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Microstructure control of the Sn-Ag-Cu-X solder alloy system through nucleation catalysis of Sn

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Microstructure control of the Sn-Ag-Cu-X solder alloy system through nucleation catalysis of Sn

by

Jason Kenneth Walleser

A thesis submitted to the graduate faculty in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE

Major: Materials Science and Engineering

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## TABLE OF CONTENTS

LIST OF FIGURES .................................................................................................................... v

LIST OF TABLES ................................................................................................................... xiii

ABSTRACT ............................................................................................................................. xiv

CHAPTER 1: INTRODUCTION ........................................................................................... 1
  History ................................................................................................................................... 1
  Motivation ............................................................................................................................. 3
  Objectives .............................................................................................................................. 3

CHAPTER 2: LITERATURE REVIEW ................................................................................... 5
  Electronic Packaging and Assembly .................................................................................... 5
    Packaging Hierarchy .......................................................................................................... 5
    Package reliability ............................................................................................................. 8
  Ag₃Sn Blades .......................................................................................................................... 9
  Joint Mechanics .................................................................................................................. 12
    Substrate/solder interfacial stress .................................................................................... 12
    A simple model for interfacial stress .............................................................................. 13
    Interfacial and Edge stresses ......................................................................................... 17
  Fracture Mechanics .......................................................................................................... 19
    Conclusions ..................................................................................................................... 22

Thermodynamics ................................................................................................................. 22
  Sn-Cu and Sn-Ag binary phase diagrams ........................................................................ 23
  The Sn-Ag-Cu phase diagram .......................................................................................... 25

Crystal Properties ............................................................................................................... 27
  β-Sn ................................................................................................................................. 28
  η-Cu₆Sn₅ ............................................................................................................................ 29
  γ-Ag₃Sn .............................................................................................................................. 32
  Sn/Sn grain boundary stress ............................................................................................ 34
LIST OF FIGURES

Figure 1. Sn-Pb eutectic alloy solidified with a lamellar eutectic microstructure [2].

Figure 2. Copper water vessel (left) circa 1500-1300 B.C. is assembled with rolled and riveted copper sheet, then sealed with Sn-Pb solder [3]. Today thousands of solder joints populate electronic devices (right) from supercomputers to cell phones.

Figure 3. Assembly levels in electronic devices; the device shown here represents a mainframe server [4, 8].

Figure 4. Reflow assembly. A circuit board populated with (a) components passes through (b) a reflow oven with a controlled temperature profile. The flux is activated, reducing the oxides. The solder melts and wets the substrate pads and component leads, and finally solidifies. An assembled device, (c), a USB memory key shown here, is the resulting product.

Figure 5. Failure at an Ag₃Sn blade under tension [12] (a) an overview, and (b) magnified view. Region A shows ductile failure of the solder bulk near the interface while Region B failed by transgranular and intergranular fracture through the Cu₆Sn₅ interface.

Figure 6. Failure at an Ag₃Sn blade under shear loading (a) near the interface layer and (b) within the solder bulk [12].

Figure 7. BGA board impact fracture of a SAC3870 sample. a) A macroscopic cross polarized optical view of a failed joint. b) Crack initiation at the corner followed by failure along an Ag₃Sn/Sn interface [13].

Figure 8. Vibrational failure along an Ag₃Sn/Sn interface [14].

Figure 9. Fracture along an Ag₃Sn blade by thermomechanical fatigue [15]

Figure 10. Thin film approximation [17]

Figure 11. Residual average stress relative to the misfit stress [18]

Figure 12. Residual shear and peel stresses near edge [18]

Figure 13. Thermomechanical fatigue crack propagated by interface stress [19]

Figure 14. Edge shear stress depends on substrate stiffness [17].
Figure 15. Plastic yielding near interface edge [18]; y-axis: stress, x-axis: relative distance from edge towards the center of a joint.

Figure 16. Delamination emerging from the film edge: (a) interior edge, and (b) edge at a corner. Delamination converging on an edge: (c) interior edge, and (d) edge at a corner. [22]

Figure 17. Crack emerging at interior; $\alpha$ (alpha) is a function of the difference in elastic modulus between the film and substrate. For Cu/Sn, $\alpha = -0.5$. [22]

Figure 18. Relative crack energy release rate for a crack emerging at a corner. Dots are finite element results [22].

Figure 19. The full Sn-Cu phase diagram shows a eutectic reaction on the tin rich side as well as 3 room temperature phases that may all appear in a solder joint, including the IMC layer(s) [2].

Figure 20. The tin rich section of the Sn-Cu phase diagram is of the greatest interest for calculation of the ternary section. This diagram used by Moon et al [25] combines the calculated Sn-Cu phase diagram by Shim with compiled experimental data.

Figure 21. The Ag-Sn phase diagram [2]

Figure 22. Calculated liquidus surface; note that the calculated ternary eutectic composition of 3.66 wt. % Ag, 0.91 wt. % Cu differs from the experimentally determined value of 3.5 wt. % Ag, 0.9 wt. % Cu [25].

Figure 23. Compliance tensor for $\beta$-Sn

Figure 24. Tin’s crystal structure is a body centered tetragonal derivative, space group I$4_1$/amd. Consequently, its mechanical properties are anisotropic. [30]

Figure 25. A more detailed phase diagram near the Cu$_6$Sn$_5$ composition showing additional high temperature $\eta$ structures; compositions are in weight percent. The $\eta^8 \rightarrow \eta^6$ transition, upon cooling, occurs somewhere within the gray region as detailed in the paragraph preceding this figure. [26, 31-33]

Figure 26. Ag$_3$Sn blades often occur in SAC solders at the IMC layer interface. This image of a deeply etched sample shows just how long these particles may grow. [8]
Figure 27. Vibration induced failure along an Ag₃Sn blade from Song et al [14]. Alloy composition: Sn-3.3Ag-0.5Cu wt. % Cooling rate: 0.5°C/s

Figure 28. SAC solder joints frequently contain only a few Sn grains [38].

Figure 29. Undercooling and recalescence in pure Sn [25].

Figure 30. Nucleation energetics for several mechanisms: (b) homogeneous, (c) planar substrate heterogeneous, and (d) heterogeneous crack nucleation. (a) Nucleation occurs at $\Delta G^*(r^*)$. Figure adapted from [39].

Figure 31. Wetting angle energy balance

Figure 32. Disregistry between planes of cubic and tetragonal crystals [40]

Figure 33. Disregistry between planes of a cubic and hexagonal crystal [40]

Figure 34. Free energy of nucleation for incoherent and coherent nucleation [42]

Figure 35. Type 1 partially coupled unaligned growth occurs at low solidification rates. 2.4 μm/s is shown here. [35]

Figure 36. Type 2 partially coupled aligned growth occurs at faster cooling rates. 3.5 μm/s is shown here. [35]

Figure 37. Type 3 fully coupled growth occurs at faster yet growth velocities. 14 μm/s is shown here. [35]

Figure 38. Type 4 microstructure forms at higher rates yet, 32 μm/s (shown here) and above, primary Sn dendrites occur with interdendritic type 3 eutectic. [35]

Figure 39. Suppression of Cu₃Sn growth by addition of Co and Fe [46]

Figure 40. Darken-Gurry plot for 4th element selection based on atomic radius and electronegativity

Figure 41. Typical DSC program profile with equal 1.5°C/s heating and cooling rates with a 30s dwell.

Figure 42. Example of an open top calorimetric joint and a cross section of a full joint.

Figure 43. Joint schematic for Ag₃Sn blade measurement

Figure 44. Chemical effect on undercooling
Figure 45. SAC3595 at low undercooling and low magnification [IID: 1-94-3; SID: 1-83-2; \(\Delta T = 4.41^\circ C\)] 58

Figure 46. SAC3595 at a higher magnification [IID: 1-94-7; SID: 1-83-2; \(\Delta T = 4.41^\circ C\)] 58

Figure 47. SAC3595 with a higher undercooling [IID: 2-121-04; SID: 1-83-4; \(\Delta T = 8.53^\circ C\)] 59

Figure 48. SAC3595 with a higher undercooling; magnified interface and Ag₃Sn blade. [IID: 2-121-5; SID: 1-83-4; \(\Delta T = 8.53^\circ C\)] 59

Figure 49. Typical SAC.Co with a large Ag₃Sn blade [IID: 2-94-26; SID: 1-154-4; SAC.15Co; \(\Delta T = 12.2^\circ C\)] 60

Figure 50. SAC.Co joints have a “coral-like” interfacial Cu₆Sn₅ IMC layer. [IID: 2-95-7; SID: 1-154-5; SAC.15Co; \(\Delta T = 14.92^\circ C\)] 60

Figure 51. SEI of SAC.25Co showing dendrite structure as well as some floating Ag₃Sn blades. [IID: 031108-01; SID: 147-07; SAC.25Co; \(\Delta T = 14.51^\circ C\)] 61

Figure 52. (BEC) The IMC layer has a finer coral-like morphology opposed to a scalloped morphology. [IID: 031108-03; SID: 147-07; \(\Delta T = 14.51^\circ C\)] 61

Figure 53. SAC.Ni at a high undercooling [IID: 1-95-04; SID: 1-69-05; SAC.15Ni; -10°C/minute; \(\Delta T = 14.31^\circ C\)] 62

Figure 54. Ag₃Sn blades are relatively common in SAC.Ni alloys. [IID: 1-95-06; SID: 1-69-05; SAC.15Ni; -10°C/minute; \(\Delta T = 14.31^\circ C\)] 62

Figure 55. Compare to previous two figures; lower undercooling results in slightly coarser dendrite structure. [IID: 1-90-09; SID: 1-69-7; SAC.25Ni; -10°C/minute; \(\Delta T = 6.02^\circ C\)] 62

Figure 56. A closer view at coarse dendrites in SAC.Ni; [IID: 1-90-05; SID: 1-69-7; SAC.25Ni; -10°C/minute; \(\Delta T = 6.02^\circ C\)] 62

Figure 57. Coarse dendrites appear to originate from the IMC layer indicating that the IMC may have catalyzed this tin dendrite. [IID: 2-123-09; SID: 1-155-05; SAC.15Fe; \(\Delta T = 5.56; f_{Eut} = 57.91\%; n_{Blades} = 0\)] 63
Figure 58. Dendrite structure is coarser at higher undercoolings. Here several distinct dendrite colonies exist with differently orientations. [IID: 2-123-01; SID: 69-09; ΔT = 16.13°C; SAC.10Fe; 5 blades]

Figure 59. SAC.25Zn with embedded (dark prismatic) η particles in β dendrites; [IID: 2-076-05; SID: 2-074-07; SAC.25Zn; ΔT = 4.32°C]

Figure 60. Secondary electron image of a SAC.05 sample; the arrow color overlay corresponds to the adjacent WDS line scan composition profile.

Figure 61. The concentration of Zn is elevated up to 600 ppm within the η phase (green). Note that the Zn composition axis is on the right. [SAC.05Zn]

Figure 62. With low Mn additions, the undercooling is extremely consistent but Ag₃Sn blades are still present. [IID: 1-123-03; SID: 1-96-06; SAC.05Mn; ΔT = 10.5°C; nBlades = 5]

Figure 63. Blades are eliminated at sufficient Mn concentrations ≥0.10 wt. %. Coarse eutectic and dendrite structure present in these samples. [IID: 1-104-02; SID: 1-98-02; ΔT = 10.44°C]

Figure 64. Embedded η particles in β; this sample was cooled at the faster 1.5°C/s (90°C/min) rate. [IID: 1-86-02; SID: 1-71-20; Cooling rate = 90°C/min; ΔT = 6.75°C]

Figure 65. WDS shows elevated Mn levels within pro-eutectic η particles as well as γ-Ag₃Sn eutectic platelets. Mn rich precipitates are circled

Figure 66. Small Mn rich particles, near the MnSn2 phase are found dispersed throughout Mn modified samples.

Figure 67. SEM image of SAC.25Al highlights tin dendrite structure and Al rich phase near at top of sample (arrow). IID: 2-131-02; SID: 2-107-06; SAC.25Al; ΔT = 6.56°C; fEut = 0.45; ΔT = 6.56°C

Figure 68. An optical image of SAC.25Al; note small dark dispersed phase, Cu₆Sn₅; nodular particles near top are Al rich. IID: 2-108-03; SID: 2-107-07; ΔT = 6.65°C
Figure 69. Nodular Al rich phase no longer present. Otherwise the structure is similar to, but
coarser than SAC.25Al. [IID: 2-131-08 SID: 2-124-04; SAC.05Al; rate = 10°C/min;
ΔT = 4.47°C]

Figure 70. A closer view of the bulk microstructure of SAC.05Al cooled at 90°C/min;
[IID:2-132-05; SID: 2-126-01; rate = 90°C/min; ΔT = 4.47°C]

Figure 71. Single reflow cycle, 330 seconds as a liquid; [IID: 1-094-13, SID: 1-083-02,
Alloy: SAC3595, ΔT = 4.5°C]

Figure 72. 10 reflow cycles, 2300 seconds as liquid; [IID: 2-053-05, SID: 2-027-03, Alloy:
SAC3595 ΔT = 15.9°C]

Figure 73. Increases in reflow dwell times (tliq = 4000 seconds shown) further coarsen the
microstructure providing a significantly more planar IMC layer. [IID: 2-063-04, SID: 2-
040-02, Alloy: SAC3595, ΔT = 16.5°C]

Figure 74. Compiled data from multiple cycling experiment, temperature reaches no higher
than 240°C for any datum. Sn data taken from Gagliano and Fine for dwell at 250°C.
[53]

Figure 75. Undercooling summary for multiple reflow cycles shows that undercooling
generally increases with the number of reflow cycles. Dashed lines due to ommitted
inconsistent points at cycles 5 and 7.

Figure 76. Compiled data for Undercooling as related to scallop spacing for SAC3595.

Figure 77. Overall blade distribution statistics for SAC.X system, all alloys. (a) blade
frequency, (b) length distribution, (c) orientation distribution relative to substrate, and
(d) interface attachment frequency.

Figure 78. An example of a bad blade: long, low angle, and protruding from interface
[P7100443 155-04 SAC.15Fe ΔT = 10.14]

Figure 79. Histogram distribution of Ag3Sn blades in SAC3595; the mean blade length is
near 40μm.

Figure 80. Distribution of Ag3Sn blades with respect to the Cu6Sn5 IMC layer
Figure 81. SAC.Co is characterized by a fine dendrite structure with evenly distributed $\eta$ particles. [IID: 031108-11 SID: 1-147-05; SAC.25Co, -10°C/min $\Delta T = 14.65°C$] 76

Figure 82. Same sample as previous figure but showing a small pro-eutectic $Ag_3Sn$ blade that might not be significantly degrade joint strength, given its small size and orientation. [IID:031108-15; SID: 1-147-05] 76

Figure 83. Blade density [number of blades/(0.001 in)$^2$] summary for SAC.X alloys cooled at 0.17°C/s (10°C/minute); Data points represent a unique sample. Points may overlap. Blue, zero concentration points represent the unmodified SAC3595 alloy. The blue line represents the mean of replicate samples. 77

Figure 84. Blade severity index for candidate alloys cooled at 10°C/minute 79

Figure 85. Refinement of Cu-Sn IMC powder as $\eta^'$ phase [31]. 80

Figure 86. Refinement of Cu-Sn IMC powder as high temperature $\eta^6$ phase [32]. 81

Figure 87. Refinement of Cu-Sn-Zn IMC powder has high temperature $\eta^6$ phase [32] 82

Figure 88. Refinement of the Cu-Sn-Zn IMC powder as the $\eta^8$ phase fits the data well with a goodness of fit of 5.03, but refinement as the $\eta^6$ phase fits better [32]. 82

Figure 89. Solderability comparison of select SAC.X alloys 83

Figure 90. The larger pro-eutectic $Cu_6Sn_5$ particles do not appear associated with any specific dendrites in SAC.Co samples. [IID: 031108-06; SID: 147-07; SAC.10Co; $\Delta T = 16.29°C$] 86

Figure 91. Interface comparison: coherent, semi-coherent, and incoherent 90

Figure 92. The external unit cells for each indicated phases are drawn to scale. The “atoms” shown are intended to indicate the Bravais lattice of each crystal structure and do not represent any specific element. From left to right, according to each phase’s space group designation, the Bravais lattices are body centered tetragonal, primitive monoclinic, and base centered orthorhombic. 91

Figure 93. (-3 3 0) "thick" plane cut shown normal to and edge on the (-3 3 0) plane. Infinitely thin planes intersect very few atoms. 92
Figure 94. A comparison of the mismatch between (-3 3 0) and (-1 0 1) planes in $\eta$ and $\beta$, respectively. Unfilled atoms are intersected by the cutting plane.

Figure 95. A bigger perspective on the (-3 3 0) and (-1 0 1) plane disregistry. X marks the origin of the registry. Tin overlapping tin is shown as dark blue, and Sn overlapping Cu is shown in red.
LIST OF TABLES

Table 1. Compliance tensor for \( \beta \)-Sn in GPa\(^{-1} \) 29
Table 2. Crystal structures similar to ice for heterogeneous nucleation catalysis 40
Table 3. XRD parameters 55
ABSTRACT

Sn-Pb eutectic solder was the alloy of choice since the dawn of the circuit board for creating interconnections between components in electronic devices. Under typical solder joint solidification conditions, eutectic Sn-37Pb (wt. %) solder freezes at a single temperature, usually under coupled growth conditions, thereby eliminating any “mushy zone,” providing a homogeneous microstructure, and avoiding micro-shrinkage voids. Unfortunately, lead is toxic, and as such, it has been banned in new electronic devices by various European Union (EU) regulations, notably RoHS. This is a primary driver for lead-free solder research. Additionally, increasing performance demands including rising device operating temperatures, increasing interconnection densities, and a greater demand (and consumer expectation) for reliability, also drive lead-free solder alloy research.

Based on performance and processing requirements—including maximum reflow temperature limits of circuit boards—and cost, Sn based alloys have emerged as the leading lead-free solder solution. Near eutectic Sn-Ag-Cu (SAC) alloys, with a eutectic temperature of 217°C, are the leading lead-free solder alloys for surface mount technology (SMT) applications. However, SAC alloys are not without problems. Unlike Sn-Pb, which contains only ductile terminal Pb and Sn rich phases, SAC solders contain relatively brittle intermetallic compound (IMC) phases in addition to the ductile β-Sn phase. As part of a eutectic-like structure, these IMC phase particles are small and act as dispersion strengthening agents. However, primary growth of these particles from the liquid, particularly the Ag₃Sn phase, may result in large faceted particles with a blade-like morphology that act as easy crack paths. Another potential problem is that SAC solder joints are often composed of only a few unique Sn grains. This combined with the anisotropic thermal expansion of Sn raises the potential for high stress at Sn/Sn boundaries under thermal strain, thus reducing thermomechanical fatigue performance.

The root of these problems and others lay in the complex solidification behavior of SAC solder joints caused by the difficulty in nucleating Sn from the liquid, which results in a high undercooling, which leads to non-equilibrium solidification. To address this problem in this study, a near eutectic (NE) SAC alloy has been modified with a number of low concentration fourth element additions
(referred to as X, as in SAC.X) in order to gain more microstructural control during solidification and in aging. The basic idea is that the addition of X may catalyze the early nucleation of Sn (at reduced undercooling), which may result in more eutectic growth and eliminate large IMC particle formation. There are several possible mechanisms possible to achieve this goal, but two were selected for this study. First, X may modify an existing primary (pro-eutectic) phase that, in turn, nucleates Sn and initiates eutectic growth. Second, X may form a new pro-eutectic phase that serves as a catalyst for Sn nucleation. In this study, X was chosen to utilize the first mechanism through the modification of pro-eutectic $\eta$-Cu$_6$Sn$_5$ where X substitutes for Cu. X candidate elements, those likeliest to substitute for Cu, were selected based on Darken-Gurry criteria for having atomic radius and electronegativity similar to Cu. The final selection was: Co, Ni, Fe, Mn, Zn, and Al.

A novel technique, referred to as the calorimetric joint, has been developed in this project to study the nucleation and solidification of these alloys that mimics as closely as possible the solidification conditions encountered in industrial electronic assembly processes. In essence, the calorimetric joint technique replaces the typical inert DSC pan with a reactive and wetting (pre-fluxed) Cu pan, thereby taking into account the formation and effect of IMC layer formation upon solidification. This technique enables the researcher to precisely control the cooling conditions and to thermally “watch” and measure solidification events, including the nucleation of Sn, as they occur in practice. The same model solder joint samples can then be cross-sectioned and their microstructures examined and correlated with the DSC scans.

It was discovered that some X additions increase the undercooling relative to the base SAC alloy while others decrease (Al and Zn) it. The variance in undercooling also changed depending on X. A high potency catalyst will result in a low average undercooling and minimal variance. Generally, it was found that as the atomic size of X increases relative to Cu, the catalytic potency increases.

Of the selected X elements, Zn and Al resulted in the least undercooling while Mn resulted in the least variance. With Al and Mn modification at sufficient concentration, a third X rich IMC phase formed. This was possibly the active catalyst for SAC.Mn. The Al rich IMC did not form when the concentration of Al was sufficiently low, Al<0.05wt. %, while the undercooling surprisingly decreased relative to SAC.15Al. Therefore, the Al rich IMC phase was not the likely
catalyst species. No new phase formed upon the addition of Zn. Instead, Zn was found concentrated within the primary $\eta$-Cu$_6$Sn$_5$ particles, which were frequently found embedded within Sn dendrites, indicating likely catalytic activity. XRD indicated that Zn stabilizes an orthorhombic form of $\eta$, denoted $\eta^6$ in place of the slightly different monoclinic $\eta^8$ modification of the $\eta$ group structure, thus providing evidence of a catalysis mechanism for Zn modification.

Low undercooling did not always indicate the absence of large pro-eutectic, blade-like Ag$_3$Sn particles, but the frequency of these blades was reduced with reduced undercooling, and sometimes eliminated. Though Mn did not result in the lowest undercooling, it suppressed Ag$_3$Sn blade formation with an addition of only 0.10 wt. %. The oxidation and wetting behavior of SAC3595.Cu alloys reduced the attractiveness of Mn despite its effect on Ag$_3$Sn suppression. Al and Zn did not have this problem and at the optimal concentration, 0.05 and 0.21wt. %, respectively, both eliminated Ag$_3$Sn blades and minimized undercooling while providing high eutectic volume solidification structures.
CHAPTER 1: INTRODUCTION

History

The word eutectic comes from the Greek word *eutektos*, meaning “easily melted” [1]. A low melting temperature is one, but not the only, virtue of eutectic alloys. The thermodynamic definition of a eutectic reaction is: a reversible transformation in which a liquid transforms into \( n \) solid phases at a single temperature upon cooling, and vice versa, where \( n \) is the number of elements in the system. Under equilibrium solidification, a eutectic alloy will completely solidify at a single temperature, usually under coupled growth conditions, eliminating any “mushy zone,” providing a homogeneous microstructure, and avoiding micro-shrinkage voids. The result is that eutectic alloys are generally very easy to deform and have generally homogeneous properties. Throughout history, beginning thousands of years ago, eutectic alloys have been used precisely for these reasons.

![Figure 1. Sn-Pb eutectic alloy solidified with a lamellar eutectic microstructure [2].](image)

Eutectic solder alloys, namely Sn-Pb (shown in Figure 1), with a eutectic temperature of 183°C, are perfect examples of an important class of eutectic alloys. Eutectic Sn-Pb solder has been used for millennia to join a variety of metals. Artists and jewelers have used it to join fine pieces of precious metal. It has been used to seal water vessels, like the copper vase from the
Bronze Age shown in Figure 2. Sn-Pb’s virtues include: a low eutectic temperature of 183°C—little more than a wood fire is sufficient to melt it—high ductility, good wetting on many metals, and a composition containing abundant, inexpensive elements.

Figure 2. Copper water vessel (left) circa 1500-1300 B.C. is assembled with rolled and riveted copper sheet, then sealed with Sn-Pb solder [3]. Today thousands of solder joints populate electronic devices (right) from supercomputers to cell phones.

Today’s most ubiquitous application of eutectic solder, particularly Sn-Pb, is within the electronics industry. Since the advent of the printed circuit board, solders have been used to connect electronic components—resistors, capacitors, transistors, and silicon based integrated circuits ever increasing in complexity—to glass/epoxy/conductor laminate printed circuit boards (PCBs) in order to create devices ranging from supercomputers to cell phones. PCBs provide mechanical rigidity and a framework for creating interconnections. The thermal stability of PCBs effectively limits the assembly processing temperatures to near 240°C [4, 5]. At high temperatures, the epoxy in PWBs breaks down and greater stresses develop within the PCBs themselves, as well as between the component and board. Consequently, it is generally best to minimize processing temperatures. With the eutectic temperature of 183°C for Sn-Pb, this is no problem.
Motivation

Sn-Pb’s biggest drawback is the toxicity of lead; it is a known neurotoxin. Consequently, health and environmental concerns have led to several European Union regulations, notably RoHS and WEEE, which severely limit lead’s use in electronic devices [6]. In today’s global market, manufacturers prefer a single solder solution, as opposed to multiple lines. Years of experience and knowledge of Sn-Pb, as well as its superior wetting ability, have made the electronic assembly industry reluctant to switch. Regardless, by law, lead-free solders are here to stay.

Aside from governmental mandate, there are other performance related reasons for switching to lead-free solder. Joint sizes are shrinking, environments are becoming harsher, and operating temperatures are increasing. All these factors place an increasing performance demand on solder. Creep, fatigue, and intermetallic layer growth become greater issues at higher temperature. For these reasons, stronger, more creep and fatigue resistant and slower diffusing solders are desirable for cutting edge applications in high power electronics and semiconductor integrated circuit packaging.

Objectives

The root objective of this research is to maximize the performance of SAC based solder alloys in electronic assembly with primary application at the package-to-board level. In terms of alloy and microstructure design, the objective of this research is to maximize the eutectic volume of the SAC system, refine the Sn grain structure, and eliminate Ag₃Sn pro-eutectic blade formation by effectively catalyzing the nucleation of β-Sn. A fine ternary eutectic structure will increase strength while fine Sn grains will mitigate thermal strain problems induced by the anisotropy of Sn. Sufficient wetting, non-toxicity, and a reasonable cost are prerequisites.

Tin is well documented as being difficult to nucleate [7, 8]. This is largely attributed to its anisotropic crystal structure. As a result, this system does not follow an equilibrium solidification path. Since the SAC alloy is 96 vol. % Sn, the nucleation and growth mechanisms of Sn largely
control the alloy’s solidification. The results of this non-equilibrium solidification are potentially large pro-eutectic intermetallic phases and β-Sn dendrites as opposed to a fine ternary eutectic structure, all features that weaken the microstructure. If, nucleation of Sn is controlled through the appropriate catalyst, the microstructure may be improved.
CHAPTER 2: LITERATURE REVIEW

Electronic Packaging and Assembly

Solder joints are found in virtually all electronic devices. Their purpose is to create electronic and mechanical interconnections between individual components within the system. Electronic packaging refers to the environmental isolation of electronic components, e.g., transistors, resistors, conductors, integrated circuits, etc [4]. An electronic device consists of multiple interconnected packages assembled to form a useful system such as a personal computer or an automotive sensor. Assembly refers to the process of connecting packages thereby creating a functional electronic device.

Packaging Hierarchy

There are multiple hierarchical assembly levels in electronic manufacturing. Packages are assembled onto packages, and in turn, assembled onto even larger packages ultimately, to user and peripheral device level. A schematic of this processing hierarchy is shown in Figure 3. This study will focus on Level 2 assembly, module to board, as shown in this figure. A brief description of each step follows.

Level 0: Integrated circuit (IC) creation
Level 1: IC to module (flip-chip)
Level 2: Module to board (SMT\(^1\), PTH\(^2\))
Level 3: Board to backplane
Level 4: Rack to rack
User Level: User interface and peripherals

---

\(^1\) Surface mount technology, read further  
\(^2\) Plated-through-hole, read further
Figure 3. Assembly levels in electronic devices; the device shown here represents a mainframe server [4, 9].

The finest assembly level is at the silicon integrated chip (IC) level. Solder is not used at this level. ICs are generally not mounted directly to a printed circuit board (PCB). It is first attached to a carrier module. The most common process used for chip to module attachment process is wirebonding. In this process, fine gold wire is ultrasonically diffusion bonded from metal pads on the chip periphery to metal pads on a module. However, advances in IC technology and constantly increasing input/output (I/O) density have promoted different interconnection techniques, including flip-chip attachment. In flip-chip assembly, 2-d arrays of tiny (~100μm) high melting solder spheres, generally a high lead solder (commonly Sn-90Pb), are used to make these connections. Instead of just around the perimeter of the chip, connections can be made over the entire area, thereby increasing I/O density. Additionally, flip-chip is a parallel processing technique—the joints are created all at once—as opposed to wirebonding, a serial process where
connections must be made one at a time. Flip-chip is demanding application. At this fine level, IMC formation can quickly consume an entire joint since the solder volume is so low, making a brittle joint. High current densities can drive electromigration. CTE and stiffness mismatch can generate large stresses. Currently, research is being performed to replace the 'hard' solders used at this level, but these high Pb solders used at this level are currently exempt from the EU ban.

While SAC lead free solder may one day be applied to flip chip technology, its immediate application, and the target of this study, is in board level assembly, where packages are connected to a PCB. There are multiple soldering processes commonly used at this level. The most important are wave soldering and reflow processing. In wave soldering, a PCB/component assembly with (metal) plated-through-hole (PTH) joints is passed over a wave of solder. The solder wets and flows through the through holes and solidifies creating a joint. In reflow soldering, solder paste is screen printed onto the pads of a PCB, components are placed, and the entire assembly is then passed through a reflow oven where the solder melts and solidifies, thereby creating a solder joint (Figure 4). The solder paste contains fine solder particles suspended in a mixture of flux and a carrier. Reflow processing is used to create surface mount technology (SMT) joints. Compared to PTH joints created by wave soldering, SMT enables higher I/O density, simpler PCB design, and component placement on both sides of the PCB. SMT joints experience more mechanical stresses than PTH, but the increased I/O density has made it the most popular board level assembly configuration. Numerous joint geometries may are used in SMT. However, the reflow processes is similar in all cases. This study will therefore focus on solder to be used in reflow processing.
Figure 4. Reflow assembly. A circuit board populated with (a) components passes through (b) a reflow oven with a controlled temperature profile. The flux is activated, reducing the oxides. The solder melts and wets the substrate pads and component leads, and finally solidifies. An assembled device, (c), a USB memory key shown here, is the resulting product.

Package reliability

Factors influencing solder reliability include solderability, impact strength, fatigue strength, and IMC layer growth rates. Kang et al review some critical mechanical and microstructural characteristics of lead-free solder joints, particularly within the SAC system in [10]. Fatigue arising from thermal mismatch strain, referred to as thermomechanical fatigue (TMF) is a major reliability concern [11]. Thermal shock and electromigration are additional concerns. Lead-free solders tend to improve fatigue performance and lessen electromigration, but they perform more poorly in shock loading [12].

For lead free solder alloys, the reflow temperature ranges from 240-260°C. This is a higher reflow temperature than for Sn-Pb since these alloys have higher liquidus temperatures and the poorer wetting—an increased superheating may compensate for the reduced wetting of some alloys [12]. The polymers used in electronic assemblies absorb water. This combined with the
higher reflow temperatures reduces reliability. Ultimately, the reflow temperature is determined by the solder alloy used. Therefore, PCB technology has some incentive to progress toward higher temperature tolerance.

**Ag₃Sn Blades**

The weakness of the Ag₃Sn/Sn interface is well documented. Results from combined fracture surface analysis and strength analysis indicate that its presence leads to a generally more brittle failure. Kim et al have performed both tensile and shear testing on SAC joints containing and found that Ag₃Sn blades cause more brittle joint failure [13]. Alloys prone to Ag₃Sn blade formation, e.g., SAC3970¹ and others high in Ag, failed more frequently in a brittle manner under tensile loading than did low Ag samples such as SAC305² (Figure 5). Corresponding fractographs indicate that the crack easily travels across the Ag₃Sn/Sn interface when oriented favorably. Similarly, in shear, the crack path often follows Ag₃Sn/Sn boundaries indicating interface sliding failure (Figure 6).

¹ Sn-3.9Ag-0.70Cu wt. %
² Sn-3.0Ag-0.50Cu wt. %
Monlevade and Peng performed board drop impact testing on three different SAC alloys. They found that under this loading, failure occurred dominantly at the solder/substrate interface, most frequently at the $\text{Cu}_3\text{Sn}/\text{Cu}_6\text{Sn}_5$ interface. However, when an $\text{Ag}_3\text{Sn}$ blade was oriented near parallel to the solder/substrate interface the crack would follow its interface as in Figure 7b [14].
Figure 7. BGA board impact fracture of a Sn-3.8Ag-0.07Cu wt. % sample. a) A macroscopic cross polarized optical view of a failed joint. b) Crack initiation at the corner followed by failure along an Ag$_3$Sn/Sn interface [14].

Song et al studied the vibration failure of two SAC alloys, one hypereutectic Ag composition Sn-4.2Ag-0.50Cu wt. % and another hypoeutectic Ag composition (SAC3350). They found that slower cooling rates resulted in a higher incidence of Ag$_3$Sn blades. When these blades did form, cracks preferred to follow them as in Figure 8 [15].

Figure 8. Vibrational failure along an Ag$_3$Sn/Sn interface [15].

Finally, Kang, Henderson et al show that TMF induced cracks also follow Ag$_3$Sn/Sn interfaces when present near the IMC layer as shown in Figure 9 [16, 17].
Joint Mechanics

Stresses in solder joints arise primarily due to differential thermal strain during solidification and thermal cycling. The differential thermal strain between the solder and substrate pad will contribute to the stress state in a solder joint, as will the differential thermal strain between each component and the PCB. These differential thermal strains will be dominantly shear type. The primary source of tensile stress will arise, in device application, from incidental impact loading, e.g., dropping your cell phone. In certain applications, primarily automotive, device vibrations will induce low stress cyclic tensile loading leading to fatigue. In these cases of tensile fatigue, the load is transmitted to the solder joint by flexure in the PCB [11]. The following discussion will focus on shear loading of joints.

Substrate/solder interfacial stress

In a solder joint, the residual stresses develop between the substrate and solder due to differences in thermal expansion. Any stresses induced by the formation of the IMC layer will be ignored here. A solder joint is initially formed by flowing liquid solder between the substrates
and allowing it to solidify. A near eutectic Sn-Ag-Cu solder has a eutectic temperature of 217°C. Typical operating temperatures of a solder joint range from 25 to 150°C. Heat is generated by the operation of devices due to electrical resistance. Power cycles provide a source for cyclic stress and result in thermomechanical fatigue. Also, note that an operating temperature of 150°C is 85% the absolute melting temperature, well within the realm of creep. The stress in a solder joint is similar to that of a thin film or a general layered composite. The joint will be modeled as such. A complete model will account for plasticity, interface strength, and crack energy. As a start, a simple elastic model will be used. Stress relief through plastic flow (including creep), thermomechanical fatigue, and fracture will be considered separately and briefly.

A simple model for interfacial stress

The simplest model for modeling the residual thermal stress is using the thin film approximation. Let there exist two unconstrained materials (Figure 10a): a film and a substrate, with lateral dimensions in the x-y plane, stress free, identical lateral dimensions. The film shrinks (unconstrained) relative to the substrate due to thermal expansion differences (Figure 10b). Normal tractions are applied to the film edges so that the film matches the substrate lateral dimensions (Figure 10c). Attach the film to the substrate. So long as these edge normal tractions exist, the film is in a state of pure biaxial normal stress (Figure 10d). If the edge stresses are removed, the strain is maintained by shear tractions at the film/substrate interface. In the case of a substrate/solder/substrate joint, the shear stress is shared by both interfaces. If the lateral dimensions are much greater than the film thickness, the shear stresses are only significant near the edges of the interface while away from the edges, the stress state is pure normal biaxial [18].
Using the thin film approximation, the uniform thermal residual (normal) stress in the thin film is:

\[
\sigma_{xx}^f = \sigma_{yy}^f = \frac{E^f}{1 - \nu^f} \cdot \Delta \alpha \cdot \Delta T
\]

Equation 1. Thin film differential thermal (normal) stresses

Where,

- \(\Delta \alpha\) = difference between coefficients of thermal expansion between the film and substrate.
- \(E^f\) = elastic modulus of the film
- \(\Delta T = T_R - T\); \(T_R\) = reference temperature where the stress in all layers is 0
- \(\nu^f\) = Poisson’s ratio for the film

Using copper as the substrate and pure tin as the solder, \(\sigma_{yy}^f = 87.8\text{MPa}\). This model requires the lateral dimensions (R) of the film to be large relative to its thickness (h), R >> h. In the BGA joint case, this isn’t necessarily the case. When the R = h, the shear stresses at the edge start to
interact, reducing normal biaxial stress [18]. Additionally, over time the residual stress relaxes due to creep. As such, this approximation represents the upper bound for lateral normal stresses in the joint.

Maintaining the semi-infinite plane assumption, this model can be modified to take into account relative differences of thickness and elastic moduli of the film and substrate. This model describes the substrate and film as an elastic bi-layer. The lateral dimensions are considered semi-infinite such that edge effects are negligible. The model of elastic misfit bi-axial loading is defined as follows:

\[ \sigma^T = \frac{E_f \cdot \Delta \alpha \cdot \Delta T}{1 - \nu_f} \]  
\[ \frac{\bar{\sigma}}{\sigma^T} = \frac{1 - 3 \Sigma \xi^2}{(\Sigma \xi^2 - 1)^2 + 4 \Sigma \xi (\xi + 1)^2} \]  

Where,

\[ \xi = \frac{h_f}{h_s} \]
\[ \sum = \frac{E_f / (1 - \nu_f)}{E_s / (1 - \nu_s)} \]
\[ h_f = \text{film thickness} \]
\[ h_s = \text{substrate thickness} \]
\[ \bar{\sigma} = \text{Average normal residual stress in the film} \]
\[ \sigma^T = \text{Misfit stress; same as stress predicted from thin film approximation} \]
The average residual stress (dashed line) decays as the relative thickness of the film layer increases, just as expected. For a solder joint on copper substrate, $\Sigma$, the relative elastic modulus, is 0.369. The normal film residual stress decays most rapidly between thickness ratios of 0.1 to 1. If $\xi$, the relative film thickness, is 0.1, then according to this model, the relative normal residual stress is 0.85 times the misfit stress, or 74.6MPa. This is not the best model since our joint is not a bi-layer which may bow, but rather, a sandwich where the opposite substrate balances forces and prevents bowing. The additional top layer would effectively increase the normal residual stress. Nonetheless, the 15% reduction in residual stress isn’t significant.
Interfacial and Edge stresses

![Diagram of stress distribution near edge](image)

**Figure 12. Residual shear and peel stresses near edge [19]**

The local stresses at the edges are different than those far from the edges. Not only are there shear stresses near the interface, but there is also a stress normal to the interface at the edge that balances the moment created by the in-plane normal stress and interfacial shear stress (see Figure 12). The interfacial normal stress is sometimes called the peel stress as it tends to peel the film off from the edge. If this stress is great enough and the interface is weak or flawed, the film may peel from the substrate, resulting in interface failure as shown in Figure 13. In service, this stress plays a part in the thermomechanical fatigue, providing the stress required to propagate cracks near the interface.

![Diagram of thermomechanical fatigue crack](image)

**Figure 13. Thermomechanical fatigue crack propagated by interface stress [20]**

Additionally, the thin film approximation given assumes a rigid substrate (Figure 14b). Substrate compliance will change the stress state, particularly at the edges (Figure 14c). Qualitatively, the edge shear stresses for both a rigid substrate and compliant substrate are shown in the following figure:
Figure 14. Edge shear stress depends on substrate stiffness [18].

Generally speaking, solder is a ductile material capable of significant plastic strain before fracture. For example, Sn-3.6Ag-1.0Cu (SAC3610)—this alloy has similar mechanical properties to SAC3595—has a shear yield strength of 47MPa followed by extensive plastic yielding, as measured by asymmetric four-point bending [21]. Sn-Pb solder has lower yield strength but a plasticity. Using the Tresca yield criterion [22], under bi-axial load with no out of plane stress, the normal yield stress is $2\tau_0$, twice the shear yield stress. Using the thin film model stress and Sn-3.6Ag-1.0Cu solder alloy, yielding would not occur due to residual stress far from the edge. If the solder is elastic-perfect plastic, the residual stress will never exceed the yield stress. This is most likely to happen at the interface where the shear stress is highest.
Figure 15. Plastic yielding near interface edge [19]; y-axis: stress, x-axis: relative distance from edge towards the center of a joint

Fracture Mechanics

Edge shear and peel stresses provide a driving force for interface debonding or the growth of cracks near the interface. Yu et al performed an extensive study of edge effects in thin film delamination, modeling the stress state near the edge and the crack energy release rate [23]. The slightly simplified model is compared to a finite element analysis and they match closely.

Linear elastic fracture mechanics is applied in Yu’s model. There exists a steady state crack energy release rate that is independent of crack size and dependent on the elastic properties of the film, the misfit stress, $\sigma_0$ ($\sigma_0 = \sigma^T$ from thin film approximation): $G_{ss} = \frac{(1 - \nu_f^2) \sigma_0^2 h}{2E_f}$ (Equation 2), where $h$ is the film thickness. The interface toughness can described by $\Gamma_i$, a function of the crack mode, e.g. tensile or shear opening, and the nature of the interface; it is an interface property. When $G > \Gamma_i$, interface fracture occurs. $G$ is the energy released per unit new surface area; a higher energy release rate requires a higher stress at the crack tip. In order to maximize the interface toughness, $\Gamma_\sigma$, should be maximized and $G$ minimized.
Two situations are modeled by Yu et al as noted in the figure to the side. Elastic plate theory is used to derive the stress state near the interface. These stresses were in turn used for calculating the stress intensities. The stress intensity is related to the crack energy release rate, $G$, by the following equation:

$$G = \frac{1}{2} \left( \frac{1}{E_f} + \frac{1}{E_r} \right) \left( K_i^2 + K_h^2 \right)$$

Equation 3. Crack energy release rate, G

Very different results for $G$ were obtained for interior and corner cracks. Compare Figure 17 and Figure 18.
Figure 17. Crack emerging at interior; $\alpha$ (alpha) is a function of the difference in elastic modulus between the film and substrate. For Cu/Sn, $\alpha = -0.5$. [23]

Figure 18. Relative crack energy release rate for a crack emerging at a corner. Dots are finite element results [23].

In the corner crack configuration (see Figure 18) the energy release rate approaches $G_{\infty}$ slower, with respect to the crack length, $a$, than the interior crack configuration. This is bad news for solder joints that resemble the interior edge crack. Also, note how the $x$-axis is scaled with the film thickness, $h$. Therefore, thicker joints will have lower crack energy rates than very thin joints.

The other interesting conclusion drawn from cases C and D from Figure 16, the internal crack propagating towards the edge will arrest before the interface fully debonds. Residual stresses alone will therefore not cause a total failure of the joint.
Conclusions

The mechanics of a complex collection of solder joints placed on a circuit board is terribly difficult to model. Residual stresses arise when different materials with different properties, e.g., thermal expansion or elastic moduli, are joined together. The local thermal strain in any solder joint depends on the joint configuration, temperature, and location on the board. Within the joint itself, IMC interface layers further complicate the system. Solder is an elastic-plastic material which allows the thermal stress to exceed the yield stress without failing, provided sufficient plasticity. Operating at 0.85T_m, solder joints are subject to creep which relaxes the stress. It is thermomechanical fatigue driven, by these residual strains which are most likely to cause failure since stresses can generally be relieved by plastic deformation.

The upper limit of the residual stress in a solder joint can be determined by the thin film approximation (see Equation 1). This case applies to a thin film (thickness much less than lateral dimensions) on a perfectly rigid substrate.

\[
\sigma_{xx}^f = \sigma_{yy}^f = \frac{E^f}{1 - \nu^f} \cdot \Delta \alpha \cdot \Delta T
\]

A fracture mechanics model was briefly discussed. While residual may not immediately cause failure of a joint, edge flaws combined with thermal cycling of the system will cause thermomechanical fatigue. In order to accurately predict the failure of any single joint due to thermal residual stresses, fracture mechanics, creep, and plasticity must all be considered.

Thermodynamics

Alloy design begins with the study of thermodynamic phase equilibria through the use of phase diagrams. The liquidus temperature, eutectic temperature, and equilibrium phase fractions are important parameters represented in phase diagrams. The reflow temperature of a solder is limited in practice by PCB materials, which are typically made of a glass/epoxy composite (130<T_g<170°C) [5]. Based on the maximum processing temperatures for assembly processes and cost considerations, tin based alloys are the only viable replacements for Sn-Pb solder [24]. β-tin is a soft, ductile anisotropic phase with a melting temperature of 232°C, which is higher
than ideal as a solder. Alloying lowers the liquidus temperature of the system as well as providing potential strengthening phases. A relatively low melting ternary eutectic alloy in the Sn-Ag-Cu system has emerged as a primary candidate system for lead-free solder.

**Sn-Cu and Sn-Ag binary phase diagrams**

Before discussing the calculation of the ternary Sn-Ag-Cu phase diagram, it is illustrative to first understand the constituent binary diagrams from which the ternary is derived. The Sn-Cu and Sn-Ag phase diagrams will be discussed. The Ag-Cu eutectic is at too high a temperature for consideration as a solder alloy and the ternary is so rich in Sn that this phase diagram is irrelevant. For alloy design near the eutectic temperature is primarily concerned with phases stable below 300°C. The roles and reactions involving these structures in the each system will be discussed here.

**Sn-Cu**

The Cu-Sn system contains 4 solid room temperature phases including two intermetallic compounds. Cu is essentially insoluble in β-Sn. The eutectic reaction occurs at 227°C. However, its composition is debatable. In the diagram [2] displayed in Figure 19, it is Sn-0.7Cu wt. %. However, some studies place it at Sn-0.90 wt. %. [24, 25] According to Moon et al, the η liquidus surface is the weakest experimental link in the phase diagram calculation, but they conclude that XCu = 0.9 fits best [25] (see Figure 20). The η and η' phases are nominally referred to as Cu₆Sn₅ and treated as a stoichiometric compound though they might properly be described as semi-stoichiometric. The η' and η [26] structures are very similar and not often distinguished from each other. The heat of transformation for the η ↔ η' transition, as determined by DSC, is between 390 and 450 J/mol depending on the thermal history of the sample [26]. Annealing and cyclic DSC experiments indicate that this is a sluggish transition [26]. The differences between these phases are discussed in the crystal properties section of this document. This being said, the η phase may appear in the bulk volume of Sn-Cu solder joints from the eutectic L → β + η reaction. It is also forms immediately during the wetting of a copper substrate. The ε-Cu₅Sn
phase is another semi-stoichiometric IMC that is treated as fully stoichiometric. While it doesn’t appear within the bulk of Sn-Cu containing solder joints, it may form as a layer between a Cu substrate and its η IMC layer.

Figure 19. The full Sn-Cu phase diagram shows a eutectic reaction on the tin rich side as well as 3 room temperature phases that may all appear in a solder joint, including the IMC layer(s) [2].

Figure 20. The tin rich section of the Sn-Cu phase diagram is of the greatest interest for calculation of the ternary section. This diagram used by Moon et al [25] combines the calculated Sn-Cu phase diagram by Shim with compiled experimental data.

Sn-Ag

The Ag-Sn system has a eutectic reaction, $L \rightarrow \gamma$-Ag$_3$Sn + $\beta$ as indicated in Figure 21 at 221°C and a composition Sn-3.5Ag wt. %. Like the Sn-Cu system, the eutectic composition is tin rich. The only important phase not yet discussed in this system is $\gamma$-Ag$_3$Sn. Ag, like Cu is essentially insoluble in $\beta$-Sn. $\gamma$-Ag$_3$Sn has a measurable composition width, but it, like Cu$_5$Sn$_3$, is generally treated as a stoichiometric compound in the near eutectic system. This is fair since the Sn rich phase boundary of Ag$_3$Sn is vertical.
The Sn-Ag-Cu phase diagram

In 2000, Moon et al. performed the most complete thermodynamic assessment to date of the Sn-Ag-Cu system [25]. Guided by previous experimental data, they gathered a complete set of experimental data near the ternary eutectic composition, then fit this data to a thermodynamic model, and finally calculated a ternary phase diagram using the CALPHAD method. The eutectic composition of from this model is Sn-3.66-0.91Cu wt. %. This composition fits within the range of the empirical data. This tin rich corner of this system is the basis for Sn-Ag-Cu solder alloy development today.

Collecting precise thermodynamic data in this system was not without challenge. Since the eutectic composition is dominantly tin, the relative volumes of the two intermetallic phases, Ag$_3$Sn and Cu$_6$Sn$_5$, are small (<5 vol. %). As a result, the DTA signal for the formation of these phases forming is small, posing an experimental challenge. Compared to Sn, the liquidus surfaces of the IMC phases are steep, i.e., small changes in Ag or Cu compositions significantly change the liquidus temperature. This corresponds to a rapidly increasing driving force with respect to temperature for their formation. This has significant consequences during solidification which will be further discussed later.
Equilibrium ternary eutectic system solidification occurs in up to 3 stages. Let $\alpha$, $\beta$, and $\gamma$ represent the system’s 3 solid crystalline phases while L is the liquid in the system.

1) $L \rightarrow \alpha$ Primary
2) $L \rightarrow \alpha + \beta$ Secondary, monovariant binary
3) $L \rightarrow \alpha + \beta + \gamma$ Tertiary eutectic

(1) and (2) occur over a range of temperatures while (3) occurs at a fixed temperature with zero degrees of freedom.

At room temperature it is body centered tetragonal (BCT) but has transforms to a brittle diamond cubic phase, $\alpha$, at 286 K (13°C). This transformation is known as tin pest. Fortunately this reaction is slow [27].

NIST performed multiple modeling iterations to reach a final refined model. The first iteration, based off SGTE pure element data and binary data from literature. A sublattice model was used to define the energy of the IMC phases [25, 28]. The calculated ternary eutectic was Sn-3.25Ag-0.69Cu wt. % at 217.4°C. The binary data for this calculated was inconsistent with the SGTE data. Modified data, consistent with the SGTE data, allowed further refinement of the system and indicated a ternary eutectic at Sn-3.42Ag-0.67Cu wt. % at 216.9°C. When a ternary interaction term was added to fit the data of Loomans and Fine [29], the eutectic is Sn-3.74Ag-0.85Cu wt. % at 215.9°C, using an interaction parameter, $L = -30\text{kJ/mol}$.

Model optimization was performed using TERGSS, based on the method of least squares, to fit the ternary excess term. The model was fit to NIST’s experimental data for the phase transitions. Heating and cycling experiment data were favored over the cooling experiment data. Even after this, some minor modifications were needed in the binary models, specifically the lattice stabilities of $\text{Ag}_5\text{Sn}$ and $\text{Cu}_6\text{Sn}_5$ were altered slightly. The final experimentally optimized calculated phase diagrams are shown below.
Crystal Properties

From the phase diagrams just shown, 4 solid equilibrium phases are indicated in Sn-Ag-Cu alloys: β-Sn [30], γ-Ag₃Sn, η'-Cu₆Sn₅ and η-Cu₆Sn₅ [26, 31, 32]. Strictly speaking, according to Larsson et al, “In the range of 25°C-415°C at least four distinct phases appear, all based on the NiAs-Ni₂In structures.”[32] These phases are, by convention, collectively referred to by their approximate stoichiometry, Cu₆Sn₅, and will be discussed later. The high temperature η to low temperature η' transition upon cooling at 187°C depicted on the phase diagram (Figure 19) is a relatively small change in structure but it is detectable with conventional thermal analysis. The intermetallic compound phases tend to facet while β-Sn does not. The relatively soft tin phase serves as a ductile matrix while the intermetallic phases may either strengthen or embrittle a joint depending on their morphology. For example, large Ag₃Sn blades can weaken a joint because it has a relatively weak interface with β-Sn which can create an easy crack path. An intermetallic
layer of Cu$_6$Sn$_5$ forms between the copper substrate surface and the solder bulk forming a strong metallurgical bond.

$\beta$-Sn

Near eutectic Sn-Ag-Cu-X alloys are mostly tin. Consequently, its properties largely determine the properties of the alloy. Tin does not have a common metallic crystal structure (HCP, FCC, BCC), but rather, its structure is a derivative of body centered tetragonal equivalent to diamond cubic compressed along its c-axis as shown in Figure 24. Its c/a ratio is 0.546. As a result of its crystalline anisotropy, its properties, including its elastic constant and coefficient of thermal expansion (CTE) are anisotropic. A schematic representation of the anisotropy of $\beta$-Sn and crystals with the same symmetry is shown in the figure below, followed by the compliance values in GPa$^{-1}$, where compliance is the inverse of the stiffness tensor. As a consequence of tin’s mechanical anisotropy, relatively large stresses may be generated between adjacent tin grains by differential thermal and elastic strain, thereby affecting the fatigue life and reliability of the joint.

Figure 23. Compliance tensor for $\beta$-Sn
Table 1. Compliance tensor for $\beta$-Sn in GPa$^{-1}$

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Figure 24. Tin's crystal structure is a body centered tetragonal derivative, space group I4$_1$/amd. Consequently, its mechanical properties are anisotropic. [30]

$\eta$-$\text{Cu}_6\text{Sn}_5$

The Cu-Sn phase diagram in Figure 19 indicates two structures near the $\text{Cu}_6\text{Sn}_5$ composition, a high temperature structure denoted $\eta$, stable above 186°C, and a low temperature structure denoted $\eta'$. Note that the $\eta$ and $\eta'$ phases are not typical stoichiometric line compounds and are more properly considered semi-stoichiometric compounds, though they are conventionally referred to as $\text{Cu}_6\text{Sn}_5$. The $\eta$ phase shifts to a more Cu rich composition towards high temperatures and may be more accurately described as $\text{Cu}_5\text{Sn}_4$ as Larsson et al have, though this study will continue to use the convention of referring to these phases generally as $\text{Cu}_6\text{Sn}_5$.

The transition noted on the phase diagram from $\eta$ to $\eta'$ is detectable using conventional thermal analysis techniques such as DSC and DTA. Electron diffraction is however capable of
discerning four phases near this composition, three of them are in the $\eta$ field of the binary phase diagram.\footnote{Henceforth, any reference to the $\eta$ phase refers to any of the high temperature phases above $\eta'$ (above 187°C). When necessary, the specific ordered structures will be referred to as $\eta^6$ and $\eta^8$.} All of them are monoclinic\footnote{Curiously, the cited authors describe the $\eta^6$ phase as monoclinic, but say that $\beta = 90^\circ$, thus making it equivalently orthorhombic. For this work, the $\eta^6$ phase will be referred to as orthorhombic.}. A more detailed phase diagram including these phases is shown in Figure 25. Very near the peritectic decomposition at 415°C, a disordered NiAs type structure exists, which will be designated as $\eta^0$ here. Just below (in temperature) this disordered $\eta^0$ phase and above the $\eta'$ ordered phase are two additional ordered phases, one with a 6-fold superstructure (denoted $\eta^6$) and the other with an 8-fold superstructure (denoted $\eta^8$) \cite{32}. These two phases are indicated on a modified phase Cu-Sn phase diagram in Figure 27.

The temperature for the $\eta^6 \leftrightarrow \eta^8$ transition is uncertain. Larsson et al place the transition at approximately 350°C, $\eta^6$ being the higher temperature phase. This conclusion is based on samples annealed at 350°C, quenched, and then observed in the TEM, where reportedly, beam induced heating causes a reversible transition between the two structures \cite{32}. Ghosh and Asta prepared $\eta$ powder for XRD by annealing at 222°C. They then indexed this pattern according to the (orthorhombic) $\eta^6$ model given by Larsson et al. This would place the $\eta^6 \leftrightarrow \eta^8$ at a lower temperature (near 222°C) than proposed by Larsson et al. This uncertainty is reflected in the phase diagram (Figure 25) as a shaded region, above which $\eta^6$ is stable, below which $\eta^8$ is stable, and within, it’s not yet certain which of these phases is stable.
Below 187°C there exists a domain twinned crystal belonging to the NiAs-Ni$_2$In structure group. Larsson et al describe the structure as “The basic hexagonal NiAs (B8) type cell is pentupled, reflected in the reciprocal lattice by a fivefold superstructure running along [11̅21]$^\prime$. The extensive domain twinning macroscopically gives rise to perfect hexagonal symmetry, which explains the previously proposed hexagonal cell [$a = 5a_{\text{NiAs}}$, $C = 5C_{\text{NiAs}}$; Bernal (1928), *Nature*, 122, 54].”[31] This domain twinning explains the hexagonal rod morphology of this phase in solidified Sn-Cu based solder alloys.

Ghosh and Asta have performed a recent review of these structures and combined them with new XRD, DSC, and ab-initio calculations [26]. Their ab-initio results compare well with the reference structures [31, 33]. They also describe the $\eta \rightarrow \eta'$ transition in detail and conclude that
it is a sluggish transition. As a nucleation catalyst for $\beta$-Sn, this study is primarily concerned with the high temperature $\eta$ phase.

The continuous layer of (high temperature) $\eta$ that forms at the solder/substrate interface immediately upon melting of the solder is responsible for the adhesion strength of SAC/Cu joints. Suh et al, showed that there is a correlation between the orientation of copper substrate grains and $\eta$ IMC layer scallops [34]. In Sn-Cu solder systems, it also occurs within the bulk as either a primary phase particles or as part of a coupled eutectic, depending on the alloy composition and processing. Generally $\eta$ pro-eutectic rods have a hollow rod structure as mentioned previously. Typical of intermetallics, it has a high yield strength and low ductility relative to metal structures. Its strength makes it a good strengthening agent, but due to its brittleness, its size should be minimized.

$\gamma$-Ag$_3$Sn

Ag$_3$Sn has a blade morphology when formed as a pro-eutectic phase and has either a rod or blade morphology depending on its growth velocity when formed by coupled eutectic growth [35]. Pro-eutectic Ag$_3$Sn have blade type morphology and are often connected to the IMC layer. While eutectic Ag$_3$Sn blades act as dispersion strengtheners, as large blades, they serve as easy crack paths.
In a study performed by Song et al, Sn-Ag-Cu alloys with hyper and hypo-eutectic Ag compositions and a constant hypo-eutectic Cu composition, cooled at two different rates, were tested under tension and vibration loading [15]. They found that the finer microstructure with only small Ag₃Sn produced by rapid cooling resulted in stronger more ductile joints in tension. Slowly cooled samples of both compositions contained pro-eutectic Ag₃Sn blades, had coarser microstructures. This resulted in lower strength and ductility. The hyper-eutectic Sn-4.2Ag-0.5Cu alloy had the most pro-eutectic Ag₃Sn. Its yield strength compared well to the hypo-eutectic Ag samples, but its elongation at failure was reduced. The common denominator between the samples with the worst performance in terms of ductility was the presence of and failure at pro-eutectic Ag₃Sn blades.
Sn/Sn grain boundary stress

Studies show that Sn grains in SAC solder joints are typically few and large, corresponding to a low nucleation rate [36]. Due to the anisotropy of tin, large stresses due to differential thermal strain between mis-oriented grains may develop. Due to the orientation dependence of the elastic response and strength, predicting failure in solder joints is difficult. Matin et al performed a thermal cycling experiment and compared the crack location to stress concentrations predicted in a finite element model and concluded that they were related [37].
Interfacial Energy and Nucleation Thermodynamics

Recall that the eutectic temperature of Sn-Ag-Cu is 217°C. Upon heating, calorimetric measurements of a SAC alloy indicate that melting occurs at this temperature. However, upon cooling under normal processing conditions, SAC alloys will not solidify until well below 217°C. This effect is known as undercooling or supercooling and is the difference between the measured temperature of solidification of a phase and its equilibrium melting temperature. This is illustrated for the case of pure tin in Figure 31. Here the sample melts at 231°C, but does not begin to solidify until about 212°C. This 19°C of undercooling is caused by the additional free energy required to form a new interface between the new solid, the nucleus, and the parent liquid. Solution thermodynamics and phase diagrams derived from its study ignore the effect of interfaces on the free energy of the system by assuming that the volume of any phase is significantly larger than its surface area. However, when studying solidification and solidification microstructures, interfacial energy cannot be ignored because of nucleation and undercooling.
Homogeneous nucleation

There are two classes of nucleation, homogenous and heterogeneous. Homogeneous nucleation occurs when a nucleus forms from its parent phase with an interface with only its parent phase. Homogeneous nucleation in practice is very difficult, if not impossible to achieve due to the presence of impurities. Heterogeneous nucleation refers to nucleation of a phase with the aid of a heterogeneous catalyst such as an impurity particle or a mold wall. These impurities lower the interface energy between the nucleus and its environment. In carefully controlled droplet emulsion experiments, pure $\beta$-Sn may undercool as much as 190K ($0.37T_m$).[7] In droplet emulsion experiments, heterogeneous nucleation is severely suppressed by isolating heterogeneous nucleation sites through a mechanism known as mote isolation. Experiments show that in the Sn-Ag-Cu system, undercooling under normal processing conditions may reach up to 30°C [8]. This corresponds to heterogeneous nucleation with a relatively weak catalyst. The solidification undercooling for most metals is only a few degrees.

Homogeneous nucleation serves as the basis for heterogeneous nucleation theory. Homogeneous nucleation occurs when a critically sized solid nucleus forms from the liquid
creating a solid/liquid interface between the liquid and the newly formed nucleus. The change in Gibbs free energy for the formation of a nucleus is:

$$\Delta G = -V_s \Delta G_v + A_{SL} \gamma_{SL}$$  \hspace{1cm} \text{Equation 4.}$$

The first term corresponds to the free energy change per unit volume while the second term corresponds to the surface energy penalty for forming this volume. The volume and area terms are functions of the geometry of the nucleus which is usually assumed to be spherical. $\Delta G_v$ is a function of chemistry and temperature, increasing as the temperature decreases. The surface energy term may or may not be constant. It is constant if the interface is isotropic—in this case the nucleus will be a sphere—or it is a function of orientation and the nucleus will be faceted. For homogeneous nucleation in the SAC system, tin’s surface energy is relatively isotropic since it doesn’t facet while the intermetallic phases are anisotropic since the do facet. The relation between the radius of a spherical nucleus and its free energy is shown in Figure 30b. Nucleation occurs when the nucleus reaches a critical size such that the next atom to join the nucleus lowers its free energy. Undercooling is the temperature at which the volume free energy change for nucleation is sufficient to form a critically sized nucleus and begin solidification. It is an indirect indicator of the surface energy barrier for nucleation and therefore should be minimized if nucleation kinetics are to be maximized.

![Figure 30](image_url)

Figure 30. Nucleation energetics for several mechanisms: (b) homogeneous, (c) planar substrate heterogeneous, and (d) heterogeneous crack nucleation. (a) Nucleation occurs at $\Delta G^*(r^*)$. Figure adapted from [39].
Heterogeneous nucleation

Nucleation occurs heterogeneously in almost all cases due to the presence of impurities with melts. These impurities lower the interfacial energy term of the nucleation equation by providing a surface with reduced interfacial energy or by reducing the necessary interface area itself. An equation for heterogeneous nucleation of an isotropic (spherical) nucleus is given below:

\[
\Delta G_{het} = (-V_s \Delta G_v + 4\pi r^2 \gamma_{SL}) S(\theta)
\]

\(\theta\) represents the wetting angle formed between the substrate, nucleus, and liquid. It is a function of the relative surface energies between each interface: substrate/liquid, nucleus/substrate, and nucleus/liquid. As the interfacial energy between the substrate and the nucleus is lowered, the wetting angle decreases and so does the free energy required for nucleation (Figure 31).

![Figure 31. Wetting angle energy balance](image)

In addition to what could be called chemical catalytic potency, the free energy of a nucleus may be lowered by changing the geometry of the catalyst. Small scratches and crevices within mold walls of solidification castings are often nucleation sites. In a crevice, a greater nucleus surface area is in contact with the catalyst, thus lowering the high energy interface area. The opening of the crevice must still be wider than the critical nucleus size for the nucleus to grow out of the crevice. In solder joints, a layer of \(\eta\)-Cu₆Sn₅ forms between the liquid solder and the copper substrate immediately upon reflow. Therefore, the liquid solder is never in contact with bare Cu during solidification. Nonetheless, the IMC layer may provide nucleation crevices at the valleys between adjacent \(\eta\) scallops.
Nucleus/Substrate Interfacial Free Energy

Interface energy arises from the difference in bonds at the surface relative to the bulk. In a body centered cubic crystal the coordination number is 8; each atom within the bulk is surrounded by 8 nearest neighbors. At the surface in a vacuum, this number is reduced by some value, depending on which plane is exposed, leaving dangling bonds. At a solid/solid interface, these dangling bonds are replaced by bonds with a different crystal. This interface energy will then depend on the structure of each crystal, the relative orientation between the two crystals, and the bonding within each crystal. Interfacial energy will decrease as surface structure and electronic nature of each interface better complement each other.

The structure of an interface may be divided into mechanical and chemical components. The mechanical component is related to physically how well the surfaces of each phase mates with each other. The chemical component of the interface relates to the bonding of specific atoms between each phase. Ultimately, structural, electronic, and chemical factors will determine the potency of any catalyst species [40].

Registry

Early nucleation studies were performed with smoke and cloud chambers. Water vapor typically undercools approximately 35°C before transforming to ice in ordinary atmosphere. Vonnegut found, in 1947, that the addition of fine AgI particles on the order of 1 μm diameter, could reduce this undercooling to 4°C [41]. This is because the structure of AgI is very close to that of ice (despite their different space groups). Note that the lattice constant for these crystals are nearly the same. It stands to reason that the close registry between these two structures, the matching of one structure to another by epitaxy, reduces the number of dangling bonds with minimal strain, thereby lowering the nucleus/substrate energy and reducing undercooling. Registry is not the only factor involved. The substrate particle size also played a role in controlling the undercooling; larger particles resulted in greater undercooling than smaller particles, but still significantly less than without.
Table 2. Crystal structures similar to ice for heterogeneous nucleation catalysis

<table>
<thead>
<tr>
<th>Substance</th>
<th>System</th>
<th>Lattice constant [angstroms]</th>
<th>δ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice</td>
<td>Hex.</td>
<td>4.535</td>
<td>7.41</td>
</tr>
<tr>
<td>AgI</td>
<td>Hex. Zn0</td>
<td>4.585</td>
<td>7.490</td>
</tr>
<tr>
<td>PbI₂</td>
<td>Hex.</td>
<td>4.54</td>
<td>8.86</td>
</tr>
</tbody>
</table>

Registry between two planes is a measure of how closely their respective structures match each other. Figure 32 and Figure 33 show two simple cases of disregistry.

\[
\delta = \left( \frac{|d_1^S \cos \theta_1 - d_1^N|}{d_1^N} + \frac{|d_2^S \cos \theta_2 - d_2^N|}{d_2^N} + \frac{|d_3^S \cos \theta_3 - d_3^N|}{d_3^N} \right)^{1/3}
\]

Equation 7. General lattice disregistry

\[
\delta = \left( \frac{|d_1^S - d_1^N|}{d_1^N} + \frac{|d_2^S - d_2^N|}{d_2^N} \right)^{1/2}
\]

Equation 6. Tetragonal lattice disregistry

Figure 32. Disregistry between planes of cubic and tetragonal crystals [40]

Figure 33. Disregistry between planes of a cubic and hexagonal crystal [40]
Unfortunately the crystals in the SAC system are not simple. The lattice parameters and cell size of the intermetallic compounds are significantly larger than that of $\beta$-Sn, nor are any of these structures simple.

### Nucleation in solder alloys

As mentioned previously, $\beta$-Sn may undercool as much as 190°C [7]. Nucleation is a complex phenomenon involving many factors. The density, potency, and type of heterogeneous nucleation site may vary and more than one type may be present in any sample. Direct observation of heterogeneous nucleation and site identification is difficult if not impossible in most cases. The usual approach is to infer information about nucleation by measuring undercooling. Kang et al illustrated these points in their work where 165 eutectic Sn-Cu solder bumps on a glass mold are solidified all at once in a DSC [43]. Each bump solidifies independently of each other resulting in a series of small solidification peaks corresponding to an undercooling range between 47 and 87°C. A similar, but lower, range of undercooling values between 43 and 60°C were found for solder bumps solidifying on a Ni/Cu UBM on Si, indicating that the substrate changes the surface energy, and consequently, the undercooling.

Three points may be taken from this experiment. First, for any given alloy sample, there are many possible nucleation sites of varying potency. Secondly, any measurement of undercooling...
should therefore take into account its variability due to these factors. Finally, the substrate plays a significant role in controlling undercooling as indicated by the reduced undercooling when a Ni/Cu UBM substrate was used.

How can the catalysis of Sn be improved? Nucleation in a system is determined by the number and potency of available catalysts. Therefore, one of the following factors must be increased: the number of nucleation sites or the potency of each site. For $\beta$-Sn, possible heterogeneous nucleation sites include topological sites on the Cu$_6$Sn$_5$ IMC layer, pro-eutectic IMC particles, or some yet unidentified catalyst. We want to avoid pro-eutectic Ag$_3$Sn particles. Therefore, this leaves increasing the number and/or catalytic potency of pro-eutectic $\eta$ particles, refining the $\eta$ IMC layer, or introducing a new phase to serve this role.

Solidification: Nucleation and Growth

Multi-component solidification is a complex phenomenon governed by many interacting factors including crystal structure, thermodynamic driving force, nucleation, and growth. The crystal structure of constituent phases determines its interfacial energy and consequently its equilibrium morphology. The thermodynamic driving force combined with interface energy controls nucleation. Combined with diffusion and interface energy, $\Delta G$ controls the growth rate and shape. At large undercooling, $\Delta G$ is high, the growth rate is fast and diffusion distance is minimized. Consequently, melts solidified under high undercooling tend to have fine structures.

The complexity of microstructures in Sn rich solder alloys is directly related to the undercooling of Sn and the existence of two minor faceting phases (Cu$_6$Sn$_5$ and Ag$_3$Sn) in a dominant non-faceting phase (Sn). The level of undercooling has significant effects on the microstructure of solidified joints including dendrite scale and pro-eutectic phase size. The volume fraction of each phase will remain the same, but the volume fraction of micro-constituents (primary like particles versus coupled eutectic-like regions) will change depending on the degree of undercooling and growth mechanisms (coupled versus uncoupled growth). For a very detailed explanation of the effects of $\beta$-Sn undercooling, see [7].
By suppressing Sn nucleation the solidification path deviates from the equilibrium solidification path. Primary intermetallic phases become capable of nucleating and growing potentially large [7, 10] while depleting the amount of Cu and Ag in the liquid. This leads to constitutional supercooling conditions in the remaining liquid which, in turn, result in $\beta$-Sn dendrite formation upon its nucleation. After its initial nucleation, $\beta$-Sn dendrites grow extremely fast. Finally, after some initial period of dendrite growth, the remaining liquid will be at a composition and temperature favorable to eutectic-like coupled growth, and this will fill the remaining sample volume.

**Directional Solidification**

The morphology of any set of solidifying phases is significantly controlled by the growth rate of each phase. The relation between growth velocity and microstructure is generally studied using directional solidification experiments. Real joint solidification is more complex than directional solidification and it would be very difficult if not impossible to measure the growth velocity within a real joint. However, directional solidification experiments can be useful gaining insight into the growth mechanisms of an alloy.

Schaefer and Lewis studied a commercial near eutectic alloy Sn-3.82Ag-0.90Cu wt. % in a directional solidification experiment [35]. This alloy is close to our SAC3595 alloy, but unlike ours, it is has a hyper-eutectic Ag composition so that Ag$_3$Sn is the equilibrium primary phase. Growth velocities of 0.826, 1.76, 2.4, 3.5, 7.1, 14, 32, and 500 $\mu$m/s were tested. The 500 $\mu$m/s sample did not exhibit directional solidification so its results were discarded. Four types of steady state directionally solidified structures were identified ranging from partially coupled growth between the Sn and IMC phases to fully coupled growth with interaction between Sn and the IMC phases as well as interaction between the IMCs. These results are shown in Figure 35 through Figure 38. These sections are transverse to the growth direction. The coupled Ag$_3$Sn morphology is fine blades while the Cu$_6$Sn$_5$ morphology is a rod.

At the slowest growth rates, unaligned Ag$_3$Sn blades grow with randomly distributed Cu$_6$Sn$_5$ rods. As the solidification velocity increases, the Ag$_3$Sn blades begin to align. These structures are
partially coupled since the IMC growth is coupled with the Sn but not with each other. At higher yet velocities, fully coupled growth occurs where the Cu₆Sn₅ rod intermetallic grows attached to the edge of Ag₃Sn blades. At yet faster rates, primary dendrites form with fine interdendritic ternary eutectic.

Figure 35. Type 1 partially coupled unaligned growth occurs at low solidification rates. 2.4 μm/s is shown here. [35]

Figure 36. Type 2 partially coupled aligned growth occurs at faster cooling rates. 3.5 μm/s is shown here. [35]

Figure 37. Type 3 fully coupled growth occurs at faster yet growth velocities. 14 μm/s is shown here. [35]

Figure 38. Type 4 microstructure forms at higher rates yet, 32 μm/s (shown here) and above, primary Sn dendrites occur with interdendritic type 3 eutectic. [35]
CHAPTER 3: EXPERIMENTAL METHODS

Alloy selection

Working from the Sn rich corner near the eutectic point of the phase diagram, a base alloy was selected as a baseline for this research. Then, new alloys were derived from this base alloy by substituting a fourth element, denoted X as in SAC.X, in place of a small fraction of copper. The effect that this addition has on the solidification path, crystal structure, and microstructure will then be measured and properties optimized.

Base alloy

The primary virtues of eutectic systems are a low melting point and single temperature solidification. However, suppressed nucleation kinetics and consequent undercooling of $\beta$-Sn prevent the initiation of coupled eutectic growth at the eutectic temperature. With proper modification, a SAC alloy may be selected such the system solidifies more like a coupled eutectic. The base alloy of composition Sn-3.5Ag-0.95Cu wt. % (SAC3595) was selected for this study [44]. It is hypo-eutectic in Ag to reduce the driving force for Ag$_3$Sn formation. A slightly hyper-eutectic concentration of Cu was selected to promote pro-eutectic $\eta$ particles that may serve as nucleation catalyst sites. All this is accomplished with only moving the liquidus temperature (for $\eta$-Cu$_6$Sn$_5$) up three degrees to 220°C.

Upon reflow of the SAC3595 base alloy upon a Cu substrate, a layer of $\eta$-Cu$_6$Sn$_5$ immediately forms. Yet, such a joint still often undercools significantly. Thus it is reasonable to conclude that the $\eta$ phase by itself is not a very potent catalyst for $\beta$. Fortunately, initial experiments showed that, occasionally, high undercooling was avoided in the SAC3595. Thus it was hypothesized that even a minor increase in catalytic potency of Cu$_6$Sn$_5$ by a minor alloy addition could promote consistently low undercooling.
X modification

Initial work on the quaternary modification of SAC alloys focused on mechanical strength and the IMC layer morphology [45, 46]. It was discovered that modification of a near eutectic (Sn-3.6Ag-1.0Cu) with as little as 0.15 Co wt. % could improved the retained joint shear strength upon aging for 72 h at 150°C. Auger elemental mapping showed segregation of Co to the η particles, with a higher concentration on the periphery of these particles [45]. This was the first evidence that a fourth element could be used to modify the η particles and the microstructure in general.

This initial success prompted further investigation of SAC.X solders. New X additions were selected upon the principle that X would substitute into the η phase in place of Cu, thus modifying the η structure. This modification of η-Cu₆Sn₅ may have multiple effects. First, the resulting strain combined with the chemical effect of the X substitution can alter the diffusion of Cu and Sn in η, an important mechanism in IMC layer growth. Results for Co and Fe do indeed show that X modification of the η phase alters the IMC layer growth; both Co and Fe reduce the growth of the Cu₃Sn layer during high temperature aging (150°C, see Figure 39) while promoting ductile shear failure within the solder joint matrix [46]. Later results on an expanded selection of X, including Si, Ti, Cr, Mn, Ni, and Zn, showed continued control of IMC layer growth and strength with X combined with substitution of X into η-Cu₆Sn₅ [47].

Figure 39. Suppression of Cu₃Sn growth by addition of Co and Fe [46]
In addition to altering diffusion, modification of the η structure will alter interface structure and consequently the interface energy of this structure. A reduction of interfacial energy may result from decreased disregistry between the η and β phase or through a change in the chemistry of the interface [40]. If the interface energy of η with β-Sn is reduced, its catalytic potency for heterogeneous nucleation of β is increased. If β is able to nucleate at a higher temperature (undercool less), more eutectic growth is possible. Additionally, if eutectic growth initiates at a higher temperature, Ag₃Sn blades have less driving force to form.

X was selected based on criteria proposed by Darken and Gurry [48]. A Darken-Gurry plot with the solvent element, focused on Cu as the solvent species is shown in Figure 42. Factors including price and ease of alloying were also considered. Hence, rhodium is out of the question, although it falls within the ellipse shown in Figure 40. From IMC layer studies on Ni substrate, it was already known that Cu-Sn-Ni forms (Cu, Ni)₆Sn₅. In a previous study [46], both Fe and Co were shown to have improved joint strength retention in aged specimens. In another [47], Zn was shown to suppress the formation of the ε-Cu₃Sn phase whose growth is often associated with strength reducing interface micro-voiding.

Part of our goal with the SAC3595.X alloy is to minimize the amount of X required for solidification control. The idea is to keep the alloy as simple as possible by not forming any new phases and to maintain a good surface finish, which the addition of an excessive amount of X may degrade. X additions were restricted to concentrations between 0.05 and 0.25 wt. %; ultimately, Ni, Co, Fe, Mn, Zn, and Al were selected as candidates.

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1 Henceforth, the base alloy Sn-3.5Ag-0.95Cu wt. % will be referred to as SAC3595. Modified alloys of the SAC3595 base will be referred to as SAC.#X where # represents hundredths of weight percent substitution of element X for Cu. Ex: SAC.25Zn refers to the composition Sn-3.5Ag-0.70Cu-0.25Zn wt. %.
Figure 40. Darken-Gurry plot for 4th element selection based on atomic radius and electronegativity

DSC

Differential scanning calorimetry (DSC) combined with microstructure examination are the primary tools that will be used to measure the catalytic effect of X. DSC is a thermal analysis technique in which heat flow into and out of a sample is measured relative to a reference sample under controlled heating, cooling, and isothermal temperature scans. More specifically this study uses power-compensating DSC. Power to two independently controlled furnaces is controlled to follow a user specified temperature-time profile and the difference between the powers is measured [49]. As a sample is melted, the sample absorbs more heat relative to the reference pan; power to the sample cell is increased, resulting in an endothermic peak. Conversely, during solidification, heat is released from the sample relative to the reference, resulting in an endothermic peak. The time, temperature, and enthalpy of transformation for these reactions can be measured. In this manner, undercooling, the difference between the equilibrium phase formation temperature and the real
measured temperature of formation corresponding to the nucleation temperature, can be measured for each sample. By integrating the heat flow with respect to time over the solidification time, the heat of solidification and melting can be measured. It should be constant from sample to sample assuming that solidification and melting is the only reaction that is being measured.

INERT SUBSTRATE DSC

The traditional goal of DSC is to chemically and thermally isolate a sample and measure its thermal behavior. For this purpose, aluminum pans suffice. Aluminum’s native oxide, Al$_2$O$_3$, chemically isolates the solder from the pan. The surface of both sample and pan are clean after scanning. Most DSC experiments fall into this class.

Two experiments were performed using Al pans. In the first, a sample is scanned once. In the second, a sample is scanned multiple times, usually ten, to measure how the undercooling of the same sample changes between solidification cycles.

Calorimetric joint method

Useful information may be obtained from traditional inert pan DSC. However, for studying the behavior of solder joints, and in particular, nucleation, it ignores two potentially critical factors. One, solder reacts with its substrate and may absorb some of it into the solder bulk through the IMC layer(s) thereby altering its composition. Two, mold walls often provide critical heterogeneous nucleation sites, but in solder systems, the mold wall is replaced by an IMC layer. By replacing an effectively inert Al pan with a reactive Cu copper pan, a calorimetric solder joint is created that takes into account IMC formation and other potential factors that may influence nucleation in real joints. Additionally, through calorimetric joints, the as solidified microstructure of a solder joint can be directly correlated to the cooling rate.

A variety of experiments may be performed using the calorimetric joint method. The user has control over the temperature scan rate, hold times, sampling rate, and equilibration conditions. For this study a Pyris 1 power compensating DSC is used. The maximum DSC cooling rate is limited by the temperature controller and the heat transfer rate capacity of the system. The conventional limit is often considered to be around 100°C/minute due to the heating and cooling devices used in the
DSC. Provided strong enough reactions, there is no limit other than perhaps time constraints on the minimum scan rates.

For this study DSC program parameters, including the heating and solidification rates and dwell times, were chosen to replicate those encountered in industrial processing, with special attention paid to BGA reflow processing. Actual DSC pan conditions will not exactly match those found in a real reflow oven because of the way heat transfer is controlled in a reflow oven versus the DSC. In a reflow oven, heating and cooling is natural convection and conduction under controlled environment temperature. In the DSC, the sample temperature is precisely controlled by measuring its temperature and adjusting the heat flow to maintain the specified rate. The advantage of measuring temperature with the DSC is that the actual sample temperature is measured.

**Experiments**

![DSC Scan Profile](image)

Figure 41. Typical DSC program profile with equal 1.5°C/s heating and cooling rates with a 30s dwell.

A typical DSC program file is shown above. A linear heating rate 20-30°C above the eutectic is followed by a short dwell, and finally cooling at the same cooling rate as it was heated. Rates of 0.17°C/s (10°C/minute) and 1.5°C/s (90°C/minute) are typically used. Equal heating/cooling rate experiments at these rates effectively simulate BGA reflow and paste soldering reflow profiles. This is
the most common experiment that was performed in this study. The sample was heated and cooled at equal rates, 1.5°C/s (90°C/min) or 0.17°C/s (10°C/min), with a dwell time of 30 seconds at a peak reflow temperature of 240°C. Other possibilities include adjusting the dwell time to measure the interface formation or using multiple solidification cycles.

Several experiments were performed to test the effect of multiple reflow cycles. In these experiments, the sample was cycled through multiple melt/solidify cycles with variable dwell times. With each excursion to the liquid state, the IMC layer has time and mobility to grow.

**Joint preparation**

The following method was used to prepare calorimetric joint samples. The result is shown in Figure 44.

1) Obtain a small segment of solder wire.
2) Flatten sample to about 100μm in rolling mill. Multiple passes may be required. Take care that the rolling surfaces are clean. Clean with acetone and alcohol as necessary.
3) Heat a hot plate to about 180°C.
4) Rinse the DSC pans with methanol (or ethanol) to remove any organic residue. Let solvent evaporate. Use the hot plate to accelerate this.
5) With a clean cotton swab, flux the pan and lid inside surfaces.
6) Place fluxed pan/lid pairs on hot plate until all liquid is driven off. Remove before any darkening or discoloration occurs. The flux solids will be white and give the copper a hazy appearance. Use these fluxed pans as soon as possible, preferably same day to avoid any undesirable corrosion. Store in cool dry area if not used immediately.
7) Cut and mass a single piece of solder ribbon near 15mg, place in fluxed pan, add lids, loosely crimp pans with tweezers.
8) Perform DSC scans using an empty pan as a reference.
Metallographic preparation

Once the joint is created, it can be prepared for optical and SEM metallography. Calorimetric joints are mounted individually in epoxy, held on edge using sample clips so a transverse cross section can be obtained. Samples are then ground with 600 grit on a rotating wheel until a large cross-section of solder is found. Samples are then polished with glycol based polycrystalline diamond suspension polishing compounds and copious amounts of lubricant.\(^1\) Polishing time at each step should be just long enough to eliminate the previous step’s scratches. Samples were cleaned with soap, (DI) water, and a cotton swab, rinsed with water, then alcohol, and finally dried with compressed air between each polishing step. Coarse polishing is performed with 3μm on a low nap nylon cloth\(^2\) with moderate sample pressure slightly greater than writing pressure used with a pencil. Fine polishing is performed with 1μm diamond suspension on a medium nap cloth\(^3\) with slightly less pressure. Final extra-fine polishing is performed with 0.05μm colloidal silica on a medium-low

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1 Allied High Tech products are used. Lubricant: Allied High Tech “Red Lube”
2 Allied High Tech “White Label” cloth
3 Allied High Tech “Final B” cloth
nap cloth. This step serves a dual purpose as the final polishing stage and etching stage, leaving the IMC particles slightly raised relative to the tin phase.

Some striking images can be created by ion milling with a gun angle at 40, 20, and 10° for 4 minutes at each. This creates additional surface relief that the IMC phases stand out against the Sn matrix, high contrast edges in secondary electron imaging. This highlights the dendritic structure.

Microstructure and analysis techniques

Ag₃Sn blade analysis

The goal is to gather data that is most relevant to how Ag₃Sn blades likely affect the joint strength based on prior research and several assumptions. First, it is assumed that blades attached to the interface are much more detrimental since the joint shear stress is typically greatest here, and therefore, the crack path is most likely to encounter blades along the interface. Secondly, it is assumed that blades forming a small angle with the substrate are most detrimental. In joint shear mode, the resolved shear stress along the blade/matrix interface increases as this angle (θ in Figure 45) decreases. In joint tension, the tensile stress normal to the blade interface also increases as θ decreases.

The following procedure was used to collect data on Ag₃Sn blades:

Figure 43. Joint schematic for Ag₃Sn blade measurement

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¹ Allied High Tech “Final P” cloth
1. Visually scan each joint cross-section with an optical microscope and count the number of Ag₃Sn blades.
2. For each cross-section containing an Ag₃Sn blade, photograph the blade.
3. With each blade photograph measure the following with a spatially calibrated image using Image Pro Plus (image analysis software):
   a. Length
   b. Length projected along the substrate/solder interface
   c. Orientation relative to the substrate (angle)
   d. Attachment to the interface (yes or no)
4. Measure the joint area by measuring the coordinates of the polygon corresponding to the area of the joint under a microscope.

Blades are, in most cases, easily distinguished in optical microscopy by their color and morphology. If there was sufficient uncertainty, backscattered electron imaging easily resolves it. The primary morphological feature of an Ag₃Sn blade is a high aspect ratio. They typically have one flat edge and one rough edge. Length and orientation are unambiguous measurements. In some cases blade attachment to the interface is a judgment call since blades near the interface but not attached within a specific cross section are likely attached just above or below the actual cross-section.

**Powder XRD**

Several powder samples of Cu₆Sn₅ and X modified Cu₆Sn₅ were prepared for XRD to examine the effect of X on the η crystal structure. Nominal 100 gram ingots of the IMC were produced from pure elements by melting and mixing them in sealed silica tube, then quenching. Unmodified Cu₆Sn₅ was produced from a Sn-38.2Cu wt. % alloy. It was assumed that X could dissolve into a maximum 15% of the Cu sites. Sn-31Cu-5.8Zn wt. % and Sn-31Cu-5.8Co wt. % samples were prepared. A central section from each ingot was cut, re-sealed in an argon backfilled silica tube, and heat treated at a temperature just below the peritectic temperature at 400°C for Cu₆Sn₅ for 500 hours for the unmodified Cu-Sn and 165 hours for the Sn-Cu-X ingots in order to transform the residual primary phase to η. This difference was not intentional, and it is assumed that the shorter time was sufficient for transformation. The heat treated samples were then removed from the furnace and water quenched within their silica tubes. Once cool enough to touch, they were broken out of
the silica tubes. The transformation from the high temperature $\eta$ to the low temperature $\eta'$ is slow [26]. Therefore, it is assumed that $\eta$ phase is retained at room temperature.

For the Sn-Cu(-X) heat treat temperature, a portion of these ingots will be a tin rich liquid. Upon cooling, this liquid will transform to $\beta$-Sn. With this composition selected, there will always be some $\beta$ in the final product at room temperature. These ingots were pulverized into coarse powder with a hammer and anvil. This coarse powder was then ground in a mortar and pestle with concentrated HCl in methanol (> 40 vol. %) to create a finer powder as well as to dissolve any tin. The powder was held in this acid suspension and periodically agitated and replenished with acid for at least a day to complete the dissolution of Sn as indicated by the cessation of bubbling (of H$_2$ product). The final product was then filtered so that only the powder remained. Room temperature XRD was performed on this powder with the PANalytical X’Pert Pro diffractometer in Metals Development, Ames Lab. Scan times were approximately 30 minutes each sample. Scan parameters are shown in Table 3.

Table 3. XRD parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation</td>
<td>Cu-Kα</td>
</tr>
<tr>
<td>Scan range</td>
<td>$20 &lt; 20 &lt; 80^\circ$</td>
</tr>
<tr>
<td>Step size</td>
<td>0.01 (20)</td>
</tr>
<tr>
<td>Step collection time</td>
<td>30s</td>
</tr>
<tr>
<td>Temperature</td>
<td>Room Temperature</td>
</tr>
</tbody>
</table>
CHAPTER 4: RESULTS

The primary type of sample used in this study was the calorimetric joint. Using the calorimetric joint method, the undercooling of experimental alloys was measured at controlled cooling rates, then cross-sectioned, and finally microstructures analyzed. Results will focus on the following main ideas:

- How does X and its concentration affect the undercooling relative to the base SAC3595 alloy?
- How does the microstructure change with the addition of each X relative to the base SAC3595 alloy?
- What is the relation between undercooling and microstructure?

Chemical effect: single reflow calorimetric joints

The chemical effect of X modification of SAC3595 on nucleation was by measured by varying the alloy composition, holding all else constant, and measuring the undercooling. The cooling rate was well controlled in the DSC. Replicate scans, generally seven, were performed for each composition. Since nucleation is a stochastic process, replicate samples are necessary to fully understand how X affects nucleation. Single data points may be misleading. In fact, the original unreplicated set of results told a different story than the full replicated results that follow.

Most experiments used a cooling rate of 0.17°C/s (10°C/min). This rate was chosen for several reasons. First, at this cooling rate the DSC signal (low signal to noise) was strong, and the DSC easily controlled the heat flow at this rate. Secondly, this cooling rate is within the range of cooling rates experienced by solder joints in reflow processing, particularly BGA joints. Joint microstructures solidified at this rate serve, in part, as a litmus test for Ag₃Sn formation since at this rate; if Ag₃Sn forms and Sn undercools significantly the Ag₃Sn will have had ample time to grow [16]. At higher cooling rates, Ag₃Sn blades were more easily kinetically suppressed. Unless otherwise specified, all data corresponds to this rate.

A general summary of results for the undercooling of β-Sn in the SAC3595.X system for samples cooled at 0.17°C/s (10°C/min) is shown in Figure 46. The experiments focused on this relatively
slow cooling rate as a litmus test. As the cooling rate decreases, if a sample nucleates pro-eutectic Ag₃Sn and undercools significantly, Ag₃Sn blades will have more time to grow and weaken the joint. Some very large blades in fact formed in some samples that will be shown later. Each center point represents the average undercooling upon the first (and only) cooling scan of at least seven replicate samples. The variance in undercooling is represented by error bars extending, one standard deviation, symmetrically, from the average. Unreplicated results are omitted from this figure. Note that only one data point is shown for Ni at 0.20Ni. Single runs at other concentrations and at faster rates were performed, but they performed poorly in reducing the undercooling as well as in suppressing Ag₃Sn. Hence, further tests were not performed. It is useful to compare both the variance as well as means. A strong catalytic effect of X is indicated by both a reduced mean and a reduced variance in undercooling. A discussion of the chemical effect of each tested X will follow.

Figure 44. Chemical effect on undercooling

SAC3595 base alloy

Ten data points for SAC3595 are represented in Figure 44. The undercooling ranged between 4.4 and 15.4°C with a mean of 6.8°C, represented by the dashed line. The variance is represented by the shaded green region extending symmetrically one standard deviation above and below the
average. To underscore the importance of replicate scans, consider that the undercooling of the first tested sample of this alloy under these conditions had the highest undercooling (15.4°C), causing the initial X modified solder results to appear more potent catalysts than they actually were. Subsequent samples solidified at a much lower undercooling.

The microstructures associated with the samples with the least undercooling are displayed in Figure 45 and Figure 46. These samples solidified with a relatively large eutectic volume and relatively large dendrites. Figure 46 nicely shows an embedded $\eta$ particle in a Sn dendrite. Given the size of this particle relative to the surrounding Sn dendrites and fine eutectic volume, it is likely a pro-eutectic phase. It is possible that this particle acted as a heterogeneous nucleation site. In Figure 45, there was unfortunately one pro-eutectic Ag$_3$Sn blade extending from the interface (just above the scale bar). Even at this relatively low undercooling, there was sufficient driving force to form this phase.

The sample shown in Figure 47 and Figure 48 solidified at a higher undercooling of 8.53°C. Compared to the sample with lower undercooling, it solidified with a finer dendrite structure and

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1 IID and SID fields within captions are unique image and sample identification numbers, respectively. They are primarily intended for this author and for archival purposes. Note, however, that figures with different SIDs indeed correspond to unique samples while figures with identical SIDs are different locations of the same sample.
finer ternary eutectic structure which are typical of higher undercooling. Ag₃Sn blades can be seen in both these figures.

Figure 47. SAC3595 with a higher undercooling [IID: 2-121-04; SID: 1-83-4; ΔT = 8.53°C]

Figure 48. SAC3595 with a higher undercooling; magnified interface and Ag₃Sn blade. [IID:2-121-5; SID: 1-83-4; ΔT = 8.53°C]

Co modification

At a cooling rate of 0.17°C/s (10°C/min), Co modification increased the undercooling of SAC3595 at all tested compositions (up to 0.25 wt. %) with no decreasing trend. Its microstructure was significantly different than SAC3595. Two replicate SAC.15Co samples are shown in backscattered electron images in Figure 49 and Figure 50. The dark phase within the solder bulk is the η-Cu₆Sn₅ phase. It is distributed evenly throughout the matrix within both the fine eutectic volume as well as within the dendrites which are relatively fine compared to the SAC3595 samples. The SEM photograph in Figure 50 shows a large Ag₃Sn blade protruding from the η-Cu₆Sn₅ IMC.

The IMC layer of Co modified samples was unique. Rather than scallops, the η-Cu₆Sn₅ layer formed a coral-like interface with the solder bulk. Compare Figure 50 (Co) to Figure 48 (SAC3595).
Figure 49. Typical SAC.\textsubscript{Co} with a large $\text{Ag}_4\text{Sn}$ blade [IID: 2-94-26; SID: 1-154-4; SAC.15\textsubscript{Co}; $\Delta T = 12.2^\circ\text{C}$]

Figure 50. SAC.\textsubscript{Co} joints have a “coral-like” interfacial $\text{Cu}_5\text{Sn}_5$ IMC layer. [IID: 2-95-7; SID: 1-154-5; SAC.15\textsubscript{Co}; $\Delta T = 14.92^\circ\text{C}$]

Figure 51 and Figure 52 show a closer view of the Sn dendrite structure and $\eta$ morphology in SAC.25\textsubscript{Co}, including the $\eta$ IMC layer. The Co addition modified the pro-eutectic $\eta$ morphology as well as the $\eta$ IMC layer morphology. The $\eta$ particles in Figure 52 are more rounded and irregularly shaped opposed to the more faceted particles shown in Figure 47 (SAC3595). The increase in Co from 0.15 to 0.25 Co did not alter the microstructure significantly.
Ni modification

SAC.Ni samples had a microstructure similar to SAC.Co samples in that they had relatively fine dendrites and $\eta$ pro-eutectic particles dispersed throughout the solder bulk, apparently independent of any other microstructure constituent. These pro-eutectic particles, however, were more faceted than in the Co modified alloys. EDS confirmed that Ni dissolved into the $\eta$ phase. Compare Figure 53 through Figure 56 below, paying special attention to the distribution of (dark) $\eta$ pro-eutectic particles and the dendrite size. The $\eta$ particles all appear distributed independent of any other phase, but they appear more frequently in the sample with less undercooling and coarser tin dendrites. Unfortunately, like Co modified samples, $\text{Ag}_3\text{Sn}$ blades appeared frequently, especially in samples with large undercooling.
Fe modification

Fe modified samples had a relatively high variance in undercooling, and its average undercooling increased linearly with respect to increasing Fe concentration. On average, SAC.Fe samples undercooled more than that of the base alloy, but some samples undercooled very little (5.56°C), for example, the (SAC.15Fe) sample shown in Figure 57. In contrast, some undercooled significantly
(16.13°C), like the (SAC.10Fe) sample shown in Figure 58. Some rather large Ag3Sn blades were observed, especially at increased undercooling.

The tin dendrite size depends once again on the undercooling. Two very distinctive microstructures, representing the extremes in undercooling for SAC.Fe, are shown in Figure 57 and Figure 58. (Though these sample alloys are slightly different, they should behave similarly.) Therefore, Fe is not an effective addition for the controlling undercooling SAC.Fe.

**Figure 57.** Coarse dendrites appear to originate from the IMC layer indicating that the IMC may have catalyzed this tin dendrite. [IID: 2-123-09; SID: 1-155-05; SAC.15Fe; ΔT = 5.56; fEut = 57.91%; nBlades = 0]

**Figure 58.** Dendrite structure is coarser at higher undercoolings. Here several distinct dendrite colonies exist with differently orientations. [IID: 2-123-01; SID: 69-09; ΔT = 16.13°C; SAC.10Fe; 5 blades]
Zn modification

To date, Zn modification has reduced undercooling the most; at 0.21 wt. %, the average undercooling was 3.3°C. At lesser concentrations, Zn had a diminished effect. One might expect that at concentrations higher than 0.21 wt. % Zn that the undercooling would be further reduced. However, this was not the case; the average undercooling increased slightly with the addition of more Zn, but its variability decreased as shown in Figure 44.

A common feature in SAC.Zn joints was primary η particles embedded in Sn dendrites as shown in Figure 59, a feature consistent with catalytic activity for tin nucleation (see Discussion). Wavelength dispersive spectroscopy (WDS) was used to measure the concentration of Zn within a selection of SAC.X samples including the SAC.05Zn sample shown in Figure 60 and Figure 61. Within the indicated embedded η particle, the concentration of Zn reached as much as 500 ppm. According to Alfred Kracher, based on the elemental standards used and background count measurement, the detection limit of the WDS is 0.02 wt. % (200 ppm) for Zn, easily below the values observed here within the embedded η particles as well as the η Cu₆Sn₅ layer. For further information on x-ray microanalysis, see [50, 51].

![Figure 59. SAC.25Zn with embedded (dark prismatic) η particles in β dendrites; [IID: 2-076-05; SID: 2-074-07; SAC.25Zn; ΔT = 4.32°C]](image)
Mn modification

Mn was unique because it so severely reduced the variability in undercooling, though its mean value was still higher than that of SAC3595. Only SAC.25Zn came close to matching its low variability. This consistency was no guarantee against Ag₃Sn blades, at least at the lowest addition of 0.05 wt. %. Blades are fully suppressed at 0.10 wt. % Mn. Unfortunately, even at this low concentration a tenacious oxide with a gold tint formed, resulting in relatively poor wetting. This oxide layer and already suppressed Ag₃Sn blades made tests at higher concentrations greater than 0.15 wt. % Mn unnecessary since additional Mn would likely exacerbate the already poor wetting.

The microstructure of all SAC.Mn samples was relatively coarse, containing large dendrites, coarse eutectic, pro-eutectic η, and, at 0.05 wt. % Mn, Ag₃Sn blades. Upon closer inspection, some small micron scale inclusions can be seen dispersed throughout the joint. Pro-eutectic η particles were frequently found embedded within Sn dendrites. A particularly striking case is shown in Figure 64. Some of these samples appeared to have a particularly high eutectic volume.
Figure 62. With low Mn additions, the undercooling is extremely consistent but Ag₃Sn blades are still present. [IID: 1-123-03; SID: 1-96-06; SAC.05Mn; ΔT = 10.5°C; nBlades = 5]

Figure 63. Blades are eliminated at sufficient Mn concentrations ≥0.10 wt. %. Coarse eutectic and dendrite structure present in these samples. [IID: 1-104-02; SID: 1-98-02; ΔT = 10.44°C]

Figure 64. Embedded η particles in β; this sample was cooled at the faster 1.5°C/s (90°C/min) rate. [IID: 1-86-02; SID: 1-71-20; Cooling rate = 90°C/min; ΔT = 6.75°C]

Several WDS line scans (Figure 65) were performed on SAC.15Mn to find where the Mn atoms sit. According to these, like Zn, Mn dissolved into η pro-eutectic particles. It also apparently dissolved some into Ag₃Sn. Small micron sized Mn rich particles formed throughout the sample. WDS places the concentration of this phase as much as 27 at. % Mn. Considering that their size approaches the X-ray interaction volume, precise measurements are not possible using WDS.
According to the binary Mn-Sn phase diagram Figure 66, the phase nearest the composition indicated by the WDS is MnSn2 [2].

Figure 65. WDS shows elevated Mn levels within pro-eutectic $\eta$ particles as well as $\gamma$-Ag$_3$Sn eutectic platelets. Mn rich precipitates are circled.

Figure 66. Small Mn rich particles, near the MnSn2 phase are found dispersed throughout Mn modified samples.
Al modification

SAC.Al samples had low undercooling across the tested composition range. SAC.05Al and SAC.25Al both had average undercooling less than that of SAC3595 at the 0.17°C/s (10°C/minute) cooling rate. SAC.10Al had a slightly higher average undercooling of 7.12°C, 5% higher than that of SAC3595. Of the 21 samples tested at the 10°C/minute cooling rate, ranging in Al concentration from 0.05 to 0.25 wt. %, only 2 samples (SAC.15Al) contained any Ag₃Sn blades. The lowest average alloy undercooling of 4.47°C was surprisingly achieved with the smallest addition of Al, SAC.05Al.

Like all the other alloys here, its microstructure contains tin dendrites, ternary eutectic and a pro-eutectic phase. The dendrite size is relatively coarse, as expected for this low undercooling. At the highest tested Al concentration, 0.25wt. %, a third intermetallic IMC phase with a nodular, isotropic morphology formed. This phase segregated towards the top as shown in both Figure 67 and Figure 68, indicating a buoyant force, i.e., a reduced density. WDS indicated that it is rich in Al and Cu, measuring 38.6Al-59.1Cu-1.2Sn-1.6Si-.35Ag at. %. Assuming that this corresponds to a binary intermetallic Al-Cu phase, the closest match in Pearson is Al₄Cu₉ [52]. In a future study positive identification of the phase and its structure requires a technique with crystal lattice level resolution such as X-ray diffraction or electron backscatter diffraction (EBSD).
Figure 67. SEM image of SAC.25Al highlights tin dendrite structure and Al rich phase near at top of sample (arrow). IID: 2-131-02; SID: 2-107-06; SAC.25Al; ΔT = 6.56°C; fEut = 0.45; ΔT = 6.56°C

Figure 68. An optical image of SAC.25Al; note small dark dispersed phase, Cu₆Sn₅; nodular particles near top are Al rich. IID: 2-108-03; SID: 2-107-07; ΔT = 6.65°C

The microstructure of SAC.05Al is shown in Figure 69 and Figure 70. At this concentration, the Al rich phase was absent, as indicated by combined SEM inspection and WDS. The detected Al signal in the Sn dendrite phase was equal to that of the signal from a Sn standard, i.e., Al does not dissolve in Sn. At this low Al concentration, small Ag₃Sn precipitate size, and an interfering Ag signal, no Al can be detected within Ag₃Sn. The only η-Cu₆Sn₅ region large enough for reliable WDS analysis is the IMC layer. The Al signal in this layer is very small, 160-230ppm, effectively at the detection limit for simple point or line scan analysis. For Al, in summary, Al did not dissolve in Sn, probably dissolved into Cu₆Sn₅ at some concentration near the detection limit of the WDS detector, and possibly dissolved into Ag₃Sn but this cannot be confirmed using WDS within the microprobe.
Multi-cycle experiments

The IMC layer morphology and its thickness change over time, especially when the solder is a liquid, as copper from the substrate diffuses towards the solder. Multiple reflow cycle and extended dwell (time above liquidus) experiments were performed to relate the reflow cycle, IMC morphology, and undercooling. Results and DSC parameters follow.

Figure 71 through Figure 74 show the coarsening of the IMC layer over time, as well the difference in microstructure caused by differences in undercooling. Over time, the morphology of the IMC layer changed from fine rounded scallops (Figure 71) to more rounded brick morphology for SAC solder shown in Figure 73. At the same time, the population density of IMC layer crevices decreased. The IMC layer coarsening of SAC and SAC.X solders is plotted in terms of the crevice spacing as a function of time at liquid in Figure 74. The time as a liquid parameter was chosen because this is when the atomic mobility is the greatest and growth the most rapid. It also allows comparison to experiments where long dwell times are used as well as multiple reflow cycles. Gagliano and Morris performed a more complete study on the IMC layer growth for liquid Sn/solid Cu couples and showed similar results [53]. Data from this study which uses SAC3595 is compared
to theirs which uses pure tin in Figure 74. The coarsening reasonably follows \( t^{1/3} \) kinetics, but varies by alloy.

Figure 71. Single reflow cycle, 330 seconds as a liquid; [IID: 1-094-13, SID: 1-083-02, Alloy: SAC3595, \( \Delta T = 4.5^\circ C \)]

Figure 72. 10 reflow cycles, 2300 seconds as liquid; [IID: 2-053-05, SID: 2-027-03, Alloy: SAC3595 \( \Delta T = 15.9^\circ C \)]

Figure 73. Increases in reflow dwell times \((t_{\text{liq}} = 4000 \text{ seconds shown})\) further coarsen the microstructure providing a significantly more planar IMC layer. [IID: 2-063-04, SID: 2-040-02, Alloy: SAC3595, \( \Delta T = 16.5^\circ C \)]

Figure 74. Compiled data from multiple cycling experiment, temperature reaches no higher than 240°C for any datum. Sn data taken from Gagliano and Fine for dwell at 250°C. [53]

Several samples of varying composition were tested in a multiple reflow experiment with short dwell times and 10 reflow cycles. The undercooling for any sample generally increased as a function of cycle number as shown in Figure 75. The undercooling was, however, not monotonically increasing. In all but one case, the first cycle resulted in the least undercooling. In a slightly different experiment, calorimetric joints were solidified once, then re-melted, held as a liquid for 5 minutes,
and re-solidified. In each case, the undercooling during the second solidification was greater than the first, consistent with the 10 reflow cycle experiment.

![Graph: Multiple reflow effect on undercooling](image)

Figure 75. Undercooling summary for multiple reflow cycles shows that undercooling generally increases with the number of reflow cycles. Dashed lines due to omitted inconsistent points at cycles 5 and 7.

A set of scallop spacing measurements were made on 5 different samples with different undercooling temperatures. The average scallop spacing was then calculated for each set and compared to undercooling in Figure 76. The experimental parameters between each sample were not consistent as noted within the figure. The experiments differed in reflow cycle number (one versus multiple solidification cycles) and cooling rate. These results indicate that factors other than the scallop spacing dominate the undercooling behavior.

- First cycle: sharpest initial crevices
- Second cycle: most rapid filling of crevices
- Subsequent cycles: coarsening, slower
Figure 76. Compiled data for Undercooling as related to scallop spacing for SAC3595.

Consistent with the kinetic undercooling effect, samples solidified at 1.5°C/s (90°C/min) undercooled more regardless of the scallop spacing; compare green to others. This would indicate that the cooling rate has a stronger effect on undercooling than the morphology. Consistent with the strongly reduced sharpness of the IMC crevices samples reflowed more than once have a higher undercooling than those reflowed only once; compare samples solidified at the same cooling rate (0.17°C/s) but with different number of reflow cycles (red vs. blue). Of the multiple reflow cycle samples cooled at 0.17°C/s, as the scallop spacing increases, so does the undercooling, if only slightly. This indicates that the scallop spacing is only weakly related to the undercooling.

Ag₃Sn Blade Suppression

Following are the results from the examination Ag₃Sn blades within calorimetric joints. First, the frequency, orientation, and interface attachment of Ag₃Sn blade is examined across all SAC.X calorimetric joints. Then, the Ag₃Sn blade suppression performance of each alloy is compared as a function of X and its concentration.
Overall SAC.X (SAC3595 included)

Figure 77 shows the overall distribution of Ag₃Sn blades and the frequency of their occurrence. In most cases, there are very few, if any, blades in any particular joint. Most blades measure near 50 μm in length. There is no strong orientation preference, though high angle (θ > 45°) blades are slightly preferred. Most blades are clearly attached to the interface. An illustration of a typical “bad” blade is given in Figure 78.

Figure 77. Overall blade distribution statistics for SAC.X system, all alloys. (a) blade frequency, (b) length distribution, (c) orientation distribution relative to substrate, and (d) interface attachment frequency.

Figure 78. An example of a bad blade: long, low angle, and protruding from interface [P7100443 155-04 SAC.15Fe ΔT = 10.14]

SAC3595

As a reference, some data was compiled for SAC3595 relating to its distribution of Ag₃Sn blades. It is shown in Figure 79 and Figure 80. The Ag₃Sn blade length distribution looks like a Weibull
distribution with an average blade length near 40 μm. As Figure 80 indicates (1 on the x-axis), 80% of the blades were attached to the interface.

![Histogram distribution of Ag₃Sn blades in SAC3595; the mean blade length is near 40μm.](image)

Figure 79. Histogram distribution of Ag₃Sn blades in SAC3595; the mean blade length is near 40μm.

![Distribution of Ag₃Sn blades with respect to the Cu₆Sn₅ IMC layer](image)

Figure 80. Distribution of Ag₃Sn blades with respect to the Cu₆Sn₅ IMC layer

Most blades are attached to the interface. (1) on the x-axis represents blades that are attached to the interface while (0) represents blades that not attached.

**Ag₃Sn Blade Summary**

No formal standard differentiation of a benign Ag₃Sn blade and harmful Ag₃Sn blade has been presented in literature examined here. The Ag₃Sn/Sn interface is clearly a weak segment within a solder joint, and it would be preferable to categorically eliminate them and their weak interface. However, which blades significantly reduce a joint’s strength and to what extent isn’t clear. Blade-like particles in some of our samples are apparently pro-eutectic Ag₃Sn, but are not necessarily large enough to be of great concern, as shown in Figure 82, which is the same sample shown in Figure 81. Considering that all the blades with cracks shown in the literature review originate from the IMC
layer, these blades are likely more detrimental than when in the bulk. This is in part due to the fact that, due to the typical loading conditions, the highest stress in most of the joints tested occurs near the interface; therefore cracks preferentially originate here. The strength of the joint under both shearing and tension decrease as the length of the Ag₃Sn blades projected along the joint/substrate interface increases. This projected length is likely the critical parameter for joint performance. The longest easy crack path will be provided by Ag₃Sn plates oriented near parallel to the interface. Under joint shear loading, they provide a long sliding path. Under joint tensile stress, they provide a long fracture path. At high angles, the projected length is minimized; the resolved shear stress under joint shear is small. Under tensile loading, the resolved shear stress is large, but the projected crack length is small and will result in the crack jumping from interface to interface with little growth along the joint’s length.

Figure 81. SAC-Co is characterized by a fine dendrite structure with evenly distributed η particles. [IID: 031108-11 SID: 1-147-05; SAC.25Co, -10°C/min ΔT = 14.65°C]

Figure 82. Same sample as previous figure but showing a small pro-eutectic Ag₃Sn blade that might not be significantly degrade joint strength, given its small size and orientation. [IID:031108-15; SID: 1-147-05]

Ideally, Ag₃Sn blades would not exist in any joint, and in some SAC alloys, they can be prevented entirely, namely in SAC%Mn where Mn≥0.10wt. %, SAC.21Zn, and SAC.(0.05, 0.25)Al. A simple count of blades for any alloy is a good start, but this isn’t necessarily the best metric. Large blades protruding from the interface at low angles, like that that shown in Figure 79, experience a greater resolved stress, and consequently, result in worse mechanical properties than sample with a few short blades in its center, like that shown in Figure 79. In order to fail, a crack must propagate
across the full length of the joint so the greater the length of this weak interface projected onto the length of the joint, the weaker it is. For a more thorough discussion of the effect of Ag3Sn blades in literature, see the Ag3Sn Blade Criteria and Fracture Energy.

The number of blades per unit area, or the *blade number density*, for each sample is plotted in Figure 83. The blue points with a concentration of zero represent the unmodified SAC3595 alloy. The blue line represents the average of each replicate set. Generally, seven replicate samples at each alloy composition are plotted; all data is shown for completeness. Notable exceptions: Ni had a tendency to produce many blades in the initial results so fewer results were collected; SAC.20Ni is the only replicated SAC.Ni alloy at the 10°C/min cooling rate. SAC.05Fe and SAC.20Fe have only one data point. One outlier point is off the scale for SAC.15Fe. This sample had a very small cross section with a single blade and is not likely representative of the entire sample. Some data overlaps, particularly when the number of Ag3Sn blades is zero.

![Figure 83. Blade density summary for SAC.X alloys cooled at 0.17°C/s (10°C/minute). Data points represent a unique sample. Points may overlap. Blue, zero](image-url)
concentration points represent the unmodified SAC3595 alloy. The blue line represents the mean of replicate samples.

A blade severity index was created (Equation 10) in order to compare the expected detrimental effects of Ag₃Sn blades for each experiment condition (alloy and cooling rate), taking into account the lengths of the blades rather than simply their count. For each sample, the sum of the lengths of its Ag₃Sn blades is normalized by the joint area. Then, each set of replicates is averaged. These results are then scaled by a constant equal to the area of an “ideal” joint cross section, k, which is defined as 0.003 by 0.250 in (0.0023 in²), approximately equal to the cross-sectional area of a mechanical joint specimen. Comparing Figure 83 and Figure 84, there was no significant change in ranking between X candidates between these two measures of Ag₃Sn suppression performance.

\[
f(X, y) = k \sum_{s}^{n_{\text{samples}}} \sum_{b}^{n_{\text{blades}}} \frac{l_{b}}{A_s}
\]

Equation 8. Blade severity index
Generally speaking, Al and Zn at the optimal concentration were most effective at suppressing Ag₃Sn blade formation and have processing and soldering advantages. One might expect that since there were no blades at 0.05wt. % Al that there would be no blades at higher Al concentrations. A bit surprisingly, this was not true. Two blades were observed in the SAC.15Al sample. Mn effectively suppresses Ag₃Sn formation at low concentrations; however, it solidifies with a tenacious oxide that doesn’t wet particularly well. SAC.Fe wets particularly well, but its Ag₃Sn blade growth behavior is not well controlled.

**XRD**

Collected diffraction data was refined [54] using the Rietveld refinement method with the PANalytical X’Pert HighScore Plus software package. Structure parameters for the η⁶, η⁸, and η' were used as listed in Ghosh and Asta [26]. The original works [31-33] by Larsson et al were also consulted for additional guidance. The XRD patterns of the η phases are all very similar. The primary difference lies between 30<2θ<40°. The (unmodified) Sn-Cu IMC powder was refined as
both $\eta'$ and $\eta^8$, both monoclinic phases. The results are shown below in the $2\theta$ range of interest. Based on the improved goodness of fit parameter (GOF) [55], 7.67 ($\eta'$) compared to 1.94 ($\eta^8$), this sample is the high temperature $\eta^8$ monoclinic phase and not the low temperature $\eta'$ monoclinic phase.

Figure 85. Refinement of Cu-Sn IMC powder as $\eta'$ phase [31].
Figure 86. Refinement of Cu-Sn IMC powder as high temperature $\eta^8$ phase [32].

The Cu-Sn-Zn IMC sample was refined against each reference structure. The results are shown in Figure 87 and Figure 88. The best fit was obtained by refinement as the orthorhombic $\eta^6$ phase with a GOF = 4.10 compared to 5.03 for refinement as the $\eta^8$ phase. The experimental data lacked the additional peaks between $30<2\theta<40$ which would be present if it were the $\eta^8$ phase. The software insisted on placing a peak near $2\theta=39^\circ$, but neither the reference pattern nor this experimental pattern contained this peak. If this peak were eliminated from the refinement, the goodness of fit would improve further.
Figure 87. Refinement of Cu-Sn-Zn IMC powder has high temperature \( \eta^6 \) phase [32].

Figure 88. Refinement of the Cu-Sn-Zn IMC powder as the \( \eta^8 \) phase fits the data well with a goodness of fit of 5.03, but refinement as the \( \eta^6 \) phase fits better [32].
CHAPTER 5: DISCUSSION

Results of this study show that the addition of X can significantly affect the undercooling and consequently the microstructure of SAC.X alloys. Here, the winners and losers, and why each alloy performed as it did will be discussed.

- What are the trends in catalytic potency and why are some X additions more powerful than others?
- What are the most likely nucleation mechanisms?
- Which alloys performed best in terms of:
  - Undercooling
  - Ag₃Sn suppression

Solderability and surface Finish

The surface finish and solderability of the base (SAC3595) alloy is comparable to other SAC alloys, i.e., acceptable but not as good as Sn-Pb. Both are related to the surface energy between the solder, atmosphere, and the substrate. Solderability generally refers to the quality and ease of creating a solder joint resulting from molten solder wetting the joint substrates. Solderability is a complex property of a solder joint that depends on processing and the environment. Substrate wetting is a good indicator of solderability [56]. The surface finish is affected in part by the oxidation performance of the alloy and substrate as well as the solder’s solidification path. Poor oxidation performance will degrade the solderability as oxides do not wet well [56]. Thus, a good solder alloy must resist oxidation in order to maximize solderability.

Figure 89. Solderability comparison of select SAC.X alloys

Solder beads of selection of alloys with strong nucleation control were created in ambient atmosphere on fluxed copper blocks to compare their surface finish and wetting. The results are shown in Figure 89. SAC3595 performed well, yielding a bright surface over most of the bead with
some surface relief due to solidification shrinkage on the top. SAC.21Zn performed well, arguably better than SAC3595 in terms of wetting angle, while its surface relief was comparable. SAC.15Mn performed the poorest among this group, forming a high wetting angle, approximately 90°. It also had the worst surface finish with a slight gold tinge, likely an oxide. The wetting angle of SAC.05Al around the bead was not uniform, though, on average, it is comparable to SAC3595. It had a dull matte surface finish.

Based on these results, the degradation in wetting caused by Mn outweighs its nucleation control benefits, at least in ambient atmosphere. Inert atmosphere reflow ovens will likely improve Mn’s standing. In light of SAC.21Zn and SAC.05Al alloys, which provide good nucleation control and wetting, Mn is effectively eliminated as a suitable modification for the SAC3595 alloy.

Trends in microstructure and undercooling

After running multiple replicate DSC runs, it became clear that there could be significant variability in the undercooling of any particular joint solidified under identical conditions. This variability was present in both inert and reactive substrates. Nucleation is a stochastic process on its own since it relies on the local random motion and arrangement of atoms in a liquid. It also varies according to the availability of heterogeneous sites. Nucleation catalysis sites, even in a well controlled alloy chemistry and solidification process can vary because of catalyst site geometry and local compositional and structural variation. Potential nucleation catalysts in SAC/Cu solder joints examined here include the growing IMC layer and pro-eutectic particles.

In accordance to the hypothesis that X substitutes into the η lattice, thereby modifying its interfacial energy, special attention was paid to the atomic radius of X and its concentration, and how these factors related to the undercooling and microstructure. Comparing the effect of Co and Ni to Fe and Mn to Zn, it was observed that as the atomic radius increased the potential for undercooling suppression generally decreased. This led to the addition of Al as an X candidate. Further discussion of this atomic radius effect is contained later in the Catalysis mechanisms section.
The base alloy (SAC3595) undercooling at 10°C/min cooling is relatively low compared to some literature results for similar SAC solders. Kang et al measured the undercooling of SAC3870 as 29.8°C when at a cooling rate of 0.02°C/s (1.2°C/min); the substrate was not identified, but it is likely non-reactive, unlike our calorimetric joints [8]. This same study also solidified solder balls (SAC3870) on Cu pads and found that Ag₃Sn blades frequently grew from the IMC layer, but the undercooling was not reported in this case. Our results for SAC3595 indicated that the Cu substrate and resulting interfacial reaction reduce the undercooling to 6.8°C on average, but also promoted Ag₃Sn blade growth off this interface. 80% of blades formed in this alloy originate from this layer while undercooling is more than halved relative to the same cooling rate and alloy solidifying in an aluminum pan.

Though the average undercooling of SAC3595 was not particularly high, Ag₃Sn blades were still capable of forming, indicating that Ag₃Sn nucleation is still thermodynamically possible above the nucleation temperature of Sn. Once nucleated, Ag₃Sn blades can grow. Consequently an improved alloy must either further reduce the undercooling of Sn, lower the driving force for Ag₃Sn formation by reducing silver’s concentration, or otherwise suppress the nucleation and growth of Ag₃Sn. While it is tempting to simply reduce the silver concentration as such alloys as SAC105 do, doing so increases the liquidus and reduces the potential eutectic volume, thereby weakening the joint. Catalyzing the nucleation of Sn at lower undercooling remains the superior approach, and some X additions accomplish this, according to the results of this study.

One indicator of pro-eutectic catalysis is the presence of a pro-eutectic phase embedded inside a secondary phase where the pro-eutectic phase is simply identified by its relative size and morphology. While it is conceivable that a secondary phase could merely grow around a secondary phase, the consistent observation of this relation combined with relatively low undercooling strongly supports this catalysis hypothesis. In several low undercooling cases of SAC3595, Cu₆Sn₅ particles occur embedded within Sn dendrites as shown in Figure 47 and Figure 48. Thus it is reasonable that pro-eutectic Cu₆Sn₅ catalyzes tin nucleation in these samples.
Co and Ni

Cobalt and Nickel had similar but distinct effects on the undercooling and microstructures of the joints tested. Both feature a well dispersed pro-eutectic Cu$_6$Sn$_5$ phase with some dissolved X. Unfortunately, both also frequently contain Ag$_3$Sn blades. The Cu$_6$Sn$_5$ particles are not strongly associated with any Sn dendrites as shown in Figure 90. The undercooling in both Co and Ni modified samples is greater on average than SAC3595 indicating that both elements suppress the nucleation of Sn. If the only chemical difference between these two alloys is that X substitutes into Cu$_6$Sn$_5$ then this supports the argument that nucleation is often catalyzed by pro-eutectic, but that Co and Ni reduce the catalytic potency of Cu$_6$Sn$_5$.

![Image](image.jpg)

Figure 90. The larger pro-eutectic Cu$_6$Sn$_5$ particles do not appear associated with any specific dendrites in SAC.Co samples. [IID: 031108-06; SID: 147-07; SAC.10Co; $\Delta T = 16.29^\circ$C]

Fe

SAC.Fe samples yielded some samples with very low undercooling and attractive microstructures like that shown in Figure 59. Unfortunately, not all samples appeared like this. Others solidified with much greater undercooling and contained many Ag$_3$Sn blades. On average, SAC.Fe undercooling was greater than that of the base alloy at tested concentrations. The average undercooling decreased linearly with increasing Fe concentration so it may effectively suppress undercooling at higher (not yet tested) concentrations. The variance in undercooling for SAC.Fe is far too high (similar to unmodified SAC3595) to be considered an effective catalyst at the tested concentrations.
Mn

Mn has recently garnered some attention by Liu and Lee [57] as a beneficial addition to SAC105 based solders, especially in impact loading. Mn certainly provided some of the most unique microstructures in the current study, like that shown in Figure 66. Based on the presence of a third Mn rich IMC phase combined with low variance in undercooling, this phase is likely responsible in part for the nucleation control during solidification. It is also noteworthy that these results show that Mn substitutes into $\eta$ as well as Ag$_3$Sn. Whether or not this has anything to do with its strong undercooling control is uncertain. Despite having an undercooling higher than that of SAC3595, it is still capable of suppressing Ag$_3$Sn blades at Mn concentrations as low as 0.10 wt. %. Unfortunately, despite its effective Ag$_3$Sn suppression at such a low concentration, its oxide that forms during reflow and relatively poor wetting remain the primary downfall of the SAC3595.Mn. Despite this drawback, use of N$_2$ or other inert gas atmospheres in reflow ovens may allow this deficiency to be overcome.

Zn

The average undercooling suppression effect of Zn increases sharply as the concentration is increases to 0.21 wt. % Zn and rises slightly at 0.25wt. % Zn while reducing its variance. The exact reason for this is uncertain. In either case, Ag$_3$Sn blade formation is suppressed. At this low undercooling, apparently there is insufficient driving force for Ag$_3$Sn nucleation, thus achieving the desired effect of reduced undercooling.

What remains to be explained (see next section) is why Zn is an effective addition to SAC3595 for reducing undercooling. According to WDS line scans like that shown in Figure 61, Zn readily substitutes into the Cu$_{6.5}$Sn$_{5.5}$ lattice—in both the IMC layer and in pro-eutectic particles—in quantities up to 600 ppm (0.06 at. %) for SAC.05Zn. The overall atomic composition of Zn in SAC.05Zn is 0.09 at. %.

Al

The major advantage of SAC.Al alloys in terms of undercooling and Ag$_3$Sn suppression is that it takes so little Al, 0.05 wt. %, to achieve a well controlled undercooling while suppressing Ag$_3$Sn.
Only Zn≥0.21 can match the undercooling control of Al. Recall that for high concentrations of Al (0.25 wt. %), a third Al rich IMC phase forms. At lower concentrations, when this phase is absent, the undercooling is actually further reduced. This indicates that the third IMC phase is not likely responsible for the reduced undercooling. In terms of the stated goal of this study to control nucleation using a minimum amount of X, such strong control with such a minute concentrations is ideal.

Al falls slightly outside the Darken-Gurry ellipse for substitution in place of both Cu and Sn. It is small relative to Sn and large relative to Cu. Hence, very little Al will severely strain the η lattice, assuming that the Al addition does not alter the η phase in some other manner. This could explain why so little Al is required to effect a significant reduction in undercooling. In order to determine the true catalysis mechanism for Al, the Al modified Cu₆Sn₅ structure must be studied at the crystal structure scale using either crystal diffraction techniques or TEM.

Catalysis mechanisms

As just discussed, each X modification of SAC3595 somehow changes the solidification behavior of the alloy. Most X, such as Co, Ni, Mn and Fe increase the undercooling over all tested concentrations. Some, notably Zn and Al, both decrease the undercooling and its variance when added at sufficient concentrations. These concentrations were 0.21 wt. % for Zn and 0.05 wt. % for Al. Now, the question is why?

Crevices and topology effect

One explanation to this question is surface topology. There are multiple instances where primary Sn dendrite arms appear to originate on the IMC surface as in Figure 57. The IMC layer forms almost immediately after reflow. In general, its morphology is dome-like hills and deep valleys as in Figure 48. With some alloys these domes appear to facet, forming ridges and crevices. Given a particular surface energy balance and wetting angle, the critical nucleus volume, and hence, nucleation undercooling, can be reduced by nucleating within one of these IMC layer crevices [39]. See Figure 30 in the Interfacial Energy and Nucleation Thermodynamics section.
During multiple solder reflow cycles, the time spent as a liquid increases with each cycle. Consequently, the IMC layer becomes thicker and coarsens with each reflow cycle. This may increase the undercooling due to a reduction in crevice nucleation sites. Crevices lower the total surface energy barrier for nucleation by reducing the exposed nucleus/liquid interface which has higher interface energy than the nucleus/solid interface from which the crevice is formed. (See Literature Review:Heterogeneous Nucleation for more in depth discussion.) Thus, as the number of crevices in the IMC layer decreases, the undercooling increases. The general effect of multiple reflow cycles is increased undercooling, regardless of any 4th element as shown in Figure 76.

In Figure 77 the undercooling is plotted as a function of IMC crevice spacing. The following experimental factors are applicable: number of reflow cycle(s) and cooling rate. The single cycle solidification points were plotted since they would have been molten for the least amount of time. However, they do not compare well to the multi-cycle experiments. Between the two single cycle experiments samples, the dominant factor is the cooling rate, not the scallop spacing. Within the multi-cycle experiment set, the data fits our hypothesis, but the effect of the scallop spacing is small.

Topological features still likely serve an important role in nucleation, but the IMC scallop spacing is not the best predictor. It in effect defines the quantity of potential topological nucleation sites, but it says little of their quality, that is their radius of curvature which is more easily relatable to the nucleation energy. Other possible measures include average curvature or maximum curvature of the interface.

\[ \eta\text{-Cu}_6\text{Sn}_5 / \beta\text{-Sn Registry} \]

Recall that the initial assumption was that X could substitute into the \( \eta \) structure in place of Cu. It was then hypothesized that this substitution would strain the \( \eta \) lattice in such a manner that its registry with \( \beta\text{-Sn} \) nuclei would improve, thereby reducing the nucleation barrier, and consequently, lower undercooling. Here, results and validity of this hypothesis will be discussed in detail. First, note that there are three possible types of interfaces, based on the degree of fit, shown in Figure 91: coherent, semi-coherent, and incoherent. Fully coherent nucleation requires a very close fit, which Turnbull estimates at \( \delta \leq 0.005 - 0.015 \). [42] Given that the \( \text{Cu}_6\text{Sn}_5 \) structures are rather complex
and have different symmetry than $\beta$-Sn, $\eta$-Cu$_6$Sn$_5$ is unlikely to be coherent catalyst. According to Turnbull, “When the disregistry $\delta<0.20$, the boundary region between the nucleus and catalyst surface can be pictured as made up of local regions of good fit bounded by line dislocations…” [42]. This is considered a semi-coherent interface [39]. This type of interface is likely the lowest energy type of interface possible and the most likely mode of catalysis possible within this system. An incoherent interface has the most unfulfilled bonds and the highest energy of these three types.

![Diagram of interface comparison: coherent, semi-coherent, and incoherent.](image)

**Figure 91. Interface comparison: coherent, semi-coherent, and incoherent**

There are multiple allotromorphs of $\eta$ that may be acting as a catalyst for $\beta$-Sn [32]. The question is which one is present during nucleation of $\beta$. The phase diagram near the Cu$_6$Sn$_5$ composition is redisplayed in Figure 93. Nucleation occurs in all alloys in this study above the $\eta \rightarrow \eta'$ transition. Therefore, $\eta'$ should not be able to exist as a catalyst phase. Of the high temperature $\eta$ phases, $\eta^6$ and $\eta^8$ are the most likely catalysts. The highest temperature disordered $\eta$ phase, $\eta^0$, not displayed in this phase diagram, is unstable below temperatures just below the peritectic decomposition temperature and is unlikely to be present at soldering temperatures [32]. The crystal structure external unit cells considered as nucleation catalysts are given below.

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1 Please see Literature Review: Crystal structures for a more in depth discussion of the transition temperatures for these phases.
Figure 92. The external unit cells for each indicated phases are drawn to scale. The “atoms” shown are intended to indicate the Bravais lattice of each crystal structure and do not represent any specific element. From left to right, according to each phase’s space group designation, the Bravais lattices are body centered tetragonal, primitive monoclinic, and base centered orthorhombic.

High density planes in $\beta$-Sn and both $\eta^8$ and $\eta^6$ structures were selected as most likely catalysis planes for nucleation since they have the lowest energy resulting from the fewest dangling bonds. Simulated XRD patterns from structures built in Carine Crystallographic software (v. 3.1) from the experimental lattice descriptions in Ghosh and Asta [26] were used to identify the high density planes in each structure. Cutting the $\eta$ structure along a high density crystal plane is difficult because any single (infinitely thin) plane within the $\eta$ structure intersects only a few atoms. However, if a “thick” cutting plane is considered, many atoms are cut. This is demonstrated in Figure 93. In the edge-on view on the left, the atoms are slightly displaced about a central plane through several unit cells. Registry with such thick planes of $\eta$ will contain an out of plane component which will generally increase the interface free energy. However, for this analysis it will be assumed that the out of plane free energy contribution is negligible relative to in-plane interfacial lattice strain.
Thus far the best candidate planes/orientations for $\beta$-Sn catalysis is $\eta^6 (-3 3 0) // \beta (-1 0 1)$ as shown in Figure 94. The lattice misfit of $\beta$ relative to $\eta^6$ is shown in parentheses. The lattice disregistry is 11.4% by Equation 2, small enough to form a semi-coherent interface. Figure 95 shows a larger perspective of this proposed epitaxial relationship. Strong registry between two atoms is represented here by dark blue and red regions indicating overlapping positions between the crystals. There are some overlapping atoms and each plane has a similar density of atoms, but a more in depth analysis is required to quantitatively compare the energies of catalysis planes.
Figure 94. A comparison of the mismatch between (-3 3 0) and (-1 0 1) planes in $\eta^6$ and $\beta$, respectively. Unfilled atoms are intersected by the cutting plane.

Figure 95. A bigger perspective on the (-3 3 0) and (-1 0 1) plane disregistry. X marks the origin of the registry. Tin overlapping tin is shown as dark blue, and Sn overlapping Cu is shown in red.
It is difficult to predict how the substitution of X into η will affect its crystal structure. It may be argued that if a larger atom replaces a smaller atom that the lattice will expand to accommodate and vice versa. In ordered phases such as η⁶, η⁸, and η¹, the strain induced by substitution of another atom will depend on exactly which site the substitutional atom occupies. How η expands or contracts will depend on exactly which sites X occupies. Recall that of the selected X candidate alloys that did not precipitate a third intermetallic phase, only 0.05Al and Zn consistently reduced the undercooling of β-Sn. Both Al and Zn have a larger atomic radius than Cu. Consequently, if Zn is substituted in place of Cu into the η lattice, the lattice will expand to accommodate for the larger Zn atom. For the planes shown in Figure 94, the disregistry along the x-axis would decrease while increasing along the y-axis if uniform expansion is assumed. Unfortunately, WDS says little about where within the η structure that Zn is located, and more detailed diffraction data, perhaps neutron diffraction, would be required to experimentally identify site substitution occupancy.

The most convincing mechanism for catalysis comes from the XRD results. The XRD results from single phase quenched and annealed η ingots described in the results section identify unmodified Cu-Sn IMC phase as the monoclinic η⁸ phase. This is as expected since the η⁶ phase is difficult to stabilize and readily transforms to η⁸ at some temperature close to 350°C. Indeed Larson et al actually observed this transition in-situ within the TEM [32]. When Zn is added to Cu₆Sn₅, XRD indicates that the η⁶ phase is retained. Thus, Zn effectively stabilizes the η⁶ orthorhombic phase and/or suppresses the η⁸ monoclinic, and β-Sn has the chance to nucleate off η⁶, perhaps even with the plane registry proposed above, instead of η⁸. At a minimum, the η⁶ phase has symmetry (orthorhombic) nearer to that of β-Sn (tetragonal), and this may make all the difference.
CHAPTER 6: CONCLUSIONS

The goal of this research was to minimize the undercooling of SAC.X joints, thereby maximizing the eutectic volume and mitigating Ag₃Sn pro-eutectic blade formation. Based on these criteria, SAC.21Zn and SAC.05Al provide the best performance. Both X candidates substitute into the η structure. A nucleation mechanism for SAC.Zn has been proposed that may also apply to Al, though it has not yet been tested.

It was discovered that some X additions (Al and Zn) decrease the average undercooling relative to the base SAC alloy while others increase it. The variance in undercooling also changes depending on X. A high potency catalyst will result in a low average undercooling with minimal variance. Generally, it was found that as the atomic size of X increases relative to Cu, the catalytic potency increases.

Of the selected X elements, Zn and Al modification result in the least average undercooling. Mn modification results in the least variance in undercooling. In the case of both Al and Mn, a third X rich IMC phase can form. This is possibly the active catalyst for SAC.Mn. However, the Al rich IMC does not form when Al≤0.05 wt. % while the undercooling actually decreases. Therefore, this Al rich IMC phase is not likely the catalyst species. No new phase forms upon the addition of Zn. Instead, Zn is found concentrated within the primary η-Cu₆Sn₅ particles, which are frequently embedded within Sn dendrites, indicating likely catalytic activity. XRD indicates that Zn stabilizes an orthorhombic form of η, denoted η⁶ in place of the slightly different monoclinic η⁸ modification of the η phase structure, thus providing evidence of a catalysis mechanism for Zn modification.

Low undercooling is not always an indicator of effectively suppressed Ag₃Sn blades, but the frequency of blades is reduced with reduced undercooling, and sometimes eliminated. Though Mn doesn’t result in the lowest undercooling, it suppresses Ag₃Sn blade formation with an addition of only 0.10 wt. %. Unfortunately, the oxidation and wetting behavior of SAC3595.Mn alloys reduce the attractiveness of Mn despite its effect on Ag₃Sn suppression. Results here have shown that Al and Zn do not have this problem at their optimal concentrations, 0.05 and 0.21wt. %, respectively.
CHAPTER 7: FUTURE WORK

Thus far cooling rate, chemical, and topological dependence of undercooling and microstructure have been investigated. Future work should focus deeper into the mechanisms of catalysis in order to further optimize the SAC.X system. Fe, Ni, Zn, Mn, Al and Co all substitute into the η structure but how exactly each modifies η has not been fully described.

Initial crystal structure studies using powder XRD have been successful for Zn modification of the η phase. Additional studies with other X modifications, especially Al, are needed to provide confirmation of the η′ stabilization nucleation mechanism. Additionally, more powerful diffraction techniques including electron diffraction or synchrotron x-ray diffraction are necessary to identify where exactly within the η lattice that the X atoms reside. TEM would be the best method to measure any epitaxial relations between the η and β phases, particularly in the case of the η particles embedded within tin dendrites.

The original intention of X modification was to strain the η IMC layer and slow diffusion during thermal aging. As increased joint performance and reliability is demanded, especially at higher temperatures, this effect becomes more important. Focus shifted early on, shortly after the development of the calorimetric solder joint technique, to nucleation catalysis, but the effect of the most effective X in this study on IMC growth and joint strength after thermal aging is worthy of study.
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