn-0.19Ni samples (a hypereutectic composition) which were held isothermally for 0, 1, 6, 10 hours or 2 months at 230°C before being heated at 0.02K/min. The first four curves contain two peaks where the relative magnitude of the two peaks depends on the holding time at 230°C. The first peak is dominant at the shorter holding times and the second peak becomes more dominant with increasing holding time. The 2 month curve contains only one peak and has an onset temperature that is higher than the other holding times.

Figures 1(b)-(e) show typical microstructures of samples that had different isothermal holding times and were then cooled from 230°C without melting. All the particles in Figure 1(b)-(e) were confirmed as NiSn₄ or Ni₃Sn₄ phase by EDX and EBSD. Table 2 shows the summary of EDX measurements. The light grey phase contains 18.5 ± 0.7 at% Ni and the dark phase contains 41.0 ± 0.7 at% Ni, consistent with NiSn₄ and Ni₃Sn₄ respectively. The slightly Sn-rich compositions are consistent with past work [9, 18] and indicate a composition range for each IMC. The EBSD patterns were consistent with the oS20-PtSn₄ structure type [15, 27] and mS14-Ni₃Sn₄ [28] based on quantitative comparison of the experimental patterns with both kinematic and dynamical simulations of the Kikuchi patterns.

Figure 1(b) shows the microstructure of samples without isothermal holding (i.e. heated to 230°C and then cooled immediately). It contains Ni₃Sn₄ particles and a much higher fraction of NiSn₄ plates plus β Sn. In Figure 1(c) and (d), as the isothermal holding time increased, the fraction of NiSn₄ decreased and the fraction of Ni₃Sn₄ increased, and the size of Ni₃Sn₄ particles increased. After 2 months holding at 230°C, there was no discernable NiSn₄ phase and all had transformed into Ni₃Sn₄ particles and β Sn as shown in Figure 1(e). From Figure 1(b)-(e), it can be concluded that NiSn₄ is a metastable phase at 230°C and is transforming into Ni₃Sn₄ and β Sn with time. The microstructures in Figure 1(b)-(d) contain both NiSn₄ and Ni₃Sn₄ and have two peaks in the DSC heating curves, where the second peak becomes more dominant with increasing holding time. Thus, the first peak is associated with the melting of

metastable $\beta\text{Sn}+\text{Ni}_3\text{Sn}_4$ eutectic and the second peak is caused by the melting of stable $\beta\text{Sn}+\text{Ni}_3\text{Sn}_4$. Since Figure 1(e) contains only βSn and Ni_3Sn_4 , the single peak in the 2 month curve in Figure 1(a) is the melting of stable $\beta\text{Sn}+\text{Ni}_3\text{Sn}_4$ eutectic.

Table 3 summarises the measured metastable and stable eutectic temperatures. The stable eutectic temperature is the average of the onset temperature of the 2-month curves for all six samples. The metastable eutectic temperature is the average of the onset temperature of the other four curves for the six samples. From this method, the stable $\beta\text{Sn}+\text{Ni}_3\text{Sn}_4$ eutectic temperature is 231.10 ± 0.03 °C and the metastable $\beta\text{Sn}+\text{Ni}_3\text{Sn}_4$ eutectic temperature is 230.99 ± 0.05 °C. The difference between the two eutectic temperatures is 0.11 ± 0.06 °C.

The measured Ni_3Sn_4 liquidus temperatures are shown in Figure 2(a). The composition error bars are the minimum and maximum values from ICP-AES chemical analysis results (Table 1) and are relatively large because the composition range is so small. The temperature error bars are the minimum and maximum values from all repeat experiments used for liquidus temperature measurement.

Figure 2(a) also shows the experimental stable phase diagram plotted using the mean stable eutectic temperature measurement, the Ni_3Sn_4 liquidus temperature results, and assuming the βSn liquidus to be linear by linking the melting point of Sn with the stable eutectic point. To further validate the stable eutectic point, the presence or absence of primary Ni_3Sn_4 particles was explored in all samples by two methods: holding in a positive thermal gradient, and isothermal holding at 1K above the stable eutectic temperature. Both methods showed that there were no primary Ni_3Sn_4 particles at Sn-0.09Ni and there were primary Ni_3Sn_4 particles in the other four compositions. Thus, Sn-0.09Ni is a hypoeutectic alloy and others are hypereutectic alloys. The stable eutectic composition is determined by these methods as 0.095 ± 0.005 wt%Ni which is in good agreement with an extrapolation of the Ni_3Sn_4 liquidus line to the mean stable eutectic temperature (Figure 2(a)).

Figure 2(b) shows the experimental stable and metastable Sn-Ni phase diagrams. The solid line is the stable $\beta\text{Sn}-\text{Ni}_3\text{Sn}_4$ phase diagram (from Figure 2(a)) and the dashed line is the metastable $\beta\text{Sn}-\text{Ni}_3\text{Sn}_4$

phase diagram. The metastable eutectic composition has been found from the intersection of the βSn liquidus line and the metastable eutectic line (Table 3). The liquidus line of NiSn_4 is unknown, but its slope should be smaller than that of the Ni_3Sn_4 liquidus line and is plotted in grey to highlight this uncertainty. Based on the stable and metastable phase diagrams, the eutectic mixtures are predicted to contain 0.33 mass% (~ 0.28 vol%) Ni_3Sn_4 and 0.99 mass% (~ 0.94 vol. %) NiSn_4 respectively at each eutectic point.

3.2 Stable and metastable eutectic morphologies

In both laboratory and synchrotron unidirectional solidification, it was possible to grow the βSn - Ni_3Sn_4 eutectic and the βSn - NiSn_4 eutectic and to study transitions between the two eutectics in all compositions from 0.09 – 0.26 wt%Ni. Figure 3 shows typical longitudinal cross-sections of the stable βSn - Ni_3Sn_4 eutectic (Figure 3(a)), the metastable βSn - NiSn_4 eutectic (Figure 3(b)), and the transition between the two (Figure 3(c)) for Sn-0.14Ni pulled at $1\mu\text{m/s}$. The Ni_3Sn_4 appears dark and the NiSn_4 is light grey.

Figure 4 gives typical examples of the 3D morphology of the intermetallics in the two eutectics after selective dissolution of the βSn matrix for compositions in the range 0.04 – 0.14wt%Ni grown at $1\text{--}2\mu\text{m/s}$. By combining Figures 3(a) and 4(a-c), it can be seen that the stable βSn - Ni_3Sn_4 eutectic grows as an irregular rod-like eutectic with complex branching. Examination of the Ni_3Sn_4 rod in Figure 4(c) shows clear growth facets and a faceted tip. It was common for eutectic Ni_3Sn_4 to grow from pre-existing primary Ni_3Sn_4 with complex branching and to gradually adjust the rod growth direction to the βSn -L interface growth direction as shown in Figure 4(a) and (b).

From Figures 3(b) and 4(d-f), it can be seen that the metastable βSn - NiSn_4 eutectic usually grows with a broken-lamellar morphology where the NiSn_4 sheets are often well aligned with one another and can grow at an angle to the pulling direction (e.g. Figure 3(b)). It was also common for there to be regions of irregular βSn - NiSn_4 eutectic where the microstructure is ‘irregular plate’ such as that after

the transition in Figure 3(c). In all cases, the eutectic NiSn_4 grew as thin faceted sheets as shown in Figure 4(d)-(f).

3.3 Stable $\beta\text{Sn-Ni}_3\text{Sn}_4$ eutectic growth mechanisms

Typical features of growth of the stable eutectic are shown in Figure 5. It is a sequence of radiographs of Sn-0.14Ni alloy growing at $V=1 \mu\text{m/s}$ in vertical unidirectional solidification where the pulling direction is downward and the isotherms are approximately stationary in the field of view. Figure 5(a)-(e) shows the stable eutectic growth front at different times (t) where the earliest time is at the bottom (Figure 5(a)) and the latest at the top (Figure 5(e)). The dark phase are Ni_3Sn_4 rods where darker regions indicate thicker rods and the $\beta\text{Sn-L}$ interface is $\sim 3/4$ of the way up each image. The white circles are shallow bubbles which are attached to the SiO_2 walls. Therefore, bubbles move downwards as the sample is pulled downwards and act as useful markers when examining Figure 5.

Four Ni_3Sn_4 rods are labelled on Figure 5. Rod-1 nucleated at a bubble in the liquid ahead of the $\beta\text{Sn-L}$ interface before $t=4540\text{s}$ in Figure 5(a). Rod-1 grows and makes contact with the $\beta\text{Sn-L}$ interface and, then, the $\beta\text{Sn-L}$ interface grows over (engulfs) Ni_3Sn_4 rod-1 by Figure 5(b). Rod-2 has similar growth behaviour as rod-1; it nucleated in the liquid ahead of the $\beta\text{Sn-L}$ interface between 4777s in (b) and 4865s in (c). As rod-1 and rod-2 nucleated in the liquid ahead of the $\beta\text{Sn-L}$ interface and the sample is of hypereutectic composition, rod-1 and rod-2 are primary Ni_3Sn_4 phases. In the radiograph sequences, new βSn does not appear to nucleate on the primary Ni_3Sn_4 rods ahead of the $\beta\text{Sn-L}$ interface. This was confirmed by *post mortem* EBSD mapping which showed that the same two βSn grains existed for the whole growth distance and no new βSn grains nucleated during growth, as shown in Figure SI-1 in the Supplementary Information. This is most likely because the nucleation undercooling for βSn nucleation on Ni_3Sn_4 is typically $\geq 5 \text{ K}$ [29], which is not reached in the location of Ni_3Sn_4 particles ahead of the main $\beta\text{Sn-L}$ front.

Some rods developed into coupled eutectic growth with Ni_3Sn_4 - $\beta\text{Sn-L}$ triple junctions, such as rod-3 and rod-4. These Ni_3Sn_4 rods lead the eutectic front (i.e. Ni_3Sn_4 protrude ahead of the $\beta\text{Sn-L}$ interface)

as is common in nf-f eutectics [30] and is clearest in Figure 5(e). In Figure 5(e), it can be seen also that rod-2 branches during growth. Snapshots from the frames where rod-2 branches are shown in Figure SI-2 in the Supplementary Information. It can be seen that branching occurs near the moment the tip of rod-2 is contacted by the eutectic front. Diverging growth of the branch and stem results in 2 rods at the eutectic front which then grow as a coupled eutectic with βSn . To investigate whether there is a crystallographic origin to the branching, we measured the orientations of multiple branches and the surrounding βSn by *post mortem* EBSD. Most Ni_3Sn_4 branches had no simple or reproducible OR with βSn . However, occasionally, we measured parallel planes the same as those recently identified in a nucleation OR when tin droplets solidify on the facets of Ni_3Sn_4 [31]: $\{-5-10\}_{\text{Ni}_3\text{Sn}_4} // \{-1-10\}_{\text{Sn}}$ and $\{100\}_{\text{Ni}_3\text{Sn}_4} // \{241\}_{\text{Sn}}$. An example of this βSn - Ni_3Sn_4 OR is shown in Figure SI-3 in the Supplementary Information where the Ni_3Sn_4 branch and stem share a common $\{201\}$ plane. This indicates that, in at least some cases, Ni_3Sn_4 branching at Ni_3Sn_4 - βSn -L junctions is assisted by the reduction in interfacial energy associated with a preferred βSn - Ni_3Sn_4 OR.

From these observations, it can be concluded that the mechanisms of spacing selection are: (i) Ni_3Sn_4 nucleation in the liquid ahead of the βSn -L interface where the spacing is wide, such as rod-1 and rod-2, (ii) Ni_3Sn_4 branching near a Ni_3Sn_4 - βSn -L triple point where the spacing is wide, such as rod-2, and (iii) Rod termination where the local spacing is narrow, such as some of the rods near label-4 in Figure 5(a).

Due to converging and diverging rod growth, the stable eutectic grew with a wide range of local spacings as shown in Figure 5(a-e). However the vertical position (temperature) of the βSn -L interface was not strongly influenced by the local spacing. For example, the βSn -L interface does not become strongly depressed behind the average front position when the local spacing is wide as shown in Figure 5(a) which is quite different to diverging growth in other nf-f systems, such as borneol-succinonitrile [30] and Fe-C [32]. The relatively flat βSn -L interface is due to the shallow βSn liquidus slope (Figure

2) which makes the solute undercooling a relatively weak function of solute accumulation ahead of the $\beta\text{Sn-L}$ interface.

Post mortem EBSD analysis of typical $\beta\text{Sn-Ni}_3\text{Sn}_4$ eutectic branches is shown in Figure 6. Figure 6(a) is a BSE-SEM image where the $\beta\text{Sn-L}$ interface growth direction was upward (the Y direction). Branches are confirmed as monoclinic Ni_3Sn_4 by the EBSD phase map in Figure 6(b). IPF-Y, IPF-Z and IPF-X maps are shown in Figure 6(c), (d) and (e) respectively and the colour scale is shown in Figure 6(c). The IPF-X and IPF-Y maps show that the different branches have different crystallographic orientations and the IPF-Z map shows that all branches share a common plane. The numbered branches in Figure 6(e) show the sequence of growth. At the beginning, only particle-1 was growing and its growth direction is along $[010]$ Ni_3Sn_4 and near-parallel with the $\beta\text{Sn-L}$ interface growth direction. Then to decrease the eutectic spacing, branch-2 developed, followed by branch-3 and -4, and then branch-5. The crystal unit cells in Figure 6(e) and pole figures in Figure 6(F) show that Ni_3Sn_4 branches 1, 3, 4 and 5 all grew along $[010]$ and share a common $\{201\}$. The angle between adjacent branches varied from 29° between 1 and 2, 21° between 1 and 3, 18° between 3 and 4, and 22° between 4 and 5. Thus, although all these branches have one parallel plane with βSn : $\{201\}_{\text{Ni}_3\text{Sn}_4} // \{100\}_{\text{Sn}}$, none of them has a simple or reproducible OR with βSn .

Combining the in-situ imaging, growth directions and the growth morphologies of Ni_3Sn_4 rods, the origin of the irregular growth can be concluded to have two origins. (1) Ni_3Sn_4 can only grow along $[010]$ and since Ni_3Sn_4 is monoclinic, $[001] \neq [010] \neq [100]$, so Ni_3Sn_4 only grows in one direction. Thus, branching requires a new orientation to nucleate on a rod which is likely to require a relatively large branching undercooling. (2) Many eutectic Ni_3Sn_4 form from primary Ni_3Sn_4 that nucleated in the liquid (Figure 5) with random orientation that will have, in most cases, $[010]$ poorly oriented with respect to the pulling direction which results in widely converging and diverging rod growth. Also, since Ni_3Sn_4

rods that nucleate in the liquid are orientated randomly and βSn requires a large nucleation undercooling [29] to nucleate on Ni_3Sn_4 , no preferred OR forms with βSn for most rods.

3.4 Metastable βSn - NiSn_4 eutectic growth mechanisms

The regular metastable eutectic grew with one of two lamellar configurations during unidirectional growth. Either the NiSn_4 sheets intersected the sample surface as shown in Figure 7(a) for synchrotron samples and Figure 4(f) for laboratory samples; or the (010) NiSn_4 lamellae were near-parallel with the sample surface as shown in Figure 7(i) for synchrotron samples and Figure 4(d) for laboratory samples.

EBSD analysis of metastable eutectic growth for both configurations is shown in Figure 7(b) and 7(ii).

In both cases, the orientation relationship is:

$$(010)_{\text{NiSn}_4} // (100)_{\beta\text{Sn}} \text{ and } [001]_{\text{NiSn}_4} // [001]_{\beta\text{Sn}} \quad \text{OR1}$$

Where the interfacial plane is $(010)_{\text{NiSn}_4} // (100)_{\beta\text{Sn}}$ in both cases but the NiSn_4 growth direction is different: $[001]$ in Figure 7(a), and $[100]$ in Figure 7(ii). From previous work [18, 19], the interface plane $(010)_{\text{NiSn}_4} // (100)_{\text{Sn}}$ has been shown to involve the closest packed planes in both the NiSn_4 and βSn and the lowest lattice mismatch ($\sim 5\%$) between the two crystals. Note that the space group used to describe NiSn_4 is different in this work (Table 2) compared with refs. [18, 19] which leads to different miller indices but the OR is the same. The two different NiSn_4 growth directions are likely because, while this crystal is orthorhombic, it has $a=6.418 \text{ \AA}$ and $c=6.384 \text{ \AA}$ and is pseudo-tetragonal. Thus, the directions $[001]$ and $[100]$ NiSn_4 are very crystallographically similar and either can be the growth direction.

A typical βSn - NiSn_4 eutectic growth front is shown in Figure 8(a) for Sn-0.14Ni growing at $V = 1 \text{ }\mu\text{m/s}$. The horizontal curved dark line is the βSn -L interface which crosses the whole sample, and the growth direction is upwards. In the region highlighted by a black rectangle, there is a faceted triangular tip of NiSn_4 growing ahead of the βSn -L interface. Figure 8(b) is a zoomed-in image showing the shape of the βSn -L and NiSn_4 -L interfaces. The NiSn_4 tip is $\sim 30\mu\text{m}$ ahead of the βSn -L interface which corresponds

to $\sim 0.24\text{K}$ hotter using the macroscopic thermal gradient at the interface. Post mortem EBSD analysis of a similar region is shown as a phase map in Figure 8(d) and Figure 8(e) gives the unit cell orientation which shows that the growth direction is $[001] \text{ NiSn}_4$. Combining these results, a schematic of the metastable eutectic growth front is drawn in Figure 8(c). Note that Figure 8(a)-(c) are through-thickness integrated images, that the sample contains only one NiSn_4 lamella in the thickness, that the NiSn_4 lamellae are significantly thinner than the sample thickness, and that the volume fraction of NiSn_4 lamellae is only $\sim 1\%$.

The same growth crystallography formed in laboratory unidirectional solidification experiments as shown in Figure 8(f) and (g). However, the laboratory samples generally formed more regular arrays of NiSn_4 sheets such as that in Figure 3(b), compared with the NiSn_4 sheets in synchrotron experiments (e.g. Figure 8(a)). This may be due to the much thinner samples used for synchrotron imaging ($20\mu\text{m}$) which may have impeded the formation of simple regular arrays with OR1.

3.5 Transitions between stable and metastable eutectic growth

The transition from stable to metastable eutectic growth was commonly observed in laboratory unidirectional solidification experiments as shown in Figure 3(c) and Figure 9. In Figure 9(a) and (c) the transition can be seen clearly from the different morphology and shade of Ni_3Sn_4 and NiSn_4 . In Figure 9(b), the transition is from irregular branching Ni_3Sn_4 rods to irregular NiSn_4 plates. In Figure 9(d), the transition is from regular parallel Ni_3Sn_4 rods to irregular NiSn_4 sheets and there is a clear transition boundary between the stable and metastable eutectics. Note that the morphology of the stable eutectic was usually more regular at higher growth rate. The metastable eutectic usually had an irregular morphology just after the transition from the stable eutectic (e.g. Figures 3(c) and 9(b)-(d)) and the regular broken-lamellar morphology typically only developed at some growth distance after the transition (e.g. Figures 3(b), 4(d)-(f) and 7).

A summary of laboratory unidirectional solidification experiments is plotted in Figure 10 as a velocity-composition ($V\text{-}C_0$) microstructure map for the range $V = 0.5\text{-}500 \mu\text{m/s}$ and $C_0 = 0.04\text{-}0.26 \text{ wt\% Ni}$.

Note that most samples started with stable $\beta\text{Sn-Ni}_3\text{Sn}_4$ eutectic growth and the indicated microstructures are those that formed after a growth distance of ~ 10 mm when a quasi-steady state had developed. It can be seen that the Sn-Ni system has a eutectic coupled zone that is skewed to the side of the faceted phase, with βSn dendrites growing at hypereutectic compositions at 'high' growth rates as is common of nonfaceted-faceted systems [33] (e.g. Al-Si [34], $\beta\text{Sn-Ag}_3\text{Sn}$ [35] etc.). Figure 10 also shows that, when the growth velocity was higher than $1 \mu\text{m/s}$, the metastable eutectic always grew (with and without βSn dendrites). When the growth velocity was $1 \mu\text{m/s}$ or below, some samples grew as fully metastable $\beta\text{Sn-NiSn}_4$ eutectic and others as fully stable $\beta\text{Sn-Ni}_3\text{Sn}_4$ eutectic (i.e. the type of eutectic varied from sample to sample). Thus, no simple transition velocity between the two eutectics was found in this work, indicating that the transition is sensitive to the initial conditions when $V \leq 1 \mu\text{m/s}$ (e.g. orientations at the start of growth etc.) and, perhaps, the transition to 100% $\beta\text{Sn-Ni}_3\text{Sn}_4$ eutectic growth at steady state occurs at a velocity slower than $0.5 \mu\text{m/s}$ which was the slowest speed used here.

Figure 11 examines the transition from metastable to stable eutectic growth in a sequence of radiographs of Sn-0.14Ni that was growing with a fully metastable eutectic front at $10 \mu\text{m/s}$ and the pulling rate was then decreased to $1 \mu\text{m/s}$. In Figure 11, the $\beta\text{Sn-L}$ interface growth direction is upward and Figure 11(a) corresponds to a frame shortly after Ni_3Sn_4 nucleated and developed into four diverging rods. Both stable Ni_3Sn_4 rods and metastable NiSn_4 sheets are present in the same image and they are still in competitive growth for all images in Figure 11.

Figure 11(a) shows stable eutectic coupled growth where Ni_3Sn_4 rods lead ahead of the $\beta\text{Sn-L}$ interface. Diverging growth of its left branch grows toward the left and has stopped one metastable NiSn_4 sheet growing. On its right, the eutectic spacing is too wide, so Ni_3Sn_4 rods-2 developed to reduce the local spacing as shown in Figure 11(b-c). Two types of metastable eutectic morphologies are observed in Figure 11(a). Sheet-1 is a NiSn_4 sheet that intersects the sample surface and the sheet with triangular tip has its main (010) NiSn_4 facet parallel with the sample surface. NiSn_4 sheet-1 grows

towards the right with a highly inclined angle and grows over and stops the NiSn_4 flat sheet as shown in Figure 11(b).

As NiSn_4 sheet-1 grows, it advances ahead of the Ni_3Sn_4 rods in Figure 11(b) and stops all Ni_3Sn_4 rods growing in Figure 11(c). At the same time, NiSn_4 sheet-3 developed on the right of Ni_3Sn_4 rod-2. In the few seconds after 4078s, the sample grows with a fully metastable $\beta\text{Sn-NiSn}_4$ eutectic. However, the sample does not achieve a steady-state. Some new Ni_3Sn_4 rods grow into the left of the field of view in Figure 11(d) and grow towards to right and, after 4324s, proceed to stop all metastable eutectic growing.

To analyse the competition between the two eutectics in Figure 11, the images are quantified in Figure 12(a) and (b). Figure 12(a) shows the $\beta\text{Sn-L}$ interface position (isotherm position) as the black solid line where the interface is hotter when the interface position is higher. It is clear that the interface moved to a colder temperature when the interface velocity increased and *vice versa*. This directly reflects the interplay between interface velocity, interphase spacing, and growth undercooling that is the basis of the Jackson-Hunt theory [36] and its extension to nf-f systems [30, 32]. The average eutectic projected spacings of the two eutectics during pulling at $1\mu\text{m/s}$ are plotted against time in Figure 12(a). Three periods of growth at $1\mu\text{m/s}$ are indicated in Figure 12(a) and Table 4: period 1 is from 30s to 1465s, period 2 is from 1868s to 4405s and period is from 4405s to 5714s. The solid blue lines with arrows show the range of stable $\text{Sn-Ni}_3\text{Sn}_4$ eutectic growth and the dashed blue lines with arrows show the range of metastable $\text{Sn-Ni}_3\text{Sn}_4$ eutectic growth.

In Figure 12(a), it can be seen that 100% metastable eutectic is growing at the end of period 1, and 100% stable eutectic is growing at the end of period 3. All three periods are at $V = 1\mu\text{m/s}$, period 1 is after growth was increased from $0\mu\text{m/s}$, and periods 2 and 3 are after the velocity was decreased from $V = 10\mu\text{m/s}$. In Figure 12(a), it can be seen that the average eutectic spacing of the two eutectics in periods 2 and 3 are smaller than the average eutectic spacings in period 1, although there is significant scatter in the local spacing data. The local spacings can be understood from the plot of

local spacing versus the depth of the depressed βSn -L interface (ΔZ) between the two adjacent eutectic rods or plates in Figure 12(b), which was measured directly from radiographs. The maximum solute undercooling is shown by the 'error bar' that was calculated by multiplying the thermal gradient and the depth of the depressed βSn -L interface. Blue open triangles are the stable eutectic data points and red squares are metastable eutectic data points. Both eutectics show a trend of increasing local solute undercooling with increasing local spacing at $V = 1 \mu\text{m/s}$, as expected by eutectic growth theory because the lateral diffusion length is longer for wider spacings. The broad range of spacings in Figure 12(b) is an indication of the difficulty the eutectics had in adjusting (decreasing) their spacing during growth which results in growth relatively far from the extremum point. Caution is required when interpreting the βSn - NiSn_4 data points, however, because with the low contrast between the thin NiSn_4 sheets and Sn, it is likely that some NiSn_4 plates are not visible so Figure 12(b) only gives a general trend in the case of βSn - NiSn_4 .

It can also be seen in Figure 12(b) that many points overlap, showing that the growth temperature of the two eutectics is similar at $V = 1 \mu\text{m/s}$. This is consistent with $1 \mu\text{m/s}$ being close to the transition velocity between the two eutectics and is one reason why the two eutectics can grow together for a long distance at $1 \mu\text{m/s}$. Different behaviour was measured in laboratory samples which generally exhibited sudden transitions from stable to metastable eutectic growth as shown in Figure 3(c) and 9 whereas synchrotron samples often had both eutectics growing together. This may be due to the thin samples used for synchrotron imaging ($20\mu\text{m}$) which may have impeded the formation of metastable βSn - NiSn_4 with simple regular arrays with OR1, and helped the stable βSn - Ni_3Sn_4 to compete over a longer distance.

3.6 Comparison with other metastable eutectics

Typically, the competition between stable and metastable eutectic growth in directional solidification is explained with a competitive growth criterion of "whichever eutectic can grow at highest temperature is selected (i.e. wins)" [33, 37, 38]. Such an analysis requires data or functions for the

growth temperature versus velocity for both eutectics. It can be seen in Figure 12(a) that when the growth velocity increases from $V = 1 \mu\text{m/s}$ to $V = 10 \mu\text{m/s}$ and from $V = 1 \mu\text{m/s}$ to $V = 5 \mu\text{m/s}$, the interface position moves downward to higher undercooling (lower growth temperature). However, there are only a small number of rods/sheets across the field of view and the growth distance is not long enough to develop a quasi-steady state and, therefore, these synchrotron experiments are not suitable for measuring the mean undercooling versus velocity. Therefore, the metastable eutectic growth temperature versus velocity data was measured in laboratory Bridgman growth experiments using a thermocouple embedded in the centre of the sample similar to [39-41]. In Figure 12(c), the open squares are measurements of metastable eutectic growth temperature versus the square root of pulling rate, and the dashed black line is the trend line of metastable eutectic growth. The data are in reasonable agreement with Eq. 1. [36] although there is significant scatter:

$$T_G = T_E - K_E \sqrt{V} \quad (1)$$

Where T_E is the (metastable) eutectic temperature, T_G is the eutectic growth temperature, V is the growth velocity, K_E is a eutectic growth constant, and the growth undercooling is $\Delta T = T_E - T_G$. For regular nf-nf eutectics, K_E is related to material properties including the liquidus slope, volume fraction of phases, diffusion coefficient, Gibbs-Thompson coefficient and interface shape (angles between S-L interfaces and the growth direction) [36]. For irregular nf-f eutectics such as grey cast iron, a similar expression has been shown to be valid which is consistent with the measurements in Figure 12(c) where the metastable constant is $K_E^m = 0.26 \text{ K s}^{0.5} \mu\text{m}^{-0.5}$.

For a metastable eutectic to be able to grow at higher temperature than a stable eutectic, the T_G versus $\sqrt{V}$ curves of the stable and metastable eutectics must cross, i.e. $K_E^m < K_E^s$. This is shown on Figure 12(c) where the stable eutectic line is shown schematically because it could not be measured. It can be seen that a critical transition velocity of $1 \mu\text{m/s}$ would require a stable eutectic constant of $K_E^s = 0.4$.

The main reason for $K_E^m < K_E^s$ in the Sn-Ni system seems to be the difference in regularity of the eutectics. The metastable $\beta\text{Sn-NiSn}_4$ eutectic grows with a reproducible OR, often in a relatively regular broken-lamellar array (e.g. Figure 3(b)). In contrast, the stable $\beta\text{Sn-Ni}_3\text{Sn}_4$ eutectic cannot achieve a regular rod array because monoclinic Ni_3Sn_4 nucleates with random orientations in the liquid ahead of the $\beta\text{Sn-L}$ interface, grows only along [010] and has significant branching difficulties.

Figure 12(c) also shows that an important factor in the metastable eutectic being selected at such low growth velocity in the Sn-Ni system is the very small difference between the stable and metastable eutectic temperatures. The difference between the stable $\beta\text{Sn-Ni}_3\text{Sn}_4$ and metastable $\beta\text{Sn-NiSn}_4$ eutectic temperatures is 0.11 K which is much smaller than 2.8K between $\alpha\text{Al-Al}_3\text{Fe}$ and $\alpha\text{Al-Al}_6\text{Fe}$ [42], and 7.4K between $\gamma\text{Fe-graphite}$ and $\gamma\text{Fe-Fe}_3\text{C}$ [1] and other reported metastable eutectics have even larger eutectic temperature differences (Table 5). Thus, in the Sn-Ni system, the difference between the eutectic constant slopes K_E^m and K_E^s does not need to be very large for the metastable eutectic to outcompete the stable eutectic.

4 Conclusions

The competition between stable $\beta\text{Sn-Ni}_3\text{Sn}_4$ and metastable $\beta\text{Sn-NiSn}_4$ eutectic growth has been studied by unidirectional solidification of Sn-xNi ($x = 0.04 - 0.26 \text{ wt\%Ni}$) at growth rates in the range $0.5 - 500 \mu\text{m/s}$ to build the understanding of why metastable $\beta\text{Sn-NiSn}_4$ eutectic forms in some electronic solder joints. The following conclusions can be drawn.

The stable and metastable eutectic temperatures have a temperature difference of only 0.11 ± 0.06 °C. The eutectic compositions for the stable and metastable eutectics are $0.095 \pm 0.005 \text{ wt\% Ni}$ and $0.11 \pm 0.005 \text{ wt\% Ni}$.

The stable $\beta\text{Sn-Ni}_3\text{Sn}_4$ eutectic grew during the early transient stages of unidirectional growth for all compositions studied and, occasionally, at quasi-steady state when $V \leq 1 \mu\text{m/s}$. It has a nonfaceted-faceted irregular-rod morphology, where the monoclinic Ni_3Sn_4 grew only along $[010]$ and branching required a new crystallographic orientation to nucleate on an existing rod. The spacing adjustment mechanisms were identified to be nucleation of Ni_3Sn_4 in the liquid ahead of the $\beta\text{Sn-L}$ front and branching of existing rods to decrease the spacing, and rod termination to increase the spacing. Since most Ni_3Sn_4 rods nucleated in the liquid with a wide range of orientations, $[010]$ growth was at a wide range of angles relative to the macroscopic growth direction which created a highly irregular eutectic. No preferred orientation relationship (OR) was measured between Ni_3Sn_4 and βSn because most Ni_3Sn_4 nucleated in the liquid ahead of the $\beta\text{Sn-L}$ front and did not change orientation during growth.

The metastable $\beta\text{Sn-NiSn}_4$ eutectic had either a broken-lamellar or irregular-plate morphology. In $20 \mu\text{m}$ thin sample growth, they have two growth configurations: either NiSn_4 sheets intersect to the sample surface or they have their main (010) NiSn_4 facet parallel with the sample surface. NiSn_4 sheets grew with faceted tips ahead of the $\beta\text{Sn-L}$ interface and with a reproducible OR of $(010) \text{ NiSn}_4 // (100) \text{ Sn}$ and $[001] \text{ NiSn}_4 // [001] \text{ Sn}$. This OR reflects a relatively good lattice match between βSn and NiSn_4 .

The transition velocity between the two eutectics was less than $1\mu\text{m/s}$. Using the competitive growth condition that the eutectic that can grow at higher temperature is selected, the low transition velocity is concluded to be partly due to the very small temperature difference between the stable and metastable eutectic points, and partly due to the growth difficulties of monoclinic Ni_3Sn_4 in the stable eutectic. In laboratory experiments, the transition was relatively sudden with a total change from stable to metastable eutectic growth over a few μm . In synchrotron experiments, there was typically a much longer growth distance over which the two eutectics coexisted. This seems to be related to the thinner samples used for synchrotron experiments ($20\mu\text{m}$) that interfered with the development of regular arrays of NiSn_4 sheets.

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Tables

Table 1 Compositions of the prepared alloys in wt%, as determined by ICP-AES.

Sample Name	Analysis 1 wt%Ni	Analysis 2 wt%Ni	Analysis 3 Wt%Ni
HP Sn-0.04 Ni	0.041	NA	NA
HP Sn-0.09 Ni	0.082	0.095	0.102
HP Sn-0.10 Ni	0.102	0.105	NA
HP Sn-0.14 Ni	0.146	0.127	0.142
HP Sn-0.19 Ni	0.185	0.210	0.184
HP Sn-0.26 Ni	0.239	0.280	0.247

Table 2. Summary of intermetallic compounds. EDX measurements are mean $\pm$ standard deviation. SG = space group [27, 28].

Phase	Appearance in OM	EDX [at % Ni]	EBSD			
			Pearson	SG	Prototype	Ref
NiSn ₄	Light grey	18.5 $\pm$ 0.7	oS20	Ccca	PtSn ₄	[27]
Ni ₃ Sn ₄	Dark grey	41.0 $\pm$ 0.7	mS14	C12/m1	Ni ₃ Sn ₄	[28]

Table 3 Experimental results of the two eutectic points.

	Temperature T_E (°C)	Composition C_E (wt%Ni)
Stable Eutectic	231.10 $\pm$ 0.03	0.095 $\pm$ 0.005
Metastable Eutectic	230.99 $\pm$ 0.05	0.110 $\pm$ 0.005
Difference	0.11 $\pm$ 0.06	0.015 $\pm$ 0.007

Table 4 Results of average eutectic spacing and average depressed depth for stable and metastable eutectics.

Period	Time (s)	Velocity ($\mu\text{m/s}$)	Average λ (μm)		Average ΔZ (μm)	
			Ni ₃ Sn ₄	NiSn ₄	Ni ₃ Sn ₄	NiSn ₄
1	30 – 1465	1	204	200.42	16.01	15.11
2	1868 – 4405	1	80.12	169.38	8.9	10.68
3	4405 – 5714	1	134.76	>> 500	10.08	NA

Table 5 Stable and metastable eutectic temperatures and compositions for different systems.

System	C_E^{stable}	$C_E^{\text{metastable}}$	T_E^{stable}	$T_E^{\text{metastable}}$	ΔT	REFs
Al-Fe	1.85 wt%Fe	3.4 wt%Fe	653.87	651.05	2.82	[42]
Fe-C	-	-	1154.5	1147.1	7.4	[1, 43]
Fe-C	4.27 wt%C	4.32 wt%C	1154.8	1147.3	7.5	[44]
Fe-C	4.26 wt%C	4.3 wt%C	1158	1147	11	[45]
Al-Ge	30.3 at%Ge	32 at%Ge	424	420	4	[45]
Ni-B	3.3 wt%B	-	1093	988	105	[46]
Ni-B	18.1 at%B	19.6 at%B	1087	1003	85	[47]
Fe-B	16.6 at%B	18.4 at%B	1177	1114	63	[47]
Al ₂ O ₃ -Y ₂ O ₃	18.4 mol%Y ₂ O ₃	23.1 mol%Y ₂ O ₃	1826	1702	124	[4]

Figures

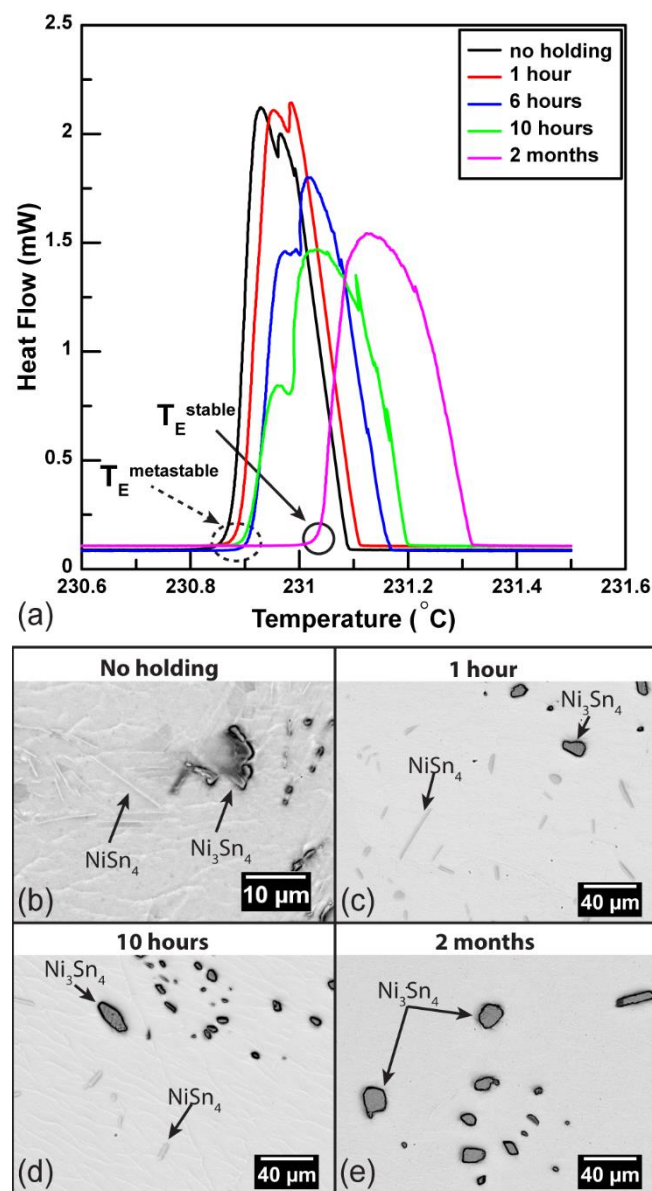


Figure 1 (a) DSC heating curves for Sn-0.19Ni after isothermal holding at 230 °C for the stated time and then heating at 0.00033K/s. (b)-(e) Microstructures after isothermal holding of 0hr, 1hr, 10hr and 2 months.

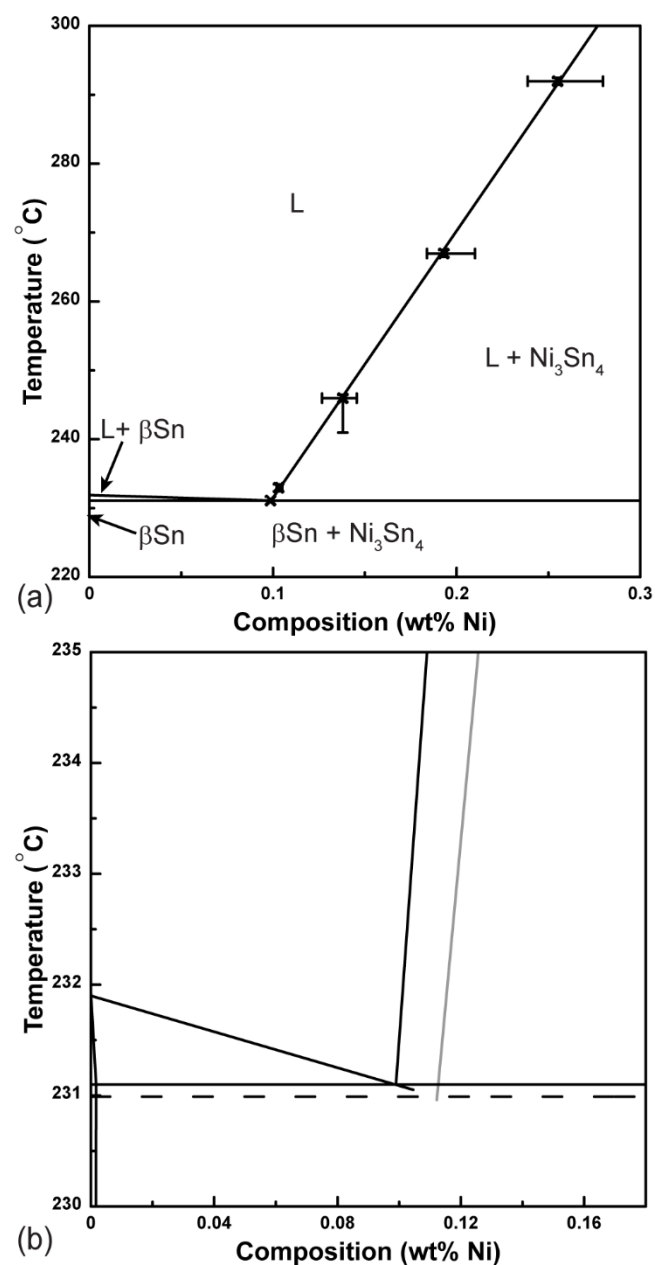


Figure 2 (a) Liquidus temperatures for Sn-xNi hypereutectic alloys where $x = 0.1, 0.11, 0.14, 0.19$ and 0.26 wt%Ni. The minimum and maximum values are indicated as the error bars for temperature and composition. (b) Experimental Sn-rich corner Sn-Ni phase diagram. The solid line is the stable phase diagram and dashed line is the metastable phase diagram. The grey line is estimated.

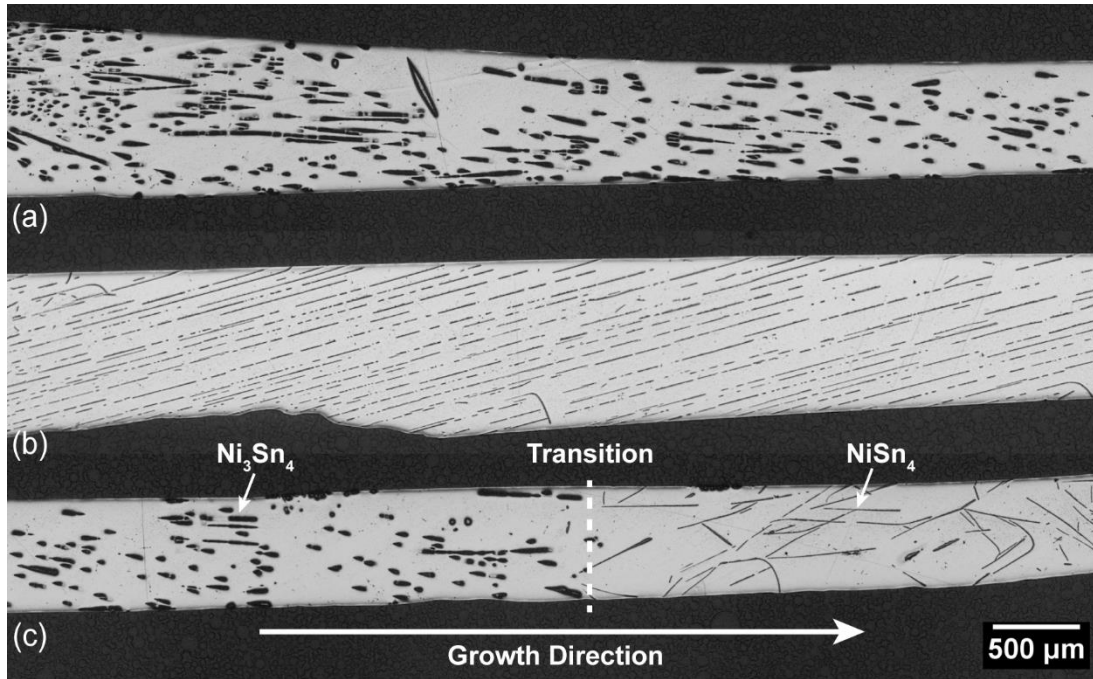


Figure 3 Typical region of (a) stable $\beta\text{Sn}+\text{Ni}_3\text{Sn}_4$ eutectic; (b) metastable $\beta\text{Sn}+\text{NiSn}_4$ eutectic; and (c) the transition between stable and metastable eutectic growth. All regions were grown at $V=1 \mu\text{m/s}$ and $G_L = 12 \text{ K/mm}$ in $\text{Sn}-0.14\text{Ni}$.

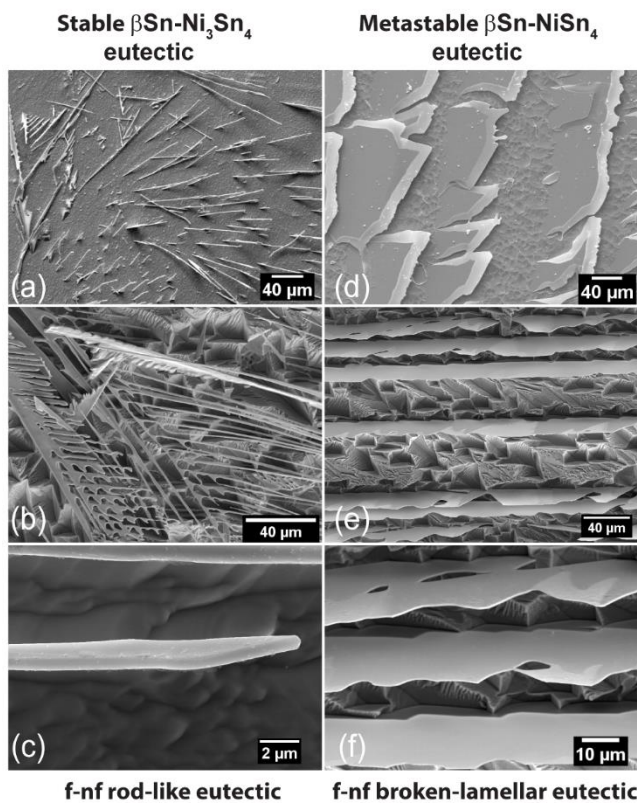


Figure 4 Typical morphologies of stable (a-c) and metastable (d-f) eutectics after Bridgman growth at $G_L=12 \text{ K/mm}$. (a) branched rods of $\text{Sn}-0.04\text{Ni}$ at $V=1 \mu\text{m/s}$; (b) branched parallel rods of $\text{Sn}-0.04\text{Ni}$ at $V=2 \mu\text{m/s}$; (c) rod-like tip of $\text{Sn}-0.14\text{Ni}$ at $V=1 \mu\text{m/s}$; (d) broken lamellar sheets with sharp growth tip of $\text{Sn}-0.14\text{Ni}$ at $V=1 \mu\text{m/s}$; (e) regular parallel sheets of $\text{Sn}-0.04\text{Ni}$ at $V=2 \mu\text{m/s}$; (f) thin sheets of $\text{Sn}-0.04\text{Ni}$ at $V=2 \mu\text{m/s}$. The growth direction for all images is from left to right.

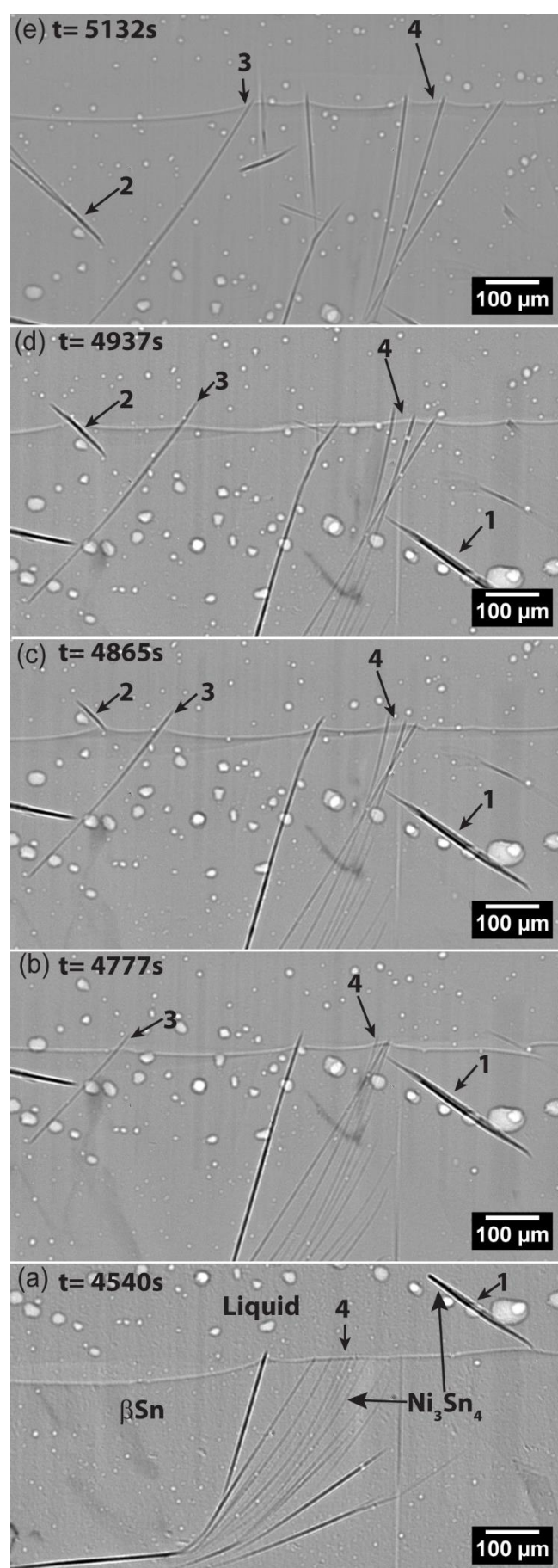


Figure 5 A sequence of in-situ radiographs showing stable eutectic growth dynamics under unidirectional solidification of Sn-0.14Ni at $G_L = 6.5$ K/mm and $V=1$ $\mu\text{m/s}$.

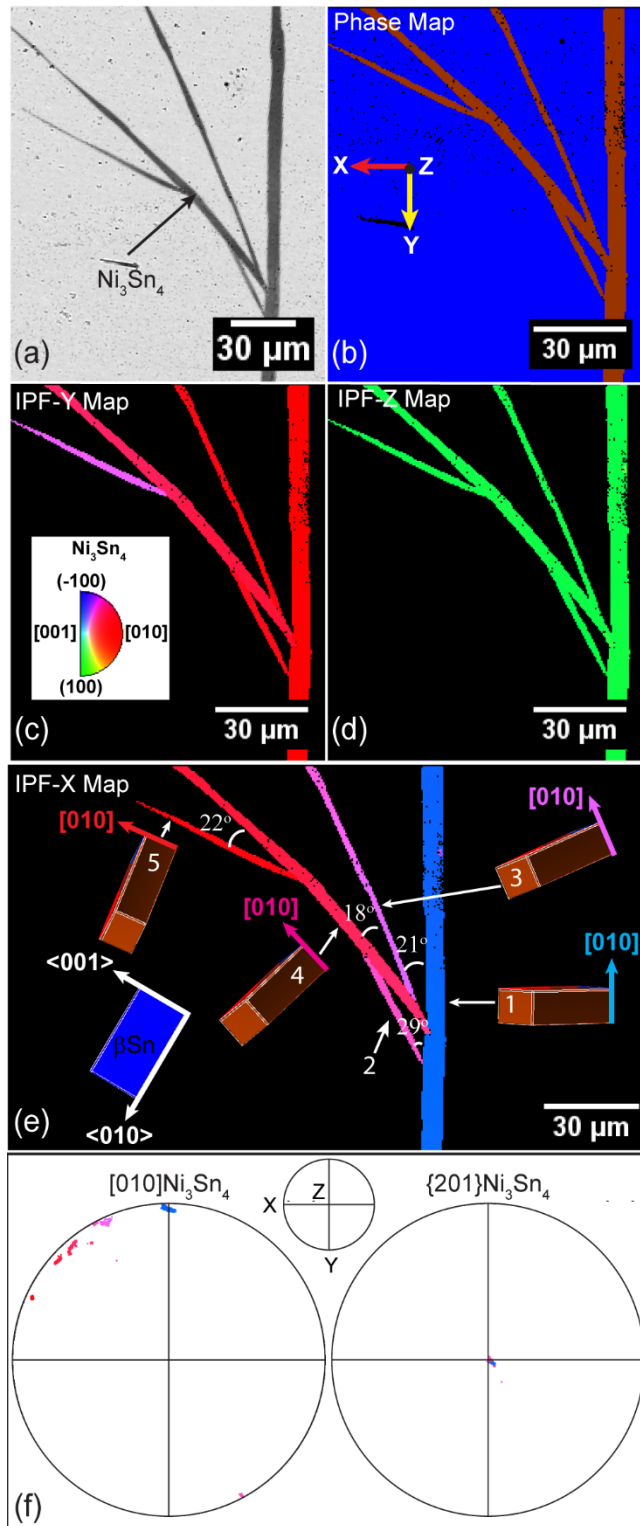


Figure 6 EBSD analysis for branched βSn - Ni_3Sn_4 eutectic grown at $V = 1$ $\mu\text{m/s}$, $G_L = 6.5$ K/mm, $C_0 = 0.09$ wt% Ni. (a) BSE image; (b) Phase map; (c) IPFY map; (d) IPFZ map; (e) IPFX map and unit crystal orientations; (f) pole figures showing the growth direction and the common plane.

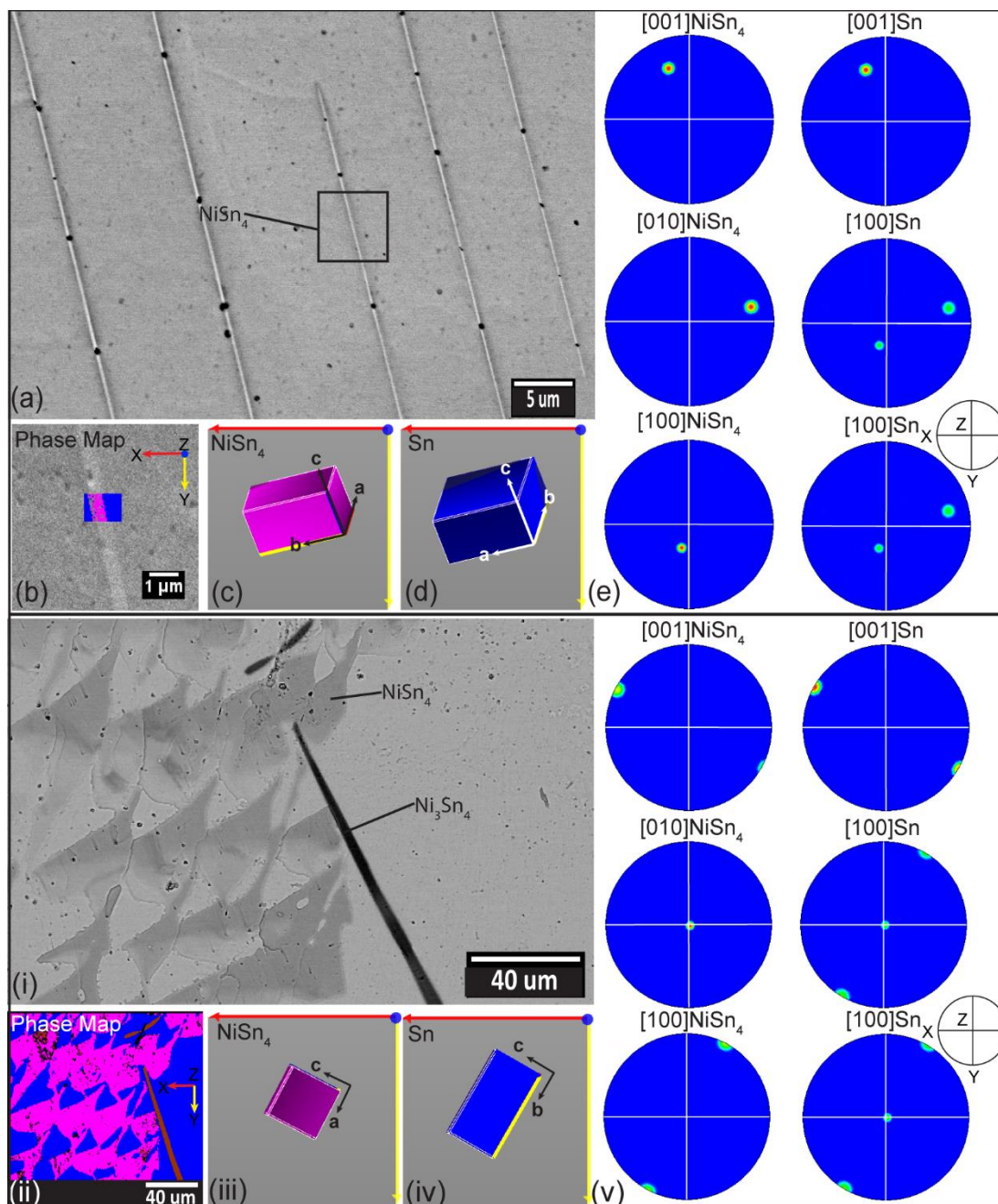


Figure 7 $\beta\text{Sn-NiSn}_4$ eutectic growth crystallography: (a)–(e) NiSn_4 sheets intersecting the sample surface at $V=1 \mu\text{m/s}$, $G_L=6.5 \text{ K/mm}$, $C_0=0.14 \text{ wt\% Ni}$. (i)–(v) $(010)\text{NiSn}_4$ is in the plane of the thin sample at $V=3 \mu\text{m/s}$, $G_L=6.5 \text{ K/mm}$, $C_0=0.09 \text{ wt\% Ni}$.

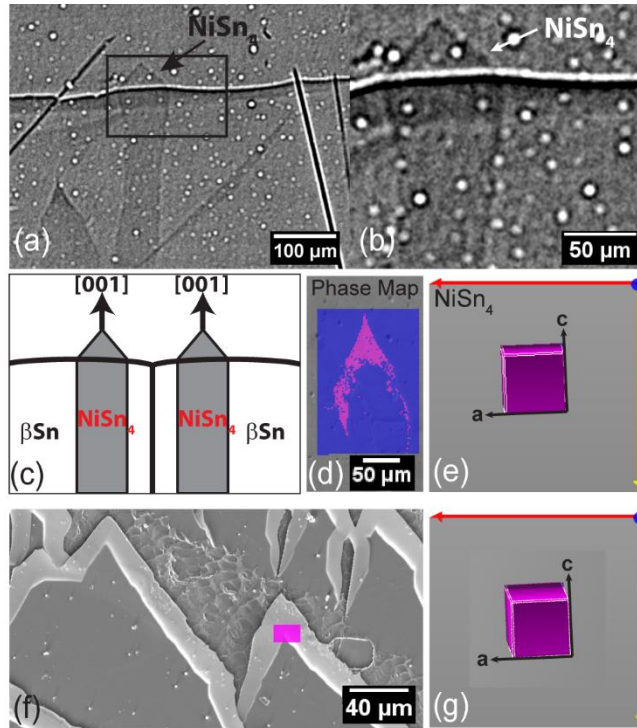


Figure 8 (a)-(b) Growth S-L interface of βSn - NiSn_4 eutectic at $V=1 \mu\text{m/s}$, $G_L=6.5 \text{ K/mm}$, $C_0=0.14 \text{ wt\% Ni}$. (c) schematic diagram of growth front. (d)-(e) EBSD analysis of the sample in (a)-(b). (f)-(g) similar growth form in laboratory UDS at $V=1 \mu\text{m/s}$, $G_L=12 \text{ K/mm}$, $C_0=0.14 \text{ wt\% Ni}$.

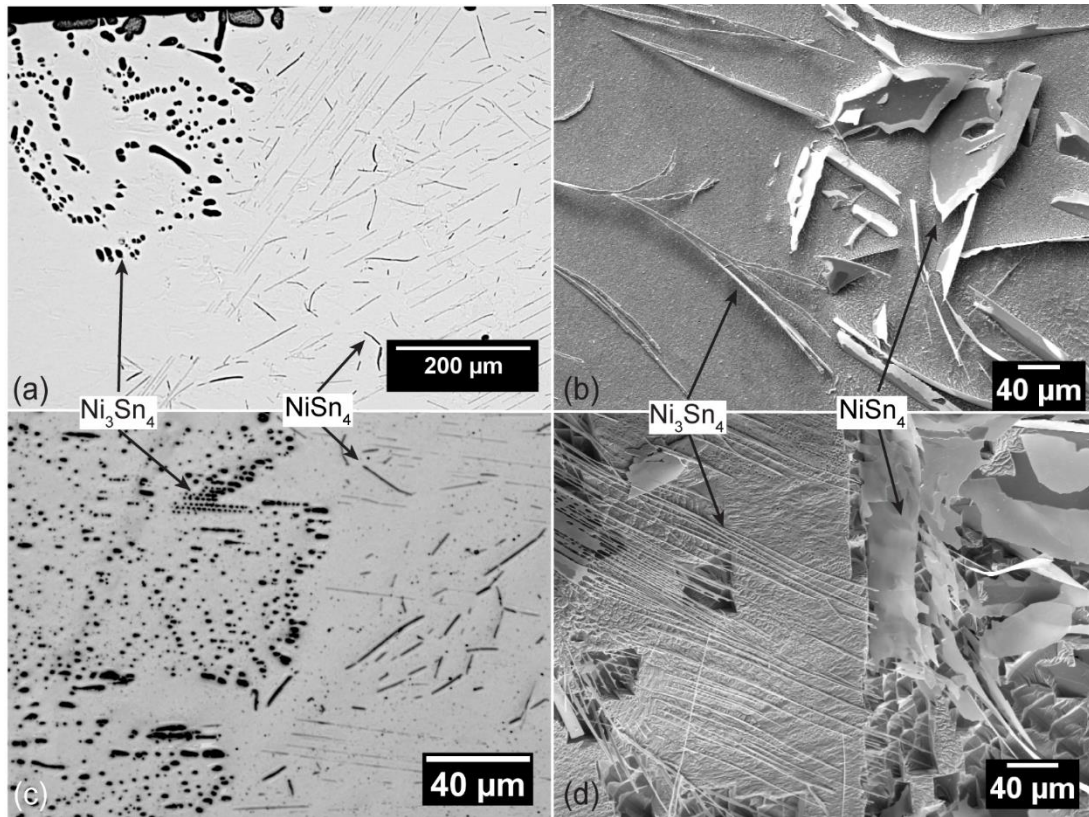


Figure 9 Typical region of transition from stable to metastable eutectics at $G_L=12 \text{ K/mm}$. (a) Sn-0.14Ni at $V=5 \mu\text{m/s}$; (b) Sn-0.04Ni at $V=1 \mu\text{m/s}$; (c) Sn-0.26Ni at $V=20 \mu\text{m/s}$; (d) Sn-0.04Ni at $V=2 \mu\text{m/s}$. (a) and (c) are optical images. (b) and (d) are SEM images and βSn has been dissolved. Growth direction from left to right.

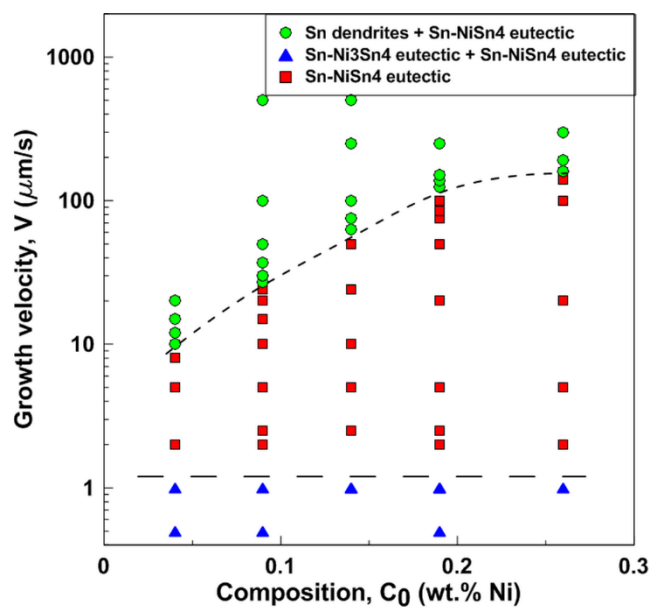


Figure 10 Growth velocity vs. composition microstructure map at $G_L = 12 \text{ K/mm}$.

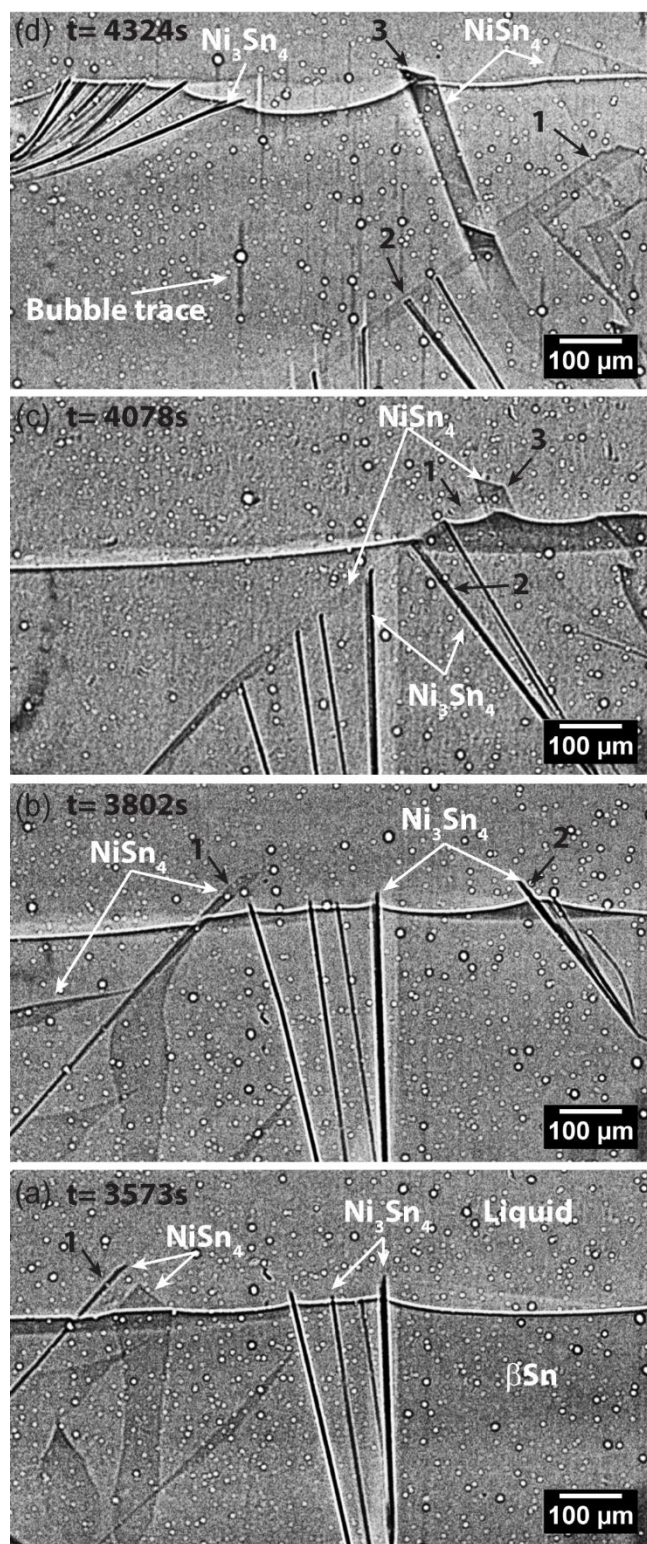


Figure 11 A sequence of in-situ radiographs showing the growth dynamics of the transition between stable and metastable eutectics at $C_0 = 0.14 \text{ wt\%Ni}$, $G_L = 6.5 \text{ K/mm}$ and $V = 1 \text{ } \mu\text{m/s}$.

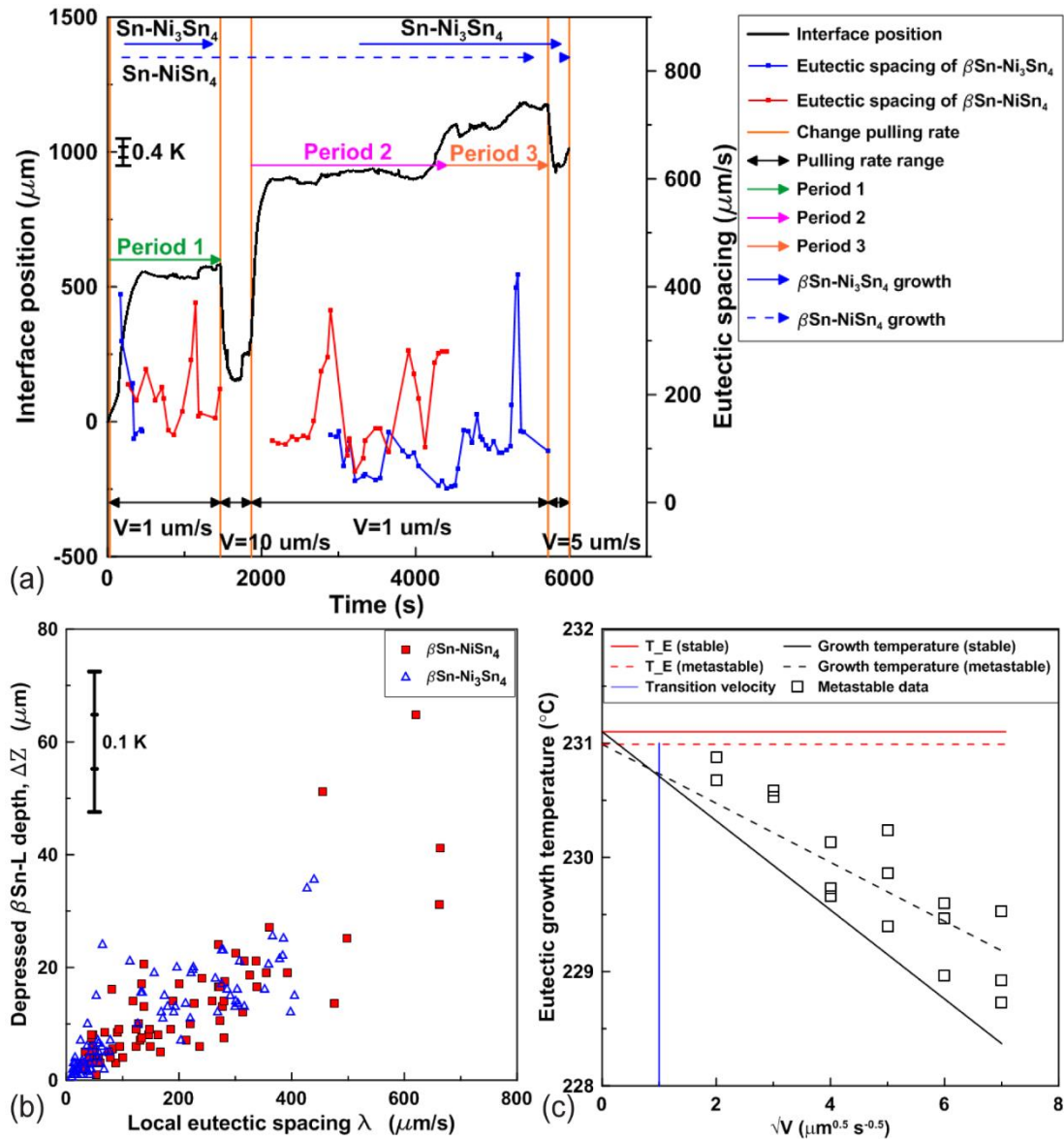


Figure 12 Measurement of interface growth details from the dataset in Fig. 11. (a) Interface position, eutectic spacing of $\text{Sn-Ni}_3\text{Sn}_4$ vs. time and eutectic spacing of Sn-NiSn_4 vs. time; (b) Measured ΔZ vs. eutectic spacing of two eutectics; (c) Eutectic growth temperatures vs. $\sqrt{V}$ map where all data were measured from laboratory UDS samples.

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