Development of Al, Mn, & Zn doped Sn-Ag-Cu-X solders for electronic assembly

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Development of Al, Mn, & Zn doped Sn-Ag-Cu-X solders for electronic assembly

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Abstract
The global electronic assembly community is striving for a robust replacement for leaded solders due to increased environmental regulations. A family of Pb-free solder alloys based on Sn-Ag-Cu (SAC) compositions has shown promise; but reliability issues in certain assembly and operating environments have arisen.
Elemental (X) additions (Al, Mn, Zn) to SAC3595 were developed recently for better control of heterogeneous nucleation in solder joint solidification. Cu substrate solderability of these SAC+X alloys was investigated at concentrations between 0.01-0.25 wt. % using globule wetting balance tests due to concern about increased oxidation during reflow. Asymmetric four point bend (AFPB) tests were conducted on as-soldered and thermally aged specimens to investigate correlation between decreased shear strength and extended aging time; a common phenomenon seen in solder joints in service. Composition dependence of these X additions also was explored in simplified Cu joints by differential scanning calorimetry (DSC) and joint microstructure analysis to determine the coupling between undercooling and solidification morphology on single and multiple reflow cycles. Interesting observations by methods such as x-ray diffraction (XRD) and nano-indentation of SAC solder joints with aluminum elemental additions led to promising results and provided a possible solution to promoting heterogeneous nucleation and high reliability in these solder alloys.
Chapter 1: General Introduction

Thesis Organization
The thesis begins with a general description of the purpose of this study. The literature review (Chapter 2) begins with history and background information about solder. An overview of the shift between Sn-Pb to Pb-free solder will be mentioned, as well as the most common Pb-free solder: Sn-Ag-Cu (SAC). As SAC solder is the frontrunner for Pb-free implementation, it was the main focus of this research. In addition, background on electronic packaging, solder wettability, thermodynamics, and microstructure components of lead-free solder, primarily SAC, will be discussed.

Additions of Al, Mn, and Zn to SAC solder were found to have favorable characteristics from previous work, providing the driving force and direction for this research. Chapter 3 presents the thermodynamic and mechanical properties of these SAC+X (Al, Mn, Zn) alloys. Thermodynamic investigation using DSC coupled with metallographic preparation looked at the relationship between thermal properties and the correlating microstructure. Due to the oxidizing nature of these additions, wettability testing of these alloys was conducted to compare with industrial alloys.

The addition of Al to the SAC system was found most intriguing, and is discussed more thoroughly in Chapter 4, as submitted to Journal of Electronic Materials. SAC+Al systems behaved unlike the Zn case and more like the Mn case by the production of a fourth phase, an intermetallic compound, Cu$_{33}$Al$_{17}$. Results concentrated on this IMC as it was found to have outstanding hardness and predictable nucleation potential.

General conclusions that can be drawn from this work about the relationships between all alloy systems that were studied are presented in Chapter 5. Along with conclusions, recommendations for future work are discussed. Possible
implementation and transfer of knowledge from the SAC+X system to SC+X is proposed, as well as the use of Cu$_{33}$Al$_{17}$ outside the field of solder.

**Purpose of Study**
The purpose of this study was primarily to verify the alloy design parameters and heterogeneous nucleation mechanisms for Sn-Ag-Cu-X (SAC+X) solder joint solidification control. Candidates based off of the SAC+X system, mainly Al, Mn and Zn, appeared as viable alloys from previous work to limit undercooling and control intermetallic growth under thermal aging conditions. This study also investigated joint mechanical properties, thermodynamics, and wettability of these SAC+X alloys, and compared the results to common industrial SAC alloys. Understanding heterogeneous nucleation mechanisms in these alloy systems also was a focus of this research, as Sn is often difficult to nucleate and does not follow an equilibrium solidification path. Finally, at least one viable commercial alloy based on the Sn-Ag-Cu-X system was to be recommended from this research for possible industrial implementation.
Chapter 2: Literature Review

Solder
The word solder means a metal or metallic alloy used when melted to joint metallic surfaces. The word originated from the Latin word solidus and later from the French derivative solidare, meaning to make solid [1]. Solders remain among the most important materials in electronic assembly because solder joints provide many beneficial characteristics that ensure a cost-effective means to serve mechanical and electrical functions. Sn-Pb solder has been primarily used in the electronics industry, most notably as a eutectic solder, i.e., 63Sn-37Pb (Figure 1), in wt.%. These eutectic or near-eutectic alloys exhibit a low melting temperature at 183°C, excellent fluidity, wettability, and consistent lamellar microstructures similar to those seen in Figure 2.

Before the 20th century, the word “solder” had a connotation with an alloy of Sn and Pb, but this is not always the case nowadays. The replacement of this favorable system was inevitable since Pb is a neurotoxin. The outlawing of Pb and other hazardous materials was felt globally when the European Union passed the Waste Electrical and Electronic Equipment (WEEE) directive [3] that dictates that all products sold within the EU must be Pb-free by July 1st, 2006. Another mandate that
works in conjunction with the WEEE is the Restriction of Hazardous Substances directive (RoHS), which restricts the use of Pb, Hg, Cd, Cr$^{6+}$, Polybrominated biphenyls (PBB), and Polybrominated diphenyl ether (PBDE) [4]. Worldwide, several Pb-free solder candidates have emerged as replacements for Sn-Pb after more than 10 years of research [5]. The leading candidates include binary and ternary alloys based on Sn-Cu ($T_e = 227^\circ C$) and Sn-Ag ($T_e = 221^\circ C$), at or near the Sn-rich eutectic regions. Included in this set are alloys based on the Sn-Ag-Cu ternary eutectic, which melts at 217$^\circ C$ [6]. No alloy can provide a drop-in replacement for all the characteristics of the Sn-Pb system, therefore compromises in melting temperature, mechanical properties, wettability, or thermodynamic properties must be taken into consideration.

**Electronic Assemblies**

The progression in the electronics industry is toward further minimization, as shown in Figure 3. Starting in the 1970s, a pin-in-hole or through-hole joint was primarily used in industry and this type of process is still widely used today for machine soldering as well as wave-soldering. With the emergence of surface mount technology (SMT), smaller components and less printed-circuit board (PCB) area are used. This helps make it possible to reduce the cost and size when compared to through-hole assembly. As more computing power becomes necessary, higher performance is needed for smaller areas as seen in Figure 4. The ball-grid array (BGA) is the next packaging system with a decrease in size, but will likely be replaced by chip-scale packages (CSPs). CSPs, commonly referred to as flip-chip packages, have solder bumps deposited on the chip pads and surrounded by an electrical insulating adhesive. This allows for flip-chips to have no solder visible on the outside once attached to the board. This type of package leads to more processing steps and requires a very flat surface. Differences in thermal expansion are also intensified as the board, solder, and adhesive are all within direct contact with each other.
Figure 3 Schematic of the evolution of the solder joint in relation to packaging architecture [5].
Figure 4 Semiconductor Industries Association data showing relevant trends driving shift in technology [5].
Package Reliability
Factors influencing new Pb-free solders are driven by the changes in packaging systems as much as by development of the alloy systems. This is because packaging arrangements rapidly lead to increased demands on solder joints in service. Factors of solder reliability include: intermetallic (IMC) growth rates, fatigue strength, solderability (wettability), thermal expansion, mechanical strength and ductility, creep resistance, resistivity, corrosion resistance, and manufacturability. Fatigue arising from thermomechanical means is a major concern within the solder community in addition to thermal shock and electromigration [7]. Pb-free joints are often found to be poorer in shock loading, as Pb-free solders are often less ductile than Sn-Pb alloys [8]. However, Pb-free solders tend to be better than Sn-Pb solders in fatigue performance. Most reflow temperatures for Pb-free solders are around 240°C, significantly higher than Sn-Pb that is refloved at 220°C. This is because the Sn-Ag-Cu alloys are based on the ternary eutectic temperature of 217°C, with 20°C of superheat being preferred for reflow ovens. The main constraint with higher reflow temperatures for PCBs is due to the fact that there is residual moisture left inside the board during the fabrication process. At temperatures above 240°C to 260°C (depending on PCB), the PCB begins to ‘bubble’ and gas pockets form resulting in delamination [9].

Thermodynamics
The alloy design of Pb-free solders begins with the thermodynamics and phase equilibria seen in relevant phase diagrams. Based on the current maximum processing temperatures for electronic assemblies and cost, Sn-based alloys are the most viable replacements of Sn-Pb solder [10]. Sn exhibits a melting temperature of 232°C, which is slightly higher than the ideal temperature of 220°C needed to maintain a 20°C reflow temperature of 240°C. Therefore, alloying Sn with other elements is needed to reduce the liquidus temperature as well as the possibility of providing favorable strengthening phases. From this initial research, alloys based on the Sn-Cu and Sn-Ag (primarily Sn-Ag-Cu) phase diagrams emerged as viable contenders to replace Sn-Pb [11].
$\beta$-Sn
Sn has been known for several thousands of years due to its easy separation from ores. Sn has been commonly alloyed with Cu to make bronze, going back to 3000 BC in Egypt. Due to Sn's unique properties (Figure 5), its uses are numerous for corrosion-resistant alloys, bearings, solders, and even easily machineable components like Napoleon's infamous buttons [12]. At room temperature, Sn has a body-centered tetragonal (BCT) crystal structure, which is uncommon among elements. This structure is known as $\beta$-Sn and is anisotropic, meaning it has different property responses in different crystallographic directions. $\beta$-Sn exhibits excellent corrosion resistance and is easily malleable. However, at temperatures below 13°C, Sn undergoes a phase transformation from $\beta$-Sn to $\alpha$-Sn. This transformation and the resulting $\alpha$-Sn are commonly referred to as 'tin pest'. The density change from $\beta \rightarrow \alpha$ is dramatic, dropping from 7.29 g/cm$^3$ to 5.76 g/cm$^3$. This causes $\beta$-Sn objects to expand in volume when changing to the $\alpha$-Sn structure, often crumbling or disintegrating. However, common additions to solder such as Ag, Cu, and Zn suppress the $\beta \rightarrow \alpha$ transformation, often well below the operating temperatures for solder joints [13].
Sn-Cu Phase Diagram

The Sn-Cu system (Figure 6), also abbreviated SC, consists of six intermetallic compounds (IMCs) at room temperature along with pure Cu and Sn. Essentially, both elements are insoluble in each other at room temperature, and both of the two lowest melting IMCs (Cu₃Sn and Cu₆Sn₅) have approximately one atomic percent of compositional range. Cu₃Sn (also referred to as ε) melts at 676°C and Cu₆Sn₅ (also referred to as η) melts at 415°C. A eutectic (Figure 7) is seen at 227°C near the Sn-rich side of the phase diagram. Some debate over the years has had the eutectic at Sn-0.7Cu [14], while others [15] at Sn-0.9Cu. However, modern phase diagrams are in agreement with the Sn-0.9Cu composition. Both the Cu₃Sn and Cu₆Sn₅ phase come into play when dealing with Sn-Cu and SAC solder joints. It is often seen that Cu₆Sn₅ forms upon initial solidification growing at a Cu substrate, while Cu₃Sn appears upon thermal aging [16]. This can be depicted in the schematic shown in Figure 8.
Figure 6 Sn-Cu phase diagram [17].

Figure 7 The Sn-rich portion of the Sn-Cu phase diagram [6].
As seen in Figure 6, one of the two IMCs which forms in solder joints and is in equilibrium at room temperature is Cu₆Sn₅. The Cu₆Sn₅ (also known as η) structure is not a typical IMC that exhibits only one composition and crystal structure, like a line compound. Rather, it is allotropic and exhibits multiple crystal structures at various temperature and compositions. This can be seen in Figure 9. A continuous layer of Cu₆Sn₅ is commonly seen in as-soldered joints adhering to solder substrates, e.g., Cu. The appearance of this IMC is often referred to as *scalloped* due to the bumpy structure seen under a microscope (Error! Reference source not found.).

Cu₆Sn₅ can also be seen in a pro-eutectic form in the solder matrix, commonly seen as a hexagonal hollow-rod structure. Cu₆Sn₅ increases solder joint strength but can lead to brittleness, which is common for most IMCs. By minimizing the extent of Cu₆Sn₅ growth, a good balance between strength and ductility can be achieved.
Figure 9 Phase diagram near the Cu₆Sn₅ composition showing η structures [18].

Figure 10 Metallographic presence of Cu₆Sn₅ adhering to Cu substrates in a Sn-Ag-Cu calorimetric joint.
**Sn-Ag Phase Diagram**

The Sn-Ag phase diagram has a eutectic reaction at 221°C, observed at Sn-3.5wt%Ag. Like the Sn-Cu binary system, the eutectic is located on the Sn-rich side of the phase diagram, seen in Figure 11. The important IMC phase to emerge from this system during soldering is Ag$_3$Sn (referred to as γ), occasionally seen as a detrimental phase in SAC solder joints when in its pro-eutectic 'blade' form (Figure 12), but more often seen as a rod-like eutectic phase in Sn-Ag or SAC eutectic solders. Like Cu, Ag is virtually insoluble in β-Sn. Much like the Sn-Cu IMC, Cu$_6$Sn$_5$, Ag$_3$Sn has a substantial composition range, but is generally referred to as a stoichiometric compound as dictated by its formula.

![Figure 11 Ag-Sn phase diagram](image-url)
$Ag_3Sn$

One of the common phases seen in Sn-Ag-Cu alloys is $Ag_3Sn$ ($\gamma$). This is considered to be the least desirable IMC that forms in this system, particularly as a large proeutectic phase, due to the inherent weakness of the $Ag_3Sn$ and Sn interfaces. As a fine rod-like phase in the ternary eutectic, $Ag_3Sn$ ($\gamma$) is also a potent strengthener. The cracking phenomena related to large $Ag_3Sn$ ‘blades’ present in solder joints, which undergo thermomechanical fatigue, can be seen in Figure 12. Deleterious crack growth was found to occur between the $\beta$-Sn and the large $Ag_3Sn$ blades. Blade formation can be controlled by minimizing Cu content and increasing the cooling rate for Sn-Ag-Cu alloys [20]. In a deep-etching experiment, it is found that these $Ag_3Sn$ blades can protrude deep within a joint (Figure 13), which gives a large amount of surface area that can fail in thermomechanical fatigue. Depending on the cooling environment and solidification rate, $Ag_3Sn$ can be found to have rod-like, spheroidal, plate-like, and even fiber eutectic in Sn-Ag (and Sn-Ag-Cu) alloys [21]. Therefore, the understanding of how to control $Ag_3Sn$ blade formation and morphology by control of joint solidification is critical to designing good Pb-free replacement alloys for Sn-Pb.

![Figure 12 Cross-views of Sn-3.8Ag-0.7Cu solder joints failed after thermal cycle testing seen at various magnifications a,b, & c ($Ag_3Sn$ blades indicated by arrows A,B,C, and D) [22].]
Sn-Cu-Ag Phase Diagram
In 2000, the most complete, up-to-date study [6] on the Sn-Ag-Cu system was conducted by researchers at the National Institute of Standards and Technology (NIST). This study focused on Sn-rich alloys in the Sn-Ag-Cu system, primarily driven by their potential use as Pb-free solders. The ternary eutectic of this system was experimentally determined by DTA at Sn-3.5±0.3Ag-0.9±0.2Cu at a temperature of 217.2±0.2°C. The calculated ternary eutectic of this system was found to be 216.3°C at a composition of Sn-3.66Ag-0.91Cu (wt. %). The calculated liquidus projection determined from this study can be seen in Figure 14. From many studies of this system, the naming convention of Sn-Ag-Cu (SAC) alloys was developed and will be used throughout this work. For example, the approximate ternary eutectic is called SAC3709, or Sn-3.7Ag-0.9Cu. This Sn-rich side of the ternary phase diagram is fertile ground for Sn-Ag-Cu solder alloy development today.
Nucleation and Solidification Behavior

Even though the eutectic temperature of the Sn-Ag-Cu system is 217°C, this is often the listed melting temperature. Upon solidification, this SAC system can go well below its listed 217°C mark and still remain liquid; this is referred to as supercooling or undercooling. The difference between the onset of melting and the onset of solidification in this study will be referred to as undercooling (ΔT). Pure Sn can often undercool well below its melting point of 232°C, which is shown in Figure 15. Sn has been found to undercool as much as 190°C under very controlled circumstances [24], but is often found to be <30°C under laboratory conditions. Thus, it can be assumed that Sn-rich alloys, like those used in this study that rely on Sn nucleation to promote the solder joint solidification reaction, will show similar behavior to that of pure Sn.
Heterogeneous nucleation is a favorable mechanism for solidifying solder joints and is the process in which nucleation occurs at the site of a defect, impurity, or the “mold wall,” in this case probably the IMC layer that forms instantly and encases the remaining liquid alloy in the solder joint. Impurities, which can also be referred to as dopants, help produce a catalyst effect that promotes solidification. For this system, Cu₆Sn₅ typically acts as a catalyst surface for β-Sn but can be doped with modifying elements to enhance its potency [25]. Impurities in a system help lower interfacial energy and, thereby, promote nucleation. With more impurities (growth initiation sites), there is a better probability to nucleate favorable phases with the number density and type of nucleation sites varying between samples. Therefore, promoting the nucleation of additional Cu₆Sn₅ phase, as a pro-eutectic, could aid in the heterogeneous nucleation of β-Sn. Also, pro-eutectic Ag₃Sn is an undesirable phase because it probably does not act as catalyst for β-Sn in addition to being mechanically detrimental to solder.
**Thermal Aging**

Thermal aging of SAC solder joints and the suppression of IMC growth was the first major reason to begin modifying SAC alloys with other constituents. Though Cu$_6$Sn$_5$ is typically found in as-solidified solder joint microstructures, Cu$_3$Sn can emerge upon thermal aging and can lead to embrittlement. Various constituents added into the SAC system were found to inhibit Cu$_3$Sn and/or Cu$_6$Sn$_5$ growth. This can be seen in Figure 16.

![Figure 16 Thermal aging of SAC alloys [16].](image)

It was found that Mn performed well in suppressing both Cu$_6$Sn$_5$ and Cu$_3$Sn growth for very small additions. Al additions to SAC alloys were found to exhibit similar behavior with growth suppression during thermal aging in later work. With Zn additions, a discontinuous layer of Cu$_3$Sn grew off of the Cu substrate, which was the best outcome for all of the tested alloys. Cu$_6$Sn$_5$ growth with Zn additions was comparable to the Al and Mn alloys. A representative image from Al, Mn, and Zn doped samples can be seen in Figure 17 through Figure 19. From this preliminary investigation, it was determined to pursue Al, Mn, and Zn for a more detailed
examination of thermal and mechanical properties for SAC+X {Al, Mn, Zn} modified alloys. In each of the figures below, the visible phases from left to right are: Cu, Cu₃Sn, Cu₆Sn₅, and the Sn-rich solder matrix.

Figure 17 SAC+0.05Al 1000hr thermally aged specimen.

Figure 18 SAC+0.10Mn 1000hr thermally aged specimen.

Figure 19 SAC+0.21Zn 1000hr thermally aged specimen.
Intermetallic Compounds in SAC+X (Al, Mn, Zn)

In previous investigations of these SAC+X (Al, Mn, Zn) alloys, it was discovered that one IMC formed that was not found in the discussed binary systems. For the Mn doped SAC alloys a third IMC phase was observed. This phase was identified by energy dispersive spectroscopy (EDS) as MnSn$_2$ and is seen circled in red in Figure 20. These particles were typically found within the ternary eutectic structure in solidified microstructures. SAC+Zn microstructures did not exhibit a new IMC phase but rather a modified pro-eutectic Cu$_6$Sn$_5$ phase as seen in Figure 21. These particles were often found residing within Sn dendrites. This modified Cu$_6$Sn$_5$ structure had a composition of 66.9Cu-20.6Sn-12.5Zn (at.%), as determined by WDS [26]. It was found that the Zn substituted for Sn in this modified structure. This correlates with the initial hypothesis of modifying the Cu$_6$Sn$_5$ structure to promote enhanced heterogeneous nucleation, but Zn did not substitute for Cu, as predicted.
Figure 21 Zn modified Cu$_6$Sn$_5$ particles found within a SAC+Zn alloy.
Chapter 3: Thermodynamic and Mechanical Properties of SAC+X {Al, Mn, Zn} Solders

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**Abstract**
The replacement of Sn-Pb solders for assembly of electronic systems is being driven by government and environmental regulations. Of the Pb-free choices, a family of alloys based on the Sn-Ag-Cu (SAC) ternary eutectic have emerged as the most viable for broad use in global electronics \[27\]. Exploration of SAC+X candidates, ie. fourth addition element modifications of SAC solder alloys, is needed to promote heterogeneous nucleation, to control solder alloy undercooling, and to select solidification product phases in the solidified microstructure. Aluminum, manganese, and zinc additions to SAC alloys have become suitable candidates for an enhanced Pb-free solder alloy and results that support this will be discussed as well as suggestions for future work. This paper will also focus on the measurement of two physical properties of the microalloyed SAC solders: maximum shear strength using asymmetric four point bend (AFPB) and solderability (wettability) tested using a wetting balance.

**Introduction**
The global electronic assembly community is striving to accommodate the replacement of Pb-containing solders, primarily Sn-Pb alloys, with Pb-free solders due to environmental regulations and market pressures such as WEEE, RoHS, and REACH \[28\], \[29\], \[30\] and market pressures. During this major transition away from eutectic or near-eutectic Sn-Pb solder (Figure 22) for electronic assembly, there is also the opportunity to make a major improvement in Pb-free joint
reliability for challenging operating environments, i.e., high temperatures and stress levels, as well as impact loading situations. Of the Pb-free choices, an array of solder alloys based on the Sn-3.7-Ag0.9Cu (wt.%) ternary eutectic \( (T_{eut} = 217°C) \) composition, also expressed as SAC3709, have emerged with the most potential for broad use across the industry [27]. However, since the SAC ternary eutectic is significantly higher than that of eutectic Sn-Pb (183°C), it can be stated that SAC solder is not a drop-in replacement [29], [31], [32].

The electronics industry has seized the challenge of adaptation and is proceeding rapidly to develop assembly techniques and to generate reliability data for SAC as a favored Pb-free solder in many electronic assembly applications. Sn-Pb solders have been limited typically to low-stress joints and reduced-temperature service, because of the soft Pb phase that is prone to coarsening and ductile creep failure. Pb-free joints with high Sn content and strong intermetallic phases can promote enhanced joint shear strength and creep resistance and can permit an increased operating temperature envelope for advanced electronic systems and devices.

![Lead-Free Soldering Implementation](image)

*Figure 22 Pb-free soldering implementation comparing Sn-Pb to Pb-free in solder shipments in kg [33].*
Studies have shown that Sn dendrites are the dominant as-solidified microstructure feature in solder joints made with many SAC alloys, which was contrary to the previous experience with Sn-Pb. It was found that relatively high but variable undercooling was commonly observed before joint solidification leading to Sn dendrites with spacing variations (that depend on undercooling and growth rate) but with very few distinct Sn grains. The unusually high undercooling of the SAC solder joints was associated with the difficulty of nucleating Sn as a pro-eutectic phase. Especially during slow cooling (e.g. in ball grid array (BGA) joints where cooling rates are less than 0.2°C/s) increased undercooling of the joints can also promote formation of undesirable pro-eutectic intermetallic (IMC) phases, specifically Ag₃Sn "blades" which tend to coarsen radically, leading to embrittlement of as-solidified solder joints. It was found that slight additions of a fourth phase, 'X', can help promote heterogeneous nucleation in solder systems, suppressing Ag₃Sn blade formation and providing a substantial amount of final ternary eutectic alloy [34], [26], [35], [36], [37].

Advancements in Pb-free solder research have demonstrated the capability to achieve increased shear strength at ambient temperatures as well as elevated temperatures near 150°C [38], similar to temperatures commonly seen in automotive electronics [39]. Due to the coefficient of thermal expansion mismatch commonly seen in printed circuit board (PCB) systems [40], shear strength will be the main focus and deciding factor for characterizing the mechanical strength of solder joints. Tensile strength studies [41] essentially showed that most Sn-based solder alloys fail near the Cu₆Sn₅ layer by localized parting with little difference between soldering alloy effects. Asymmetric four point bend (AFPB) testing was determined to be the preferred way of examining shear strength since it puts the solder joint in a state of pure shear in the middle of the test specimen [42].

McCormack and Jin stated, “for the Pb-free substitute solders to be acceptable for industry-wide applications, they have to exhibit various desirable material
characteristics in terms of melting temperature, solderability (wettability), electrical and thermal conductivity, thermal expansion coefficient, mechanical strength and ductility, creep resistance, thermal fatigue resistance, corrosion resistance, manufacturability, and cost” [43]. While no one alloy or alloy system exhibits the best characteristics in each field, it is important to realize that the fundamental principle behind soldering is solderability, also known as wettability. Wettability measurements can be obtained in various ways using multiple methods like the edge dip method, rotary dip method, dip and look method, spread method, and the globule method. For this research, a wetting balance using the globule method was used to investigate wettability of various solder alloys. As it is often difficult to compare wettability measurements between studies due to various test parameters [44], a force curve versus time is the standard measurement for wetting balance machines and baseline alloys were also tested for direction comparison.

**Experimental Methods**

**Experimental Methods: Alloy Preparation**

For the experiments described in this study, a series of solder alloys (Table 1) were prepared from elemental Sn, Ag, Cu, Al, Mn, and Zn all of 99.99% impurity, by encapsulating the weighed constituents for each alloy in a quartz tube that was backfilled and sealed with 1/3 atm of UHP He gas after mechanical pump evacuation to a level of 50 mtorr. The strategy for this study was to substitutionally alloy Al, Mn, or Zn for Cu and to remain close to the baseline composition of SAC3595. Each sample was heated in an air atmosphere furnace to melt the constituents and to superheat the alloy to a temperature of 1200°C. After achieving the selected superheat, each encapsulated alloy was held for four hours to ensure homogenization before chilling in ice water to promote ingot solidification without tube fracture.
Table 1 Summary of alloys for experiment given in wt%.

<table>
<thead>
<tr>
<th></th>
<th>3595</th>
<th>3595+0.01</th>
<th>3595+0.05</th>
<th>3595+0.10</th>
<th>3595+0.15</th>
<th>3595+0.20</th>
<th>3595+0.25</th>
</tr>
</thead>
<tbody>
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<td>Sn</td>
<td>95.55</td>
<td>95.55</td>
<td>95.55</td>
<td>95.55</td>
<td>95.55</td>
<td>95.55</td>
<td>95.55</td>
</tr>
<tr>
<td>Ag</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Cu</td>
<td>0.95</td>
<td>0.94</td>
<td>0.9</td>
<td>0.85</td>
<td>0.8</td>
<td>0.75 (0.74Zn)</td>
<td>0.7</td>
</tr>
<tr>
<td>Al, Mn, Zn</td>
<td>0</td>
<td>0.01</td>
<td>0.05</td>
<td>0.1</td>
<td>0.15</td>
<td>0.20 (0.21Zn)</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**Experimental Methods: DSC**

Significant useful information can be obtained from traditional differential scanning calorimetry (DSC). However, when studying solder joints and undercooling behavior of solder in a traditional inert DSC pan, there isn’t a direct correlation between what is tested and what would potentially be used in industry. By replacing an effectively inert aluminum pan (with internal surfaces “lined” with non-wetting aluminum oxide film) with a reactive (pre-fluxed) copper pan, a *calorimetric solder joint* can be created which would give direct correlation to what happens in real solder joining systems that commonly involve organic solderability preservative (OSP) and copper contacts [34]. With the use of a copper pan, the solder can react on the inner pan walls to form an IMC layer, similar to what is seen in industrial practice. Furthermore, the calorimetric solder joints can be metallographically prepared after solidification so that any correlation between thermal transformation behavior and microstructure can be observed.

Various experiments were performed using the calorimetric joint method. Temperature scan rates, hold times, sampling rate, sample size, and scanning temperatures were all varied to see the effects on the calorimetric joints. For this study, a Pyris 1 power compensating DSC was used. The DSC program parameters were selected to closely replicate typical BGA reflow processing in an industrial setting, the most challenging situation for as-solidified joint embrittlement from Ag₃Sn blades. Though the amount of solder and test vessel used in DSC were not exactly the same as BGA reflow processing, Cu-Cu substrates and thermal excursion parameters were selected to mimic a BGA reflow event in a laboratory setting.
A typical DSC profile used in this experiment can be seen below. An initial hold of 30 seconds was used to allow for the program and sample temperature to achieve a thermal equilibrium. A linear heating rate of 10°C/min (0.17°C/s) was used to bring the solder joint up to temperature from 160°C to 240°C. The specimens were then held for 30 seconds at temperature and cooled linearly from 240°C to 160°C at 10°C/min. For several samples, multiple reflow cycles were used to study the dependence on cycle number of microstructure coarsening and of undercooling. For these studies, the DSC profile in Figure 23 was used and repeated for the number of indicated cycles.

![DSC Scan Profile](image)

Figure 23 Heating and cooling schedule for each reflow cycle of the calorimetric solder joint samples.
Joint Preparation

The following method was used to prepare calorimetric joint samples [26].

1. A small segment of drawn solder wire (0.067” dia.) was obtained.
2. The wire sample was flattened to 100μm in a manual rolling mill in multiple passes, forming a solder alloy ribbon. The rolling surfaces were cleaned with acetone and alcohol, as necessary.
3. A hot plate was pre-heated to 180°C.
4. A copper DSC pan set (pan & lid) was cleaned with a solvent to remove any organic residue and the solvent was allowed to evaporate.
5. Johnson’s No. 1 Stainless Steel Flux (Johnson Mfg., Princeton, Iowa) was used to prepare the Cu DSC pan set surfaces, following the manufacturer’s guidance.
6. With a clean cotton swab, flux was applied to the pan and lid inside surfaces.
7. The fluxed pan and lid set were placed on the hot plate (at 180°C) by using tweezers, remaining until all liquid evaporated. The pan set was removed before any darkening or discoloration occurred. When properly prepared the flux solids will be white and give the copper surfaces a hazy appearance.
8. The fluxed pans were used as soon as possible, preferably within hours to avoid any undesirable moisture absorption and/or corrosion.
9. Small shears were used to cut a single piece of solder ribbon that weighed ~25mg. The precise weight (accurate to ±0.1mg) of each sample was recorded and the ribbon was placed in a fluxed pan, a lid was added, and the pan was crimped with tweezers to retain the lid.

Experimental Methods: Metallographic Preparation

Calorimetric joints were prepared metallographically as individual samples by the following steps:

1. A brass metal pipe smaller than ½” was obtained.
2. A square piece of electrical tape was stretched across one opening of the brass pipe section to make a reservoir. Electrical tape was wrapped around the outside surface of the pipe.
3. A DSC pan was inserted into a sample clip and tweezers were used to lower it into the pipe. The sample was stuck to the electrical tape. The sample was oriented parallel to the length of the pipe.
4. An epoxy-resin was prepared and used to fill up the brass pipe section per given instructions.
5. The electrical tape was removed after proper curing time was observed.
6. 400 grit abrasive was used to de-burr the edges of the brass pipe and to slowly grind into the DSC sample until an acceptable cross-section was visible. The sample was rinsed with methanol and dried.

7. Step 6 was repeated for 600 and 800 grit abrasive.

8. Using 3µm diamond suspension on an Allied High Tech “White Label” cloth, the sample was polished for approximately one minute.

9. Using 1µm diamond suspension on an Allied High Tech “Final B” cloth, the sample was polished for approximately one minute.

10. The sample was set face down on a vibratory polisher using a Buehler “MasterTex” cloth and polished for 5-7 minutes using 0.05µm colloidal silica Allied High Tech “Master Polish”. It was rinsed with methanol and dried. This step was used to produce slight surface relief by preferentially removing tin from the polished surface.

**Determination of Ag₃Sn Blade Phase Content**

Data was gathered from previous work that characterized how Ag₃Sn blades likely affect the joint strength based on several assumptions [26]. It was determined that blades over 50µm in length are indicative of joints that have the highest susceptibility for failure. As length of Ag₃Sn blades increase, there is a higher probability that a blade will connect both IMC interfaces allowing for an easy crack path if put into shear. Therefore, for this study all Ag₃Sn blades greater than 50 µm in length that were seen in a cross section were recorded for analysis. Blades are, in most cases, easily distinguished in optical microscopy by their morphology and color. If there was sufficient uncertainty about the phase identity of a possible blade, backscattered electron imaging (BSE) was used to easily resolve it. The primary morphological feature of an Ag₃Sn blade is a high aspect ratio. They typically have one flat edge and one rough edge. Since the length of the cross sections for the solder joints microstructures was not consistent throughout the entire study it was determined that a normalized measurement, such as \( \text{Ag₃Sn blades (over 50µm in length) per 1,000 µm of interface} \), was to be used to correctly compare blade counting statistics.
**Asymmetric Four Point Bend Testing**

A butt-joint was fabricated by soldering together two 1 inch x 1 inch x ¼ inch oxygen-free high thermal conductivity (OFHC) Cu blocks with a uniform solder joint width. The Cu faces to be joined were first polished through a standard 240-320-400-600 grit metallographic polishing sequence [26]. The surfaces were then cleaned for 30 seconds in a 50:50 HCl:distilled water mixture followed by a distilled water rinse, a final methanol rinse, and drying with an air gun. The faces were then fluxed with a thin layer of *Johnson #1 flux* and allowed to dry.

The blocks were then loaded into a soldering fixture as shown in Figure 24. A uniform gap was maintained between the blocks by a strip of stainless steel shim stock on both ends of the joint. The gap was maintained at a distance of 3 mils or approximately 75µm. Light fluxing was applied to both surfaces in the gap and to the beveled Cu near the joint gap in order to maintain a clean surface prior to soldering. A screw in the soldering fixture was used to hold a thermocouple against the end of one Cu block. The soldering fixture was placed on a hot plate and heated to 255°C. At 255°C, wire solder was placed onto and drawn across the length of the joint. The joint was maintained in the 255-260°C temperature range for 30 seconds. It was then placed on a Cu cooling block and allowed to cool to 150°C. The fixture was then placed under running DI water to cool to room temperature.
Bars for AFPB were electro-discharge machined (EDM) from the resulting butt joint. The AFPB bar dimensions were 34mm x 3.1mm x 4mm with the solder joint situated at the bar midsection. Two notches (Figure 25) of 1 mm length were EDMed on the top and bottom of the solder joint leaving a joint height of 2 mm. The bar was centered within the AFPB fixture by manual alignment with scribe marks on the upper and lower fixtures, as shown in Figure 26.
The AFPB fixture was loaded into an Instron Model 1125 with a 1000 lb load cell. The sample was then tested in compression mode with a rate of 0.1mm/minute. A data set of compressive load versus ram extension was obtained as shown in Figure 27.

Figure 26 AFPB fixture and specimen configuration.

Figure 27 Raw data for compressive load versus ram extension for AFPB solder joint.
The compressive load data was converted to shear force for an AFPB sample as described by Equation 1:

\[
V = P \frac{(x - y)}{(x + y)}
\]

where \( V \) is the shear force, \( P \) is the applied compressive load, and \( x \) and \( y \) was the outer and inner span lengths of the test fixture, 30mm and 4mm, respectively. The shear stress was calculated by dividing by the area of the solder joint between the two notches.

The maximum shear strength was measured as shown in red in Figure 28. A minimum of seven bars were measured for a given solder composition from which the average maximum shear stress was computed.

![Figure 28 Raw data converted to shear stress versus ram extension for AFPB solder joint; max. average shear stress indicated by red line.](image)
Wettability Testing

Solderability, also known as wettability, is a measurement that can be easily obtained from a wetting balance. A typical wetting balance is a vertical load cell placed above a molten solder bath in which a test vehicle is dipped into solder and a change in force on the vehicle is measured versus time. The measured force, $F$, can be related to the buoyancy force and the meniscus force once the load cell compensates for the initial weight of the test vehicle. A simplified wetting balance (meniscopgraph) schematic can be seen below Figure 29. As the sample is dipped into the solder bath, multiple forces react with the test vehicle and are shown in Figure 30.

![Figure 29 Schematic of wetting balance [46].](image)

![Figure 30 Measured force ($F$), contact angle ($\theta$), and surface tension at the solid-liquid ($\gamma_{sl}$), solid-vapor ($\gamma_{sv}$), and liquid-vapor ($\gamma_{lv}$) interfaces in the wetting balance test [47].](image)

With all of the above principles in mind, an equation relating the meniscus and buoyancy forces can be described by Equation 2, or alternatively

Equation 3, using the measured force ($F$), contact angle ($\theta$), surface tension at the solid-liquid ($\gamma_{sl}$), solid-vapor ($\gamma_{sv}$), and liquid-vapor ($\gamma_{lv}$) interfaces, the liquid meniscus parameter ($P$), volume of the partially submersed sample ($v$), the liquid density ($\rho$), and the acceleration of gravity ($g$) for the wetting balance test.
To eliminate much of the possible variation from test vehicle fabrication, a spool of 99.9999% Puratronic® copper wire with a 0.5mm diameter was obtained from Alfa-Aesar and was used for the wetting balance experiments. The copper wire was sectioned into ~2.5cm segments using a Tronex 5113 Razor Flush® wire cutter [48] to obtain a moderately flat surface with minimal shear as seen in Figure 31.

Both ends of the copper wire segments were used in succession in the wetting balance experiments and a total of 20 measurements were obtained for each of the given alloys seen in Table 2. The SAC305 alloy tested in this study was obtained from Gen3 Systems and the SN100C alloy was obtained from Nihon-Superior, Inc. The remaining series of solder alloys seen in Table 2 were prepared in a similar manner to those from Table 1. Small segments of solder were then drawn into wire
with a diameter of 0.067". From the wire, the solder was sectioned into 200±10 mg portions to be used on a Gen3 Systems MUST System 3 Pb-free solderability tester. The segments of wire were tested via the parameters seen below in Table 3.

Table 2 Alloys used in wettability experiment.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>0.010%</th>
<th>0.025%</th>
<th>0.050%</th>
<th>0.100%</th>
<th>0.150%</th>
<th>0.200%</th>
<th>0.250%</th>
</tr>
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<tbody>
<tr>
<td>Sn-0.9Cu</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Sn-3.5Ag</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SN-100C</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>SAC 305</td>
<td>X</td>
<td></td>
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<td>SAC 3595</td>
<td>X</td>
<td></td>
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<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>0.21%</td>
</tr>
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</table>

Table 3 Wettability test conditions.

<table>
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<tr>
<th>Test Variable</th>
<th>Condition</th>
</tr>
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</tr>
<tr>
<td>Substrate removal speed (mm/s)</td>
<td>1</td>
</tr>
<tr>
<td>Substrate immersion time (s)</td>
<td>10</td>
</tr>
<tr>
<td>Substrate immersion depth (mm)</td>
<td>5</td>
</tr>
<tr>
<td>Wire diameter (mm)</td>
<td>0.5</td>
</tr>
<tr>
<td>Length of Wire (cm)</td>
<td>2.5</td>
</tr>
<tr>
<td>Solder bath temperature (°C)</td>
<td>255</td>
</tr>
<tr>
<td>Solder globule mass (mg)</td>
<td>200</td>
</tr>
<tr>
<td>Flux type</td>
<td>Actieve 5 (IPC Flux #2)</td>
</tr>
</tbody>
</table>

Wettability Test

The following method was used to conduct a wetting balance (wettability) test.

1. 0.5mm diameter copper wire was obtained.
2. 2.5cm segments of the wire were cut using a Tronex 5113 Razor Flush® wire cutter.
3. Each segment was cleaned with a solvent of acetone or ethanol.
4. A Globule 2 stage was loaded on the wetting balance machine.
5. The Globule 2 stage was heated to 255°C and previous solder was removed.
6. Stage was cleaned with solvent and flux to obtain a clean surface, devoid of previous solder debris.
7. A 200mg pellet of solder was placed on the clean sample stage.
8. A segment of wire was placed inside component clip #18 placed on the Linear Variable Differential Transformer (LVDT).
9. The end of the wire segment was dipped in the (provided) rosin flux to prepare the surface.
10. Once the solder was melted and heated to the reflow set point on the sample stage, it was fluxed with a cotton swab using the same flux as that used on the copper wire.
11. Sample stage was raised to approximately 2cm below the sample clip.
12. The stage was oriented such that the tip of the fluxed copper wire sat directly above the uppermost part of the molten solder ball.
13. The wettability test was conducted using the parameters from Table 3.
14. The sample stage was lowered and the data was acquired.
15. The copper wire was rotated 180° in the component clip so the other end could be utilized.
16. After ten wettability tests were completed for one solder pellet, it was removed and the stage was cleaned before another set of runs commenced.
17. Steps 5-16 were repeated for the desired number of tests for each alloy.

For each of the alloys in Table 2, twenty measurements were collected and analyzed. A series of 10 typical wetting balance curves can be seen in Figure 33. From the data for an alloy, several values were obtained from the curve: the start of wetting and 2/3 maximum force. Important events occurring during the wetting curve can be seen in Figure 32. The time (in seconds) was reordered for both of these events and subtracted to get the wetting time that is also expressed in seconds. This value is considered to be the true wetting time [49].
Figure 32 Wetting curve with start of wetting (red), 2/3 max force (green) and max force (blue) indicated.

Figure 33 A collection of 10 wettability curves for sample alloys.
Equation 4 Wetting time equation [49].

\[
\text{Wetting Time} = \text{Time to} \frac{2}{3} \text{Max Force} - \text{Start of Wetting}
\]

The true wetting time used in this study is expressed in Equation 4. The wetting times for the alloys were compiled and analyzed to find the mean wetting time. The values were then plotted against other alloys to compare the average wetting time as well as the standard deviation between wettability measurements. Alloys that exhibited consistent values of the shortest time were considered to have the best wettability.

Experimental Results

DSC

**Aluminum Alloys**

Small additions of Al were added to the base SAC 3595 alloy (Table 1) and were found to lower the undercooling, in general, with increasing concentration. As revealed in Figure 34, the average undercooling for SAC 3595 was 12±2.2°C and the lowest undercooling for an Al addition was 6±2.1°C at 0.25Al. While the undercooling was suppressed, the standard deviation within each sample remained consistent at ±2.0°C. Undercooling also had a strong correlation with increasing concentration. The melting point of the alloy remained at 217°C and the liquidus stayed below 222°C for all alloys. Each bar in Figure 34 represents a different composition consisting of seven DSC traces and shows a typical spread in exotherms and solidification temperatures as depicted in Figure 35 for SAC3595+0.10Al.
Figure 34 SAC3595+Al undercooling dependence on concentration.

Figure 35 Representative thermograms for SAC+Al alloys, showing heating (top) and cooling (bottom) traces.
For several samples, it is possible to see two freezing events indicated by two distinct exotherms (see Figure 36). This can be indicative of having two separate nucleation events on different sides of the DSC pan or of two phases in the microstructure, e.g. Cu₆Sn₅ (interfacial and pro-eutectic), Sn, and ternary eutectic that froze in sequence. Increasing the amount of solder in the DSC pan from ~15mg to ~30mg made the multi-peak exotherms occur less frequently.

**Manganese Alloys**

Small additions of Mn were added to SAC3595 as per Table 1. The Mn effect on the base alloy was found to be surprisingly potent. With the smallest addition of 0.01wt%, the undercooling decreased significantly to an average of 4.4±0.3°C, and remained near 4°C until the maximum tested concentration of 0.25wt%, as seen in Figure 37. The deviation in undercooling varied slightly throughout the alloy ranges, but remained consistent around ±0.3°C.
The undercooling of SAC+Mn alloys remained constant (Figure 37) as did the isotherms that were obtained. In Figure 38, representative isotherms for SAC+0.15Mn can be seen. Tight control on the melting and liquidus temperatures (217°C and 220°C, respectively) was seen for all Mn alloys. It was also apparent from the tight undercooling spread in the data that there was close control in the solidification temperature. Similar to the SAC+Al alloys, double peaks would often be seen during solidification that could indicate two distinct solidification events.
Figure 38 Representative thermograms for SAC+Mn alloys, showing heating (top) and cooling (bottom) traces.

Figure 39 SAC+Mn thermograms that exhibit multiple peaks on cooling (bottom).
Zinc Alloys
Zn additions ranging from 0.01wt% to 0.25wt% were added substitutionally (for Cu) to the base alloy of SAC3595 as listed in Table 1. As seen in Figure 40, undercooling was significantly reduced from the base value of 12°C for all additions of Zn. While the decrease in undercooling was not as abrupt as in the SAC+Mn alloys, the lowest observed undercooling of 2.9±0.2°C for this study was repeatedly achieved in the SAC3595+0.21Zn, as seen in Figure 41. The deviation in undercooling decreased with increasing zinc concentration from ±1.2°C for SAC3595+0.01Zn to ±0.2°C for SAC3595+0.25Zn. This would suggest that zinc is a potent catalyst for heterogeneously nucleating tin, which would result in a minimized undercooling when compared to the base alloy with no zinc. SAC+Zn alloys solidified in a similar manner as the SAC+Al and SAC+Mn alloys showing two distinct exotherms, as shown in Figure 42.

![Figure 40 SAC+Zn undercooling dependence on concentration.](image)
Figure 41 Representative thermograms for SAC+Zn alloys, showing heating (top) and cooling (bottom) traces.

Figure 42 SAC+Zn thermograms that exhibit multiple peaks on cooling (bottom).
DSC Multiple Reflow Cycles
While all of the observations above were done for one thermal cycle, thermal joints often undergo multiple cycles in production. Continuing to promote a reproducible low undercooling after multiple reflow cycles is needed in a robust Pb-free solder. Since undercooling is directly correlated with microstructure, producing alloys that maintain a significant reduction in undercooling for multiple reflow cycles will create joints with a similar beneficial microstructure. As seen in Figure 43, SAC3595 had a consistent undercooling of ~12°C for all five of its cycles. The sample of SAC3595+0.20Al had more deviation between each of its reflow cycles, but was consistently lower than SAC3595 with an initial undercooling of 3.7°C and an average undercooling of 4.1°C for all five cycles. SAC3595+0.10Mn had an average undercooling of 3.9±0.8°C for five cycles. This alloy behaved similar to the SAC3595+0.20Al, as it varied in undercooling significantly. The best alloy tested under multiple reflow cycles was SAC3595+0.21Zn, having an average undercooling of 2.8±0.2°C for five reflow cycles. The Zn alloy consistently exhibited the lowest undercooling for each cycle and had the least deviation between reflow cycles. For each of the SAC+X {Al, Mn, Zn}, it can be said that they are powerful catalysts that help reduce undercooling during multiple cycles with a heterogeneous nucleation effect that does not diminish in spite of the joint microstructure evolution that results from each melt/freeze event.
Optical Microstructure Analysis

Aluminum Alloys
SAC+Al samples had a variety of different undercoolings based on the concentration of Al added substitutionally for Cu. Calorimetric joint samples or pans that exhibited the highest, lowest, and average undercooling for each of the varying compositions were metallographically prepared. The average undercooling sample for each of the given Al alloys can be seen in the series of micrographs in Figure 44 through Figure 50. Each micrograph has a 200μm scale bar (full scale) displayed.
Figure 44 SAC3595 representative joint, $\Delta T=14^\circ C$.

Figure 45 SAC3595+0.01Al representative joint, $\Delta T=8.7^\circ C$.

Figure 46 SAC3595+0.05Al representative joint, $\Delta T=11.1^\circ C$. 
Figure 47 SAC3595+0.10Al representative joint, ΔT=7.7°C.

Figure 48 SAC3595+0.15Al representative joint, ΔT=8.7°C.

Figure 49 SAC3595+0.20Al representative joint, ΔT=6.1°C.
All of the alloys had similar microstructures that consisted of primary Sn dendrites, ternary eutectic and pro-eutectic phases. The dendrite size was relatively coarse, compared to the baseline SAC3595 and depended on the undercooling of the sample and the nominal Al concentration, to some extent. Ag₃Sn blades were visible at low and high concentrations of Al, but very few could be seen at concentrations of 0.05Al, 0.10Al, and 0.15Al.
As Al concentration increased, an increase in ternary eutectic phase fraction was seen (Figure 52), as well as the appearance of a new, small, equiaxed (<5µm) phase. The ternary eutectic phase fraction of SAC3595 was 0.32±0.16. With the smallest addition of Al, the phase fraction of ternary eutectic was 0.31±0.06. As more Al was added to the system, the ternary eutectic phase fraction reached a maximum of 0.64±0.07 in SAC3595+0.25Al.
Manganese Alloys

SAC+Mn samples exhibited a unique concentration effect in which each alloy had similarly low undercooling. Pans which displayed the highest, lowest, and average undercooling for each of the varying compositions were metallographically prepared. The average undercooling pan for each of the given manganese alloys can be seen in the micrographs in Figure 53 through Figure 58. For all figures, the scale bar is 200μm (full scale).
Figure 53 SAC3595+0.01Mn representative joint, ΔT=4.3°C.

Figure 54 SAC3595+0.05Mn representative joint, ΔT=4.4°C.

Figure 55 SAC3595+0.10Mn representative joint, ΔT=4.3°C.
Figure 56 SAC3595+0.15Mn representative joint, ΔT=4.4°C.

Figure 57 SAC3595+0.20Mn representative joint, ΔT=3.9°C.
All of the alloys had similar microstructures that consisted of primary tin dendrites, ternary eutectic, and pro-eutectic phases. The dendrite size was relatively fine and was particularly uniform for each specimen. Since undercooling is directly related to microstructure, it makes sense that each composition had similar microstructure features since they had nearly identical undercoolings. $\text{Ag}_3\text{Sn}$ blades were visible at concentrations of 0.01Mn, 0.05Mn, and 0.10Mn. For most SAC alloys, by limiting the undercooling or cooling rate, a suppression of $\text{Ag}_3\text{Sn}$ blades is often seen. However, having $\text{Ag}_3\text{Sn}$ blades in samples that exhibited the same undercooling as blade-free samples was observed for the SAC+Mn system. In the SAC+Mn solders, the initial concentration of Mn seemed to be the determining factor, i.e., a threshold concentration of Mn was reached that suppressed blade formation. Thus, this concentration effect may relate to the Mn-induced nucleation mechanism, where alloying additions greater than 0.15Mn suppressed $\text{Ag}_3\text{Sn}$ blades and helped to promote nucleation of $\text{MnSn}_2$ and the ternary eutectic, as well as pro-eutectic $\text{Cu}_6\text{Sn}_5$ and then Sn, completing joint solidification before the blades could form.
Zinc Alloys
SAC+Zn samples displayed a variety of undercoolings based on the concentration of Zn added substitutionally for Cu. Pans which showed the highest, lowest, and average undercooling for each of the varying compositions were metallographically prepared. The average undercooling pan for each of the given Zn alloys can be seen in the micrographs in Figure 60 through Figure 65. Each scale bar in the micrographs is 200μm.
Figure 60 SAC3595+0.01Zn representative joint, $\Delta T=10.9^\circ C$.

Figure 61 SAC3595+0.05Zn representative joint, $\Delta T=5.9^\circ C$.

Figure 62 SAC3595+0.10Zn representative joint, $\Delta T=4.6^\circ C$. 
Figure 63 SAC3595+0.15Zn representative joint, $\Delta T=4.2^\circ C$.

Figure 64 SAC3595+0.21Zn representative joint, $\Delta T=2.8^\circ C$. 
All of the alloys had similar microstructures that consisted of primary Sn dendrites, ternary eutectic, and pro-eutectic phases. The dendrite size is relatively coarse and depends on the undercooling of the sample. As seen in the above figures, Ag₃Sn blades were visible at concentrations of 0.01Zn, 0.05Zn, and 0.21Zn, the last of which showed the lowest undercooling. If we ignore the results for 0.21Zn, the trend again looks like a type of threshold concentration effect, similar to the Mn results, discussed above. Having Ag₃Sn blades in the sample with 0.21Zn which exhibited the same or greater undercooling as blade-free samples with lower and higher concentration of Zn was not expected for this SAC+X system. Although this may say something about a possible shift in phase fields and a different mechanism for nucleation in SAC+Zn alloys at higher Zn concentration, it is also possible that there might be some influence of a larger solder volume on Ag₃Sn blade nucleation and growth. The larger solder volume might be deduced from the increased solder joint cross-section size in Figure 64 compared to the other Zn alloy micrographs, but this should be possible to investigate by some simple repeat experiments.
Asymmetric Four Point Bend

Shear stress data for the AFPB bars was conducted on a variety of industrial solder alloys as well as microalloyed SAC3595. AFPB bars were tested under three conditions: as-soldered and after thermal aging at 150°C for 100 and 1,000 hours. Once removed, the aged AFPB bars were air cooled on a copper block and then tested. Figure 67 shows the summary of results from the industrial alloys, including the baseline SAC 3595 alloy. Figure 69 shows maximum shear stress data for SAC3595, along with at least one specimen for each from the Al, Mn, and Zn series.

For the baseline alloys tested, the SAC alloys exhibited similar trends with decreasing maximum shear strength with increased aging time. For the two alloys without Ag additions, SN100C and Sn0.95Cu (SC95), the initial maximum shear stress was approximately 10MPa less than the SAC alloys. However, after an aging time of 1000 hours, the shear strength of the SAC alloys approached the non-Ag alloys. The aging trend can be described in Figure 68, in which all numbers are normalized to the largest maximum shear stress measurement at no aging time. As
seen in Figure 68, the non-Ag alloys exhibited significantly less shear stress reduction than the SAC alloys, but had a lower initial maximum shear stress.

Figure 67 Maximum shear stress measurements for baseline alloys.

Figure 68 Normalized maximum shear stress measurements for baseline alloys.
For the SAC+X alloys tested, all samples exhibited a similar trend of decreasing maximum shear strength with aging time as shown in Figure 69. Four alloys had similar maximum shear stress measurements at 0 hours of aging: SAC3595 and SAC3595+Mn of different concentrations. Each of the SAC+Mn alloys exhibited a similar rate of decreasing maximum shear stress when compared to each other. Figure 70 shows the aging trend so that all values are normalized to the maximum shear stress at no aging time. As seen in Figure 70, the Zn alloys had different trends with the low addition of 0.05Zn losing shear strength with aging time at a faster rate than the 0.21Zn alloy. An interesting observation can be made for the SAC+Al alloy in which it had a lower but more stable shear stress with aging and retained the most strength of any of the alloys investigated. Even though SAC+Al series had approximately 10 MPa less shear strength than the base alloy SAC3595, the strength was retained through the aging process.

![SAC3595+X Shear Stress Measurements](image)

Figure 69 Maximum shear strength for SAC+X (Al, Mn, and Zn) alloys.
Wettability Testing
Wettability testing was conducted on the SAC3595+X alloys. A set of baseline alloys consisting of SAC305, SAC3595, SN100C, Sn-0.9Cu, and Sn-3.5Ag were also tested for comparison. SAC305 is a popular solder ball alloy often used in industry [50]. SN100C is the trade name of a eutectic Sn-0.7Cu alloy micro-alloyed with Ni and Ge that is also commonly used in industry [51]. SAC3595 was the ternary alloy tested in this study on which the SAC+X {X=Al, Mn, or Zn} was based. For each of the alloys, 20 wettability measurements were obtained. The average of the 20 measurements along with their standard deviation for each of the tested alloys in this study can be seen in Figure 71 and Figure 72.
The wetting balance results for each of the alloys are shown in Figure 72. Moderate Al additions resulted in better wetting behavior than the base alloy. 0.01Al was the alloy in the Al series that exhibited the worst (longest) wetting time of 0.25 seconds and the highest standard deviation of ±0.2 seconds. This trend was seen again at a concentration of 0.25Al where the wetting time was 0.23±0.18 seconds.

The Mn additions resulted in better wetting behavior at the upper and lower limit of concentration additions. 0.01Mn was the alloy in the Mn series that exhibited the best (shortest) wetting time of 0.068 seconds and a low standard deviation of ±0.008 seconds. This trend is seen again for a concentration of 0.25Mn where the wetting time was 0.07±0.007 seconds. At moderate additions between 0.5-0.2Mn, the spread in the data was greater and a slight increase in wetting time was observed. However, for all of the alloys tested in this Mn series, an average wetting time between 0.068 and 0.11 seconds was seen. Throughout the Mn alloys, it was often seen that a dull, matte looking layer would form on the surface of a molten solder pellet. Once fluxed, this film would disappear, but would re-emerge approximately 30 seconds after the flux had been applied. Though the wettability of
the Mn alloys wasn’t affected by this film, it is possible that the wetting time would be significantly poorer if the samples had not undergone a flux immediately before the test.

The Zn additions resulted in better wetting behavior as more Zn was alloyed into the system. 0.01Zn and 0.05Zn exhibited nearly the same wetting time of 0.11±0.037 seconds and 0.11±0.05 seconds, respectively. At a concentration of 0.10Zn, the best wetting time of 0.069±0.015 seconds was achieved, but the smallest deviation between tests was 0.07±0.01 seconds at 0.21Zn. The best combination of lowest wetting time and smallest deviation was obtained at the concentrations of 0.10Zn and 0.21Zn.

![Wettability Summary of SAC+X Alloys](image)

Figure 72 Summary of all SAC+X wetting times, along with 3 baseline examples.
Discussion

Trends in Undercooling

*Aluminum Alloys*
With increasing Al from the base alloy of SAC3595 to SAC3595+0.25Al, it was seen that the undercooling was decreased from 12±2.2°C to 6±2.1°C, respectively. Al was a potent catalyst to promote heterogeneous nucleation in SAC solder joints. Generally with the SAC alloys, as undercooling was limited, a refinement of the microstructure as well as a suppression of pro-eutectic Ag₃Sn was seen. For SAC+Al alloys, this was not the case since Ag₃Sn blade formation seemed to be independent of undercooling. With 0.25Al, which exhibited the lowest undercooling of 6°C, there were a significant amount of Ag₃Sn blades.

*Manganese Alloys*
With SAC+Mn alloys, a strong correlation was observed between Mn content and undercooling suppression. Even in the case of SAC+0.01Mn, there was a decrease in undercooling from 11.9±2.2°C for SAC3595 to 4.4±0.3°C for SAC3595+0.01Mn. Undercooling remained consistent around 4°C for concentrations of 0.01 to 0.25Mn while the standard deviation also remained below ±0.3°C. Each DSC trace for the Mn alloys was similar to that seen in Figure 38. Data suggests that manganese is a potent catalyst capable of providing a minimized undercooling even for additions as small as 100ppm.

*Zinc Alloys*
SAC+Zn alloys showed a concentration effect when compared with undercooling. The undercooling was minimized from 12±2.2°C for SAC 3595 to 3.5±0.2°C for SAC 3595+0.25Zn. Concentrations greater than 0.10Zn produced undercoolings less than 4.5±0.2°C. SAC+0.01Zn had an undercooling of 10.7±1.2°C which was close to the SAC3595. This would suggest that near the composition of SAC3595+0.05Zn, a different solidification behavior became dominant and heterogeneous nucleation
was able to take place. SAC3595+0.21Zn was the alloy with the lowest undercooling (2.9±0.2°C) of all of the samples investigated in this study.

**Trends in Microstructure**

**Aluminum Alloys**

Results of this study show that the addition of Al to SAC3595 had a significant concentration effect and that the microstructure varied widely relative to how much Al was substitutionally alloyed. With the base alloy of SAC3595, large Ag₃Sn blades were seen in the microstructure as well as large Sn dendrites. With slight additions of Al, the amount of Ag₃Sn blades decreased and the ternary eutectic microstructure was refined. With concentrations of Al between 0.05-0.10Al, no Ag₃Sn blades were seen. However, with Al concentration greater than 0.15Al, blades became visible and prevalent in the microstructure once again.

**Manganese Alloys**

Results of this study showed that minor additions of Mn into SAC3595 promoted heterogeneous nucleation, and limited Ag₃Sn blade formation for compositions greater than 0.15Mn. The microstructure for each of the SAC+Mn was similar in the sense that all of them formed Cu₆Sn₅ IMC on the copper substrate, Sn dendrites, and a ternary eutectic consisting of Cu₆Sn₅, Sn, and finely dispersed Ag₃Sn. For some of the alloys, Ag₃Sn blade formation was seen for the Mn alloys that still exhibited a low undercooling. This may suggest that the alloy system was not able to actively promote pro-eutectic Cu₆Sn₅. By increasing the Mn concentration, it was possible to maintain a low undercooling around 4°C and to also suppress Ag₃Sn blades. By suppressing Ag₃Sn for a wide range of alloy compositions, it was possible to avoid the creation of detrimental phases in solder joints for a wide alloy range.

**Zinc Alloys**

Research suggests that minor additions of Zn in SAC3595 promoted heterogeneous nucleation and limited Ag₃Sn blade formation in compositions of 0.10-0.15Zn, and 0.25Zn. The microstructure for each of the SAC+Zn was similar in the sense that all of them formed Cu₆Sn₅ IMC on the copper substrate, Sn dendrites, and a ternary
eutectic consisting of Cu₆Sn₅, Sn, and finely dispersed Ag₃Sn. For some of the alloys, Ag₃Sn blade formation was seen for the Zn alloys closest to the base alloy and also for the composition of SAC3595+0.21Zn. This suggested that the alloy was near the eutectic region of the ternary phase diagram and not all of the Zn was going into suppressing Ag₃Sn blade formation. A type of phase stability happened near the composition of SAC3595+0.21Zn and Ag₃Sn blades can be suppressed by having a higher or lower Zn concentration. By suppressing Ag₃Sn, it was possible to avoid the creation of detrimental phases in solder joints that could cause premature impact failures.

**Asymmetric Four Point Bend**

Results from the AFPB study are seen in Figure 67 through Figure 70, which show the maximum shear stress measurements. For the baseline samples, all of the SAC alloys showed considerable decrease in shear strength when aged, more than the two non-silver samples, e.g., SN100C performed the best by losing only 11% of its maximum shear strength. The baseline SAC alloys preformed in a similar fashion to each other, with SAC3610 having the highest average maximum shear stress of 46.3±2.5MPa. SAC3595 had an average maximum shear stress of 40.9±3.7MPa.

For the case of SAC+X, only the Mn series had a similar average shear stress of 40MPa between tested compositions. The SAC alloys containing the Al and Zn additions had approximately 10MPa less shear strength then the base SAC3595 alloy. These alloys with 0.05Al and 0.21Zn retained their strength longer after aging than other SAC+X alloys, settling between 24-30MPa at 1000 hours. The alloy that exhibited the best retention of shear strength was the 0.05Al alloy, as seen in Figure 70, which only lost 5.8% of its as-soldered shear strength.

One possibility for future work could be the creation of samples joined with a SC+Al alloy for AFPB testing. The idea behind this alloy would be to combine the shear strength advantages of removing Ag and adding Al for applications like BGA joints that can tolerate the rise in melting behavior of about 10°C. This might be
advantageous for solder joints that undergo numerous thermal cycles while needing to retain strength throughout long service life.

**Wettability**
A summary of the wettability study can be seen in Figure 72. The lines seen in blue, red, and purple correspond to the average wetting time show in Figure 71 for SAC305, SAC3595, and Sn-0.9Cu respectively. As seen in the graph, all of the SAC+X alloys exhibited lower wetting times than the best baseline alloy (SAC305). Additions of Mn and Zn preformed the best to minimize the wetting time, around 0.1 seconds, for most of the alloys between 0.01-0.25wt%. All three additions had similar wetting behaviors between 0.05-0.15wt%. At the extreme concentrations, Al preformed the worst out of all the SAC+X alloys. Furthermore, even minor additions as low as 100ppm provided substantial wetting improvement when alloyed to the base composition of SAC3595.

The Mn-containing alloys have some reaction on their free surface with air that gives a golden color but this did not prevent good wetting in the joints, during hand soldering of the AFPB samples. Also, the wetting balance results were promising in an air atmosphere. However, our experience with attempts to have BGA spheres produced of SAC+0.10Mn in a nitrogen atmosphere (in an extension of this study) showed that the melt absorbed nitrogen, which seemed to raise the surface tension [52] too high for successful atomization processing. This is consistent with the phase diagram studies of Mn-N [53], [54] which showed that multiple Mn-N phases are thermodynamically stable at operating temperatures of reflow furnaces and that nitrogen exhibits slight solubility in manganese at elevated temperatures. Since most industrial reflow furnaces use a N₂ purging gas, it may expected that reflow of a SAC3595 alloy that contains even small Mn additions would dissolve N₂ and exhibit too high of a surface tension and viscosity to coalesce, flow, and properly form solder mount joints. Further characterization using TEM or auger microscopy of this phenomenon is needed, but it is believed that the adsorbed film would be MnN.
Even though the Al alloys didn’t perform as well as the Mn and Zn alloys in air atmosphere wettability, the SAC3595+0.05Al alloy was comparable to the other alloy additions at 0.05wt% with an average wetting time of approximately 0.1 seconds. With concentrations less than 100ppm and at a concentration of 0.25Al, wetting time increased. Throughout the Al series, a wider deviation was seen for each composition, but the average wetting time was still close to the other alloys in the series. Therefore, it is advantageous to explore the implementation of SAC+Zn or SAC+Al in the microelectronics industry.

**Conclusions**
The goal of this research was to observe and analyze the microstructural effects of Al, Mn, and Zn doped SAC solder joints. All of the investigated alloys were found to lower undercooling and suppress Ag₃Sn blade formation at certain compositional ranges. Al concentration had little effect on the variance of undercooling but was found to decrease the overall undercooling to 6±2.1°C for SAC3595+0.25Al. Mn had a steady effect on undercooling and was found to keep undercooling consistently near 4°C. Zn was found to suppress the undercooling to its lowest value of 2.9±0.2°C at SAC3595+0.21Zn. Given the microstructural and thermal effects examined in this study, it can be said that Al, Mn, and Zn all helped promote heterogeneous nucleation for compositional ranges specific to each alloy. However, of the elemental additions studied, only Zn and Al are considered most promising for industrial use since Mn additions are known to react with N₂ gas that is commonly used for reflow atmospheres. Zn modification requires a fairly high level of addition (0.15-0.25 wt %), while Al requires a lower concentration to be effective (potentially as low as 0.05 wt %). It is proposed that alloys based on either the SAC+Zn or SAC+Al systems are the most viable candidates from this study for a robust, stable, and cost-effective Pb-free alloy for many electronic soldering applications.
Chapter 4: Heterogeneous Nucleation Mechanisms in SAC + Al Alloys

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**Abstract**

The global electronic assembly community is striving to accommodate the replacement of Pb-containing solders, primarily Sn-Pb alloys, with Pb-free solders due to environmental regulations and market pressures. During this major transition away from eutectic or near-eutectic Sn-Pb solder ($T_{eut} = 183°C$) for electronic assembly, there is also the opportunity to make a major improvement in Pb-free joint reliability for challenging operating environments, i.e., high temperatures and stress levels, as well as impact loading situations. Of the Pb-free choices, an array of solder alloys based on the Sn-Cu-Ag (SAC) ternary eutectic ($T_{eut} = 217°C$) composition have emerged with the most potential for broad use across the industry [27]. Exploration of SAC+X candidates, ie. 4th addition element modifications of SAC solder alloys, is needed to promote heterogeneous nucleation, to control solder alloy undercooling, and to select solidification product phases. Aluminum additions to SAC alloys have emerged as a viable candidate for an enhanced Pb-free solder alloy and results that support this will be discussed as well as suggestions for future work.

**Introduction**

The electronics industry has seized the challenge of adaptation and is proceeding rapidly to develop the assembly techniques and to generate the reliability data for tin-silver-copper (SAC) alloy solder [55], [11], and [56] as a favored Pb-free solder in many electronic assembly applications as seen in Figure 22. Compared with Sn-Pb
solders that have been limited typically to low-stress joints and reduced-temperature service because of the soft Pb phase that is prone to coarsening and ductile creep failure, the high Sn content and strong intermetallic phases of a well-designed SAC alloy solder can promote enhanced joint shear strength and creep resistance and can permit an increased operating temperature envelope for advanced electronic systems and devices.

![Lead-Free Soldering Implementation](image)

**Figure 73 Lead free soldering implementation comparing tin/lead to lead free in solder shipments in Kg [33].**

Results of SAC alloy development have demonstrated increased shear strength at ambient temperature and elevated temperatures, e.g., 150°C. Joints made from a variety of SAC solders have also demonstrated resistance to isothermal fatigue and resistance to degradation of shear strength from thermal aging for temperature excursions up to 150°C, a current test standard for under-the-hood automotive electronics solder.

An observation that arose from initial widespread testing of SAC solder alloys was the occasional embrittlement of SAC solder joints due to micro-void nucleation, growth, and coalescence, if the exposure to elevated temperatures was sufficiently
high, typically greater than about 150°C, and the exposure was sufficiently long, greater than about 500 to 1000h. This occasional joint embrittlement after thermal aging was observed at elevated Cu content in SAC solder alloys and typically was associated with excessive growth of layers of Cu-base intermetallic compounds, \( \text{Cu}_{6}\text{Sn}_{5} \) and, especially, \( \text{Cu}_{3}\text{Sn} \). It should be noted that US Patent 6,231,691 provides a solder to suppress this thermal aging phenomenon through minor additions (< 1 wt.%, but usually 0.2-0.3 wt.%) of a fourth element, such as Ni, Fe, and/or Co, and "like-acting elements," to the SAC solder to suppress solid state diffusion at the solder/substrate interface that contains the Cu-base intermetallic compound (IMC) layers [57]. Later testing showed that a Mn addition was one of the most effective like-acting elemental additions, suppressing growth of both types of intermetallic layers after extensive thermal aging. This type of minor alloy addition to prevent embrittlement has become increasingly important since narrow solder joint gaps are becoming more common with miniaturization of electronic circuits.

Studies have shown that Sn dendrites are the dominant as-solidified microstructure feature in solder joints made with many SAC alloys, not a fine (tertiary) eutectic, contrary to the previous experience with Sn-Pb. Also, it was found that a relatively high but variable undercooling was observed commonly before joint solidification leading to Sn dendrites with spacing variations (that depend on undercooling and growth rate) but with very few distinct Sn grains. The unusually high undercooling of the SAC solder joints was associated with the difficulty of nucleating Sn solidification, as a pro-eutectic phase. Especially during slow cooling, e.g., in ball grid array (BGA) joints where cooling rates are less than 0.2°C/s, increased undercooling of the joints also can promote formation of undesirable pro-eutectic intermetallic phases, specifically \( \text{Ag}_{3}\text{Sn} \) "blades," that tend to coarsen radically, leading to embrittlement of as-solidified solder joints.

The primary goal of this work has been to address several problems, such as thermal aging from IMC growth and voiding, and as-soldered embrittlement from \( \text{Ag}_{3}\text{Sn} \) blade growth. Therefore, a 2009 paper [25] proposed the study of minor alloy
additions of Mn, Zn, and Al and reported promising results. Of the listed elemental additions, Zn and Al are most promising for industrial use (due to common use of inert N\textsubscript{2} gas). Zn modification requires a fairly high level of addition (0.20-0.25 wt%), but Al requires far lower concentration to be effective (potentially as low as 0.05 wt%). This paper examines the effects of Al additions over a wide range, from 0.01 to 0.25 wt%, to explore this addition more thoroughly.

**Experimental Methods**

**Experimental Methods: Alloy Preparation**

For the experiments described in this paper, a series of solder alloys (Table 1) were prepared from elemental Sn, Ag, Cu, and Al, all of 99.99% impurity by encapsulating the weighed constituents for each alloy in a quartz tube that was backfilled and sealed with 1/3 atm of UHP He gas after mechanical pump evacuation to a level of 50 mtorr. Each sample was heated in an air atmosphere furnace to melt the constituents and to superheat the alloy to a temperature of 1200°C. After achieving the selected superheat, each encapsulated alloy was held for 4h to ensure homogenization, before chilling in ice water to promote ingot solidification without tube fracture.

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**Experimental Methods: DSC**

From a traditional DSC, significant useful information can be obtained. However when studying solder joints and undercooling behavior of solder in a traditional inert DSC pan, there isn’t a direct correlation between what is tested and what would potentially be used in industry. By replacing an effectively inert aluminum pan with a reactive copper pan, a calorimetric solder joint can be created which
would give direct correlation to what happens in real solder joining systems that commonly involve OSP/copper contacts [34]. With the use of a copper pan, the solder can react on the inner pan walls to form an IMC layer, similar to what is seen in industrial practices. Furthermore, the calorimetric solder joints can be metallographically prepared after solidification so that a direct correlation between thermal behavior and microstructure can be observed.

Various experiments were performed using the calorimetric joint method. Temperature scan rates, hold times, sampling rate, sample size, and scanning temperatures were all varied to see the effects on the calorimetric joints. For this study, a Pyris 1 power compensating DSC was used. For this study, DSC program parameters were selected to closely replicate typical BGA reflow processing in an industrial setting, the most challenging situation for as-solidified joint embrittlement from Ag₃Sn blades. Though the amount of solder and test vessel used in DSC were not exactly the same as BGA reflow processing, Cu-Cu substrates and thermal excursion parameters were selected to mimic closely a BGA reflow event in a laboratory setting.

A typical DSC profile used in this experiment can be seen below. An initial hold of 30 seconds was used to allow for the program and sample temperature to achieve a thermal equilibrium. A linear heating rate of 10°C/min (0.17°C/s) was used to bring the solder joint up to temperature from 160°C to 240°C. The specimens then were held for 30 seconds at temperature and cooled linearly from 240°C to 160°C at 10°C/min. For several samples, multiple reflow cycles were used to study coarsening of the microstructure and the undercooling dependence on cycle number. For these studies, this typical DSC profile was used and repeated for the number of indicated cycles.
Joint Preparation

The following method was used to prepare calorimetric joint samples.

1. A small segment of drawn solder wire (0.067” dia.) was obtained.
2. The wire sample was flattened to about 100μm in a manual rolling mill in multiple passes, forming a solder alloy ribbon. The rolling surfaces were cleaned with acetone and alcohol, as necessary.
3. A hot plate was pre-heated to about 180°C.
4. A copper DSC pan set (pan & lid) was cleaned with a solvent to remove any organic residue and the solvent was allowed to evaporate.
5. Johnson’s No. 1 Stainless Steel Flux was used to prepare the Cu DSC pan set surfaces, following the manufacturer’s guidance.
6. With a clean cotton swab, flux was applied to the pan and lid inside surfaces.
7. The fluxed pan and lid set was placed on the hot plate (at 180°C) by using tweezers, remaining until all liquid was evaporated. The pan set was removed before any darkening or discoloration occurred. When properly prepared the flux solids will be white and give the copper surfaces a hazy appearance.
8. The fluxed pans were used as soon as possible, preferably within hours to avoid any undesirable moisture absorption and/or corrosion.
9. Small shears were used to cut a single piece of solder ribbon that weighed about 25mg. The precise weight (accurate to ±0.1mg) of each sample was

Figure 74 Heating and cooling schedule for each reflow cycle of the calorimetric solder joint samples.
recorded and the ribbon was placed in a fluxed pan, a lid was added, and the pan was crimped with tweezers to retain the lid.

10. DSC scans were performed using an empty pan as a reference.

**Experimental Methods: Metallographic Preparation**

Once a calorimetric joint is created, it can be prepared for optical and SEM metallography. Calorimetric joints were prepared individually by the following steps:

1. A brass metal pipe smaller than $\frac{1}{2}$" was obtained.
2. A square piece of electrical tape was stretched across one opening of the brass pipe section to make a reservoir. Electrical tape was wrapped around the outside of the pipe and cut off so that the open end was completely exposed.
3. A DSC pan was inserted into a sample clip and tweezers were used to lower it into the pipe. The sample was stuck to the electrical tape.
4. An epoxy-resin was prepared and was used to fill up the brass pipe section per given instructions.
5. The electrical tape was removed after proper curing time was observed.
6. Using 400 grit abrasive, the edges were de-burred of the brass pipe and was used to slowly grind into the DSC sample until acceptable cross-section was visible. The sample was rinsed with methanol and dried.
7. Step 6 was repeated for 600, and 800 grit abrasive.
8. Using 3um diamond suspension on a Allied High Tech “White Label” cloth, the sample was polished for approximately one minute.
9. Using 1um diamond suspension on a Allied High Tech “Final B” cloth, the sample was polished for approximately one minute.
10. The sample was set face down on a vibratory polisher using a Buehler “MasterTex” cloth and polished for 5-7 minutes using 0.05μm Allied High Tech “Master Polish”. It was rinsed with methanol and dried. This step was used to produce slight surface relief by preferentially removing tin from the polished surface.

**Experimental Methods: XRD**

Two types of X-ray diffraction (XRD) measurements were made for this research in an attempt to identify a special phase that appeared to segregate by buoyant forces and to have exceptional hardness from nanoindentation measurements (see below).
The first XRD analysis was made on an as-cast ingot that had been polished smooth to a 1μm finish. The ingot sample composition was SAC3595+0.20Al that had been melted in a quartz tube and water quenched. The resulting ingot was metallographically prepared in a transverse section. The test parameters for this test can be seen in Table 5 below.

Table 5 Summary of X-ray diffraction parameters used for ingot sample.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation</td>
<td>Cu-Kα1</td>
</tr>
<tr>
<td>Scan Range (°2θ)</td>
<td>10-100</td>
</tr>
<tr>
<td>Step Size (°2θ)</td>
<td>0.017</td>
</tr>
<tr>
<td>Scan Step Size (s)</td>
<td>479</td>
</tr>
<tr>
<td>Divergence Slit Size(*)</td>
<td>0.5</td>
</tr>
<tr>
<td>Anti-Scatter Slit Size(*)</td>
<td>1</td>
</tr>
<tr>
<td>Stage</td>
<td>Spinning</td>
</tr>
<tr>
<td>Generator Settings</td>
<td>40mA, 45kV</td>
</tr>
</tbody>
</table>

The second type of XRD measurement was made on a chill cast specimen of 78.6495wt%Cu-21.3505wt%Al. This sample was heat treated, crushed, and analyzed. Both sets of XRD measurements were made using a PANalytical X'Pert Pro diffractometer located in Metals Development at Ames Laboratory USDOE. The test parameters for this XRD analysis can be seen in Table 6 below.

Table 6 Summary of X-ray diffraction parameters used for crushed powder sample.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation</td>
<td>Cu-Kα1</td>
</tr>
<tr>
<td>Scan Range (°2θ)</td>
<td>20-50</td>
</tr>
<tr>
<td>Step Size (°2θ)</td>
<td>0.008</td>
</tr>
<tr>
<td>Scan Step Size (s)</td>
<td>479</td>
</tr>
<tr>
<td>Divergence Slit Size(*)</td>
<td>0.5</td>
</tr>
<tr>
<td>Anti-Scatter Slit Size(*)</td>
<td>1</td>
</tr>
<tr>
<td>Stage</td>
<td>Spinning</td>
</tr>
<tr>
<td>Generator Settings</td>
<td>40mA, 45kV</td>
</tr>
</tbody>
</table>
**Experimental Methods: Nanoindentation**

Two sets of nanoindentation measurements were made for this research. The first nanoindentation set was conducted on a SAC3595+0.05Al DSC calorimetric joint. Four areas were analyzed: the copper DSC pan, the Cu$_6$Sn$_5$ layer, the Sn matrix, and the area noted as the Sn-Cu-Al. This rejected solute phase (Sn-Cu-Al) area was adjacent to the Cu$_6$Sn$_5$ scallop-shaped intermetallic interface, where it is believed that aluminum was rejected into the Sn matrix as the Cu$_6$Sn$_5$ solidification front advanced. Ten hardness measurements were made for each phase using the same test parameters. A cube-corner diamond tip geometry was used with a 1mN maximum force. No holding time at maximum force was used for this series of measurements.

The second set of nanoindentation results were collected on a SAC3595+0.20Al DSC calorimetric joint, i.e., richer in Al content. The areas that were analyzed in this test included: Sn matrix, Cu$_6$Sn$_5$, Ag$_3$Sn, and Cu$_{33}$Al$_{17}$, as identified in the XRD measurements described above. The main difference in test parameters between the first and second test was that a holding time of 10 seconds was used for the second set and that no holding time was used for the first. By adding a hold time at the maximum load, time dependent effects such as creep would be less visible in the resulting data [58].

**Experimental Results**

**DSC**

Small additions of aluminum were added to the base SAC 3595 alloy (Table 4) and were found to lower the undercooling with increasing concentration. As revealed in Figure 34, the average undercooling for SAC 3595 was 12°C, and the lowest undercooling for aluminum additions was 6°C at an addition of 0.25Al. While the undercooling was decreased with increasing concentration, the melting point of the alloy consistently remained at 217°C and the liquidus was consistently below 222°C.
for all alloys. A sample set for one alloy of seven DSC traces from seven independent samples can be seen in Figure 35, showing a typical spread in exotherms and solidification temperatures. Seven samples per composition were run for one reflow cycle for all of the tested alloys. The isotherms in Figure 35 are for SAC3595+0.10Al.

![SAC 3595+Al Undercooling](image1)

Figure 75 SAC3595+Al undercooling dependence on concentration.

![SAC 3595+0.10Al](image2)

Figure 76 Representative isotherms for SAC+Al alloys.
On some samples, it is possible to see two freezing events indicated by two distinct exotherms (see Figure 36). This can be indicative of two separate nucleation events on different sides of the DSC pan that froze at different temperatures or of two phases in the microstructure, e.g., Cu₆Sn₅ (interfacial and pro-eutectic) and Sn (and ternary eutectic), that froze in a sequence. With increasing the amount of solder in the DSC pan from ~15mg to ~30mg, the multi-peak exotherms were seen less frequently.

![Isotherms which exhibit multiple peaks.](image)

The undercooling of SAC3595 alloys with increasing concentrations of aluminum can be seen in Figure 34. More quantitatively, by alloying SAC3595 solder with aluminum, the undercooling was decreased from 12±2.2°C to 6±2.1°C at SAC3595+0.25Al. While the undercooling was suppressed, the standard deviation within each sample remained consistent at ±2.0°C.

While all of the observations above were done for one thermal cycle, thermal joints often undergo multiple cycles in production. Exhibiting a low undercooling for
multiple reflow cycles is needed in a robust lead-free solder. Since undercooling is directly correlated with microstructure, being able to produce alloys that exhibit significant reduction in undercooling for multiple reflow cycles will be able to produce joints that are microstructurally similar. As seen in Figure 43, this sample of SAC3595 had a consistent undercooling of ~12°C for all five of its cycles. This sample of SAC+0.20Al had more deviation between each of its reflow cycles, but was consistently lower than SAC3595, with an initial undercooling of 6.4°C and an average undercooling of 4.1°C for all five cycles.

**Figure 78** SAC+Al undercooling at multiple reflow cycles.

**Optical and SEM Microstructure Analysis**
SAC+Al samples had a variety of different undercoolings based on the concentration of aluminum added substitutionally for Cu. Three DSC pans out of seven for each of the varying were metallographically prepared for each aluminum concentration, i.e., pans that exhibited the highest, lowest, and average undercooling. The average undercooling pan for each of the given aluminum alloys can be seen in the series of micrographs in Figure 79 through Figure 50.
Figure 79 SAC 3595 representative joint, \( \Delta T = 14^\circ C \).

Figure 80 SAC3595+0.01Al representative joint \( \Delta T = 8.7^\circ C \).
Figure 81 SAC3595+0.05Al representative joint, $\Delta T=11.1^\circ C$.

Figure 82 SAC3595+0.10Al representative joint, $\Delta T=7.7^\circ C$.

Figure 83 SAC+0.15Al representative joint, $\Delta T=8.7^\circ C$. 
Figure 79 through Figure 50 show a summary of optical micrographs of each alloy in this study that had exhibited an average undercooling, where the alloy and undercooling are listed for each micrograph. Each scale bar (end-to-end) in the micrographs is 200μm.
All of the alloys had similar microstructures that consist of primary tin dendrites, ternary eutectic, and pro-eutectic phases. The dendrite size is relatively coarse and depends on undercooling of the sample. Ag₃Sn blades are visible at low and high concentrations of aluminum, but very few seen at concentrations of 0.05Al, 0.10Al, and 0.15Al. As aluminum concentration increases, an increase in ternary eutectic phase fraction was seen (Figure 52), as well as the appearance of a new small equiaxed (<5μm) phase. The initial ternary eutectic phase fraction was 0.32±0.16. With the smallest addition of aluminum, the phase fraction of ternary eutectic was 0.31±0.06. As more aluminum is added to the system, the ternary eutectic phrase fraction reaches is maximum at SAC3595+0.25Al of 0.64±0.07.

![Figure 86 Fraction of ternary eutectic measured in SAC+Al alloys.](image)

SEM and WDS analysis was conducted on the bottom interface of a SAC3595+0.05Al sample after a single DSC reflow cycle. As seen in the image and resulting microprobe data below (Figure 87 and Figure 88), an increase of aluminum is found at near the Cu₆Sn₅ IMC layer. A halo effect can be seen in the SEM micrograph which corresponds to an increase in aluminum signal. From the micrograph below, it appears that the Cu₆Sn₅ contains some aluminum, but enrichment of Al is found
between and surround Cu$_6$Sn$_5$ scallops. This aluminum enrichment could help lead to the formation of Cu$_{33}$Al$_{17}$ particles since Cu diffusion near the interface is large as well. EDS was conducted on the Cu$_{33}$Al$_{17}$ phase. EDS analysis indicated that the composition was 62.9 at%Cu-36.9at%Al-0.2at%Ag.

The composition of this microprobe analysis was conducted on a sample that did not exhibit a large fraction of Cu$_{33}$Al$_{17}$ particles. This lean Al addition may not be sufficient to cause significant nucleation of Cu$_{33}$Al$_{17}$ IMC phase, but does promote nucleation of Sn by substitution into Cu$_6$Sn$_5$ at interfacial layer.

Another set of WDS analysis was conducted on a SAC3595+0.10Al sample, which is a sample that exhibits the most Cu$_{33}$Al$_{17}$, but no Ag$_3$Sn blades. As seen below in Figure 89 below for a WDS scan taken between two scallops, an enrichment in aluminum is seen that extends slightly into the copper as well as into the solder matrix. Figure 90 shows a WDS scan which was taken on a Cu$_6$Sn$_5$ scallop. Aluminum is seen alloying with the Cu$_6$Sn$_5$ IMC, but not seen in great amounts out into the solder matrix, starting at approximately 4µm. Both Figure 89 and Figure 90 indicate that
there is a solubility limit for Al in Cu$_6$Sn$_5$ and that Al concentrates outside the scallops when the initial IMC forms.

Further examination of the Cu$_{33}$Al$_{17}$ was needed, and conducted on SAC 3595+0.20Al, the alloy which contained the most Cu$_{33}$Al$_{17}$ particles of any of the given alloys. When examining interfaces under the SEM at high magnification on
backscattered electron mode, it can be seen that the new Cu$_{33}$Al$_{17}$ phase is faceted, hexagonal in shape and primarily seen on the top surface (lid side) of the calorimetric joints. The phase appears dark in back scattered electron mode when seen in an SEM(Figure 91). The size of this phase varies from 2-5μm with an average size near 3 μm. As seen in Figure 50, the particles are can be seen in direct contact with the Cu$_6$Sn$_5$ interfacial layer, attached to the copper substrate, as well as adjoined to pro-eutectic Cu$_6$Sn$_5$. WDS analysis of the particles was 62.2at%Cu-37.2at%Al-0.6at%Sn, and matches closely with the Cu$_{33}$Al$_{17}$phase [59] and the initial EDS analysis.

![Figure 91 Dark, dispersed phase seen on top surface of SAC+0.20Al.](image1)
![Figure 92 Scratches and pullout from new IMC phase indicated by arrows.](image2)

**Quantitative Metallography**
Phase fractions of the Ag$_3$Sn and Cu$_{33}$Al$_{17}$ were compared at varying aluminum additions of (0, 0.01, 0.05, 0.10, 0.15, 0.20, 0.25%Al in SAC 3595). Blade counting for the alloys was conducted on visible Ag$_3$Sn blade seen protruding from either the top or bottom calorimetric joint interface. Blades of length of ≥50 μm were recorded. Phase fraction of Cu$_{33}$Al$_{17}$ particles can also be seen a graph below. The total number of particles were counted per DSC joint, as well as the total interface length per DSC pan. From these values for both Ag$_3$Sn and Cu$_{33}$Al$_{17}$, the number of IMC’s per 1000μm of interface was graphed per alloy.
Figure 93 Ag$_3$Sn blades/1000µm of interface for SAC+Al alloys for given interface.

Figure 94 Cu$_{33}$Al$_{17}$ particles/1000µm of interface for SAC+Al alloys for given interface.
Ag₃Sn blades were prevalent in the base SAC 3595 alloy as well as the 100ppm concentration. Blade suppression was seen for the alloys with small additions of aluminum greater than 0.01wt%, but blades became visible again the higher concentrations. Blades were seen slightly more frequently on the bottom interface than the top interface at lower concentrations, but also had a greater deviation per sample. At aluminum concentrations of 0.15, 0.20, and 0.25; Ag₃Sn blade formation was more consistent per sample and was just as likely to occur on the top interface as the bottom. The need for an Ag₃Sn suppressant can be articulated in the base SAC 3595 where a wide range in the number of blades can be seen.

Cu₃₃Al₁₇ particles show a different behavior than Ag₃Sn blade formation. As the phase fraction increases with increasing aluminum it reaches an apex until 0.25wt%, which subsequently drops Cu₃₃Al₁₇ fractions comparable to 0.05Al. A significant piece of data was that 98% of all particles seen in the SAC+Al were found on the top interface. This suggests that the particles are affected by gravity, and a buoyancy effect is seen in the solder joint microstructures. Particles that were seen on the bottom were often seen growing off of the Cu₆Sn₅ layer like seen in Figure 95.

![Image](image.png)

Figure 95 Cu₃₃Al₁₇ particle on bottom interface, shown attached to Cu₆Sn₅ interface.
Particle concentration per 1000μm of interface increased for the given alloy selection until 0.25Al. At higher levels of aluminum, less pro-eutectic Cu$_6$Sn$_5$ was seen in the microstructure due to a reduction of copper. With insufficient copper, an excess of aluminum was seen which would retard formation of Cu$_{33}$Al$_{17}$ particles. An interesting behavior is that by substitutionally alloying Al for Cu, the Ag$_3$Sn blade formation and Cu$_{33}$Al$_{17}$ particle formation displays an inverse relationship. As Cu is alloyed out of the system, Al is forming Cu$_{33}$Al$_{17}$ and going into solution in the matrix as well as into Cu$_6$Sn$_5$. With the addition of aluminum, a heterogeneous nucleation mechanism is being created which inhibits blade formation. With a decrease concentration of Cu at 0.20Al and 0.25Al, Ag3Sn blade formation is seen once again while Cu$_{33}$Al$_{17}$ are prevalent.

**XRD**

Phase identification of the particles was conducted on a SAC3595+0.20Al sample, which showed the most particle count per 1000μm of interface. Approximately 30 grams of solder was placed into a quartz tube and brought up to 300°C. Once the solder was molten, the tubes were quenched in a room temperature water bath. Transverse sections of the quenched ingots were metallographically prepared and as seen in Figure 96. An agglomeration of particles was seen on the top surface. Knowing that the an increased phase fraction of particles were seen the closer to the cast surface, a cross section of an ingot was ground to approximately 1mm below the cast surface for preliminary XRD analysis.
Figure 96 Cu33Al17 particles seen near top surface of SAC3595+0.20Al sample water quenched in air.

Figure 97 Initial X-ray diffraction scan near top surface of SAC3595+0.20Al sample.
Analysis of the XRD data shows large signal from \( \beta \)-Sn. Peaks were matched to \( \beta \)-Sn, Ag\(_2\)Sn, and Cu\(_6\)Sn\(_5\). Some peaks were not identified, and were assumed to be the IMC particle phase. Initial verification of the phase was between Cu\(_9\)Al\(_4\) and Cu\(_{33}\)Al\(_{17}\) due insufficient counts as well as peak overlap with \( \beta \)-Sn. Given that many of the highest intensity peaks for the particle phase overlap with \( \beta \)-Sn, phase extraction was needed to verify the IMC particle phase.

![Al-Cu phase diagram](image)

Figure 98 Al-Cu phase diagram [59].

A chill casting of the alloy composition 62.2at\%Cu-37.8at\%Al was made, heat treated at 600°C for 3 days, and crushed for powder XRD analysis. The composition of this experiment was chosen based on the WDS analysis, and assuming a pure binary alloy. The scanning range for this experiment was conducted between 30° 2\( \Theta \) and 50° 2\( \Theta \) due to the difference between the Cu\(_9\)Al\(_4\) and Cu\(_{33}\)Al\(_{17}\) patterns. In the XRD run, double peaks at 40.6° 2\( \Theta \), 46° 2\( \Theta \), and 49° 2\( \Theta \) are distinctly visible in the
theoretical pattern and not the Cu$_9$Al$_4$ pattern. From these differences, it can be concluded that the powder XRD sample is composed Cu$_{33}$Al$_{17}$, and thus the IMC phase seen in SAC solder joints is Cu$_{33}$Al$_{17}$.

Figure 99 Powder X-ray diffraction run with Cu$_{33}$Al$_{17}$ and Cu$_9$Al$_4$ theoretical patterns overlaid.

**Nanohardness**

As seen in Figure 92, gouges and unusual scratches were seen in micrographs of SAC+Al alloys. The location of scratches were often correlated with areas that exhibited pullout of the Cu$_{33}$Al$_{17}$ phase. With this idea in mind, nanohardness was conducted on the particles to determine hardness. A set of nanohardness measurements were taken on a SAC3595+0.05Al DSC joint. Hardness measurements were taken on the copper DSC pan, Cu$_6$Sn$_5$, the tin matrix, and the area noted as the Sn-Cu-Al. This rejected solute phase (Sn-Cu-Al) is the area of the joint close the Cu$_6$Sn$_5$ scallop-shaped intermetallics, where it is believed that aluminum is rejected into the matrix as the Cu$_6$Sn$_5$ solidification front advances. As seen in Figure 100, Cu$_6$Sn$_5$ is 17x harder than the SAC solder matrix, and 12x harder than the Sn-Cu-Al phase. The difference in hardness between the solder matrix and the Sn-Cu-Al could be beneficial to mechanical properties as it would provide an
intermediate step between the hard Cu₆Sn₅ IMC and the relatively soft solder matrix.

![Hardness of Phases(MPa)](image)

Figure 100 Initial nanohardness measurements conducted on SAC+0.05Al.

A second set of nanohardness measurements were made on a SAC3595+0.20Al DSC joint. The hold time at maximum load was adjusted from 0 seconds for the first set of data measurements to 10 seconds for these set of measurements. The largest effect of creep during nanoindentation is the initial penetration [58], so by increasing the hold time, time dependent effects like creep are lessened. In this set, measurements were made in the tin matrix, an Ag₃Sn blade, and a Cu₆Sn₅ IMC to verify the nanohardness method and machine with literature values. As seen in Figure 101, the hardness measurements obtained with the higher maximum load displacement correlates well with literature values for the three phases [60].
Figure 101 Nanohardness measurements on SAC3595+0.20Al showing literature values for hardness [60].

Figure 102 Nanohardness measurements showing hardness of Cu₃₃Al₁₇ phases taken in tin and Ag₅Sn blade.
After verification of the machine, hardness measurements were made on the \( \text{Cu}_{33}\text{Al}_{17} \) particles. Two types of measurements were made for the \( \text{Cu}_{33}\text{Al}_{17} \) particles; one was particles inside an \( \text{Ag}_3\text{Sn} \) blade and the other were made on particles inside the tin solder matrix. As seen in Figure 102, the hardness measurements made on the particles in the tin matrix were 31.4±5.8 GPa compared to particles in the \( \text{Ag}_3\text{Sn} \) blade were 49.1±2.5 GPa. The difference in apparent hardness can be attributed to the hardness of the phase surrounding the particles. The relatively soft tin matrix has more compliance and is more ductile than the harder \( \text{Ag}_3\text{Sn} \) IMC. The true hardness of the particles is most likely closer to the hardness found of \( \text{Cu}_{33}\text{Al}_{17} \) in \( \text{Ag}_3\text{Sn} \) rather than \( \text{Cu}_{33}\text{Al}_{17} \) in Sn.

**Discussion**

**Trends in Undercooling**

With increasing Al from the base alloy of SAC3595 to SAC3595+0.25Al, it is seen that undercooling is decreased from 12±2.2°C to 6±2.1°C, respectively. Al is a potent catalysis to promote heterogeneous nucleation in SAC solder joints. Generally with SAC alloys, as undercooling is limited, a refinement of the microstructure as well as a suppression of \( \text{Ag}_3\text{Sn} \) is seen. For SAC+Al alloys, this seems to not be the case. \( \text{Ag}_3\text{Sn} \) blade formation is independent of undercooling in SAC+Al alloys. With 0.25Al, which exhibited the lowest undercooling of 6°C, had a significant amount of \( \text{Ag}_3\text{Sn} \) blades. It is important to mention that the formation of \( \text{Cu}_{33}\text{Al}_{17} \) particles is also independent of undercooling, as the maximum particle concentration was reached at 0.20Al, whereas the undercooling was minimized at 0.25Al. As \( \text{Cu}_{33}\text{Al}_{17} \) particles utilize more copper, the thermodynamically stable phase field shifts out of the favorable \( \text{Cu}_6\text{Sn}_5 \) and most likely into Sn as seen below in Figure 103. Therefore, SAC+Al alloys do not act as true ternary eutectic alloys as such additions like Co, Mn, and Zn do.
Trends in Microstructure

Results of this study show that the addition of aluminum to SAC3595 have a significant concentration effect and the microstructure varies widely to how much aluminum is being substitutionally alloyed. With the base alloy of SAC3595, large Ag₃Sn blades can be seen in the microstructure as well as large tin dendrites. With slight additions of aluminum, the amount of Ag₃Sn blades decreases and the ternary eutectic microstructure starts being refined. With concentrations of Al between 0.05-0.10Al, no Ag₃Sn blades are seen. However, with aluminum concentration greater than 0.15Al, blades become visible once again and become prevalent in the microstructure. With Al additions greater than 0.01Al, a fifth phase, determined to be Cu₃₃Al₁₇, is seen in SAC+Al soldered microstructures. Cu₃₃Al₁₇ particle concentration increases with increasing aluminum concentration until its apex at 0.20Al, which afterwards decreases at the concentration of 0.25Al. With the formation of Cu₃₃Al₁₇ particles, a depletion of aluminum can be accounted for, and reduces the nominal value of copper in the overall solder joint. In other SAC alloys, the primary IMC which forms with Cu would be Cu₆Sn₅, and later Cu₃Sn in as aged
microstructures. However, in SAC+Al alloys, there is a dual competition for Cu which can either go into Cu$_{33}$Al$_{17}$ or Cu$_6$Sn$_5$. As more Cu$_{33}$Al$_{17}$ particles form with increasing Al, an increase in Ag$_3$Sn blade formation is seen that corresponds to the decrease of copper in the solder matrix.

**Trends in Hardness**
Nanohardness was a vital tool in examining physical properties of the important Cu$_{33}$Al$_{17}$ phase. The hardness of the Cu$_{33}$Al$_{17}$ phase was proportional to the underlying structure residing beneath the particles. The hardness of Cu$_{33}$Al$_{17}$ in tin dendrites was 31.4±5.8 GPa compared 49.1±2.5 GPa to particles surrounded by Ag$_3$Sn blades. Data suggests that the compliance of the tin produced a false, lower hardness reading than for readings in Ag$_3$Sn.

Further investigation using nanoindentation is needed to determine true hardness of the Cu$_{33}$Al$_{17}$ particles. For all of the indents, a cube-corner tip was used; which is a more aggressive tip than a standard Berkovich tip commonly used on nanoindenters [60]. Although results using the cube-corner match closely with literature, increasing the maximum load to 2mN and using a Berkovich indenter would be the preferred sample arrangement in future studies. Phase extraction of these particles is also desirable to verify hardness without effects of other solder phases.

**Nucleation Sequence**
By using a calorimetric joint and doing microstructural analysis, it possible to see the sequence of nucleation in the solder joints. When solder is brought up to its melting temperature, Cu$_{33}$Al$_{17}$ is the first to form. Seen growing off of Cu$_{33}$Al$_{17}$, Cu$_6$Sn$_5$ is the next to form as it expels Cu$_{33}$Al$_{17}$ off the Cu substrate. As Cu$_{33}$Al$_{17}$ gets expelled pass the solidification front, it floats towards the top interface in the still molten solder via a buoyancy effect. On occasions, the particles are seen still attached to the lower interface or even large pro-eutectic formations. This would indicate that the nucleation and the buoyancy effect of the particles occur briefly before joint solidification. In the final sequences, tin dendrites freeze after the
Cu₆Sn₅ IMC attached to the Cu interface. Lastly, the Sn-Ag-Cu ternary eutectic is the last to freeze, which fills in between where the tin froze.

It is possible that Cu₃₃Al₁₇ and Cu₆Sn₅ exhibit an epitaxial relationship which promote nucleation and phase stability of the particle phase in the solder joint microstructure. Cu₃₃Al₁₇ is a R3M (160) type of space group which is trigonal, but also exhibits hexagonal symmetry. The density Cu₃₃Al₁₇ is 6.45 g/cc. Further investigation of epitaxial and as well as structure information regarding Cu₃₃Al₁₇ is needed for better understanding of how SAC+Al alloys behave. TEM, OIM, further XRD, and perhaps synctrotron radiation could be utilized to characterize epitaxial properties regarding Cu₃₃Al₁₇ and Cu₆Sn₅, and the overall microstructure.

Future work should focus more onto the mechanism of catalysis as well as the reason for nucleation sequence. Particle ripening and thermal again experiments would be vital to the understanding how Cu₃₃Al₁₇ evolves with solder joints in service. Though hardness of the particles was determined, future work could involve the testing of physical joints in drop shock and shear to see the effect of Cu₃₃Al₁₇ at one interface.

![Comparison of SnCuAl and SnAgCuAl Alloys](image)

*Figure 104 Undercooling dependence of SAC and SC alloys with dopants.*
Another set of experiments was conducted with SC+Al (Figure 104), and was found to have similar outcomes to the SAC+Al alloys. This is possible as it was found that Cu33Al17 particles were limited on the amount of copper residing in the alloy, not Ag. Since Cu33Al17 formation is independent of Ag, SC+Al could be a viable contender in situations where SAC is not desirable and lowest melting point is not a criterion.

**Conclusions**

The goal of this research was to see the microstructural, thermal, and physical effects of aluminum on SAC solder joints. Aluminum was found to minimize undercooling, which would maximize eutectic volume and later Ag3Sn pro-eutectic formation. Aluminum concentration had little effect on the variance of undercooling, but decrease the overall undercooling from 12±2.2°C to 6±2.1°C for SAC3595 and SAC3595+0.25 Al, respectively.

One unusual outcome from this research was the discovery of a fourth phase that forms in SAC+Al solder joints and could have several beneficial properties. While the addition of Al decreases undercooling, Ag3Sn blade formation is more coupled to the formation of Cu33Al17 particles, which pull copper out of the solder that could form the ternary eutectic, thus a dual competition for copper is seen in SAC+Al alloys. The amount of particle formation is correlated directly to the amount of aluminum added into the system and indirectly to how much copper is being used in forming Cu6Sn5. Cu33Al17 formation also was related to joint geometry, as 98% of all particles were found to be on the top interface of each joint, which suggests a buoyancy effect that is consistent with the reduced density of the Cu33Al17 phase compared to Sn. Interestingly, the Cu33Al17 hardness was found to be 12x more than any of the other phases prevalent in SAC+Al microstructures. A maximum hardness of 49.1 ±2.5 GPa taken on particles residing within Ag3Sn blades was found. The particles were often found in contact with Cu6Sn5, suggesting possible epitaxy and
catalysis mechanism. SAC3595+0.10Al was found to be the alloy in which the most particles were formed and no Ag₃Sn blades were present.
Chapter 5: General Conclusions

Conclusion
Many different aspects of lead free solder were investigated in this study, ranging from: undercooling suppression, nucleation control, microstructure evolution, solderability, and mechanical strength. Additions of Al, Mn, and Zn to the SAC system were found to suppress undercooling by different heterogeneous nucleation mechanisms, as evidenced by the different composition dependence for each one. Al, Mn, and Zn additions also were found to be effective for nucleation control under multiple (reflow) cycles, where previous work had demonstrated enhanced IMC growth control under extended high temperature thermal aging conditions. In a deviation from the initial hypothesis, the alloy additions of Al and Mn did not fully substitute in the SAC alloy for Cu, but rather produced a 3rd IMC of Cu$_{33}$Al$_{17}$ and MnSn$_2$, respectively. Wetting balance measurements showed that low concentrations (< 0.25 wt. %) of Al, Mn, and Zn in SAC 3595 caused no decrease in wetting behavior on Cu in air, to counter the concern about the effect of the oxidizing elements on solderability. Al exhibited the worst wetting behavior of the three alloying additions to SAC, however all three modified SAC alloys had better wetting than the baseline selection of SAC and SC industrial alloys, including SAC305 and SN100C. Two solder alloys based on Sn-Cu (without Ag) showed the best retention for strength under thermal aging, but had a lower initial maximum shear stress, compared to several unmodified alloys. Al and Zn doped SAC alloys also showed the same excellent retention of shear strength with extreme thermal aging when compared against other SAC alloys, but started at about the same reduced strength as the non-Ag alloys. In general it was found that low level alloying additions of Al, Mn, and Zn were the most viable for an optimum combination of thermal aging resistance, wettability in air, and nucleation control. Al additions between 0.05 to 0.15 wt.%, Mn additions between 0.15 to 0.20 wt.%, and Zn additions between 0.10 to 0.15 wt.% were found favorable for beneficial modification of SAC3595.
A surprising outcome of this work was the discovery of the $\text{Cu}_{33}\text{Al}_{17}$ IMC phase in SAC+Al alloys. The probable nucleation sequence seen for this alloy is: $\text{Cu}_{33}\text{Al}_{17} \rightarrow \text{Cu}_6\text{Sn}_5 \rightarrow \beta\text{-Sn} \rightarrow$ ternary eutectic. This new IMC particle phase exhibited outstanding hardness, nearly 50GPa when tested inside an $\text{Ag}_3\text{Sn}$ blade, as well as a buoyancy effect visible in the microstructure. This buoyancy effect that seems to cause the IMC particles to float up to the top interface of the solder joint could act as a particle strengthening mechanism, providing reinforcement against stresses induced upon thermal cycling. $\text{Cu}_{33}\text{Al}_{17}$ could also be applied in uses outside the solder field, like cutting tool abrasives and wear resistant materials, where the nucleation and growth of particles of ultra-hard $\text{Cu}_{33}\text{Al}_{17}$ maybe be possible by a flux growth approach in Sn.

**Future Work**

Thus far cooling rate, chemical, and topological dependence of undercooling and microstructure have been investigated at very low level (<0.25 wt.%) substitutional concentrations. Future work should focus deeper into the mechanism of catalysis to optimize the SAC+Al and SAC+Zn systems, especially, to ensure $\text{Ag}_3\text{Sn}$ blade-free solder joints with the minimum addition level, preserving their desirable low melting behavior. From an applications perspective, it is also desirable to do some drop shock (impact) testing of boards assembled with SAC solder with the recommended Al and Zn additions. It is important to compare these choices to other alternatives, particularly for drop impact resistance in both as-solidified and thermally aged conditions.

Because Al pulls Cu out of the base alloy in the form of $\text{Cu}_{33}\text{Al}_{17}$, increasing nominal Cu concentration in this system should be investigated to see if the phase fraction of the particles increases with increasing Cu. Therefore, increasing Cu concentration, while still remaining close to the ternary eutectic is possible. The composition near Sn-3.5Ag-1.1Cu-0.2Al (wt. %) could be investigated for BGA types of applications, because it exhibits the same Cu/Al ratio as an alloy that contains particles and is also blade free. Thermal cycling of BGA joints made from SAC+Al should be
conducted to see if the hypothesis that the particles act as reinforcement against premature failure hold true. Also, testing of SAC+Al alloys in BGA joints also should be conducted in the form of thermal aging and impact resistance to see if $\text{Cu}_{33}\text{Al}_{17}$ is favorable. Wettability experiments on SAC+Al and SAC+Zn could also be conducted using a $\text{N}_2$ purge, similar to what is commonly seen in industry in order to correlate better between laboratory and manufacturing environments.

Further examination of $\text{Cu}_{33}\text{Al}_{17}$ could be conducted in the form of nano-hardness. The extraction of the IMC may be necessary in order to determine true mechanical properties without the effect of other phases. It is seen that $\text{Cu}_6\text{Sn}_5$ grows off of $\text{Cu}_{33}\text{Al}_{17}$, so epitaxial relations between these two IMCs should be considered. Grain mapping in the form of orientation imaging microscopy (OIM) or electron backscatter diffraction (EBSD) could be used to aid in this investigation, as well as microstructural analysis by TEM.

It is highly likely that the knowledge obtained from this study with respect to the SAC+Al system could be applied to SC+Al solders for applications that are tolerant of higher temperature reflow conditions ($\geq 250^\circ\text{C}$). In this situation, SC+Al (without an Ag addition) could intrinsically avoid the detrimental $\text{Ag}_3\text{Sn}$ blade phase and may possibly be used as a cost-effective Pb-free alloy with beneficial microstructure control and stability. This is possible because some preliminary data shows that Ag does not modify the $\text{Cu}_{33}\text{Al}_{17}$ nucleation and growth mechanisms. SC+Al alloys could combine favorable characteristics of SAC+Al and Sn-Cu systems and might be used as a replacement for current alloys based on that system.
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