Transient Liquid Phase Bonding for High Temperature Interconnects

John R. Holaday

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TRANSIENT LIQUID PHASE BONDING
FOR HIGH TEMPERATURE INTERCONNECTS

by
John R. Holaday

A Dissertation
Submitted to the Faculty of Purdue University
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To my advisor, instructors, peers, friends, and family

who have all kindly and patiently provided guidance and support
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<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>TLPB</td>
<td>Transient Liquid Phase Bonding</td>
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<tr>
<td>RoHS</td>
<td>Reduction of Hazard Substances Act</td>
</tr>
<tr>
<td>WEEE</td>
<td>Waste Electrical and Electronic Equipment</td>
</tr>
<tr>
<td>IGBT</td>
<td>Insulated-Gate Bipolar Transistor</td>
</tr>
<tr>
<td>IMC</td>
<td>Intermetallic Compound</td>
</tr>
<tr>
<td>LTP</td>
<td>Low-melting Temperature Phase</td>
</tr>
<tr>
<td>HTP</td>
<td>High-melting Temperature Phase</td>
</tr>
<tr>
<td>TLPS</td>
<td>Transient Liquid Phase Sintering</td>
</tr>
<tr>
<td>LPDP</td>
<td>Liquid Phase Diffusion Bonding</td>
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<tr>
<td>SLID</td>
<td>Solid-liquid Interdiffusion</td>
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<tr>
<td>NIST</td>
<td>National Institute of Science and Technology</td>
</tr>
<tr>
<td>SAC</td>
<td>Sn-Ag-Cu</td>
</tr>
<tr>
<td>MSL</td>
<td>Moisture Sensitivity Level</td>
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<tr>
<td>CTE</td>
<td>Coefficient of Thermal Expansion</td>
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Author: Holaday, John, R. PhD  
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Major Professor: Carol Handwerker

Transient liquid phase bonding (TLPB) is a type of interdiffusion bonding between metals that has been proposed for a variety of electronic interconnect applications. TLPB has been studied as an alternative to other high temperature interconnect materials such as high-Pb solders. The goal of eliminating Pb and other toxic materials from electronics manufacturing processes, and most importantly, waste streams has been part of an ongoing effort internationally to improve the sustainability of electronics manufacturing. Pb containing solders have largely been eliminated from most consumer applications, but continuing exemptions for high-Pb solders have been provided by regulators due to the lack of suitable replacement for high temperature interconnects. TLPB takes advantage of the formation of solid intermetallic compounds (IMC) formed by interdiffusion between a liquid phase, low-melting temperature component, such as Sn or a Sn alloy, and a solid, high-melting temperature component, such as Cu, Ni, or Ag. In conventional soldering, relatively thin layers of IMC form at interfaces and are dispersed in the bulk of the solder which has been heated above the liquidus temperature of the solder alloy and solidified by cooling. In TLPB, isothermal solidification occurs by the complete consumption of the low-melting temperature phase in the formation of IMC. Under the correct conditions, the resulting IMCs will exhibit a melting temperature greater than the initial processing temperature. The elevated melting temperature of the IMC is intended to facilitate high temperature operation and hierarchical device fabrication.

Research studies involving TLPB can be categorized into two types of work. Proof-of-concept studies have demonstrated the feasibility of producing TLP bonds using materials and methods either common to current commercial electronics manufacturing or with some novel processing or design improvement. Complete isothermal solidification in which the bonds have been shown to remain solid up to an increased melting temperature by characterization of shear strength above the initial processing temperature are key results that have been achieved using a
variety of materials and processes. Characterization of the resulting phases and microstructures via cross-sectioning and inspection using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX or EDS) have been used to show complete or adequate conversion of the low-melting temperature component to IMC as well. Powder compacts in a reducing atmosphere or paste formulations comprising mixtures of the low-melting temperature component, the high-melting temperature component, a flux, and or binding agents are most commonly used. Thin layers of these components in a planar configuration can also be used. An important result in any of these approaches is to form a dense enough bond such that adequate mechanical, thermal, and electrical performance of the interconnect can be achieved with each component in the scale of tens of microns such that interdiffusion can occur rapidly enough. Most studies have employed materials already widely adopted in electronic interconnects such Sn, Ag, Cu, Ni, Bi, or In in pure and or alloyed forms.

A second type of TLPB research has focused instead on characterizing underlying processing mechanisms such as the kinetics of IMC formation in specific TLPB candidate systems such as Cu-Sn or Ag-Sn. Solid-liquid interdiffusion couples were processed at several temperatures for various durations. Cross-sections inspected using SEM and EDS were used to inspect the rate of formation of interfacial IMC layers. In some cases, differential scanning calorimetry (DSC) was used to measure heat flows during thermal processing. By analyzing the melting and solidification events in conjunction with the known sample dimensions and mass, the amount of IMC formed for each condition could be estimated as opposed to direct observation of cross-sections. An analytical model of the intermetallic growth kinetics would then be presented based on the observed rates. Other researchers prioritized investigating the thermodynamic implications of alloying either the low-temperature component or the high-temperature component. Once again, SEM and EDS were used to identify the phases formed and DSC was used to identify significant phase transitions relative to temperature. Typically, some discussion of key thermodynamic characteristics affected by the alloying type employed with the goal of identifying processing or applications limits for a specific material set.

In the work presented in this thesis, a comprehensive approach is taken to TLPB design encompassing both practical bond engineering concerns but also applying analysis of key materials science concepts. First, the key thermodynamic concepts required for successful TLPB are examined. Cu-Sn, Sn-Ag-Cu, and Sn-Bi-Cu example TLPB are used to introduce the concept
of TLPB in further detail. Further introductions cover manufacturing and design constraints, wetting and microstructural inhomogeneities, and the technical demands for various applications.

Rather than making basic modifications to existing TLPB formulations, a framework for interpreting equilibrium binary and ternary phase diagrams to predict non-equilibrium TLPB behavior was implemented. Detailed thermodynamic data in the form of calculated phase diagram (CALPHAD) databases exist for a broad set of Sn alloys. This framework was applied to screen potential TLPB formulations from a larger design space. Ternary diagrams were generated at regular temperature intervals using Thermo-Calc in order to compare outcomes over possible processing temperature ranges. Evaluations of binary and ternary phase diagrams are presented for several Sn alloys with Ag, Cu, and Ni as the high-melting temperature phase. Known interfacial reaction products were also discussed to demonstrate circumstances in which a different phase is known to form than that expected based on the proposed thermodynamic interpretation method. This analysis was performed to provide insights into potential TLPB formulations regarding effective composition ranges, resulting phases, processing temperatures, and operating temperature ranges.

Competing approaches to high temperature interfaces were also reviewed to better understand the requirements for commercially viable TLPB design. Various high temperature solder alloys have been investigated, and some are currently used in niche applications. Inclusion of precious metals or mechanical performance limits the practicality of the most promising alloys although Zn-Sn solders exhibits promising properties. Sintered Ag also exhibits excellent electrical, mechanical, and thermal properties. Examples of novel TLPB geometry, processing techniques, and optimization were also reviewed. These studies demonstrate that design and process optimization on an application basis will be needed to make TLPB a competitive technology.

Application of the thermodynamic framework lead to the identification of a novel Bi-rich, Sn-Bi-Cu TLPB formulation. The relatively low eutectic temperature (139°C) of Sn-Bi is an attractive characteristic for use in TLPB, specifically where low temperature processing is desirable. Ideally, the melting temperature and thus the maximum operating temperature is elevated to that of the precipitated Bi phase (~271°C) that forms after Sn is consumed by the formation of Cu₆Sn₅ and Cu₃Sn. Previous investigations of Sn-Bi TLPB focused on characterizing the reaction of eutectic Sn-Bi and Sn-rich, Sn-Bi with Cu. Unfortunately, eutectic
Sn-Bi reacted with Cu results in a persistent melting event at 200°C due to the presence of Cu$_6$Sn$_5$. Analysis of the ternary phase diagrams and invariant reactions in the Cu-Sn-Bi ternary reveal that a shift in the IMC phase in equilibrium with Bi causes a liquid forming reaction at 200°C. This reaction can be avoided by using a Bi-rich, Sn-Bi composition such that Cu$_3$Sn forms at the Cu-SnBi interface as opposed to a layered Cu$_6$Sn$_5$ and Cu$_3$Sn structure. The concept of processing regimes and processing regime maps was introduced as a method to clarify description of the temperature and composition ranges resulting in the same processing outcomes.

Experimental assessment of Bi-rich, Sn-Bi was performed with Cu and Ni. Interfacial reactions between Sn-80Bi (wt. %) and Cu substrates confirmed the direct formation Cu$_3$Sn. Planar TLPB assemblies were fabricated by quickly soldering together substrates in a planar configuration with a bondline thickness of 10 to 20µm. These assemblies were then thermally processed using the DSC, cross-sectioned, polished, and examined via SEM. DSC and and EDS confirmed complete isothermal solidification in less than 60 minutes at 300°C. Solid-liquid interfacial reaction couples were also heated in a tube furnace. Interfacial reactions were also tested to confirm the viability of Bi-rich Sn Bi where Ag or Ni interfaces will be bonded. Experimental results demonstrated that Sn-Bi-Cu is a practical TLPB system when a Bi-rich low-melting temperature phase is processed above 200°C.

Transient liquid phase bonding is a compelling method for forming high temperature interconnects. Bi-rich, Sn-Bi with Cu has been demonstrated to be a novel, thermodynamically viable TLPB system. Although further development will be needed to characterize and refine mechanical performance. The thermodynamic framework developed for TLPB also establishes the opportunity for additional novel formulations to be developed.
1. INTRODUCTION

1.1 Contributions to TLPB Design Presented in This Thesis

This work presents a review of prior literature relating to transient liquid phase bonding as well as new contributions to the field. In Chapter 1, prior experiments and examples of alloy systems were discussed to highlight the opportunities and challenges of developing viable TLPB systems for various applications. In Chapter 2, an original analysis of existing thermodynamic data is presented to show how thermodynamic modeling using CALPHAD databases can be leveraged for TLPB design. Isothermal sections of ternary phase diagrams including Ag-Cu-Sn, Cu-Ni-Sn, Cu-Sn-Bi, Ni-Sn-Bi, Ag-Sn-Bi, In-Sn-Ag, In-Sn-Cu, and In-Sn-Ni were computed at regular intervals and evaluated using the framework developed to predict TLPB behavior. Literature is reviewed where applicable for each system to test expected interfacial reactions and identify metastable phase formation. Competing technologies for high temperature interfaces and novel TLPB formulations and processing techniques are compared in Chapter 3. Chapter 4 presents a novel formulation for TLPB based on a Bi-rich, Sn-Bi alloy as a low melting temperature component with Cu or Ni as the high temperature component. Isothermal sections of the ternary phase diagrams and the framework from Chapter 2 were used to identify the thermodynamic advantages of Bi-rich, Sn-Bi alloys versus eutectic Sn-Bi. Experiments were performed to confirm the expected behavior of the system. Copper substrates and substrates with a Ni metallization were pre-soldered using a Sn-80Bi alloys (wt.%) and isothermally processed using DSC to characterize isothermal solidification in a planar TLPB geometry using this novel formulation. Measurements of IMC growth were performed with a series of solid-liquid diffusion couples for the Cu-Sn-Bi and Ni-Sn-Bi systems and compared with isothermal solidification times in thin planar bonds. The implications of these results for TLPB alloy design were discussed.

1.1.1 Introduction - Challenges in Replacing High-Pb Solders and Creating Even Higher Temperature Bonding Technologies

Since the beginning of integrated circuit manufacturing and circuit board assembly, Sn-Pb soldering has been the workhorse system for providing reliable interconnections, time and time again, as the underlying technologies, geometries, and number of interconnects per circuit
board have changed. The global electronics industry has transitioned to lead-free components in consumer electronic devices due to the known risks of lead to human health as reflected in the European Union’s Reduction of Hazardous Substances Act (RoHS) (European Parliament 2011) and the Waste Electrical and Electronic Equipment (WEEE) (European Parliament 2012) directive and similar bans in other regions. With electronics industry supplying a global marketplace, where compliance with EU regulations has driven the transition toward a more restricted set of materials in consumer products regardless of where they are sold, particularly for solder alloys used in circuit board assembly and packaging. (European Parliament 2011) (European Parliament, 2012) (Puttlitz and Stalter 2004)(Bradley et al. 2007). However, the transition to Pb-free electronics is far from complete: the RoHS exemptions for high-Pb, high-temperature alloys used in wafer bumping, substrate bumping, and die attach will likely continue until a practical replacement becomes available. (Frear 2006) (Tu et al. 2003)

At the same time, new devices and applications are demanding ever higher performance solder alloys for assembly than currently exist, leading to continuing research in new Pb-free alloys and interconnect solutions that meet these enhanced performance challenges. More compact auto engine compartments require placing control systems closer to the engines and actuators, which increases exposure of vulnerable integrated circuitry to higher temperatures, vibration, and thus, conditions for fatigue and failure. Semiconductors based on GaN, III-Vs, SiC, and diamond operate at significantly higher temperatures than Si, whose maximum operating temperature is approximately 200°C. This creates the need for new, RoHS-compliant bonding solutions for die-attach, insulated-gate bipolar transistor (IGBT) attach, and power electronics to replace high-Pb solders, Pb-free solders, and thermal interface materials used today. (Chin et al. 2010) (Manikam and Kuan Yew 2011) (Harris and Matthews 2009) (Chidambaram et al. 2011)(Greve et al. 2013)(Moeini et al. 2015) (Greve et al. 2014)(Li et al. 2011)

The challenges in developing a high temperature Pb-free solder or alternative interconnect solution for die attach, wafer and substrate bumping, and other joining applications can be further illustrated by examining the use of the Sn-Pb system in terms of its processing temperatures, thermal, and mechanical behavior, and the microstructures created under certain processing conditions. Tin-lead alloys have many advantageous properties for electronics, including forming a simple binary eutectic with a eutectic temperature of 183°C, excellent and reproducible mechanical properties, damage tolerance, and thermomechanical fatigue and
impact/drop shock resistance, good electrical conductivity, excellent wetting characteristics, and a classic eutectic solidification morphology with two primary solid solution phases. As shown in the Pb-Sn phase diagram in Figure 1-1, the large solid solubility of Sn in Pb (18.9 wt. % at 183°C) leads to a range of useful, tunable solidus temperatures from 183°C to close to the melting point of Pb (327°C), and, therefore, with a tunable “mushy” (liquid + solid) zone width based on alloy composition (NIST 2002a). Soldering is first performed at the chip or die attach level with high-Pb, Pb-Sn solders with a high solidus temperature and narrow mushy zone on melting. A commonly used high temperature solder composition of Pb-Sn is 95Pb-5Sn (wt. %), with a solidus temperature of 320°C. Once solidified, packaged components are soldered onto circuit boards without melting the high-Pb solder by using the Sn-Pb eutectic composition of 62.13Sn-37.87Pb (wt. %), with its eutectic temperature of 183°C or using Pb-free solders, such as in the Sn-Ag-Cu system with a eutectic composition of 95.6Sn-3.5Ag-0.9Cu wt. % and a eutectic temperature \( T_e \) of 217°C. (Moon et al. 2000) Numerous other board level assembly solders are available commercially and widely used, including the Sn-Ag eutectic \( T_e=221°C \), near eutectic Sn-Cu alloys \( T_e=227°C \) with various alloying additions, and for even lower temperature assembly, Sn-Bi eutectic alloys \( T_e=139°C \).
While there are many alloy compositions with liquidus temperatures in the 260°C – 310°C range, there are no drop-in, Pb-free solders which have solidus temperatures in the same range as high-Pb solders. For example, Sn-Cu alloys with 2-3 wt% Cu have liquidus temperatures in that range, but a solidus temperature of 227°C. Based on an examination of the binary phase diagrams with one low melting point element \( T_m < 400°C \), or with a low temperature eutectic, and the community’s experience with designing Pb-free alloys to replace the Sn-Pb eutectic, it is unlikely such a solder is possible other than the ones reviewed by Chen et al., Zeng et al. and Suganuma et al. (Chen et al. 2006)(Suganuma et al. 2009) (Zeng et al. 2012)

Non-solder alternatives have been developed resulting in a range of commercial products being currently offered, including sintering of Ag and Cu nanoparticles, core-shell nanoparticles, mixtures of coarser Cu with Ag nanoparticles, Ag-filled adhesives, Bi-Ag-X alloys, transient liquid phase sintering, and foil-based transient liquid phase bonding. For any to be acceptable substitutes for high-Pb solders in a given application or for a higher temperature application, the interconnects/bonds must:
1. Perform within an acceptable range of the electrical, thermal, and mechanical requirements for the application.

2. Form at temperatures less than or equal to commercial high-Pb solders it is replacing (< 300°C) or at any temperature limits determined by the systems to be joined.

3. Perform reliably for typical operation and use conditions, including during thermal cycling to low and high temperatures depending on the operating ranges, which can reach 400°C for some applications.

4. Exhibit acceptable mechanical, thermal, and electrical performance after long-term aging and use.

5. Be manufacturable in high-volume electronics with an extremely low level of manufacturing defects commensurate with performance requirements.

In this chapter, we focus specifically on approaches for creating transient liquid phase systems that meet these criteria and defining the ranges of compositions and processing conditions appropriate for their use in specific applications. Of particular importance is our current understanding of (1) what it will take to achieve the manufacturability required for a Pb-free technology that could replace high-Pb solders in current applications, (2) how these can be extended to higher temperature applications, and (3) how transient liquid phase bonding compares with other alternative technologies.

### 1.2 Transient Liquid Phase Bonding: Key Thermodynamic Concepts

The defining characteristic of transient liquid phase bonding is the formation of a solid bond by isothermal solidification reactions as opposed to melting, wetting, and solidification of a liquid alloy during cooling, i.e. soldering. In conventional soldering, a relatively low melting temperature component, such as a Sn alloy, is heated above its liquidus temperature. The liquid metal wets the surfaces to be joined, with some intermetallic formation possible, and cooled with the majority of liquid remaining. During cooling, a solid joint is formed by solidification. There can be significant undercooling of liquid tin, leading in most cases to formation of Sn dendrites even for a eutectic alloy. In contrast, TLPB technologies produce solid bonds between a low melting temperature phase (LTP) and the two high melting temperature substrate phases (HTP) by several possible routes: (1) by intermetallic compound (IMC) formation that consumes at least one component of the LTP, changing the composition of the liquid, and continuing to react
until no liquid remains, (2) by interdiffusion into the HTP to form a solid solution, and (3) by precipitation of another phase in ternaries and higher order phase diagrams as the phase equilibrium reactions at the liquid-solid interface change from a (liquid + IMC) to a three phase equilibrium (liquid + IMC + precipitate).

The history of using these reactions for non-electronics applications from ancient times to the 1980’s, is described in a review paper by MacDonald and Eager (1992). (MacDonald and Eager 1992) In the comprehensive TLPB study of Ag-Sn-Ag, Li, Agyakwa, and Johnson reviewed the literature for electronics applications in detail, starting with the pioneering work of Bernstein and Bartholomew from the 1960’s in bonding Ag, Au, and Cu with indium as the initial liquid for “using low-temperature processing conditions to produce high-temperature bonds for a multitude of semiconductor and non-semiconductor brazing and bonding applications.” (Li et al. 2010) They reviewed other research and its relevance to electronics, including the Roman and Eager studies of commercial solder alloys as the low temperature phases to bond Ag, Au, and Cu substrates as well as bonding of Ni, Pd, Pt, and Zr substrates and use of ternaries and quaternaries in the Cu-In-Sn-Bi system (Roman and Eagar 1992). Transient liquid phase bonding processes in Sn-based systems have been referred to by various names and acronyms by different research groups. The terms “transient liquid phase sintering” (TLPS), “liquid phase diffusion bonding” (LPDB), “transient liquid phase bonding” (TLPB), and “solid-liquid interdiffusion” (SLID) have all been used to describe bonding of two substrates via isothermal solidification reactions between a low melting temperature phase and the high melting temperature substrates. (McCluskey and Greve 2014)(Moeini et al. 2015)(Choquette and Anderson 2015) (Reeve et al. 2016). In this paper, the term TLPB will be used, although all can be used interchangeably.

Two binary and two ternary phase diagrams are used here to illustrate these three TLPB routes for isothermal solidification. The Cu-Sn binary system is the classic TLPB system, given the ubiquity of Cu and Sn in electronic interconnects. The Cu-Ni binary system, a simple isomorphous system, is used to illustrated how interdiffusion alone can lead to isothermal solidification. A ternary system is required for precipitation to occur when the other two processes deplete the liquid from one of the components leading to the formation of a new phase. The first ternary presented here is the Sn-Ag-Cu system in which IMC formation of the low melting liquid phase with the substrate eventually leads to precipitation of an IMC between Sn
and the non-reacting component. After complete isothermal solidification, the melting temperature of the bond is not as high as the melting points of the individual phases because of additional reactions that can occur with ternary alloys (and those with more elemental components.) The second ternary is the Sn-Bi-Cu system in which Bi precipitates as the Sn-Cu IMCs grow. This ternary system is shown because the melting temperature of solidified bonds can be substantially lower than the melting temperatures of the individual phases. The possible reactions, the temperatures over which they can occur, and the temperatures of stability of the final bonds can be understood from the showing how the compositions shift as reaction, diffusion, and precipitation proceed.

1.2.1 Cu-Sn Binary System: Reaction, Intermetallic Formation, and Interdiffusion.

The binary Cu-Sn phase diagram is shown in Figure 1-2, with the five possible temperatures ranges and reactions for Cu bonding with a transient Sn-Cu liquid phase (NIST 2002b). Note that the Cu solubility of the liquid (Sn) changes temperature, as does the solubility of Sn in (Cu). (Note that the use of parentheses denotes a liquid solution or solid solution phase, such as (Sn), which is a liquid contains both Sn and Cu, or (Cu) is solid Cu into which Sn is dissolved.) Although only the two lower temperature regimes are applicable to electronics manufacturing, all ranges are included for completeness, particularly to illustrate how to interpret binary phase diagrams in the context of TLPB. The importance features to note in each regime are what the solidus and liquidus temperatures are across the phase diagram, what phases are stable and at what composition, and how they change from the initial compositions as intermetallic forms isothermally.

Above the eutectic temperature of Sn-Cu (227°C) up to approximately 415°C (A in Figure 1-2), Sn liquid reacts with Cu substrates to form two intermetallics, Cu₆Sn₅ and Cu₃Sn, as shown schematically in Figure 1-3. For a limited amount of Sn relative to the Cu substrates, the liquid (Sn) can be completely consumed by the formation of these two intermetallics. At the point when the liquid is consumed, the two intermetallics and Cu will remain, which means that the joint can be heated up to 415 °C, the lowest melting temperature of the three phases remaining, i.e. of Cu₆Sn₅, without liquid formation. As a condition of thermodynamic equilibrium in binary systems, only two phases can be in equilibrium except at invariant points. An invariant point in a binary is at a specific temperature and composition at which three phases
can coexist, such as the eutectic composition and temperature. An additional type of invariant point in this binary is the peritectic at 415 °C when Cu₆Sn₅ decomposes into liquid (Sn) and Cu₃Sn. In the case of A, continued annealing after isothermal solidification leads to the disappearance of one of the two phases; in this case to the disappearance of Cu₆Sn₅ when the initial amount of Cu is significantly greater the amount of Sn and the final equilibrium is between Cu₃Sn and (Cu), a Cu-Zn solid solution. This TLPB reaction was studied in great detail by Li, Agyakwa, and Johnson (Li et al. 2011). Starting at 348°C, an additional phase between Cu and Cu₃Sn is stable with the composition Cu₄₁Sn₁₁. Continued annealing of isothermally solidified joints at temperatures between 348°C and 415°C can lead not only to disappearance of Cu₆Sn₅ but also to the disappearance of Cu₃Sn, leaving behind Cu₄₁Sn₁₁ and (Cu).

Between 415°C and 638°C (B in Figure 1-2), reaction of liquid (Sn) with Cu leads to formation of Cu₃Sn in direct contact with the Sn-Cu liquid, with additional solid phases present at equilibrium between Cu₃Sn and Cu. The melting temperature of the isothermally solidified bond is then 677°C due to the stability of Cu₃Sn above 638 °C. Between 638 °C and 757°C (C in Figure 1-2) reaction between liquid Sn and Cu leads to the formation of solid solution γ (gamma phase), the stable phase in contact with (Sn). The melting temperature of the solidified joint is determined by the specific composition of solid solution γ that is formed. Continued annealing in this range can lead to the disappearance of γ and Cu₃Sn, leaving behind β and (Cu). In D, β is the stable intermetallic phase with a wide range of solid solubility in contact with the liquid and (Cu). Ranges A – D are where intermetallic formation leads to isothermal solidification. In E in Figure 1-2, there are no stable intermetallic phases between the (Sn) liquid phase and (Cu). This means that, in this temperature range, isothermal solidification only occurs by diffusion of Sn into the Cu substrate to form (Cu). This is the same concept shown for the Cu-Ni system described below. Note that diffusion of Sn into Cu to form the solid solution (Cu) may also contribute to isothermal solidification at lower temperatures even when there are intermetallic compounds present. The contribution of Sn diffusion into (Cu) is dependent on the relative rates of intermetallic formation and interdiffusion of Sn in Cu, i.e., on temperature and the IMC and Cu microstructures.
Figure 1-2 Cu-Sn phase diagram from NIST annotated with the five ranges over which transient liquid phase bonding can be performed. Modified from (NIST 2002b).

Figure 1-3 (a) Schematic of planar geometry for transient liquid phase bonding in the Cu-Sn system (b) after partial reaction in region A in Figure 1-2(c) after complete reaction

1.2.2 Cu-Ni Binary System: Diffusion alone

The Cu-Ni system is an isomorphous system, with only a liquid phase and a face-centered cubic (FCC) solid solution phase, as shown in the phase diagram in Figure 1-4. When pure liquid Cu is brought into contact with pure Ni in this temperature range, dissolution of the Ni into the Cu liquid will occur until the liquid becomes saturated with Ni. Simultaneously, Cu diffuses into Ni
to form the solid solution. Isothermal solidification of a Ni-Cu-Ni structure can occur if the relative volume of the initial Cu liquid is small compared to the Ni such that the final composition of the bond is completely within the FCC-solid solution phase. A thermodynamic and kinetic model for isothermal solidification by diffusion in a single solder phase developed by Illingworth, et al. has relevance for electronics if temperatures are high enough for solid state diffusion in the HTP to be significant (Illingworth et al. 2007).

![Cu-Ni phase diagram](image)

Figure 1-4 Cu-Ni phase diagram calculated using ThermoCalc with the two-phase region indicated where isothermal solidification can occur by interdiffusion

1.2.3 Precipitation of an additional phase in a ternary system

1.2.3.1 Sn-Ag-Cu System: IMC formation with precipitation of a second IMC

In this analysis of the Sn-Ag-Cu system, we will first discuss reactions at temperatures where the Cu$_6$Sn$_5$ and Ag$_3$Sn are the stable phase that form between a Cu or Ag substrates and (Sn) liquid. Four isothermal sections in the Sn-Ag-Cu phase diagram (Moon et al. 2000) are used here to show the reaction pathways for isothermal solidification of a Sn-3.0Ag-0.5Cu (wt. %) alloy (SAC305) in contact with Cu at 270°C, 240°C, 223°C, and 219°C (Figure 1-5(a-d)). In Figure 1-5(a-c), the liquid dissolves additional Cu until it becomes saturated with Cu while the Ag and Sn content remain constant before IMC formation begins. For Figure 1-5d, the initial alloy contains some solid Sn but melts to form a liquid in contact with Cu$_6$Sn$_5$. The composition of the saturated liquid solution in contact with Cu$_6$Sn$_5$ is a function of temperature, as represented by
the tie lines. As the Cu₆Sn₅ and the Cu₃Sn layer between the Cu₆Sn₅ and Cu grow, the liquid becomes enriched in Ag as shown by the arrows in Figure 1-5 until the terminal liquid composition is reached for each temperature, as indicated by the starred compositions. As the Cu-Sn IMCs continue to grow, Ag₃Sn precipitates in the liquid to maintain the terminal liquid concentration.

If SAC305 is used to bond two Ag substrates at 270 °C, the path is reversed as seen in Figure 1-6(a). The Ag₃Sn intermetallic forms at the interface between the liquid and the Ag substrates. The Cu concentration in the liquid increases, reaching the same terminal liquid in equilibrium with Ag₃Sn and Cu₆Sn₅. With further Ag₃Sn growth Cu₆Sn₅ precipitates in the liquid until the liquid is consumed. The temperature dependence of the terminal liquid solution can be easily seen by following the Cu₆Sn₅ - Ag₃Sn two-phase trough in the liquidus projection indicated by the arrow in Figure 1-6b. The final structures contain precipitated intermetallic particles along the bond’s centerline. With further annealing, there may be additional solid state transitions that change the tie lines between solid phases but are not considered here.

However, the melting temperature of the resulting joint is not at 414 °C due to additional transitions that can occur at lower temperatures in this ternary (NIST 2002c). The reaction L + Cu₃Sn ↔ Cu₆Sn₅ + Ag₃Sn occurs at approximately 356 °C, as shown in the isothermal ternary sections in Figure 1-7b.
Figure 1-5 Isothermal sections of the Sn-Ag-Cu ternary a 270°C, b 240°C, c 223°C, and d 219°C (Modified from (Moon et al. 2000))
Figure 1-6 a Isothermal section of the Sn-Ag-Cu ternary phase diagram showing the reaction path for SAC305 with a Ag substrate at 270°C and b is the liquidus projection of the Sn-Ag-Cu ternary diagram at 355°C with the terminal liquid compositions occurring on the join between the Cu6Sn5 and Ag3Sn primary phase fields, indicated by the arrow, as modified from (Moon et al. 2000)
Figure 1-7 a Calculated isothermal sections of the Sn-Ag-Cu ternary diagram showing the Class II reaction occurring at a 344°C and b 350°C. showing the terminal liquids in equilibrium with Cu₆Sn₅ (stars). In a this composition forms a three phase triangle with Cu₆Sn₅ and Ag₃Sn, whereas in b the three phase triangle is between Cu₆Sn₅ and Cu₃Sn

1.2.3.2 Sn-Bi-Cu: IMC formation with Bi precipitation

A second example of a reaction to precipitate an addition phase is also presented here for the Sn-Cu-Bi system. This system was chosen because of the Type 2 reaction that occurs in this system above approximately 200 °C, in which Bi + Cu₆Sn₅ transforms into Cu₃Sn and liquid. What this means is that any reaction path below 200 °C in which the final microstructure contains Cu₆Sn₅ and Bi will form a liquid at higher temperatures, and not at the melting point of Cu₆Sn₅ in the binary Cu-Sn diagram (NIST 2002d). These reactions are shown in two isothermal sections for the Sn-Bi-Cu phase diagram shown in Figure 1-8. At temperatures below approximately 200 °C (Figure 1-8a), Sn-Bi liquids in contact with Cu form Cu₆Sn₅ and Cu₃Sn on Cu, with the liquid decreasing its Sn concentration until the terminal liquid composition (indicated by the grey star) is reached. Further reaction to form the intermetallics leads to the precipitation of Bi to maintain the constant terminal liquid composition. Isothermal solidification can go to completion in this way. If the as-solidified bond is heated to slightly higher temperatures (Figure 1-8b), the Class 2 reaction will lead to liquid formation, with no solid Bi remaining. This is because, as seen by
comparing Fig.8a and Fig. 8b, Cu$_6$Sn$_5$ is not in equilibrium with solid Bi at this temperature. Cu$_6$Sn$_5$ is only in equilibrium with Cu$_3$Sn and the terminal liquid (black star). In this case, further growth of Cu$_3$Sn at the expense of Cu$_6$Sn$_5$ may occur until it is completely consumed. At this point the liquid is in equilibrium with Cu$_3$Sn and Bi, and Bi can precipitate. Isothermal solidification will then occur by growth of Cu$_3$Sn and Bi precipitation until all the liquid is consumed. The final as-solidified bond is in the three-phase stability triangle of Cu, Bi, and Cu$_3$Sn.

![Figure 1-8](image1.png)

Figure 1-8 Calculated isothermal sections of the Cu-Sn-Bi ternary phase diagram showing class 2 reaction between a 202°C and b 203°C

These examples illustrate the critical relationship between the thermodynamic properties of systems, the processing temperatures which can be used, and their resulting application and use temperatures. The binary phase diagrams provide all relevant information on what phases might occur and at what temperature. For ternaries and higher order systems, “Class 2” reactions may occur that can dramatically decrease the temperatures where liquid forms. In order to understand what may occur in ternary and higher order systems, one cannot, therefore, estimate their behavior based on the behavior of the individual binaries. In the sections below, more examples will be explained in detail and how they determine the possible processing and application/use temperatures for specific compositions.
1.3 Transient Liquid Phase Bonding: Key Kinetic Concepts

For TLPB technologies to be adopted, the rate of reaction to form an isothermally solidified bond must be rapid enough to be consistent with commercial manufacturing, i.e. it must be quick enough to be practical. Four parameters come together in a simple geometric and kinetic model for how quickly such a reaction can occur. These parameters are: (1) IMC growth rate as a function of temperature, time, and composition, (2) the total volume of low melting phase that must be consumed for isothermal solidification to occur, (3) the interfacial area where the reaction is taking place, and (4) the uniformity of the microstructure.

1.3.1 IMC Growth Rates

Extensive observations of IMC growth kinetics have been performed by the Pb-free solder research community. These studies are typically focused on IMC formation at the interface between copper contacts, any metallization, and the bulk solder alloy. Interdiffusion studies related to Kirkendall void formation also provide a valuable source of data for TLPB design. Study of IMC formation specifically for TLPB has also been performed for the key IMC phases typically utilized. Here we introduce some of the relevant literature results for Ag₃Sn, Cu₃Sn, Cu₆Sn₅, and Ni₃Sn₄.

There have been many studies reporting the kinetics of Cu₆Sn₅ and Cu₃Sn growth in the Cu-Sn system. Li et al. measured IMC growth in Cu/Sn/Cu arrays using a combination of differential scanning calorimetry and measurement of IMC growth from cross-sections (Li et al. 2011). Measurement of IMC thickness was then used to determine the residual Sn content from DSC heat flow measurements. This technique was used to gather a comprehensive dataset for IMC growth in Cu-Sn and to develop a model that includes consumption of Cu₆Sn₅ via Cu₃Sn formation. Based on this dataset, the change in total IMC thickness with time was found to be proportional to $Kt^{1/2}$ - the typical equation assumed to correspond to lattice diffusion control, with $K$ that includes the temperature dependence. With this data set and the derived equation, it is then possible to predict the necessary processing time for complete isothermal solidification of a known layer thickness in the Cu-Sn system and for complete conversion to Cu₃Sn. The Arrhenius method was used with the resulting kinetics constants for 260°C, 300°C, and 340°C to arrive at an activation energy of 84.6+/− 25.8 kJ/mol for Cu₃Sn and 19.7 +/− 13.1 kJ/mol for
Cu₆Sn₅. A summary by Laurila et al. (2005) provides further background on reactions between Sn and Cu and the effects of ternary additions (Laurila et al. 2005).

Li et al. 2010 also studied the growth kinetics of Ag₃Sn in Ag/Sn/Ag couples at 260°C, 300°C, and 400°C using a combination of DSC experiments coupled with microstructural characterization using an SEM (Li et al. 2010). Ag₃Sn growth was shown to conform to a time dependence of \( t^{1/3} \) where the exponent of 1/3 is assumed to correspond to a grain boundary diffusion-type controlled growth. The IMC growth rate and morphology was shown to be consistent with grain boundary diffusion / molten channel-controlled growth, i.e., the growth morphology showed irregular, facetted growth front, with a reported activation energy of 37.2 +/- 18.9 kJ/mol (Li et al. 2010).

The kinetics of Ni-Sn formation are generally slower than for the Cu-Sn or Ag-Sn intermetallics, with Ni₃Sn₄ IMC growth reported to dominate at lower temperatures and to be parabolic. Tomlinson and Rhodes investigated interfacial IMC formation between Sn and Ni, Ni-P, and Ni-B surfaces from 180°C to 220°C. An activation energy of 128 kJ/mol was observed (Tomlinson and Rhodes 1987).

As seen in Figure 1-2a for the simple case of Cu-Sn, a Sn film of thickness \( L \) is placed between two planar Cu substrates of area \( A \). Intermetallic formation to form Cu₆Sn₅ and Cu₃Sn only occurs at the interfaces between the Cu and Sn, so the consumption of the Sn to isothermally solidify the structure and form the bond is limited by the area of contact, which in this case is \( 2A \), with the effective thickness of Sn to be consumed by intermetallic formation of \( L/2 \), with a total volume of liquid Sn to be consumed of \( 2A*L/2 = A*L \). Reaction occurs by interdiffusion as described by He et al., Kumar et al, and Park et al., with the reaction rate decreasing as the layer thickness increases, and increasing as the temperature increases (He et al. 2004)(Kumar et al. 2011)(Park et al. 2014). The simplest form of the relationship between IMC thickness and time at a given temperature is that the thickness of the IMC layer formed after time \( t \) is proportional to the product of a kinetic coefficient \( (K) \) and \( t^{1/2} \). Therefore, when this equation applies, the time required for isothermal solidification goes up as the square of the layer thickness, as shown in Figure 1-9.

The \( Kt^{1/2} \) equation is frequently interpreted as a measurement of lattice diffusion for forming the combined growth of Cu₆Sn₅ and Cu₃Sn, but this does not reflect the actual diffusion pathways that lead to IMC growth. Even in the growth of a single IMC, the rate of reaction is
determined by the specific contributions of grain boundary, lattice, and interfacial diffusion, as well as other microstructural and physical characteristics of the bonds that affect their evolution with time and temperature. When two IMCs are evolving, the rate of growth of both IMCs is coupled.

Park et al.’s phase field calculations take these contributions into account and successfully captures the scalloped morphology of the Cu_{6}Sn_{5} (Park et al. 2012). Phase field modelling allows the identification of relative diffusion rates for the various diffusion pathways rather than relying on a single diffusion term. Accurate representation of observed morphology indicates realistic diffusion terms for grain boundary diffusion, interfacial diffusivity between phases, bulk diffusivity, etc. These models were in term used to create processing maps for Cu-Sn TLPB (Figure 1-9) in terms of processing temperature, Sn bond line thickness, and time for complete conversion. The maximum acceptable processing time determines the maximum bond line thicknesses and temperatures that can be used for a given system with its kinetics and geometry (Park et al. 2014). Using the results from Park et al. in Figure 1-9a, only the temperatures and bond line thicknesses below the horizontal dotted line can produce isothermal solidification in less than 20 minutes. As another example, assume that a practical lower limit of bond line thickness is 10 µm and an upper limit of processing time is 5 minutes. Only the conditions represented by the small shaded triangle in the top left corner of the Park et al. processing map in Figure 1-9b produce isothermal solidification for temperatures up to 310°C.
Figure 1-9  

a) Sn elimination time with respect to temperature and initial Sn layer thickness, with the maximum processing time line drawn at 20 minutes to illustrate a possible practical limit.  

b) Contour map representing Sn elimination time with respect to temperatures (240°C - 310°C) and Sn layer thicknesses 4 - 28 µm. The shaded area shows the range of temperatures and thicknesses near 10 µm possible for a maximum 5 minute processing time (Modified from Park et al. 2014)
The final critical point to be made here is that the growth rate of an intermetallic can be dramatically affected by alloy composition and the presence and stability of grain boundaries/interfaces in the IMCs. This can occur even when comparing two systems in which the IMCs being formed are the same. Although the \( t^{1/2} \) and \( t^{1/3} \) dependence is assumed to reflect growth only by lattice diffusion and grain boundary/interface diffusion, respectively, growth of IMC layers occurs by a combination of grain boundary, lattice, and surface or interfacial diffusion, with grain boundaries serving as fast diffusion paths between the two bounding phases. Having a higher density of grain boundaries, i.e., a smaller grain size, in the IMC layer will lead to faster growth. The grain size at any given stage in processing will also be determined by the rate of coarsening of the IMC by surface/interfacial diffusion and grain boundary motion. One example is TLPB in the Sn-Cu-Ni system. Using Cu-Ni solid solution substrates of different compositions in contact with initially pure Sn, several papers have report that the intermetallic growth rate of \( \text{Cu}_6\text{Sn}_5 \) can be higher by orders of magnitude when it forms on Cu-Ni alloys rather than on Cu. (Vourinen et al. 2008) (Paul, 2004)(Baheti et al. 2017a) (Baheti et al. 2016)(Choquette and Anderson 2015) (Reeve, et al. 2016) Furthermore, the \( \text{Cu}_3\text{Sn} \) IMC appears to become unstable for \( \text{Cu}_x\text{Ni} \) compositions for \( (x \geq 10) \). Using a particle-based TLPB approach, Choquette and Anderson determined that, depending on the volume fraction of liquid, \((\text{Cu},\text{Ni})_6\text{Sn}_5\) growth could be fast enough to completely solidify bonds/solder joints after 90 seconds above 250 °C (Choquette and Anderson 2015). Another example is the Cu-Sn-Bi system, in which the effective diffusion coefficient for \( \text{Cu}_3\text{Sn} \) appears to be two orders of magnitude faster than in the Cu-Sn system at the same temperature. In both cases, the IMC growth morphologies were different from their Cu-Sn counterparts, with a significantly smaller, yet stable IMC grain size for the former as shown in Figure 1-10(Paul 2004) (Baheti et al. 2016) (Baheti et al. 2017b), and faceted, irregular IMC growth for the latter. The practical implication for these observations is that growth rate and microstructural evolution experiments are needed for calibration of any new materials system. The results from these two systems are described in greater detail below.
Figure 1-10 Micrograph showing the grains of the Cu₆Sn₅ phase in diffusion couple annealed at 215 °C for 400 h for (a) binary Cu/Sn and (b) ternary Cu(5Ni)/Sn (Paul 2004).

1.3.2 Effect of Reaction Geometry on Isothermal Solidification Rate: Changing the Volume of Low Temperature Phase and Interfacial Area for Reactions

The time for isothermal solidification can be reduced by increasing the interfacial area over which the reaction is occurring, while keeping a fixed volume of low melting point phase. For example, if the reaction configuration is changed by adding a Cu foil of the same size as the substrates being joined while keeping the total Sn volume constant, as illustrated in Figure 1-11a-c, the interfacial area for reaction doubles and the Sn layer thickness that must be consumed by IMC formation is thus reduced by a factor of 2. According to the simple equation above, this would reduce the reaction time by a factor of 4. Bajwa and Wilde demonstrated that creating a multilayer geometry can be an effective strategy for reducing the time required for isothermal solidification, achieving mechanical, thermal, and electrical properties of multi-layer Ag-Sn-Ag bonds that were equivalent to sintered nanosilver (Bajwa and Wilde 2016).
Another geometry that reduces the reaction time is by combining particles of the high temperature phase with low temperature phase to increase the interfacial area available for reaction. This geometry, referred to here as transient liquid phase sintering (TLPS), is shown schematically for the Sn-Cu system in Figure 1-11d. For a constant total volume of copper and of tin, reducing the Cu particle size increases the total area over which reaction can occur, thus decreasing the effective Sn layer thickness with the time for complete conversion being proportional to the Sn layer thickness squared. A typical microstructure of a TLPS bond using
Cu HTP particles and a Sn-Bi matrix is shown in Figure 1-11e. Note that there is significant porosity remaining in addition to a dense network of Cu particles, IMC, and residual Sn.

1.4 Manufacturing and Design Constraints

In addition to the reaction itself, manufacturing processes for a specific application impose additional constraints that must be considered in choosing TLPB formulations and selecting the materials to be bonded. Processing takes place above the liquidus of a relatively low-melting temperature phase, commonly Sn or a Sn-based alloy, which melts and reacts with a high temperature phase to isothermally solidify the bond. As with soldering, there are many other additional processing steps that affect the microstructure, properties, performance, and reliability of the resulting bonds:

1. Fluxing or pre-processing of the substrates.
2. Application of the foil, preform, or paste onto one substrate and then capping with the additional substrate. Some pressure is required to set the initial configuration.
   Additional pressure may be needed in subsequent steps.
3. Heat up of the assembly to be bonded, with or without pressure.
4. De-gassing of the flux during heat up, with rearrangement and densification in the solid state occurring in particle/paste based systems.
5. Melting of the LTP.
6. Wetting of the HTP (substrates and particles) by the liquid phase and capillary flow to redistribute the liquid.
7. Dissolution of HTP into the LTP until LTP is saturated.
8. Reaction at the maximum temperature to form the desired intermetallic and precipitate phases until no liquid remains and without formation of porosity.
9. Cooling of the assembly to room temperature without cracking or debonding.

All steps must be successful for useful bonds to form.

Since TLPB is a reaction-based process, maintaining appropriate stoichiometry is necessary to ensure complete conversion of the LTP to desired IMC and precipitate phases. For example, if we consider the complete conversion of Sn to form Cu$_6$Sn$_5$, the molar ratio of Cu:Sn must be greater than 6:5. If we take into account the density and atomic volumes of Cu and Sn, the minimum molar ratio can be converted into volume and mass-based ratios and fractions that
are useful for selecting HTP and LTP particle sizes and estimating minimum reaction time for isothermal solidification from IMC growth rate data. Ratios and fractions for conversion into the most common Ag, Cu, and Ni Sn-based IMCs formed during TLPB are presented in Table 1-1. In some cases, the fraction of LTP required to produce bonds exhibiting reasonable adhesion and density exceeds the maximum LTP:HTP ratio for complete conversion. Increasing the ratio of LTP to HTP typically improves wetting of the surfaces to be bonded. For TLPS systems, it also promotes particle rearrangement and densification. For a constant interfacial area of HTP, increasing LTP volume increases the thickness of IMC per unit area that must be formed, and therefore increases the minimum process time.

Various techniques for assembling TLPB structures have been used in research studies and a few have been incorporated into commercial products. Screen-printable TLPS pastes containing a polymer added for increased stability have been developed in the Sn-Cu-Bi system (Ormet Circuits 2012) as a replacement for lead-free solders, Cu-via fill, TIMs, and high-Pb solder paste. A TLPB foil, an LTP preform, or a TLPS preform could be applied using die attach equipment currently used for die attach adhesive films. Plating and other deposition techniques of the LTP have also been used instead of, or in addition to foil, to promote substrate wetting. Additionally, novel or hybrid approaches may be employed, such as the multilayer described above. All design choices result in tradeoffs in process requirements, bond quality, application space, and market appeal.

Foil or LTP pre-form configurations simplify the design process by minimizing flux and densification issues, but process time increases with bond line thickness since the two interfaces being bonded function as the only source of HTP. This becomes of particular concern when metallization layers are thin. For example, electroless Ni layer thicknesses are limited to 3-6 µm according to IPC Standard 4552 (IPC 2012). For example, for complete conversion of two 3µm Ni layers to Ni$_3$Sn (one on each surface to be bonded) without complete consumption of the Ni, the total bond line thickness of Sn must be less than 5 µm. This is a challenge for initial bonding due to issues of substrate planarity, deposition control, and substrate wetting. If the reaction layer is only Ni$_3$Sn$_4$, the maximum allowable Sn thickness would be approximately 20 µm. Acceptable reflow times and temperatures, ability to provide pressure, and post-assembly annealing capabilities also constrain the composition and maximum TLP thickness.
The key advantage of a LTP-HTP paste is that the maximum bond line for complete conversion is independent of bond line thickness due to the presence of the HTP in the bulk of the bond. This is in contrast to a foil-based format where the bonding interface is the only source of HTP, as described above. Since reaction rates are a function of HTP surface area, LTP volume, and interdiffusion rates, paste-based technologies (TLPS) provide an opportunity for controlling the reaction rate by independently changing HTP volume, HTP interfacial area, and LTP volume. In addition, paste-based formulations introduce the variables of particle size, particle size distribution, and morphology, flux and binder characteristics and amounts, LTP to HTP ratios, and overall bond line thickness. There can be issues in reducing the particle size of the HTP to increase the interfacial area and thus decrease the processing time; for example, poor wetting and oxidation may be more pronounced at smaller particle sizes. Additional issues are presented in the next section.

### Table 1-1 LTP to HTP Ratios and Fractions for Binary Intermetallic Compounds

<table>
<thead>
<tr>
<th>Phase</th>
<th>Maximum Volume Ratio of LTP to HTP</th>
<th>Maximum Volume Fraction of LTP</th>
<th>Maximum Mass Ratio of LTP to HTP</th>
<th>Maximum Mass Fraction of LTP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag3Sn</td>
<td>0.52:1</td>
<td>0.34</td>
<td>0.37:1</td>
<td>0.27</td>
</tr>
<tr>
<td>Cu3Sn</td>
<td>0.76:1</td>
<td>0.43</td>
<td>0.62:1</td>
<td>0.38</td>
</tr>
<tr>
<td>Ni3Sn</td>
<td>0.67:1</td>
<td>0.45</td>
<td>0.81:1</td>
<td>0.45</td>
</tr>
<tr>
<td>Cu6Sn5</td>
<td>1.89:1</td>
<td>0.66</td>
<td>1.56:1</td>
<td>0.61</td>
</tr>
<tr>
<td>Ni3Sn4</td>
<td>3.22:1</td>
<td>0.78</td>
<td>2.70:1</td>
<td>0.73</td>
</tr>
</tbody>
</table>

### 1.5 Wetting and Microstructural Inhomogeneities

In the previous section, changing the LTP to HTP ratio and the LTP layer thickness lead to straightforward conclusions about the kinetics. For a constant interfacial area of HTP, increasing LTP volume increases the thickness of IMC per unit area that must be formed, and therefore increases the minimum process time. In addition, increasing the ratio of LTP to HTP typically improves wetting of the surfaces to be bonded. For systems containing HTP particles, it also promotes rearrangement and densification. However, uniform, predictable wetting of the HTP is required for these relationships to be true, and ultimately for producing a commercially viable TLPB technology.
1.5.1 Incomplete Wetting.

If the low temperature phase does not completely wet the high temperature phase, the actual thickness of the low temperature phase to be consumed by isothermal solidification will be larger than the optimal for that system, meaning that the solidification time required goes up by \((\text{thickness})^2\) or \((\text{thickness})^3\). Furthermore, the bond will contain significant voids and stress-concentrating defects. This partial wetting situation is shown in Figure 1-12a for a fluxed 10 µm Sn foil placed between two singulated, leadframe Cu sheets (5.6mm x 5.6 mm and acid etched). The trilayer assembly was heated using a hot plate to 260 °C and held for 40 minutes. As a result of non-uniform melting and wetting, the sheets contained wetted and non-wetted regions as shown in Figure 1-12b-d, with the wetted regions being considerably thicker than 10 µm for conservation of mass. Along the edges of the wetted regions, the low temperature phase retracts as the IMC forms, leading to bare IMC where the liquid was previously and an incipient “crack” along the interface as shown in Figure 1-12d. This solidification phenomenon is known as “hot tearing.” Wetting in TLPB with foil systems can be improved by creating a more uniform temperature field during heating, applying pressure to redistribute the liquid between the two substrates, using a reducing atmosphere, improving planarity of the substrates, and ensuring there is enough liquid to completely wet the surfaces during heating before IMC growth begins to form bridges between the two substrates.

Complete wetting in the Cu-Bi-Sn system with the target bond line thickness was achieved by preheating two fluxed substrates on a hot plate, dropping two 500 µm diameter solder balls on one substrate where the solder balls then wet and spread across the substrate, then putting the second substrate in contact with the molten solder, and pressing the two together with slight pressure. The total time above liquidus was 5 to 10 seconds. The joined substrates were cooled and then subsequently annealed to isothermally solidify the bonds. Several other studies have shown that fully wetted structures are possible in foil-based systems if the pressure is high enough, if the surfaces being joined are sufficiently planar for the LTP volume used, and if the other effects are controlled.
Figure 1-12 Bond in foil-based TLPB Sn-Cu using 10 µm pure Sn foil, with no-clean RMA flux and low pressure (28 kPa) joining Cu lead frame substrates at 260°C for 40m showing a region of good wetting, b Schematic TLPB cross-section illustrating ideal wetting condition (top) and final partial wetting condition (bottom) with exaggerated defects (non-planarity, irregular growth fronts, and hot tearing) c Edge of wetted region showing hot tearing and d exposed Cu-Sn IMCs.
1.5.2 Liquid Redistribution and Porosity Formation in TLPS Systems.

Porosity of the same scale as the low melting phase particle size can also occur in a particle-based TLPS systems due to the melting and redistribution of the low melting point phases into agglomerated HTP particle clusters. Furthermore, both pockets of liquid and voids can be created due to the simple geometrical arrangement of particles, as shown in Figure 1-11e and Figure 1-13. This represents a significant deviation from an ideal uniform layer thickness of low temperature melting phase. Flanagan et al. 2012 and Greve et al. 2013, 2014 noted that such porosity can remain in the isothermally solidified bond if the Cu and low temperature phase particles are mixed together to form a paste (Flanagan et al. 2012). When the low temperature phase particles melt, the liquid wets the Cu particles, pulling the Cu particles together due to capillary forces, but not necessarily with much Cu particle rearrangement. When the IMC forms between adjacent Cu particles the structure becomes rigid. This leaves behind voids where the low temperature phase particles had been and which cannot be removed due to the rigid interconnected structure of the IMC. In addition, the role of paste formulation is important as well, including particle size differences, LTP composition differences, and fluxes. Pan and Yeo 2014 performed a process optimization study with three different pastes containing Cu, Sn alloy particle sand Sn-Bi alloy particles, flux, and polymer additive. They demonstrated that reflow parameters could be controlled to significantly decrease formation of large voids and improve the resulting mechanical and thermal properties of bonded structures, as shown in Figure 1-14.

Figure 1-13 Cross-section of as-fabricated Cu-Ni-Sn TLPS bond using Cu-10wt%Ni HTP particles and Sn-Ni LTP, showing formation of (Cu,Ni)-Sn IMC and unreacted Sn at particle junctions. Pockets of residual tin between HTP particles in a TLPS Cu-Ni-Sn bond (Choquette and Anderson 2015)
In a recent study, Chen et al. eliminated these issues with TLPS by using Cu-Sn core-shell particles to form a preform at 30MPa and applying light loads during processing/reaction (Chen et al. 2016). From this process, high density bonds could be formed with minimal porosity and acceptable mechanical, thermal, and electrical properties for IGBT applications. It should be noted that process optimization studies must be performed for all new formulations in the specific applications and geometries being considered.

1.5.3 Porosity Formation during Isothermal Solidification and Solid-State Transformations

Porosity formation in TLPB systems can have several other root causes that should be avoided. These include: (1) Sn consumption by solid-state IMC formation during heat-up before a liquid forms, (2) volume changes during bond formation and IMC equilibration after isothermal solidification, (3) debonding due to consumption of the HTP, and (4) flux entrapment. In terms of porosity formation during solid state reactions, Bosco and Zok demonstrated that if IMC formation in the Cu-Sn system is completed before forming any liquid, significant porosity forms along the midline of the bond (Bosco and Zok 2004). The critical limits for porosity
formation are determined by the LTP thickness, the target reaction temperature, and the heating rate to the reaction temperature. This is particularly an issue for electroplated LTP phases on metal substrates, where in systems such as Sn-Cu, IMC growth begins at room temperature. This may have contributed to porosity formation in thin Sn-Ag TLPB bonds formed at a heating rate of approximately 10°C/minute up to 300°C (Shao et al. 2017). Midline porosity formation was also observed by Chuang et al. for Sn-Ni bonds that were partially reacted above the LTP liquidus temperature and then subsequently annealed below the solidus temperature to consume the Sn (Chuang et al. 2012). As with Bosco and Zok, they attributed porosity formation to the impingement of a few large IMC particles along the midline that limited volume change accommodation as IMC growth continued in adjacent areas. They discovered that adding 2.4 wt% Ag to Sn eliminated void formation, likely by rapid coarsening of the Ag₃Sn to fill in the pores.

A second cause of void formation is due to volume changes as the phase fractions of the IMCs change during equilibration after isothermal solidification. Bundiman et al. observed pronounced void growth along the midline in as-solidified Ni-Sn TLPB bonds composed of Ni₃Sn₄ and Ni formed at 300°C was subsequently reacted to form Ni₃Sn₂ and Ni₃Sn at 600°C, as shown in Figure 1-15. (Budhiman et al. 2017). Void formation was exacerbated by the squeezing out of Sn to the edges of the bond during initial bonding where it continued to form IMC during the high temperature anneal. A third root cause of porosity is dewetting of the underlying substrate when a thin, plated HTP layer forms an IMC not only with the HTP but also with the underlying under-layer metallization (Chu et al. 2015). Flux entrapment can also create a physical barrier to impingement of the two reaction fronts, leading to midline porosity formation (Chu et al. 2015).
Figure 1-15 Optical microscopy cross sections of Ni-Sn TLPB bond showing (top) $\text{Ni}_3\text{Sn}_4$/Ni bond fabricated at 300°C for 20 minutes using a pressure of 0.5 bar. Note unreacted Sn forced out of bond during fabrication and small line of midline porosity in $\text{Ni}_3\text{Sn}_4$. (bottom) Significant void formation after annealing at 600°C for 24 h accompanying transformation to $\text{Ni}_3\text{Sn}$ and the formation of $\text{Ni}_3\text{Sn}_2$ where residual Sn had been. (Budhiman et al. 2017)

1.6 Commercial Electronics Applications and Technical Demands

1.6.1 Application temperatures

Transient liquid phase bonding has been proposed for a variety of electronics applications in which high temperature compatibility is necessary. Automotive, aerospace, and deep well applications are commonly cited in literature as industries demanding operation at increased temperatures (Chin et al. 2010). Changes in semiconductor market for power electronics also demands new interconnect solutions. These power electronics devices are more efficient but tend to operate at higher temperatures with greater thermal fluxes due to their small footprint compared to Si-based devices. Back-side attach or die-attach is a common application of high-Pb solders which is currently exempt from RoHS regulations which have driven most of the global consumer market towards the use of Pb-free solders.

Electrification in both the automotive and aerospace industries is expected to increase demand for interconnect technologies that can sustain high-temperature applications under harsh conditions (Chin et al. 2010). As noted by Chin et al. from a report by DaimlerChrysler, devices installed in the engine compartment are expected to withstand operating temperatures up to 200 °C. The proliferation of sensors and electronics controls throughout the vehicle also means that interconnect technologies will need to tolerate even higher temperature extremes, up to
300 °C for wheel mounted components, 500 °C for combustion systems, and 800 °C in exhaust systems. Thermal management for power electronics is increasingly a concern for the aerospace industry as fly-by-wire technologies become more common.

1.6.2 Application Requirements

The possible application temperatures span the ranges for high Pb solders (room temperature to 200 °C) up to 800 °C for exhaust systems. Regardless of the high-temperature application, the following performance, properties, and processability requirements must be met, as summarized from reviews of Chin et al. 2010 and Manikam et al. 2011 with some additions and modifications (Chin et al. 2010) (Manikam and Kuan Yew 2011). They are:

- For solders:
  - Appropriate solidus and liquidus temperatures for the specific application, for example, ≥ 260 °C for high-Pb solder replacement and even higher for other applications
- For non-solder alternatives:
  - Processable at reasonable temperatures, with no liquids forming near the use temperature.
- Acceptable wettability and adhesion
- Low toxicity
- Reasonable cost
- Thermal conductivity > 20–30W/m·K
- High electrical conductivity
- Good corrosion resistance
- Ductility for stress relaxation within the bond
- Thermal shock reliability
- Thermo-mechanical fatigue resistance
- Ability to accommodate CTE mismatch between the die and substrate
- Long-term stability under use temperatures
- Manufacturable in high-volume manufacturing
- Reworkable
The inability to meet these requirements with an alternative in high-volume manufacturing for a broad range of applications has led to the continuation of RoHS Exemption 7(a) for "Lead in high melting temperature type solders (i.e. lead-based alloys containing 85% by weight or more lead)."

The properties, performance, and processing requirements listed above can be examined in terms of intrinsic versus extrinsic behavior for a given technology. For example, the thermal and electrical conductivities of pure single crystal metal are intrinsic properties. In most applications, however, dopants, impurities, second phase particles, and defects such as dislocations and grain boundaries create scattering sites that lead to a decrease in conductivity. The microstructure creates most of the extrinsic behaviors of materials, having a dramatic effect on electrical and thermal conductivity, as well as on most of the other requirements listed above. For example, the presence and spatial distribution of porosity can dramatically decrease thermal and electrical conductivity, as is well known for solder interconnects. Consider the following three cases of solids with porosity: (1) 50% porosity distributed as isolated pores in a dense matrix, (2) a particle compact with 50% porosity but no particle-particle bonding, and (3) a dense solid with an interface crack with a substrate. In the first case, the thermal and electrical conductivities would be decreased by approximately 50% from the bulk values. For the second case, there are only point contacts between the particles, leading to very high contact resistance/low conductivity (Kammer et al. 2015). In the third case, if the crack spans the entire interface, the conductivity of the structure is dictated by the conductivity across the air gap. Microstructure and microstructure evolution dictate the extrinsic behavior of TLPB interconnects and must be optimized for the specific application.

A common method for taking multiple criteria into account when down-selecting technologies for specific applications is through a weighted decision matrix assessment. A weighted decision matrix for comparing die attach material candidates is illustrated in
Table 1-2, a draft matrix created by the iNEMI High Temperature, Pb-free Die Attach Material Project. The importance of specific characteristics depends on the demands of the application and specific characteristics of the full system. In some cases, there will be pass-fail level that a technology must meet, such that failing by one characteristic eliminates it from further consideration. The numerical scores (0-5) are assigned to difference performance levels set by the application, where a higher score is better. Each score is multiplied by its weigh factor (not shown here), and all scores are summed for a given technology to come up with an overall score that can be compared with alternatives. In many cases, the real value of setting up a weighted decision matrix is to clarify the requirements for an application, examine where various technologies fall short, and determine whether other parts of the design or processing might be used to overcome such limitations. In some cases, it is found that certain criteria are not absolute, and can be traded-off for others, i.e., the weighting factors can be modified after further analysis of the results.
Table 1-2 Scoring factors related to key characteristics for commercial applicability intended for comparing different die attach technologies (iNEMI High Temperature, Pb-free Die Attach Material Project)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Is it a solder material?</td>
<td></td>
<td>X No</td>
<td>Yes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cost relative to high lead solder (Pb5Sn)</td>
<td></td>
<td>X &gt;100x</td>
<td>10-100x</td>
<td>5-10x</td>
<td>2-5x</td>
<td>&lt;2x</td>
<td></td>
</tr>
<tr>
<td>Melting Temperature of Final Bond</td>
<td>°C</td>
<td>X &lt;260</td>
<td>&gt;=260</td>
<td>&gt;=280</td>
<td>&gt;=300</td>
<td>&gt;=350</td>
<td></td>
</tr>
<tr>
<td>Service Temperature</td>
<td>°C</td>
<td>X &lt;150</td>
<td>&lt;=175</td>
<td>&lt;200</td>
<td>&lt;250</td>
<td>&gt;250</td>
<td></td>
</tr>
<tr>
<td>Stiffness (Modulus)</td>
<td>GPa</td>
<td>X Greater than 100</td>
<td>80 to 100</td>
<td>50 to 80</td>
<td>20 to 50</td>
<td>Less than 20</td>
<td></td>
</tr>
<tr>
<td>Feasible Applications</td>
<td></td>
<td>X Transistor</td>
<td>Diodes</td>
<td>Thyristors</td>
<td>Rectifiers, Inverters</td>
<td>Power MOSFET, IGET</td>
<td></td>
</tr>
<tr>
<td>Surface Metallization Compatibility</td>
<td></td>
<td>X Cu</td>
<td>Cu, Ag</td>
<td>Cu, Ag, NiAu</td>
<td>Cu, Ag, NiAu, NiPdAu</td>
<td>Cu, Ag, NiAu, NiPdAu, Ag thick film</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>W/mK</td>
<td>X 0 to 10</td>
<td>10 to 25</td>
<td>25 to 50</td>
<td>50 - 100</td>
<td>&gt; 100</td>
<td></td>
</tr>
<tr>
<td>Electrical Resistivity</td>
<td>μΩ*m</td>
<td>X Greater than 100</td>
<td>Less than 100</td>
<td>Less than 50</td>
<td>Less than 1</td>
<td>Less than 0.2</td>
<td></td>
</tr>
<tr>
<td>Moisture Sensitivity Level (MSL)</td>
<td></td>
<td>X 6</td>
<td>3</td>
<td>2a</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Reliability (cycles to failure)</td>
<td>°C</td>
<td>X 125Peak</td>
<td>150 Peak</td>
<td>165 Peak</td>
<td>175 Peak</td>
<td>200 Peak</td>
<td></td>
</tr>
<tr>
<td>CTE</td>
<td>PPM per °C</td>
<td>X &gt;80</td>
<td>40-80</td>
<td>20-40</td>
<td>10 - 20</td>
<td>&lt; 10</td>
<td></td>
</tr>
<tr>
<td>Processing Temperature</td>
<td>°C</td>
<td>X &lt;200</td>
<td>200 ~250</td>
<td>250 ~300</td>
<td>300 to 400</td>
<td>&gt;400</td>
<td></td>
</tr>
<tr>
<td>Pressing Pressure</td>
<td>MPa</td>
<td>X &gt; 50 MPa</td>
<td>&gt;10MPa</td>
<td>1-10MPa</td>
<td>&lt;1MPa</td>
<td>None Need</td>
<td></td>
</tr>
<tr>
<td>Processing Atmosphere</td>
<td></td>
<td>X Other:</td>
<td>Vacuum</td>
<td>Forming Gas</td>
<td>N2</td>
<td>Air</td>
<td></td>
</tr>
<tr>
<td>Pressing Time</td>
<td></td>
<td>X &gt;1hour</td>
<td>&lt;1hour</td>
<td>&lt;30min</td>
<td>&lt;10min</td>
<td>&lt; 1 min</td>
<td></td>
</tr>
<tr>
<td>Maturity</td>
<td></td>
<td>X R&amp;D level</td>
<td>-</td>
<td>Small-Scale Mass Production</td>
<td>-</td>
<td>Large-Scale Mass Production</td>
<td></td>
</tr>
<tr>
<td>Material Type</td>
<td></td>
<td>X Paste</td>
<td>-</td>
<td>Preform</td>
<td>Wire</td>
<td>Film</td>
<td></td>
</tr>
<tr>
<td>if it is a paste, paste type</td>
<td></td>
<td>X Dispensing</td>
<td>-</td>
<td>Printing</td>
<td>-</td>
<td>Both</td>
<td></td>
</tr>
<tr>
<td>Cleaning</td>
<td></td>
<td>X Other</td>
<td>Chemical Wash</td>
<td>Water Wash</td>
<td>-</td>
<td>None Need</td>
<td></td>
</tr>
<tr>
<td>Rework</td>
<td></td>
<td>X No, component would be destroyed</td>
<td>Rework possible, but will require more steps</td>
<td>-</td>
<td>Mostly compatible</td>
<td>Yes, compatible with conventional rework techniques</td>
<td></td>
</tr>
<tr>
<td>Die Size Compatibility</td>
<td></td>
<td>X &lt; 4mm²</td>
<td>4-16 mm²</td>
<td>16-36 mm²</td>
<td>36-100 mm²</td>
<td>&gt;100 mm²</td>
<td></td>
</tr>
<tr>
<td>Electromigration potential</td>
<td></td>
<td>X Likely</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Unlikely</td>
</tr>
</tbody>
</table>
The scoring system shown here values high melting temperatures, high operating temperatures, high thermal and electrical conductivities, and low CTE, as seen by the relative scores. The scoring for reliability, corrosion resistance, electromigration and other complex criteria will generally be based on performance in a standardized test as compared with a benchmark material, or on a series of laboratory tests that evaluate properties affecting the more complex criteria. For example, for reliability these might consist of thermal cycling tests of an assembly in terms of cycles to failure under specific testing conditions for the former, and of stress-strain behavior in a tensile test, fracture toughness, various elastic moduli, ductility, impact testing, and creep rate for the latter.

Another method for performing a quantitative, yet more visual comparison on a characteristic-by-characteristic basis is using a “radar” chart as illustrated in Figure 1-16. For candidate systems that meet the pass-fail down-selection criteria, the characteristics are distributed around the outer circumference of a facetted circle. The score for each characteristic for a technology is marked on one of the 6 levels as determined by their scores (0-5). The order of the characteristics can be changed to reflect priorities, and the tradeoffs in individual characteristics can become more apparent than by using a composite score.

Figure 1-16 Schematic radar chart comparing two die-attach technologies using multiple characteristics to illustrate the tradeoffs between technologies
Table 1-3 Properties of intermetallic phases commonly utilized for TLPB (Room temperature properties published by NIST) (Fields et al. 1991)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Cu$_6$Sn$_5$</th>
<th>Cu$_3$Sn</th>
<th>Ni$_3$Sn$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition Temperature (°C)</td>
<td>415</td>
<td>638</td>
<td>798</td>
</tr>
<tr>
<td>Vickers Hardness (Kg/mm$^2$)</td>
<td>378 +/- 55</td>
<td>343 +/- 47</td>
<td>365 +/- 7</td>
</tr>
<tr>
<td>Toughness (MPa$\sqrt{m}$)</td>
<td>1.4 +/- 0.3</td>
<td>1.7 +/- 0.3</td>
<td>1.2 +/- 0.1</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>85.56 +/- 1.65</td>
<td>108.3 +/- 4.4</td>
<td>133.3 +/- 5.6</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.309 +/- 0.012</td>
<td>0.299 +/- 0.018</td>
<td>0.330 +/- 0.015</td>
</tr>
<tr>
<td>Thermal Expansion (PPM/°C)</td>
<td>16.3 +/- 0.3</td>
<td>19.0 +/- 0.3</td>
<td>13.7 +/- 0.3</td>
</tr>
<tr>
<td>Thermal Diffusivity (cm$^2$/sec)</td>
<td>0.145 +/- 0.015</td>
<td>0.240 +/- 0.024</td>
<td>0.083 +/- 0.008</td>
</tr>
<tr>
<td>Heat Capacity (J/gram/°C)</td>
<td>0.286 +/- 0.012</td>
<td>0.326 +/- 0.012</td>
<td>0.272 +/- 0.012</td>
</tr>
<tr>
<td>Resistivity (µΩ*cm)</td>
<td>17.5 +/- 0.1</td>
<td>8.93 +/- 0.10</td>
<td>28.5 +/- 0.1</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>8.28 +/- 0.02</td>
<td>8.90 +/- 0.02</td>
<td>8.65 +/- 0.02</td>
</tr>
<tr>
<td>Thermal Conductivity (W/cm*°C)</td>
<td>0.341 +/- 0.051</td>
<td>0.704 +/- 0.098</td>
<td>0.196 +/- 0.019</td>
</tr>
</tbody>
</table>
2. GENERAL THERMODYNAMIC FRAMEWORK FOR DESIGN OF TLPB TECHNOLOGIES

The processing temperatures and times, operation temperatures and times, and durability requirements in terms of phase stability of the isothermally solidified bonds can be translated to thermodynamic constraints based on composition and temperature. Extensive databases and literature exist detailing the equilibrium phases and reaction kinetics for a wide range of low-melting temperature metals in contact with high-melting temperature metals. Here we present a framework for combining these data with thermodynamic assessments for TLPB design. Simple criteria are introduced for evaluating specific binary, pseudo-binary, and multi-component systems. In addition, “processing regime maps” and “reaction diagrams” are used as two visualization techniques to extend interpretation of thermodynamic data by using diffusion couple/interdiffusion experiments to identify missing or metastable phases during reaction for designing ternary and high order multi-component TLPB systems.

Table 2-1 List of binary and ternary systems analyzed using the thermodynamic framework

<table>
<thead>
<tr>
<th>Binary</th>
<th>Ternary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-Sn</td>
<td>Ag-Cu-Sn</td>
</tr>
<tr>
<td>Cu-Sn</td>
<td>Cu-Ni-Sn</td>
</tr>
<tr>
<td>Ni-Sn</td>
<td>Ag-Sn-Bi</td>
</tr>
<tr>
<td></td>
<td>Cu-Sn-Bi</td>
</tr>
<tr>
<td></td>
<td>Ni-Sn-Bi</td>
</tr>
<tr>
<td></td>
<td>In-Sn-Ag</td>
</tr>
<tr>
<td></td>
<td>In-Sn-Cu</td>
</tr>
<tr>
<td></td>
<td>In-Sn-Ni</td>
</tr>
</tbody>
</table>

The general thermodynamic criteria for TLPB are based on (1) the melting temperature of the LTP for the desired reaction with an HTP, (2) the formation of selected IMC(s) that incorporate appropriate component(s) of the liquid, (3) for ternaries and above, three phase equilibria linking a terminal liquid composition, the IMC, and any other phases that precipitate during isothermal solidification, (4) and the temperature of liquid-forming reaction for product phases for specific operating temperatures in specific applications.

Criterion (1) applies to both binary and multi-component systems. For instance, processing in common binaries such as Cu-Sn, Ni-Sn, and Ag-Sn must occur above the melting
temperature of pure Sn, 232°C. In the case of ternaries and multicomponent systems, processing must occur above the solidus temperature of the LTP, and usually above the LTP liquidus temperatures such that a sufficient liquid fraction exists to for wetting of the HTP.

Application of criterion (2) requires that the relevant liquid compositions be in equilibrium with an IMC phase incorporating the desired component of the liquid at processing temperatures. As some solubility of the HTP component(s) may exist in the liquid, it is equilibria of the HTP-saturated liquids that is relevant. When the IMC layers form by interdiffusion, local equilibrium is generally assumed to be satisfied at each interface. In a ternary, one of the components may not be incorporated into the IMCs. Such a system would invoke criterion (3) which requires that a solid phase form isothermally from the non-reacting component through its equilibrium with both the terminal liquid composition and the desired IMC phase. Criterion (4) indicates that the phase(s) formed during processing must remain stable and solid up to the intended operation temperature. Consideration of criterion (4) has implications for processing conditions for creating specific phases that are not only stable during processing, but also during operation.

The three most important binaries for TLPB – Cu-Sn, Ag-Sn, and Ni-Sn – are examined below based on these criteria. In binaries, the possible processing and use ranges based on the four criteria can be read directly off the phase diagrams: the positions of three phase invariants (eutectic and peritectic reactions) are points in the two dimensional temperature-composition phase diagram plot. The identification of these invariants in the binary systems helps understand how more complex reactions occur when an additional element is added to form a ternary.

In ternary systems, the equilibria from the binaries are not the only reactions that occur. For example, for a three-component system, there can be points of four-phase equilibria, such as the ternary eutectic in which a liquid transforms at a specific composition and temperature into three phases. Similarly, there are peritectics, eutectoids, and peritectoids. Of particular importance to TLPB are additional four phase invariants where two solid phases transform into a liquid plus another solid phase. The four phase invariant reactions involving a liquid phase are classified as follows:

- Class I invariants: ternary eutectic reaction where liquid ↔ α + β + γ
- Class II invariants: quasi-peritectic reaction where liquid + α ↔ β + γ
- Class III invariants: ternary peritectic where liquid + α + β ↔ γ
These are identified in specific systems by comparing isothermal sections of the ternary phase diagram, as well as through thermodynamics calculations through CALPHAD-based software. For TLPB design, four phase reactions all in the solid state (eutectoid, quasi-peritectoid, and peritectoid) are also important since formation of a higher temperature phase by continuing interdiffusion may require the disappearance of a phase that had previously formed during isothermal solidification. A range of ternary examples will be shown to illustrate the phases that result in different composition and temperature regimes and how that limits processing conditions and composition ranges.

In this section, we show that phase diagrams serve as the beginning point in TLPB design. Phase diagrams show what phases to expect within certain composition and temperature ranges at equilibrium. Achieving equilibrium means that, in a two component system, there will only be two phases present. The TLPB process is an interdiffusion process, inherently non-equilibrium, and multiple phases generally remain in the isothermally solidified bond, depending on the temperature, time, and starting compositions and geometries. Furthermore, some equilibrium phases in the phase diagram may not form during interdiffusion and isothermal solidification. In the following sub-sections, TLPB alloy design is discussed in terms of these invariant reactions, predicted phase sequences from phase diagrams, and the phases as a function of composition, temperature, time, and sample geometry.

2.1 Binary TLPB Systems

2.1.1 Cu-Sn

The Cu-Sn phase diagram (Figure 1-2) was described above in Section 1.2.1. If we start with pure Sn in contact with Cu. The five ranges for isothermal solidification are shown as A: 227 °C-415 °C for Cu₆Sn₅, B: 415°C – 638 °C for Cu₃Sn, and three higher ranges for C:γ, D: β, and E: (Cu). As described in detail in the (NIST 2002b), there are 13 invariant equilibria in the Cu-Sn system with five involving a liquid phase and are therefore relevant to reacting pure Sn with pure Cu:

- Liquid ↔ Cu₆Sn₅ + (Sn) at 227 °C
- Liquid + Cu₃Sn ↔ Cu₆Sn₅ at 415 °C
- γ ↔ Liquid + Cu₃Sn at 638 °C
41

- Liquid + $\beta \leftrightarrow \gamma$ at 757 °C
- Liquid + (Cu) $\leftrightarrow \beta$ at 796 °C

Section 1.2.1 above provides additional details about the expected reactions during isothermal solidification as a function of temperature. One additional feature to note in the Cu-Sn system is the extended temperature range for operation if a bond reacted in A until it contains no Cu$_6$Sn$_5$ or B. In this situation, the lowest melting point IMC in the system is Cu$_3$Sn. If the Cu$_3$Sn is heated above 638 °C, the Cu$_3$Sn remains stable until 677 °C when it transforms congruently into $\gamma$. This provides an additional 39 °C of solid phase stability for bonds isothermally solidified with no remaining Cu$_6$Sn$_5$.

The microstructure and phase content in a specific bond will evolve after isothermal solidification as a function of annealing temperature and time, which can be interpreted based on thermodynamics. Bosco and Zok demonstrated that annealing a Cu-Sn-Cu TLPB bond with a 20 µm thick Sn layer at 400 °C produced only the Cu$_4$Sn$_1$1 phase ($\delta$) in contact with (Cu) (C). When the as-solidified bond was heated to 550 °C, $\delta$ transformed into $\gamma$ (D), which then transformed peritectically into $\delta$ and a dispersion of (Cu) particle, as expected from the phase diagram. After annealing the original $\delta$ bond at 600 °C, there was only (Cu), a solid solution of Sn in Cu (E) (Bosco and Zok 2004) (Bosco and Zok 2005).

2.1.2 Ag-Sn

The Ag-Sn binary phase diagram shown in Figure 2-1 indicates three temperature ranges for isothermal solidification: A - 220 °C - 480 °C for Ag$_3$Sn, B - 480 °C - 724 °C for $\zeta$ Ag, and C - 724°C - 962 °C for (Ag) (NIST 2002e). In A two IMC phases Ag$_3$Sn and $\zeta$ Ag are shown for reaction between Sn and Ag, however typically only Ag$_3$Sn is observed during interdiffusion experiments. The lack of a second IMC layer during interdiffusion simplifies analysis of the Ag-Sn binary in A. There are only three ternary invariants in this system:

- Liquid $\leftrightarrow$ Ag$_3$Sn + (Sn) at 220 °C
- Liquid + $\zeta$ Ag $\leftrightarrow$ Ag$_3$Sn at 480 °C
- Liquid + (Ag) $\leftrightarrow$ $\zeta$ Ag at 724 °C

This makes the use of Ag-Sn straightforward and simple in TLPB systems in terms of phase evolution. For more details on the phase evolution in Sn-Ag, see (Lis et al. 2014). As noted above, processing conditions must be controlled to avoid porosity formation that result
from its rapid intermetallic growth rate compared with Cu-Sn, as well as from changes in volume with continued annealing after isothermal solidification.

Figure 2-1 Ag-Sn phase diagram annotated for three separate TLPB reaction regimes (Modified from NIST 2002e)

2.1.3 Ni-Sn

The Ni-Sn binary system is highly relevant to TLPB due to the use of ENIG, Au/Ni, and Au/Ni-P surfaces finishes in electronics. The Ni-Sn phase diagram in Figure 2-2 shows three eutectic reactions, one peritectic reaction, two eutectoid reactions, and three congruent points. If we only consider reactions between Sn and Ni$_3$Sn$_2$ as relevant for TLPB, the invariant reactions are:
Figure 2-2 Phase diagram for Ni-Sn calculated using ThermoCalc, and annotated for two specific TLPB reaction regimes

- Liquid $\leftrightarrow$ Ni$_3$Sn$_4$ + (Sn) at 232 °C
- Liquid + Ni$_3$Sn$_2$ $\leftrightarrow$ Ni$_3$Sn$_4$ at 795 °C
- Liquid $\leftrightarrow$ Ni$_3$Sn$_2$ at 1294 °C

This leads to two relevant temperature regimes for TLPB: 

**A**: between 232 °C and 795 °C, and 

**B**: between 795°C and 1294 °C. Although the simplicity of the binary system makes it very attractive, Ni is often used in conjunction with a Au surface finish layer, and co-deposited with P or W. Having P turns the reaction into a ternary, and can add additional stability issues, including needle-like IMC growth, formation of Ni-P and Ni-P-Sn ternary compounds, and IMC spalling during reaction. (Lin et al. 2007)(Jang et al. 2000). In addition, the tendency for porosity formation noted above for Ni-Sn will require careful geometric design and process control for its successful application. As observed for the solid state reaction (Chuang et al 2012), it may be possible to eliminate some porosity by the use of a Sn-Ag LTP rather than just Sn.
2.2 Ternary Systems

Ternary systems offer broader opportunities for bond formation by having three phases in equilibrium, the transitions that can occur as one of the intermediate IMC phases disappears by continued diffusion, and Class II reactions that eliminate formation of a phase that limits the temperature of use. The systems described here are all Sn-based, and include: (1) Ag-Cu-Sn, (2) Cu-Ni-Sn, and (3) Ag-Bi-Sn, Bi-Cu-Sn, Bi-Ni-Sn. The systems Ag-Bi-Sn, Ag-Cu-Sn, and Bi-Cu-Sn have been well-studied in terms of their thermodynamics and interdiffusion/reaction paths and the thermodynamics framework can be straightforwardly applied. The two systems involving Ni - Cu-Ni-Sn and Bi-Ni-Sn - offer interesting opportunities for TLPB even though there are gaps in knowledge of their thermodynamic transitions and interdiffusion/reaction path behavior.

2.2.1 Ag-Cu-Sn

Section 1.2.3.1 above gives an introduction into the lowest temperatures reactions relevant to TLPB for the Ag-Cu-Sn system (NIST 2002c). To consider the whole range of possible processing and temperatures, there are nine ternary invariants in the Ag-Cu-Sn system that must be considered, as follows:

- $L \leftrightarrow Cu_5Sn_5 + Ag_3Sn + (Sn)$ occurs at approximately 216 °C
- $L + Cu_5Sn \leftrightarrow Cu_6Sn_5 + Ag_3Sn$ occurs at approximately 356 °C
- $L + \zeta-Ag \leftrightarrow Cu_3Sn + Ag_3Sn$ occurs at approximately 459 °C
- $L + (Ag) \leftrightarrow \zeta-Ag + Cu_3Sn$ occurs at approximately 574 °C
- $L + (Ag) + Cu_{10}Sn_3 \leftrightarrow Cu_3Sn$ occurs at approximately 611 °C
- $L + (Ag) + \gamma \leftrightarrow Cu_{10}Sn_3$ occurs at approximately 613 °C
- $L \leftrightarrow \gamma + Cu_{10}Sn_3 + Cu_3Sn$ occurs at approximately 550 °C
- $L + (Cu) \leftrightarrow (Ag) + \gamma$ occurs at approximately 636 °C
- $L + \beta \leftrightarrow (Cu) + \gamma$ occurs at approximately 642 °C

These ternary invariants change the processing and use temperature limits relative to the binaries. For example, if $Cu_5Sn_5$ is present in the isothermally solidified bond, the maximum use temperature is below 356 °C rather than 415 °C where $Cu_6Sn_5$ becomes unstable in the Cu-Sn binary.
2.2.2 Cu-Ni-Sn

The Cu-Ni-Sn ternary systems has been studied at low temperatures for transient liquid phase bonding due to several unique characteristics of the binary phase diagrams. The Cu-Ni system has a well-known isomorphous phase diagram as illustrated in Figure 1-4. Both Cu and Ni also exhibit solid solubility in binary intermetallic compounds, such as (Cu, Ni)$_6$Sn$_5$. Trace amounts of Ni have been shown to suppress the IMC’s allotropic phase change upon cooling, i.e., stabilizing the high temperature hexagonal (Cu, Ni)$_6$Sn$_5$ (Nogita and Nishimura 2008). In addition to phase stability, Cu-Ni alloying may also affect reaction kinetics since it is known to affect the rate of solid Cu-Ni substrate dissolution in molten Sn and IMC growth rates (Korhonen et al. 2000). The implications of Cu-Ni characteristics encountered in recent experiments are discussed in conjunction with several examples.

The ternary invariants for the Cu-Ni-Sn system have not yet been determined but the phases in equilibrium at various temperatures have been determined by Schmetterer et al. (Schmetterer et al. 2009). At 400 °C, liquid Sn appears to be in equilibrium with (Cu, Ni)$_6$Sn$_5$ and (Ni,Cu)$_3$Sn$_4$. At 500 °C, Sn liquid is in equilibrium with (Cu, Ni)$_5$Sn and (Ni, Cu)$_3$Sn$_2$, while at 700 °C, Sn liquid is in equilibrium with γ and (Ni, Cu)$_3$Sn$_2$. There are ternary phases reported.

Greve et al. demonstrated Sn-Cu-Ni bonding of Ag-metallized, Si dies to Ni substrates using a paste (Greve et al. 2014). The pastes included pure Cu, Ni, and mixtures of pure Cu/Ni powders HTP particles in combination with a Sn-3.5Ag LTP. Processing occurred in an inert atmosphere at 300°C for approximately 30 minutes. Pressure was applied (0.2 MPa) to minimize void formation. The Ni-Sn and (Cu, Ni)-Sn microstructures exhibited few voids. Residual Sn in the structure indicated incomplete conversion of the liquid Sn. Elevated die shear testing indicated that the bonds withstood 10 MPa well beyond the melting temperature of Sn-3.5Ag. Bonds formed from the mixture of Cu and Ni withstood the 10 MPa die shear test up to approximately 435°C which is consistent with the melting temperature of Cu$_6$Sn$_5$, 415°C. The failure temperature implies that the bonding was supported by a matrix of IMC despite pockets of unreacted Sn. Similarly, bonds withstood up to 600°C (test limit) in the case of Ni HTP with Sn, consistent with the melting temperature of Ni$_3$Sn$_4$, 798°C. The microstructures of the mixed Cu and Ni exhibited competing formation of Cu$_6$Sn$_5$ and Ni$_3$Sn$_4$ at the Cu and Ni interfaces, respectively. The phases and compositions of IMCs are known to shift with aging in reactions with BGAs where one substrate is Cu and the other is Ni.
As opposed to mixing Cu and Ni powders, Choquette and Anderson fabricated bonds using a Cu-Ni-Sn TLPB system incorporating a Cu-10Ni wt. % HTP alloy powder with a Sn-0.7Cu-0.5Ni LTP powder (SN100C, Nihon Superior). Bonds were processed using a reflow process with 30s above liquidus (227°C) to a peak temperature of 250°C. The microstructure in Figure 1-13 illustrates the layer of (Cu, Ni)$_6$Sn$_5$ (mid-gray) between Sn (light phase), and the Cu-10Ni particles. Note the lack of (Cu, Ni)$_3$Sn between the remaining Cu-10Ni particles and the (Cu, Ni)$_6$Sn$_5$ layer... Evidence presented by Baheti et al. suggested that at 200°C (Cu, Ni)$_3$Sn is not thermodynamically stable when Ni concentrations are equal to or greater than 7.5 wt% Ni. Difficulty of nucleating the thermodynamically stable phase was also suggested by Baheti et al. (2016). Vuorinen et al. (2007) instead attributed the lack of (Cu, Ni)$_3$Sn to a kinetic origin based on experiments at 240°C. Rapid growth of the (Cu, Ni)$_6$Sn$_5$ phase appears to prevent formation of the thermodynamically stable (Cu, Ni)$_3$Sn (Vuorinen et al. 2008). Evidence of (Cu, Ni)$_3$Sn in equilibrium with Cu-Ni alloys at 240°C presented by Lin et al. supports the kinetic explanation (Lin et al. 2002).

The most important feature of this system is, therefore, that it can be treated as two pseudo-binaries. This can be understood by comparing the 240 °C isothermal section of the phase diagram (Figure 2-3a) with what we refer to as a “reaction diagram” (Figure 2-3b). This isothermal reaction diagram schematically shows the phases observed during the short annealing times required for LPDB systems. Many binary and ternary phases present in the equilibrium phase diagram are missing in the diffusion couples as discussed above. The Cu-Ni HTP alloys in contact with Sn form either (Cu, Ni)$_6$Sn$_5$ or (Ni, Cu)$_3$Sn$_4$ depending on the HTP alloy composition, and at low Ni concentrations (Cu, Ni)$_3$Sn is also observed. This diagram helps to visualize the resulting phases forming from diffusion couples in various HTP and LTP composition regimes. Further development of such diagrams may prove useful for TLPB design applications.
Figure 2-3  

a) Calculated metastable equilibria in the Sn-Cu-Ni systems at 240 °C. The possible τ-phase is indicated and dotted lines in the Cu-Ni side of the diagram beyond the formation of (Cu, Ni)_3Sn_5 and (Ni, Cu)_3Sn_4 reflect the uncertainties in the phase equilibria. Plot for 240 °C based on 200 °C isotherm from (Baheti et al. 2016) without the Cu-Ni miscibility gap. 

b) Schematic reaction diagram represents the phases observed in diffusion couples composed of Cu-Ni HTP and Sn at around 240 °C. The gold circles indicate the final phases remaining after complete consumption of the Sn for a Cu-10 wt. %Ni HTP alloy. (Reeve 2016)

2.2.3 Sn-Bi LTP with Cu, Ni, or Ag

Alloys in the Sn-Bi system are attractive as the LTPs due to the low-temperature eutectic reaction in Sn-Bi occurring near 139°C at 57 wt% Bi - 43 wt% Sn. The Sn-Bi system is a simple eutectic system with no IMCs. The element Bi also forms simple binary eutectics with Ag (T_e = 262.5°C) and Cu (T_e = 270.6°C), without any IMCs. The Ni-Bi phase diagram contains two IMCs, NiBi and NiBi_3, with two peritectic reactions and the NiBi_3-Bi eutectic reaction (T_e = 270.6°C). Given the deep Sn-Bi eutectic, the maximum effective addition of Bi is limited only by the invariant reactions and the reaction paths for isothermal solidification. In the Ag-Bi-Sn and Bi-Cu-Sn systems, there is very low solid solubility of Bi in the IMCs and, with no Ag-Bi or Cu-Bi IMCs, (Bi) is the only Bi-containing phase which melts at 271 °C. The Bi-Ni-Sn system contains both Ni-Sn and Bi-Ni IMCs which make the phase diagrams and reaction paths more complex.

2.2.4 Ag-Bi-Sn

The ternary invariants for Ag-Bi-Sn are all eutectics (NIST 2002f) (Ohtani et al. 2001):

- Liquid ↔ Ag_3Sn + (Sn) + (Bi) at 137 °C
• Liquid ↔ Ag₅Sn + ζ-Ag + (Bi) at 252 °C
• Liquid ↔ (Ag) + ζ-Ag + (Bi) at 263 °C

The implication for Ag-Bi-Sn TLPB is that bonds containing Ag₅Sn will contain liquid above 252 °C, therefore limiting their processing and use to between 137°C and 252 °C. If the bond contains only the ζ-Ag intermediate phase along with (Ag) and (Bi), the bond is stable up to 263 °C.

2.2.5 Bi-Cu-Sn

There are nine ternary invariants for the Bi-Cu-Sn, with the most important for isothermal solidification being (NIST 2002d):
• Liquid ↔ Cu₆Sn₅ + (Sn) + (Bi) at 137 °C
• Liquid + Cu₃Sn ↔ Cu₆Sn₅ + (Bi) at 200 °C
• Liquid + Cu₄₄Sn₁₁ ↔ Cu₃Sn + (Bi) at 270.2 °C
• Liquid + (Cu) ↔ Cu₄₄Sn₁₁ + (Bi) at 270.3 °C

The implications for these invariants are that a bond containing (Sn) forms a liquid above 137 °C, Cu₆Sn₅ above 200 °C, Cu₃Sn above 270.2 °C, and Cu₄₄Sn₁₁ above 270.3 °C, respectively. The other five invariants can be found in the NIST Webpage for Phase Diagrams and Computational Thermodynamics, but were not included here because they involve reactions at temperatures above the Bi melting temperature, where all of the Bi is in the liquid, and bonds cannot be isothermally solidified.

Initial research on Cu-Sn-Bi for TLPB focused on eutectic Sn-Bi paired with Cu filler particles at low temperature to take advantage of the Sn-Bi eutectic temperature of 137 °C, allowing significantly lower processing temperatures than conventional Sn-Pb or SAC soldering. The Sn component of the LTP is intended to react with Cu to form IMC while the rejected Bi solute forms a solid precipitate. D’Hondt and Corbin performed DSC and EDS analysis on mixtures of Sn and Bi with Cu filler particles as well as eutectic Sn-Bi with Cu filler particles at temperatures below 200 °C (D’Hondt and Corbin 2006). Analysis of the microstructures and heat flow profiles revealed a “persistent liquid forming reaction” above 200°C, the Class II reaction between the solid Bi phase and Cu₆Sn₅. This acts as limit for Criterion 4. However, analysis of computed isothermal sections of the ternary phase diagram shows that high-Bi non-eutectic compositions can be utilized to avoid the formation of Cu₆Sn₅, as shown in Figure 2-4.
Increasing Bi content and processing temperatures result in the formation of Cu$_3$Sn and avoids Cu$_6$Sn$_5$ formation entirely. The Criterion 4 limit is then elevated to the melting temperature of Bi, 271°C which is in the lower range of melting temperatures for high-Pb, Sn-Pb solders. (Reeve et al 2016)

Figure 2-4 Calculated isothermal sections of the Cu-Sn-Bi ternary phase diagram at a 170°C and b 260°C illustrate different phases in equilibrium with Cu saturated Sn-Bi liquid based on temperature and composition. At 170°C, all compositions of liquid are in two phase equilibrium with Cu$_6$Sn$_5$ as opposed to 260°C where liquids between the stars are instead in equilibrium with Cu$_3$Sn. (TCSLD3 for Thermo-Calc)

2.2.6 Bi-Ni-Sn

The system Bi-Ni-Sn is different from Ag-Bi-Sn and Bi-Cu-Sn in that Bi-Ni IMCs form, in addition to the Ni-Sn IMCs. There are multiple metastable NiBi and metastable and stable ternary phases that have been reported in the literature. The binary invariants for the Bi-Ni system are(Liu et al. 2016):

- Liquid ↔ Bi$_3$Ni + (Bi) at 271 °C
- Bi$_3$Ni ↔ liquid + BiNi at 465 °C
- BiNi ↔ liquid + (Ni) at 637 °C

For the ternary Bi-Ni-Sn, there are two low temperature ternary invariants identified using ThermoCalc

- Liquid ↔ Ni$_3$Sn$_4$ + (Sn) + (Bi) at 137 °C
- Liquid + Ni$_3$Sn ↔ Ni$_3$Bi$_2$ + Bi$_3$Ni at 300 °C
At temperatures below 271 °C, all Sn-Bi TLP alloys can isothermally solidify with the formation of Ni$_3$N$_4$ and (Bi). The Class II invariant reaction can be seen by comparing the crossing tie lines in Figure 2-5a and Figure 2-5b, limiting isothermally solidified bonds containing Ni$_3$Bi$_2$ and Bi$_3$Ni to use below 300 °C. Another important feature to note in both sections is that, above 271°C, all Sn-Bi liquids containing less than approximately 94 mole% Bi in contact with Ni form Ni$_3$Sn$_4$ which is not in equilibrium with any Ni-Bi IMC at any temperature. This means that the bonds cannot isothermally solidify unless all Ni$_3$Sn$_4$ is replaced by Ni$_3$Sn$_2$ which can be in equilibrium with Bi$_3$Ni. Interdiffusion experiments by Wang et al. have shown that the situation is more complex than appear from the ternary phase diagram. At 300 °C and >5 wt% Sn in the Sn-Bi alloy in contact with Ni, Ni$_3$Sn$_4$ is indeed observed. With a Bi-2wt% Sn alloy at 300 °C, Ni$_3$Sn$_2$ was observed at interface with the TLP along with NiBi phase. As shown by the dotted lines in Figure 2-5, Ni$_3$Sn$_2$ is not in equilibrium with NiBi. Additional interdiffusion experiments with a limited supply of Sn-Bi TLP are needed to determine whether there are processing regimes where Bi-Ni-Sn bonds can solidify above the melting temperature of Bi.

![Figure 2-5 a](image_url)

**Figure 2-5 a** Calculated ternary isotherm showing the terminal liquid (star) in contact with Ni$_2$Sn$_3$ and Bi$_3$Sn (circles) while the dotted line shows the non-equilibrium phases observed during reaction at below the Class II reaction temperature. **b** Above the Class II reaction temperature, Ni$_3$Sn$_2$ and Ni$_3$Sn are in equilibrium with liquid. The reaction path was found to contain Ni$_3$Sn$_2$ in contact with NiSn.
2.2.7 In-Sn LTP with Ag, Cu, or Ni.

In the binary, Sn and In react to form binary IMCs with extensive solid solubility; the Sn-In binary eutectic reaction is between two intermetallics and occurs near 120 °C and 50.9 wt.% In (51.7 at.% In). Both In and Sn form IMCs with Ag, Cu, and Ni. There have been a few observations of ternary compounds, but there are regions of complete solid solubility across the ternaries and more limited solubility of the third element in some binary IMCs. The ternary AgSn-In is minimally compatible with TLPB, because In-Sn alloys react with Ag to form Ag-In IMCs with limited solid solubility of Sn. With low temperature processing, this can lead to the precipitation of a Sn-In IMC that melts at 222 °C, and therefore, does not offer any advantages over conventional Pb-free solder alloys. In contrast, the ternary Cu-Sn-In is a promising TLPB system because the Cu$_6$(Sn, In)$_5$ phase in equilibrium with near-eutectic liquid compositions incorporates both components of the LTP, as seen in the calculated Cn-Sn-In isothermal section of the ternary phase diagram in Figure 1-10, and has been shown to solidify isothermally by Sasangka et al. (Sasangka et al. 2011). The ternary Ni-Sn-In exhibits similar characteristics to Cu-Sn-In, but the solubility of In in Ni$_3$Sn$_4$ is more limited. As with the Ag-In-Sn system, alloys of In-rich Ni-Sn-In are likely to form undesirable low-melting temperature In-Sn IMCs rather than Ni$_3$(Sn, In)$_4$. The ternaries of In-Sn LTPs with Cu and Ni exhibit promising characteristics over specific composition and temperature ranges and are, therefore, recommended for further investigation, particularly the Cu-In-Sn system.
Figure 2-6 Isothermal section of the Cu-Sn-In phase diagram at 170° C generated using Thermo-Calc V.3 with database TCSLD1. All initial LTP liquid compositions can possibly be isothermally solidified forming a Cu6(Sn, In)5 ternary solid solution. Experimental measurements of the specific reaction paths for different LTP compositions and the relative diffusivities of Sn and In in the IMCs still must be evaluated to determine what ranges can be used. (Reeve 2016)
3. COMPARISON OF TLPB WITH COMPETING TECHNOLOGIES AND OPPORTUNITIES FOR FURTHER DEVELOPMENT

3.1 Comparison of TLPB with Competing Technologies

A thorough discussion of TLPB design must compare it to competing bonding approaches for high-temperature interconnects such as high-temperature solders, sintered Ag, and Ag-filled epoxies. Several authors have reviewed and compared bonds using different technologies, however the individual technologies may not have been optimized, making comparisons generally qualitative. Here we will briefly introduce several of these techniques, noting features and limitations of each, and present the few comparisons in which both technologies have been optimized.

3.2 Solders

As previously discussed, high-Pb solders have remained commercially important and exempt from RoHS regulation due to multiple characteristics. Pure Sn and Pb melt at 232°C and 328°C and form a simple binary eutectic as shown in binary phase diagram in Figure 1-1. Alloys using predominately Pb are therefore used for high-temperature applications (> 260°C) and hierarchical soldering. The reliability characteristics are also well known due to their extensive use. High melting temperatures, thermal fatigue resistance, electromigration resistance, long-term reliability, resistance to the formation of IMC’s are key characteristics of Pb-Sn alloys that have led to the continued exemptions for Sn-Pb (Menon et al. 2015).

**Au-Sn** solder alloys are currently utilized in high-temperature applications such as microwave devices, laser diodes, RF power amplifiers, and flip-chip bonding (Ivey 1998)(Kim et al. 2004)(Doesburg and Ivey 2000)(Manikam and Kuan Yew 2011). The thermal conductivity of Au-Sn, 57 W/mK, exceeds that of Pb-Sn, 35 W/mK for Pb-5Sn (Chidambaram et al. 2011)(Chidambaram et al. 2012). However, Au-Sn is much stiffer compared to “soft” solders such as Sn-Pb which limits use to small die area applications. Additionally, diffusion barriers such a Ni, Pd, or Pt may be needed to prevent the formation of intermetallics.

**Au-Ge** solder may be used for relatively high melting temperature applications since it is a simple binary system with a eutectic reaction near 360°C with ~30 at. % Ge. The melting
Temperature may be further reduced using small alloying additions such as In, Sb, or Sn (Chidambaram et al. 2011). Au-Ge also exhibits greater thermal conductivity, 44 W/mK, than Pb-5Sn, 35 W/mK. Au-Ge is also relatively stiff, but small additions of Sb (5 at. Sb) have been shown to improve ductility (Chidambaram et al. 2011). However, Sb is toxic, but much less toxic than Pb. Another limitation is that Ge cannot be easily electrodeposited. Corrosion is also a concern due to the large electromotive force between Au and Ge (Chidambaram et al. 2011).

**Au-In** has been demonstrated by Chin et al. for interdiffusion bonding of GaAs at processing temperatures as low as 200°C while withstanding temperatures as high as 450°C (Lee et al. 1993).

**Bi-Ag** is another simple binary eutectic system, with the binary eutectic at 261. Elemental Bi melts at 270°C, but it is relatively brittle and has a low thermal conductivity (9 W/mK) relative to other solders. The addition of Ag and other dopants have been shown to improve ductility (Manikam and Kuan Yew 2011). Increasing Ag content has also been shown to improve the wetting performance of Bi on Cu substrates. Various dopants have been explored in literature (Manikam and Kuan Yew 2011). Commercial ternary Bi-Ag-X solder alloys have been developed using Sn as a dopant to promote wetting by forming Cu₆Sn₅, limiting operation to approximately 200°C (Zhang and Lee 2013).

**Zn-Al** eutectic near 380°C, 6 wt. % Al, exhibits a promising melting range without any IMCs, but the alloys are very stiff and brittle (Suganuma et al. 2009). Various dopants have also been demonstrated (Manikam and Kuan Yew 2011). However, poor wetting and oxidation of Zn and Al are significant bonding and reliability concerns (Chidambaram et al. 2011).

**Zn-Sn** is a simple binary eutectic without any IMCs. Unlike other “hard” solders, it is extremely ductile and inexpensive compared to Au alloys. These alloys exhibit excellent wetting characteristics (Suganuma et al. 2009). The thermal conductivity of Zn-Sn alloys, in the range 100 to 110 W/mK for 10 to 30 weight percent Sn, exceeds that of Pb-5Sn (35 W/mK) (Suganuma et al. 2009). Zn-Sn is also extremely ductile. Reliability testing showed no significant reduction in shear strength after 3 reflow cycles up to 260°C, demonstrating potential for hierarchical soldering applications. Exposure to 85°C 85 % RH for 1000 hours only resulted in several microns of oxide at the free surface. Shear strength was maintained up to 2000 thermal cycles (-40 to 125°C) using a TiN barrier layer. Due to formation of Zn-Cu IMCs, the TiN layer is needed to suppress IMC formation. Successful barrier layers have been demonstrated for
soldering at 360 to 380°C for 60s (Suganuma et al. 2009). Solder alloy properties are summarized in Table 3-1 based on data published by Menon et al. and Suganuma et al (Menon et al. 2015) (Suganuma et al. 2009).

Table 3-1 High melting temperature solder alloys and relevant properties (Menon et al. 2015)(Suganuma et al. 2009)

<table>
<thead>
<tr>
<th>Solder Composition</th>
<th>Melting Temperature (°C)</th>
<th>Thermal Conductivity (W/mK)</th>
<th>CTE (ppm/°C)</th>
<th>Modulus (GPa)</th>
<th>0.2% Yield Strength at RT (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-20In</td>
<td>695</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au-12Ge</td>
<td>356</td>
<td>44</td>
<td>13</td>
<td>72.7</td>
<td>185</td>
</tr>
<tr>
<td>Au-20Sn</td>
<td>280</td>
<td>57</td>
<td>16</td>
<td>59</td>
<td>275</td>
</tr>
<tr>
<td>Au-3Si</td>
<td>363</td>
<td>27</td>
<td>12</td>
<td>83</td>
<td>220</td>
</tr>
<tr>
<td>Bi-11Ag</td>
<td>262-360</td>
<td>9 (for 100%Bi)</td>
<td></td>
<td>37.2</td>
<td>~33</td>
</tr>
<tr>
<td>Bi-11Ag-0.05Ge</td>
<td>262-360</td>
<td></td>
<td></td>
<td>37.2</td>
<td>~33</td>
</tr>
<tr>
<td>Pb-5Sn</td>
<td>23</td>
<td></td>
<td>30</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>Sn-5Sb</td>
<td>48</td>
<td></td>
<td>23</td>
<td></td>
<td>~40</td>
</tr>
<tr>
<td>Zn-(10-30)Sn</td>
<td>360</td>
<td>100-110</td>
<td>30</td>
<td></td>
<td>~30</td>
</tr>
<tr>
<td>Zn-(4-6)Al-(Ga, Ge, Mg, Cu)</td>
<td>~380</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3 Sintered Ag

Silver sintering for die-attach applications has garnered significant interest due to the excellent electrical and thermal conductivity of pure Ag (419 W/mK). Sintering also allows for relatively low processing temperatures (100-300°C) compared to the melting temperature of Ag (961.8°C) (Siow 2014) (Paknejad and Mannan 2017). The sintering process is used with nano or micro scale Ag particles mixed into a paste using an organic binder. Joining of particles and densification occurs by diffusion such that the total surface area and corresponding surface energy are reduced. Pressure may also be applied during processing to promote densification, however complete densification may not be desirable due to the stiffness of Ag. Instead some remaining porosity is often engineered into the bond to improve compliance. More recently, nanoscale Ag particles have been used to develop bonds that do not require the application of pressure.

Parameters such as sintering pressure, processing temperature profile, choice of organic paste constituents, particle size distribution, processing atmosphere, and the type of surface metallization are known to affect resulting bond characteristics. Paknejad and Mannan recently
performed a review of the Ag sintering literature in which they extracted these parameters and compared performance based on shear strength as well as thermal cycling performance (Paknejad and Mannan 2017). Average initial shear strength was shown to increase with increased pressure, but a decline is observed for pressures in excess of 7.5 MPa. A clear trend was not observed comparing initial shear strength to peak process temperature. The combination of parameters must be optimized for a given paste formulation as opposed to simply assuming that increased processing pressures or temperatures result in greater shear strength. Surface metallization was found to have some effect on average initial shear strength, particularly for pressureless bonding. Long term annealing and thermal cycling performance of sintered Ag bonds are also sensitive to surface metallization composition and roughness (Siow 2014). Silver and other noble metals are known to function well as bonding surfaces for Ag sintering. Other metals such as Ni must be thick enough to prevent oxidation of the underlying Cu. Oxidation increases CTE mismatch between the sintered Ag bond and the substrate which causes early thermal-fatigue failure. Comparison of shear strength after thermal cycling favored lower sintering pressures. These results suggest a tradeoff between increased initial shear strength with greater pressure versus increased thermal cycling lifetimes due to greater porosity with lower processing pressures. Practical optimization of sintered Ag bonds will likely require application specific testing.

### 3.4 Electrically Conductive Adhesives

Electrically conductive adhesives (ECA) utilize a polymer, typically epoxy, to provide the mechanical connection and filler particles, such as Ag flake, to provide electrical and thermal connectivity. Conventional ECAs utilizing epoxy benefit from epoxy’s excellent adhesion, low shrinkage, and resistance to mechanical shocks at reasonable cost (Meschi Amoli et al. 2015) A recent review by Amoli et al. addresses various approaches involving particle scale and morphology for improving ECA performance. Silver Ag flake has been used extensively in ECAs due to the excellent thermal and electrical conductivity of Ag, however metals such as copper and nickel have used as well. Use of ECAs is limited by their electrical and thermal conductivities: ECAs offer much lower thermal conductivity (~10 W/mK) and electrical conductivity ($10^{-3}$ to $10^{-4}$ ohm cm) compared to the other technologies discussed here. Since thermal and electrical conductivity in ECA’s depends upon a network of touching particles,
contact resistance between particles limits the overall performance. The intuitive solution would be to increase the fraction of filler relative to the epoxy content. However, increasing the filler content beyond the percolation threshold no longer affects conductivity significantly. The percolation threshold for a given ECA represents the concentration in which a continuous linkage of particles occurs. Increasing filler concentration beyond the percolation threshold provides little advantage while degrading mechanical performance due to the reduction of the epoxy network. Many parameters such as filler size, shape, and dispersion affect the percolation limit. Recent developments have focused on the inclusion of micro or nano scale particles. For instance, Wu et al. demonstrated a 10 wt% reduction in the percolation limit using nanoscale particles as opposed to micron-sized Ag particles (Wu et al. 2007).

3.5 Comparisons of Mechanical Properties with TLPB

The first demonstration of the potential of TLPB was in 1966 by Leonard Bernstein of Fairchild Semiconductor who introduced “solid-liquid interdiffusion” bonding for semiconductor device assembly to solve limitations related to hierarchical soldering. Bernstein identified 5 distinct steps that take place during processing: wetting, alloying, liquid diffusion, gradual solidification, and solid-diffusion, a subset of the processing steps identified here in this chapter. Mechanical properties of Ag-In, Au-In, and Cu-In lap shear bonds were measured using lap shear samples fabricated from 200°C to 450°C for 10-120 min. Successful bonding in some of the samples was demonstrated by heating lap shear bonds under load above the melting temperature of the initial low melting temperature component. The paper concluded that a viable proof of concept utilizing these techniques had been demonstrated. Multi-component alloys incorporating Sn were suggested for future work. (Bernstein 1966) Bernstein and Bartholomew published an additional paper in 1966 in which bonds were fabricated using a greater variety of materials, including HTP bonding surfaces included gold, copper, nickel, Dumet, Kovar, nickel-plated molybdenum, Au-Pt paste on ceramic, and nickel-plated metallized ceramic. After processing at 300°C for 60 minutes with pressure applied, high tensile strength was observed in the Ag-In bonds. Thermal cycling from liquid nitrogen to boiling water was performed on some of the bonds for 150 cycles without showing obvious damage. (Bernstein and Bartholomew 1966)
**Cu-Sn** Greve et al. demonstrated that Cu-Sn bonds processed at 280°C for 30 minutes using Cu particles-40wt%Sn LTP exhibited an average die shear strength of 14.6 MPa at 400°C and 10.5 MPa at 600°C (Greve et al. 2013). The Cu-Sn, core-shell structures developed by Chen et al. exhibited an average die shear strength of 29.4 MPa at 400°C (Chen et al. 2017). However above that temperature liquid forms due to presence of Cu₆Sn₅.

**Cu-Ni-Sn** Greve et al. demonstrated Sn-Ni and Sn-Cu-Ni bonding of Ag-metallized, Si dies to Ni substrates using TLPS pastes. The pastes included pure Cu, Ni, or mixtures of pure Cu/Ni powders HTP particles in combination with a Sn-3.5Ag LTP. Processing occurred in an inert atmosphere at 300°C for approximately 30 minutes. Pressure was applied (0.2 MPa) to minimize void formation. The Ni-Sn and (Cu, Ni)-Sn microstructures exhibited few voids. Residual Sn in the structure indicated incomplete conversion of the liquid Sn. However, elevated temperature die shear testing indicated that the bonds withstood 10 MPa well beyond the melting temperature of Sn-3.5Ag. Bonds formed from the mixture of Cu and Ni withstood the 10 MPa die shear test up to approximately 435°C which is consistent with the melting temperature of Cu₆Sn₅, 415°C. The failure temperature implies that the bonding was supported by a matrix of IMC despite pockets of unreacted Sn. Similarly, Ni-Sn bonds withstood up to 600°C (test limit) consistent with the melting temperature of Ni₃Sn₄, 798°C. The microstructures of the mixed Cu and Ni exhibited competing formation of Cu₆Sn₅ and Ni₃Sn₄ at the Cu and Ni interfaces, respectively. The phase and composition of IMCs are known to shift with aging in reactions with BGAs where one substrate is Cu and the other is Ni. (Greve et al. 2014) (Greve et al. 2013) As noted above in Section 2.2.6 additional experimental work is required to establish the temperature of stability.

**Ag-Sn TLPB compared with Sintered Ag** Bajwa and Wilde compared the performance of Ag-Sn multilayer TLPB preforms to optimized sintered Ag before and after 1000 thermal cycles (-40 to 150°C) (Bajwa and Wilde 2016). Average shear strength for SiC Schottky diodes (1.66 mm × 1.52 mm) mounted on AlN was 45 and 39.8 MPa for sintered Ag and Ag-Sn TLPB, respectively. After thermal cycling, average die shear force was reduced to 40 MPa and 37.5 MPa, respectively. These results indicate similar bond strength in direct comparison between TLP and Ag sintering which is consistent with values reported elsewhere. Paknejad and Mannan’s review of sintered Ag die attach materials indicated initial die shear strengths up to 60 MPa. Depending on processing conditions and particle size used, the typical initial die shear strengths ranged from 10 to 30 MPa after sintering. These results are similar to the die shear forces measured by Pan
and Yeo for their hybrid epoxy-Cu-Sn-Bi TLPS materials varied from 46 MPa at 25°C to 31 MPa at 140°C. These experiments provide compelling evidence that the mechanical performance of TLP bonding is competitive with sintered Ag and the hybrid technology.

### 3.6 Novel Processing Techniques and Application of Design Criteria for TLPB

A brief review of these candidate systems is given here in order to provide further background on TLPB implementation and to highlight the improvements and best practices developed by other researchers. These experiments show that TLPB development, particularly Cu-Sn TLPB, has moved beyond proof-of-concept towards a processing optimization. The practical importance of design parameters and constraints discussed earlier in this chapter is demonstrated in this section.

#### 3.6.1 Process Optimization

Luu et al. 2013 assessed processing parameters for Cu-Sn bonds for wafer level bonding. Die and cap wafers incorporating a thin membrane were bonded under vacuum to evaluate hermetic sealing capability. Emphasis was placed on optimizing the deposited Sn and Cu layer thickness in coordination with the heating and pressure profiles. During the heating process, Cu-Sn IMC forms before the melting temperature of pure Sn. Ensuring an adequate remaining Sn layer at the time of melting was identified as a key feature of successful bonding. The application of pressure was necessary to redistribute liquid Sn and to break up oxides at the interface. However, excess pressure resulted in squeeze out of Sn. A bonding profile utilizing 1.5 MPa pressure, bonding temperature of 270°C, and a 1.5 µm Sn thickness resulted in a 100% yield after dicing and an 80% sealing yield. (Luu et al. 2013)

Liu et al. 2012 investigated intermetallic formation in Cu-Sn SLID for wafer level bonding and 3D integration. Rather than forming a complete bond, Si was electroplated with Cu (5 µm) and Sn (3 µm) layers. The Sn layer remained a free surface to simplify characterization steps. IMC growth was consistent with literature, but the fine Cu grain size due to deposition method was shown to increase interdiffusion rates. At small scales, ramp rates must be fast enough to prevent complete conversion of the Sn layer to IMC before liquid formation. However, fast ramp rates were shown to cause droplet formation of the molten Sn, leading to uneven IMC formation. (Liu et al. 2012)
Bosco and Zok examined the critical interlayer thickness for Cu-Sn-Cu bonds. Preliminary experiments using a 10 \( \mu \text{m} \) Sn interlayer heated to 550°C at a rake of 5°C per minute under slight pressure exhibited significant void formation. The cavities were attributed to the formation of IMC during the relatively slow heating process. A series of solid state (\(<232°C\)) IMC growth experiments were conducted to determine the minimum Sn interlayer thickness such that sufficient Sn remains as it melts to accommodate redistribution. Based on these experiments, the critical interlayer thickness was determined as a function of heating rate. Subsequent Cu-Sn-Cu bonds starting with 20 to 30 \( \mu \text{m} \) of Sn resolved the porosity issues apparent in the 10 \( \mu \text{m} \) layer thickness. (Bosco and Zok 2004)

Garnier et al. also investigated the use of Cu-Sn TLP bonding for 3D integration. (Garnier et al. 2013) Four different configurations of Cu-Sn bonds linking Al pads between dies were compared. The pads were 25 \( \mu \text{m} \) in diameter with a 50 \( \mu \text{m} \) pitch. Typical steps were used to prepare for electrodeposition of 1-2 \( \mu \text{m} \) of Cu on both top and bottom wafers. A 5 \( \mu \text{m} \) Sn layer was electrodeposited on the top wafers. Half of the bottom wafers received a 3\( \mu \text{m} \) Sn layer. A 1 minute thermal treatment at 200°C was applied to half of each of the corresponding wafers to establish an existing layer of IMC at the Cu-Sn interface. Bonding occurred at 250°C for 1 minute under pressure. Cross-sections of the as fabricated bonds indicate complete conversion liquid Sn to IMC. Measurements of electrical resistance and mechanical shear force were collected before and after 500 thermal cycles from -40 to 125°C at a ramp rate of 14°C/min. Configurations initiated with Sn on both sides outperformed those with only Sn on the top. However, differences in performance may be attributable to the variation in total bondline thickness, 5 \( \mu \text{m} \) Sn vs. 8\( \mu \text{m} \) Sn, rather than defects arising from the initial lack of Sn on the bottom side. Most interesting, the configurations that underwent a thermal treatment to initiate IMC formation before bonding also outperformed their counterparts although the mechanism is unclear. Cross-sections of the thermally treated bonds appear to maintain a great bondline thickness which may be attributable to reduction in liquid Sn at bonding. These results suggest that thermal treatment before bonding to initiate IMC formation may provide benefits in other bonding configurations.

These experiments demonstrate the importance of maintaining proper ratios of Cu and Sn. Consideration of IMC formation both before and after melting of the LTP must be considered. TLPB has been shown to be more sensitive to ramp rates compared to other
processes. Inclusion of organic binders and solvents complicates this issue since slower ramp rates are needed to accommodate off-gassing. Careful design and process optimization on an application by application basis may be necessary.

3.6.2 Novel Processing and Geometry

Ehrhardt et al. presented two methods for forming Cu-Sn bonds. The more conventional approach utilized a mixture of 8-45 µm diameter Cu powder, SAC405 solder, and a solvent without reducing properties. A die was pressed into the printed paste using an unspecified pressure. An initial soldering step above the melting temperature of the majority Sn component was performed first. Without a fluxing agent, the Cu oxide prevents formation of IMC. This allows for redistribution of the Sn without the formation of an initial IMC network that prevents rearrangement and densification. During a second step, an activation gas was used to reduce the Cu oxides and initiate isothermal solidification. In a second process, a die is pressed into a printed mixture of Cu and a flux-free solvent. The same gas is used to reduce Cu oxides to avoid the use of flux. A source of solder is placed adjacent to the die on the substrate. Upon melting, capillary forces draws the Sn-rich liquid into the bond which infiltrates the Cu particles. Minimal void formation and complete conversion of the Sn to IMC was demonstrated at a processing temperature near 250°C using these techniques. Passive thermal cycling from -55 to 125°C resulted in vertical crack formation that propagated through the Si die. In other instances, crack propagation from the edge of the bond and failed adhesion of the die-side metallization was observed. This work demonstrates that novel configurations and processing techniques can be used to improve bond quality, specifically void formation. (Ehrhardt et al. 2014). Hongtao Chen et al. demonstrated a novel core shell approach to TLPB using Cu particles electroplated with Sn. Cu-Sn preforms were fabricated by electroless plating of 30 µm Cu particles with 2-3 microns of Sn. The cleaned powder was then pressed into approximately 400 µm thick preforms using 30 MPa of pressure with a 1 minute dwell. Complete conversion of the Sn layer to Cu₆Sn₅ and Cu₃Sn was demonstrated using a 12 minute reflow process with a peak temperature of 250°C. Bond fabrication using the preforms required application of < 0.5 MPa to ensure complete contact at the interfaces. The average shear strength at 400°C was 29.35 MPa. Electrical resistivity was 6.5 µ*ohm*cm. Thermal conductivity was 128 – 154 W/mk. Thermal cycling results were also promising. The use of preforms made from core-shell particles was
demonstrated to be a cost-effective method to fabricate durable, void-free TLP bonds under reasonable processing conditions. (Chen et al. 2016)

Bajwa and Wilde demonstrated TLPB preforms fabricated by electroplating alternating layers of Ag and Sn. The overall composition of the preforms was approximately 80 percent Ag. Three layer and nine layer preforms were made by depositing the layers onto a steel plate. Bonds were produced from the preforms by heating to 240°C at 35°C/min and using a contact pressure of 5 MPa. The shear strength of resulting joints was 35 MPa even after thermal shocking. SiC Schottky diodes were mounted using both the Ag-Sn preforms and Ag sintering. Electrical and thermal performance was comparable to sintered Ag. Thermal cycling from -40 to 150°C for 1000 cycles also showed promising results. The use of alternating layers was demonstrated to be a practical method for forming durable, void free TLP bonds with performance comparable to sintered Ag. (Bajwa and Wilde 2016)

3.7 Final Comments on General TLPB Development

In this chapter, approaches for creating transient liquid phase technologies that meet specific thermodynamic and kinetic criteria for well-defined ranges of compositions and processing conditions appropriate for their use in specific applications were described. In addition, we have discussed our current understanding of (1) what it will take to achieve the manufacturability required for a Pb-free technology that could replace high-Pb solders in current applications, (2) how these can be extended to even higher temperature applications, and (3) how transient liquid phase bonding compares with other alternative technologies. The Sn-based LTP systems presented in this chapter continue to dominate research in this field, however, it is possible to use Sn-free LTP compositions based on In, Zn, and Bi as the basis for other technologies, as shown in the earliest reported TLPB research for electronics.
4. ADVANTAGES OF BI-RICH SN-BI

4.1 Introduction

In chapter two, thermodynamic criteria for effective transient liquid phase bonding was introduced and applied to the use of Sn-Bi as a low-melting temperature component. The Sn-Bi-Cu ternary has long been identified as a promising system for TLPB, with most previous studies focused on high-Sn or near eutectic LTP compositions (D’Hondt and Corbin 2006)(Mokhtari and Nishikawa 2016)(Pan and Yeo 2014)(Liu and Shang 2001). A major limitation with such TLPB compositions in the Sn-Bi-Cu TLPB system is the reaction of \( \text{Cu}_6\text{Sn}_5 + \text{Bi} \) near 200°C to form liquid thus limiting the use temperature as identified by D’Hondt et al. (D’Hondt and Corbin 2006)(Mokhtari and Nishikawa 2016). This chapter demonstrates a novel method for increasing the melting temperature of Sn-Bi-Cu TLP bonds from approximately 200°C to that of Bi (271°C) by using high-Bi, Sn-Bi LTP compositions processed above 200°C. The tradeoff between lower processing temperatures (Sn-Bi eutectic at 139°C) and increasing operating temperatures above 200°C due to the direct formation of \( \text{Cu}_3\text{Sn} \) is presented below. This behavior is experimentally demonstrated in planar TLP bonds and solid-liquid diffusion couples. Increasing the proportion of Bi is shown to reduce processing times because of the overall reduction in Sn that must form IMC. Microstructural observations are also provided to inform further development of TLPB using Sn-Bi.

4.2 Thermodynamic Analysis of Bi-rich, Cu-Sn-Bi

The binary Sn-Bi system is a simple binary eutectic (138 °C) with no IMC phases and some solubility of Bi in Sn and Sn in Bi. The Bi-Cu system is also simple binary eutectic but with little-to-no solubility in either Bi or Cu.
Figure 4-1 Binary phase diagrams in the Sn-Bi-Cu system (top) Bi-Sn, (middle) Bi-Cu, (bottom) Cu-Sn shows that only Cu-Sn IMCs are expected.
Since it is well established that Cu-Sn-Bi does not form any ternary phases, the isothermal sections of the ternary phase diagram contain 2 or 3 phase equilibrium regions linking the following phases: liquid, solid Cu, solid Sn, solid Bi, \( \text{Cu}_6\text{Sn}_5 \), and \( \text{Cu}_3\text{Sn} \). (Note that only phases that form below the maximum temperature relevant for TLPB in the Sn-Bi-Cu system are considered, i.e., 271°C, the melting temperature of Bi.) The behavior of a given system will tend to result in similar behavior over specific and low-melting temperature component composition ranges, referred to in this chapter as processing regimes. Isothermal sections of the ternary phase diagrams were calculated at regular intervals using Thermo-Calc and the TCSLD3 solder alloy database. Three processing regimes were identified within the Cu-Sn-Bi system. Isothermal sections as well as step-by-step descriptions of expected phase evolution are provided below.

### 4.2.1 Cu-Sn-Bi Regime Map

The temperature and Sn-Bi LTP compositions associated with the three regimes described below have been generated from calculated ternary isothermal sections using TCSLD3. A regime map, shown in Figure 4-2, was generated to identify the phase in equilibrium with the Cu-saturated, Sn Bi which determines processing and operating temperature limits. In each of the three regimes, there is a terminal liquid composition reached as the IMCs grow that changes as a function of temperature. As shown, the terminal liquid compositions for Regime 1 coexists with \( \text{Cu}_6\text{Sn}_5 \) and Bi and for Regime 3 with \( \text{Cu}_3\text{Sn} \) and Bi. Additional IMC growth in those two regimes is accompanied by a decrease in the fraction liquid and Bi precipitation until the liquid is consumed. In Regime 2, growth of \( \text{Cu}_6\text{Sn}_5 \) stops when the terminal liquid composition is reached, and isothermal solidification is only possible when the \( \text{Cu}_6\text{Sn}_5 \) formed in the initial stages of growth is completely transformed into \( \text{Cu}_3\text{Sn} \), a process taking significantly longer than the direct formation of the IMC in equilibrium with both the terminal liquid and solid Bi.
Figure 4-2 Processing regime map identifying LTP compositions and processing temperatures associated with each processing regime based on CALPHAD phase equilibria in the Cu-Sn-Bi system

4.2.1.1 Processing Regime 1

For processing Regime 1, the entire range of Sn-Bi LTP compositions are suitable for TLPB with Cu from 139 to 200°C but application temperatures are limited by the Class II reaction to below 200°C. In this regime Sn reacts with Cu to form Cu₆Sn₅, leading to an increasing Bi concentration in the remaining liquid until a terminal liquid is reached for the three phase equilibrium with solid Bi. As Cu₆Sn₅ formation continues, Bi precipitates in the liquid until all Sn is consumed by IMC formation and the liquid is consumed. In this range of temperatures, all compositions in the Sn-Bi binary will undergo this final Bi precipitation reaction as Cu₆Sn₅ grows. For example, a near eutectic Sn-Bi liquid in contact with Cu at 170°C as depicted in the Regime I section of the isothermal solidification schematic shown in Figure 4-6. The liquid becomes enriched with Bi as Cu and Sn interdiffuse to form Cu₆Sn₅. As seen in the corresponding isothermal section of the Cu-Sn-Bi phase diagram in Figure 4-3, a Cu saturated, liquid Sn-Bi LTP is in 2-phase equilibrium with Cu₆Sn₅ (Region “A”). Cu₃Sn is in 2-phase equilibrium with both Cu and Cu₆Sn₅ thus forming a three-phase region. Based on these conditions, a Cu₆Sn₅ layer will form in contact with the liquid and a Cu₃Sn layer forms between
Cu and Cu$_6$Sn$_5$. Since the Cu$_6$Sn$_5$ and Cu$_3$Sn layers incorporate only Sn from the liquid phase, the liquid become enriched with rejected Bi solute as the intermetallic layers continue to grow, until the liquid composition reaches the maximum Bi concentration in the liquid in equilibrium with Cu$_6$Sn$_5$, i.e., the terminal liquid composition. This terminal liquid composition is in 3-phase equilibrium with Cu$_6$Sn$_5$ and solid Bi (Region “B” in Figure 4-4). Further growth of the Cu$_6$Sn$_5$ layer is accompanied by Bi precipitation until all of the liquid is consumed as illustrated in the third frame in Figure 4-6. As reported previously, complete isothermal solidification of a Cu-Sn-Bi TLP bond is achievable within the 138-200°C processing regime. Above approximately 200 °C the Cu-Sn-Bi ternary system exhibits the following Class II reaction at 195.9 °C: Cu$_3$Sn + L → Cu$_6$Sn$_5$ + Bi (NIST 2002d). D’Hondt et al. observed this reaction at 191°C in a series of DSC experiments for TLPB samples that had been isothermally solidified at lower temperature. Mokhtari observed this transformation with an onset temperature ranging from 192.8 to 201°C. This transition is shown in the regime map in Figure 4-2.

Figure 4-3 Calculated isothermal section of the Sn-Cu-Bi phase diagram at 170°C.
Figure 4-4 Calculated isothermal section of the Cu-Sn-Bi phase diagram at 210°C

4.2.1.2 Processing Regime 2

Processing Regime 2 occurs for Sn-rich LTP liquid compositions above 200°C. The Cu-Sn-Bi isothermal section at 210°C in Figure 4-4 shows that Sn-Bi liquids composed of up to 65 wt. % Bi are in 2-phase equilibrium with Cu$_6$Sn$_5$ (Region “A” in Figure 4-4). Isothermal solidification within this temperature and composition regime will initially proceed in the same way as the 138-200°C processing regime with the formation of a Cu$_6$Sn$_5$ layer in contact with the liquid with a Cu$_3$Sn layer forming between Cu$_6$Sn$_5$ and Cu (Figure 4-6). Intermetallic growth leads to increasing Bi concentration in the liquid up to 65 wt. % Bi which is in three-phase equilibrium with Cu$_6$Sn$_5$ and Cu$_3$Sn (Region “B” in Figure 4-4). Additional Cu$_6$Sn$_5$ cannot form once this liquid composition is reached since liquid compositions above 65 wt. % Bi are in two-phase equilibrium with Cu$_3$Sn only (Region “C” in Figure 4-4), not with solid Bi. The presence of Cu$_6$Sn$_5$ in contact with the liquid thus pins the liquid composition. The Cu$_3$Sn IMC will
continue to grow at the expense of Cu₆Sn₅ and Cu. Liquid consumption can resume only when Cu₆Sn₅ is completely consumed by Cu₃Sn growth and Cu₃Sn comes into contact with the liquid, Region C in Figure 4-4. With continued growth of Cu₃Sn, the liquid becomes enriched in Bi, until the terminal liquid composition is reached and Bi precipitates occurs. Although possible, the kinetics of Cu₃Sn growth makes such a conversion impractical for processing times less than 1 hour. Thus above 200°C, the terminal liquid in three-phase equilibrium (region “B”) with Cu₆Sn₅ and Cu₃Sn will be persistent for typical processing temperatures and times. Note that the upper bound for Regime 2 is the melting point of Bi. A calculated isothermal section at 260 °C is shown for comparison with of the compositional ranges of Regions A, B, C, and D. of the terminal liquid compositions

### 4.2.1.3 Processing Regime 3

Processing Regime 3 occurs for Bi rich liquid compositions at temperatures above approximately 200°C. The 260°C isotherm in Figure 4-5 shows that Bi rich liquid compositions are in two-phase equilibrium with Cu₃Sn (Region “C”) as opposed to Cu₆Sn₅ (Region “A”). By starting with an LTP with greater than 65 wt. % Bi at 260°C, Cu₃Sn forms in two phase equilibrium with the liquid until it reaches the terminal liquid composition noted in Figure 4-5(c). This composition is in three-phase equilibrium with solid Bi and Cu₃Sn (Region “D”), with further growth of the Cu₃Sn layer accompanied by precipitation of solid Bi. Regime 3 is limited by the melting point of Bi Complete consumption of Sn with high Bi alloys (Sn-xBi, for x= 90%, 95%, 98%) annealed at 300°C was reported by Wang, et al. (2012) with the formation of a Bi liquid in contact with Cu₃Sn.
Figure 4-5 Calculated isothermal section of the Cu-Sn-Bi phase diagram at 260°C
4.3 Cu-Sn-Bi IMC Formation Experiments

4.3.1 Alloy fabrication

A Sn-Bi alloy composed of 80 percent Bi by weight was fabricated by melting Sn and Bi shot together in a ceramic crucible on a hotplate set at 500°C. Sufficient rosin flux was added to the crucible to immerse the metal and prevent oxidation. The molten alloy was poured onto a room temperature copper sheet coated with boron nitride to form a sheet. The composition of the resulting sheet was verified using SEM/EDS of metallographic cross-sections. Using the calculated phase diagrams as the reference, the solidus and liquidus temperatures were measured.
and verified using DSC. The DSC sample was heated from 0°C to 400°C at 20°C per minute and cooled at 10°C per minute.

Sn-Bi solder spheres of the same composition (80 wt. % Bi) were procured from the Indium Corporation. Optical micrography was used to confirm an approximate diameter of 500µm. Composition was also verified via EDS in cross-sections of as-fabricated samples where the solder spheres were used.

4.3.2 Reactions between Sn-Bi alloys and Cu

4.3.2.1 Substrate preparation.

The Cu substrates used were 5.6 by 5.6 mm Cu pads produced for the central pad in a QFN package. The copper substrates were separated from sheets and cleaned using phosphoric acid for 10 minutes followed by rinsing in RO water, acetone, and ethanol sequentially. Finally, a proprietary (Indium Corp.) flux was applied to ensure adequate wetting.

4.3.2.2 Fabrication and heat treatment of reaction couples between solid Cu and liquid Sn-Bi alloys.

For intermetallic growth rate measurements, individual copper substrates were placed in a ceramic boat with a Sn-80 wt. % Bi alloy on top of each substrate. Excessive liquid was provided to prevent the composition of the liquid from changing appreciably during heating. Reaction couples were isothermally aged in a preheated tube furnace at 260°C and 235°C for 20, 40 and 60 minutes in flowing nitrogen (>100 SCCM) used to limit oxidation. After isothermal treatment, the samples were removed from the furnace and air cooled. The resulting couples were cross-sectioned and polished using standard metallographic techniques. SEM/EDS was used to identify the IMC phases present. For the IMC growth rate measurements, SEM micrographs of the cross-sections were measured using ImageJ. Measurement of the IMC thickness was performed by overlaying a series of lines with 1 µm spacing on SEM micrographs of the interface between the Cu pads and the Sn80Bi material.

4.3.2.3 Cu-(Sn-Bi)-Cu TLPB Assemblies

Assemblies of Cu-(Sn-Bi)-Cu assemblies were fabricated using the substrates and solder spheres described above. A hotplate was used to pre-solder the assemblies before aging experiments and DSC analyses. Fluxed Cu substrates were heated on a hotplate set to 350°C. On
one of the substrates, a small sphere of Sn-80Bi was melted. The second heated, fluxed substrate was then flipped onto the molten Sn-80Bi such that capillary forces pulled the two substrates together as illustrated in Figure 4-7. The resulting assemblies were then air cooled.

Figure 4-7 Schematic illustration of procedure used to fabricate TLPB test assemblies

Four assemblies were placed between preheated ceramic substrates and isothermally annealed in air at 260°C for one hour. Additional pre-soldered assemblies were trimmed to fit inside Al DSC pans with an internal radius of 8 mm. Three temperature profiles corresponding to the three processing regimes were used. The DSC samples were heated in the DSC at a rate of 20°C/min from 0°C to 170°C, 210°C, and 260°C, respectively; held at peak temperature for 1 hour; and cooled back to room temperature at 10°C/min. Melting and solidification events were observed during heating and cooling. Each sample was subsequently heated to 400°C at 20°C/min and cooled back to RT at 10°C confirm the presence and or absence of Cu₆Sn₅. The temperature profile is illustrated schematically in Figure 4-8. The 170°C assembly was expected to exhibit melting peaks near 191°C. The 260°C assembly was expected to exhibit melting between 250 and 271°C.
A second series of assemblies were created and processed using the DSC to carefully control heating time. The post-processing heating cycle was eliminated to observe the microstructure only after the initial isothermal hold. Durations of 20, 30, 40, 50, 60, and 180 minutes at peak temperatures of 210°C, 260°C, and 300°C were selected to compare IMC morphology with variation in processing conditions.

4.4 Results and Discussion

4.4.1 Composition of Sn-Bi Alloy

A Sn-80 wt% Bi alloy was desired because this composition lies in Regime 1 for temperatures below 200°C and in Regime 3 for temperatures above 200°C. This alloy was used to assess the growth rate of Cu3Sn above 200°C. The Sn-80Bi starting composition was confirmed using a combination of DSC and EDS measurements. As shown in Figure 4-9, the liquidus temperature was 210°C and the solidus temperature was 139°C, as expected from an alloy of 80 wt. % Bi (70 at. % Bi). Based on these results, the composition of the alloy was confirmed to be within 10 percent of the nominal target composition of Sn-80 wt. % Bi.
4.4.2 Cu-(Sn-Bi LTP)-Cu TLPB Assemblies

Sandwich assemblies were prepared and subsequently annealed to demonstrate isothermal solidification. Cross-sections of Cu-(Sn80Bi)-Cu assemblies before isothermal treatment revealed adequate wetting and minimal formation of intermetallic phases during initial assembly. Large facetted Bi phases were observed along with the Sn-Bi eutectic as consistent with the Bi rich composition of the LTP as shown in Figure 4-10.

Figure 4-10 SEM micrograph of as-fabricated Cu-Sn80Bi-Cu assembly demonstrates adequate wetting and minimal formation of IMC’s during assembly.

4.4.3 Cu-(Sn-Bi)-Cu TLPB Assemblies: DSC

The assemblies isothermally treated at 170°C for 1 hour using the DSC did not exhibit a solidification peak during cooling from 170°C to RT as shown in Figure 4-11. This result
indicates that all of the Sn-Bi liquid was converted to solid phases during the isothermal hold. During heating from RT to 300°C the sample exhibited a melting event near 191°C which indicates that Cu₆Sn₅ remains after the isothermal hold. This result is consistent with previous work in the Cu-Sn-Bi system. The DSC results are also consistent with anticipated behavior based on the discussion above.

![DSC graph](image)

Figure 4-11 DSC results from a Cu-(Sn-80Bi)-Cu assembly isothermally treated at 170°C for 1 hour and subsequently heated to 300°C and back to room temperature (shown above) reveals a melting event near 200°C which is consistent with Cu₆Sn₅ reacting with the rejected Bi phase to form liquid.

The assemblies isothermally processed using the DSC at 210°C and 260°C both exhibited melting temperatures near 271°C during heating to 300°C as shown in Figure 4-12 and Figure 4-13, respectively. Results of the complete DSC profile are shown on the left, and the signal when heating from RT to 300°C are shown on the right for clarity. The lack of a melting event near 200°C (dashed box) for the 210°C and 260°C runs indicates that the reaction of Cu₆Sn₅ and Bi to form liquid did not occur. Thus, the only IMC phase present was Cu₃Sn.
Figure 4-12 DSC results from a Cu-(Sn-80Bi)-Cu assembly isothermally treated at 210°C for 1 hour and subsequently heated to 300°C and back to room temperature reveals a melting event near 271°C which is consistent with the rejected Bi phase melting. Note the lack of melting activity near 200°C indicates that Cu₆Sn₅ was not present.

Figure 4-13 DSC results from a Cu-(Sn-80Bi)-Cu assembly isothermally treated at 260°C for 1 hour and subsequently heated to 300°C and back to room temperature reveals a melting event near 271°C which is consistent with the rejected Bi phase melting. Note the lack of melting activity near 200°C indicates that Cu₆Sn₅ was not present.

The Cu-(Sn-Bi)-Cu assemblies isothermally treated via DSC were retained for microstructural analysis. Because the samples were heated to 300°C, complete conversion of the Sn-Bi liquid to Cu₃Sn + Bi was observed in all of the assemblies. EDS was used to identify the phases as annotated in the figures. A representative microstructure presented in Figure 4-14
illustrates that Cu$_3$Sn formed at each interface with a rejected Bi phase forming along the center of the bondline. A Bi-rich phase also forms at the interface between Cu$_3$Sn and the Cu substrates. Since the entrapped Bi layer is very fine, an EDS line scan was used to verify that the layer was in fact Bismuth. The results of the line scan shown in Figure 4-15 exhibits an increase in Bi signal between the Cu$_3$Sn and Cu interfaces. The EDS maps shown in Figure 4-16 further illustrate the presence of Bi between Cu and Cu$_3$Sn. The segregation of Bi between the Cu layer and the Cu$_3$Sn layer is consistent with observations by P.L. Liu et al of Bi segregation at the interface between eutectic Sn-Bi and Cu (Liu and Shang 2001). This behavior is known to cause embrittlement of Cu.

Figure 4-14 SEM micrograph of a cross-section of a Cu-(Sn80Bi)-Cu assembly isothermally processed at 210°C and briefly heated to 300°C shows complete conversion of LTP to Cu$_3$Sn + solid Bi.
Figure 4-15 Plot of ZAF atom percent of each component versus position for an EDS line scan (right) and corresponding image (left) shows that the lighter phase between Cu₃Sn and the Cu substrate is Bi.

Figure 4-16 EDS maps a cross-section of a Cu-(Sn80Bi)-Cu assembly isothermally processed at 260°C for 1 hour and briefly heated to 300°C shows complete conversion of LTP to Cu₃Sn + solid Bi.

4.4.4 Cu-Sn-Bi Solid-Liquid Diffusion Couple Results

Cross-sections of the Cu substrates held in contact with an effectively infinite source of Sn-80 wt. % Bi liquid at 260°C for 1 hour and then cooled to room temperature are shown in
Figure 4-17. A layer of Cu$_3$Sn formed between the Cu substrate and the Sn-80wt. % Bi liquid at 260°C as expected from Wang et al (2012) and the ternary phase diagram. Note the Cu$_3$Sn forms both as a roughly continuous layer along the Cu substrate and as very large needles growing into the solidified liquid region. These large Cu$_3$Sn needles may have formed during cooling from 260°C to approximately 200°C. Note also that these is a thick layer of Cu$_6$Sn$_5$ that formed on the Cu$_3$Sn layer during solidification below 200°C.

![SEM micrograph of a cross-section of a Cu substrate in contact with Sn-80wt%Bi at 260°C for 1 hour exemplifies Cu$_3$Sn layer measured to determine IMC growth rates](image)

The observed rate of growth of the Cu$_3$Sn layer within Regime 3 deviates from that observed when Cu$_3$Sn forms between a Cu$_6$Sn$_5$ layer and Cu in conventional Sn-rich systems. Cu$_3$Sn growth was assessed using effectively infinite, solid-liquid diffusion couples of pure Cu and the Sn-80wt%Bi alloy at 235°C and 260°C for 20, 40 and 60 minutes each. The thickness of the Cu$_3$Sn layer was measured from SEM micrographs of cross-sections of the solidified couples. Measurements of Cu$_3$Sn thickness for each condition are reported in Table 4-1. Since the IMC layer thickness is not uniform, these measurements were performed by measuring the length IMC thickness at 1 µm intervals. Relatively large standard deviations are reported due to the rough interface between Cu$_3$Sn and the solidified Sn-Bi alloy rather than measurement error. Li and Johnson measured IMC growth in pure Cu-Sn couples where both Cu$_6$Sn$_5$ and Cu$_3$Sn formed, and their results for 260°C showed a thicker layer of total IMC for the durations
measured. At 260°C, Cu₃Sn formed more rapidly than the Cu₃Sn layer beneath Cu₆Sn₅ reported by JF Li et al. (Li et al. 2011).

Table 4-1 Average Cu₃Sn layer thickness measured from Cu-Sn80Bi (wt. %) diffusion couple cross-sections

<table>
<thead>
<tr>
<th>Isothermal Hold Time (minutes)</th>
<th>Temperature (°C)</th>
<th>Mean Cu₃Sn Layer Thickness (µm)</th>
<th>Standard Deviation (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>235</td>
<td>2.3</td>
<td>0.55</td>
</tr>
<tr>
<td>40</td>
<td>235</td>
<td>2.5</td>
<td>0.52</td>
</tr>
<tr>
<td>60</td>
<td>235</td>
<td>4.1</td>
<td>1.42</td>
</tr>
<tr>
<td>20</td>
<td>260</td>
<td>3.3</td>
<td>0.59</td>
</tr>
<tr>
<td>40</td>
<td>260</td>
<td>3.8</td>
<td>0.81</td>
</tr>
<tr>
<td>60</td>
<td>260</td>
<td>4.5</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Despite the rate of Cu₃Sn formation in Cu-Sn80Bi being slower than the combined formation of Cu₆Sn₅ and Cu₃Sn in pure Cu-Sn couples at the temperatures investigated, overall isothermal solidification occurs more quickly than pure Sn-Cu TLPB for the same bondline thickness due to both co-precipitation of Bi and there is less Sn present in the liquid that must be consumed. As an example, consider a 10 µm layer of Sn in contact with Cu versus a 10 µm layer of Sn-80wt% Bi as illustrated in the schematic diagram in Figure 4-18. The schematic compares the isothermal solidification behavior of pure Sn to that of Sn-80wt%Bi in contact with pure Cu, illustrating that significantly more IMC must form for complete isothermal solidification of pure Sn based on conservation of mass. Because the composition of Cu-Sn intermetallics are fixed, the layer thicknesses necessary for complete isothermal solidification may be calculated based on conservation of mass, the density of each phase, and the molar mass of each phase. Assuming constant area for planar bonding, the area will cancel out such that layer thickness ratios may be used. For Sn-Cu TLPB, the ratio of thickness Sn consumed to Cu₃Sn formed may be calculated as

\[
\frac{\left(118.69 \frac{\text{g}}{\text{mol Sn}}\right)}{3 \left(63.546 \frac{\text{g}}{\text{mol Cu}}\right) + \left(118.69 \frac{\text{g}}{\text{mol Sn}}\right)} \times \frac{8.97 \frac{\text{g}}{\text{cm}^2} \text{Cu}_3\text{Sn}}{7.36 \frac{\text{g}}{\text{cm}^3} \text{Sn}} = 0.468 \frac{\text{Sn}}{\text{Cu}_3\text{Sn}}
\]

which means that 0.468 µm of the Sn layer thickness will be consumed by 1 µm of Cu₃Sn formation. The same calculation may be performed for Cu₆Sn₅ as
which shows that 0.685 µm of Sn layer will be consumed by 1 µm of Cu₆Sn₅ formation. Continuing with the 10 µm reaction example, the pure Sn sample will thus require a minimum of 14.6 of Cu₆Sn₅. Forming the only Cu₆Sn₅ is a best-case scenario for pure Sn TLPB for the purpose of comparison. For the Sn-80wt%Bi sample the volume fraction of the Sn component may be approximated as

\[
\frac{20 \text{g}}{7.36 \text{g/cm}^3 \text{Sn}} \left( \frac{80 \times 9.78 \text{g/cm}^3 \text{Bi} + 20 \times 7.36 \text{g/cm}^3 \text{Sn}}{\text{Sn}_{80\text{Bi}}} \right) = 0.158 \frac{\text{Sn}}{\text{Sn}_{80\text{Bi}}}
\]

therefore one may consider the effective Sn height for the 10 µm layer to 1.58 µm. Dividing the 1.58 µm effective Sn layer by the Sn to Cu₅Sn ratio yields a result of 3.4 µm of Cu₅Sn needed to consume all of the Sn from a 10 µm layer of Sn-80wt%Bi. The thickness of the rejected Bi layer is simply 1-0.158 since Bi is the only remaining component. The results of this example are illustrated in Figure 4-18. This result illustrates the advantage of Bi-rich TLPB. Since IMC formation is the rate limiting step for isothermal solidification in TLPB, a Bi-rich system with the same initial bondline will solidify more rapidly.

Figure 4-18 Schematic comparing the isothermal solidification behavior of pure Sn to that of Sn-80wt%Bi in contact with pure Cu illustrates that significantly more IMC must form for complete isothermal solidification of pure Sn based on conservation of mass.
4.4.5 Microstructural Evolution

A second set of pre-soldered Cu-Sn80Bi-Cu assemblies were processed via DSC for 20, 30, 40, 50, 60, and 180 minutes at 210°C, 260°C, and 300°C. All three temperatures fall within Regime 3 given the 80 wt. % Bi composition. Complete conversion to Cu$_3$Sn and Bi for all 18 conditions is apparent in the composite SEM micrograph in Figure 4-19. The morphology of the Cu$_3$Sn phase is consistent within the temperature range tested. Some bridging was observed in the thinner bondline samples which may affect mechanical performance. Variation in bondline was attributed to inconsistencies introduced in the pre-soldering method of assembly fabrication and initial solder sphere volume. The most notable trend is increasing penetration of the Bi layer between Cu$_3$Sn and the Cu substrates with temperature and time. Bi is not present between Cu$_3$Sn and Cu at 210°C. This result suggests a thermodynamic origin to the Bi layer. It also indicates the layer formation can be prevented if detrimental to mechanical bond strength.
Figure 4-19 Compilation of SEM micrographs of Cu-Sn80Bi-Cu assembly cross-sections comparing microstructure after different processing temperatures and durations shows increasing penetration of Bi phase between Cu$_3$Sn and Cu substrates with increasing time and processing temperature. Note the variation in bondline thickness is due to variation in initial solder volume angle between substrates rather than process conditions.

### 4.5 Estimated versus Observed Cu-Sn-Bi IMC Bond Conversion Times

As previously described above, measurements of Cu$_3$Sn formation in the Cu-Sn-Bi system were shown to be faster than observed in pure Cu-Sn. The growth rate with time at 235°C and 260°C was measured using an effectively infinite amount of Cu-Sn80Bi in contact with Cu to determine at least at that composition how the presence of Bi in the liquid affected the time for isothermal solidification and whether a full analysis of the effect of Bi on IMC growth rate would need to be performed for all compositions between Cu-Sn80Bi and the terminal liquid composition.
As a first estimate of the effect of Bi on Cu3Sn growth and, therefore, the time for isothermal solidification, an estimated diffusion coefficient was calculated from the data presented above Table 4-1 on Cu3Sn layers thickness measured as a function of time in solid-liquid diffusion couples with an infinite amount of liquid at. By doing the following analysis The effective diffusion coefficient corresponding to the form $X = kt^{1/2}$ where $X$ is the IMC thickness (µm), $k$ is the growth coefficient, and $t$ is time (seconds) was approximately 0.068 µm/s$^{1/2}$ at 235°C and 0.079 µm/s$^{1/2}$ at 260°C. These coefficients were then used for a preliminary analysis of the time necessary to process a planar bond as a function of bondline thickness and composition. For the purposes of this analysis, the thickness of IMC formed in the solid-liquid diffusion couple where an effectively infinite amount of liquid is present was assumed to apply to the case of a finite volume of liquid used in an actual bond. The rate of IMC formation was also assumed to remain constant across Bi-rich compositions of Sn-Bi in Regime III.

Conservation of mass was applied using the relationships described in Section 4.4.4 for the hypothetical planar Cu-Sn-Bi bond. The initial bondline was divided by the volume Sn consumed per volume IMC formed to establish the necessary IMC layer thickness to completely consume the Sn for a given bondline and composition. The time needed to form the necessary IMC layer was determined using the coefficients described above. These results were plotted as a contour map as a function of Bi content and bondline as shown in Figure 4-20.

![Figure 4-20 Contour maps illustrating the minimum processing time (minutes) at 260°C (left) and 235°C (right) for a given initial bondline and LTP. A data point from the results presented in Section 4.4.5 are for each temperature to show that these results are a useful estimate conversion time for actual TLPB interfaces.](image)
These estimated times can be compared with the results from the planar bonds processed using DSC. The Cu-Sn80Bi-Cu assemblies processed using a DSC in Section 4.4.5 demonstrated that complete conversion of the Sn-Bi (80 wt.% Bi) to Cu3Sn and Bi occurred in a sample held at 260°C for 20 minutes with a bondline of approximately 16 µm. Likewise, assemblies with a 13 µm thick bondline held at 210°C for 20 minutes showed complete isothermal solidification. These conditions are marked with an “X” in Figure 4-20 for 260°C and 235°C. Note that the 210°C samples were compared to the isothermal solidification time estimates at 235°C since the lower temperatures were different for the two sets of experiments. As seen in Figure 4-20, an isothermal solidification time of approximately 20 minutes was estimated for both these conditions. Since complete conversion did occur in these samples at least as quickly as the predicted time, this empirical fit is useful for approximate planning purposes, but a more detailed model that considers the physics of interdiffusion is needed, particularly since the growth rate data in the Cu-Sn-Bi varies significantly from pure Cu-Sn.

Variation in IMC formation rates in a finite liquid versus an infinite liquid sample is expected since the composition of the liquid continues to change as Sn is consumed by IMC formation up to the point of reaching the terminal liquid composition. This deviation can be explained by examining the following equation

\[ \phi = \frac{J_i^s - J_i^l}{c_i^s - c_i^l} \]

where \( \phi \) is the rate of movement of the interface between solid and liquid (in this case solid Cu3Sn and liquid Sn-Bi), \( J_i \) is flux of the species \( i \) (Sn in this case) into the solid or into the liquid, and \( c_i \) is the concentration of the species \( i \). The rate of movement of the interface between Cu3Sn and liquid Sn-Bi will vary as the concentration of Sn in the liquid decreases. This shift in concentration in the liquid is also present in the solid-liquid diffusion couples where a boundary layer at the interface is likely to have formed. This means that there is likely a very rapid formation of IMC to some undetermined thickness followed by slower growth. Additional solid-liquid diffusion couple experiments using Sn-Bi alloys of 70 wt. and 90 wt.% Bi and very short durations (less than 1 minute) are suggested to sort out these effects. Ideally, a diffusion physics-based model of IMC growth with changing liquid composition should be developed to predict conversion times in finite liquid scenarios, i.e. thin bondlines.
4.6 Cu-Sn-Bi Discussion and Conclusion

A methodology for interpreting thermodynamic data for multicomponent transient liquid phase bonding systems has been introduced and demonstrated for the Cu-Sn-Bi system. This method was used to predict advantages of utilizing a Bi-rich, Sn-Bi alloy as the low melting temperature component in Cu-Sn-Bi TLP bonding. Complete isothermal solidification without the formation of $\text{Cu}_6\text{Sn}_5$ was demonstrated and shown to increase the solidus temperature of resulting TLP bonds to that of the Bi phase based on DSC experiments using Cu-Sn80Bi-Cu assemblies. Measurements of intermetallic formation between Cu and Sn80Bi establish that the rate of IMC formation for $\text{Cu}_3\text{Sn}$ deviate from that observed in previous Sn-Cu IMC kinetics studies. To develop commercially viable Bi-rich, Cu-Sn-Bi TLPB systems, further investigation of the kinetics of reaction will be necessary. Specifically, additional solid-liquid diffusion couple experiments with very short durations and other Bi-rich compositions will be necessary to gain further insights into formation of $\text{Cu}_3\text{Sn}$ Bi in the presence of Bi where Sn. Die shear testing at room temperature and elevated temperature will also be needed.

4.7 Thermodynamic Assessment of Ni-Sn-Bi

As discussed in Chapter 2, Ni-Sn-Bi does not conform to the pattern of forming the IMC phase in equilibrium with the saturated liquid. $\text{Ni}_3\text{Sn}_4$ is known to form despite Ni-Bi intermetallics being the equilibrium phase. This result is convenient when using a Bi-rich, Sn-Bi alloys with Ni for TLPB since only Sn must consumed for isothermal solidification. The melting temperature of Bi (271°C) becomes the upper limit for operating temperatures. The benefit of using Ni with Sn-Bi as opposed to Cu is that a Bi-rich composition is not required to elevate the melting temperature of the bond, thus lower temperature processing is possible.

4.8 Ni-Sn-Bi Experiments

The Sn-80Bi wt. % alloy created using the steps described in Section 4.3.1 was used again for Ni-Sn80Bi, solid-liquid diffusion couples. The diffusion couples were treated in a tube furnace for 20, 40, and 60 minutes, but at 260°C and 300°C in flowing nitrogen (>100 SCCM) used to limit oxidation. After isothermal treatment, the samples were removed from the furnace and air cooled. The resulting couples were cross-sectioned and polished using standard
metallographic techniques. SEM/EDS was used to identify the IMC phases present. For the IMC growth rate measurements, SEM micrographs of the cross-sections were measured using ImageJ. Measurement of the IMC thickness was performed by overlaying a series of lines with 1 µm spacing on SEM micrographs of the interface between the Cu pads and the Sn80Bi material.

4.9 Ni-Sn-Bi Results and Discussion

The Ni-Sn-Bi interdiffusion couples exhibited a scalloped morphology resembling a typical Cu₆Sn₅ as shown in Figure 4-21. Measurements of average intermetallic thickness are listed in Table 4-2. The intermetallic thickness for a given duration was lower compared to the values observed in Table 4-1 for Cu-Sn-Bi. Note that the relatively large value of the standard deviation is a result of the uneven growth of the Ni₃Sn₄ layer observed rather than measurement error. Again, the significance of the growth rate of Ni₃Sn₄ is also offset by the reduced Bi content in Bi-rich compositions. In implementation of Ni-Sn-Bi, a tradeoff is faced between reducing the melting temperature of the low-melting temperature phase using increased Sn and longer process times due to the increased Sn that must be consumed in the formation of Ni₃Sn₄.

![Figure 4-21 SEM micrograph of Ni-Sn80Bi solid-liquid couple held at 300°C for 60 minutes shows a thin layer of Ni3Sn4 with a scalloped morphology.](image-url)
Table 4-2 Average Ni$_3$Sn$_4$ layer thickness measured from Ni-Sn80Bi (wt. %) diffusion couple cross-sections

<table>
<thead>
<tr>
<th>Isothermal Hold Time (minutes)</th>
<th>Temperature (°C)</th>
<th>Mean Ni$_3$Sn$_4$ Layer Thickness (µm)</th>
<th>Standard Deviation (µm)</th>
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4.10 Comparison of Cu-Sn-Bi and Ni-Sn-Bi IMC Formation

The mean IMC layer thicknesses reported in Table 4-1 and Table 4-2 were plotted versus isothermal hold time as shown in Figure 4-22. Measurements of mean IMC thickness for both Ni and Cu in contact with Sn-Bi (80 wt.% Bi) at 260°C were reported. These results indicate that IMC formation was more rapid in the Cu-SnBi couples versus the Ni-SnBi couples. The additional experiments and modeling suggested for Cu-Sn-Bi are also suggested for Ni-Sn-Bi.

Figure 4-22 Plot of mean IMC thickness versus isothermal hold time comparing Ni-(Sn80Bi) and Cu-(Sn80Bi) diffusion couples shows more rapid formation of Cu$_3$Sn compared to Ni$_3$Sn$_4$. 
4.11 Discussion of Mechanical Reliability of Sn-Bi TLPB

In lieu of mechanical testing of Cu-Sn-Bi and Ni-Sn-Bi TLP bonds, a brief description of the mechanical properties of constituent phases of a bond are described here. As discussed in previous chapters, acceptable mechanical performance of alternatives to Pb-free solders is one of the key issues regarding alternatives to high-Pb solders. Compliance of Sn-Pb solders is useful for large area bonds where significant stresses are present due to mismatch in the coefficient of thermal expansion between materials used in electronic devices and packaging. The elastic modulus of high-Pb solders is approximately 20 GPa whereas the moduli of IMC phases are generally much higher than that of high-Pb solders. The moduli of Cu$_3$Sn and Ni$_3$Sn$_4$ are 108 and 133 GPa, respectively. One advantage of a Bi-rich alloy, is the layer of rejected Bi solute that precipitates as a solid Bi phase has a modulus of approximately 30 GPa. This is even lower than the modulus of pure Sn (44 GPa).

A planar bond composed of layers of Cu$_3$Sn and Bi can be considered as a layered composite to estimate the overall bond modulus using the V. The phase volume fractions for Cu$_3$Sn and Bi expected for a Sn-Bi alloy of 80 wt. % Bi are approximately 0.41 Bi and 0.59 Cu$_3$Sn based on the calculations in Section 4.4.5. Applying a simple rules of mixtures model (Reuss and Voigt) to this composition results in modulus with a lower bound of 42 GPa and an upper bound 62 GPa. This composite effect is beneficial compared to schemes in which only IMC is present in the bond due to the relatively low modulus of Bi. Further analysis and experimental testing will be needed to investigate concerns regarding the brittle nature of Bi as opposed to other solder materials currently used.
5. CONCLUSIONS AND FUTURE WORK

This work has explored the challenges and opportunities of transient liquid phase bonding for electronics interconnects. The existing TLPB methods summarized in this work have demonstrated the possibility of forming dense, mechanically robust bonds using a variety of methods. Future applications demanding higher operating temperatures and the pursuit of more sustainable electronics manufacturing methods, specifically the elimination of high-Pb alloys in power electronics and other high temperature applications have renewed interest in TLPB. The challenging requirements for the commercial adoption of these methods were enumerated and translated into thermodynamic and kinetic requirements.

Rather than attempting to make incremental process improvements to existing TLPB formulations, an analytical approach to developing future formulations was undertaken. The thermodynamic characteristics of an effective TLPB formulation require the formation of desirable phases, particularly IMC phases. The Cu-Sn binary was used as an example of characteristics desired in TLPB. A framework for predicting the behavior of ternary and binary systems was presented and applied to a series of Sn alloys. Sn-based systems are desirable due to the well characterized IMC phases and the extent of thermodynamic data available. Effective processing temperatures and composition ranges were identified for several binary and ternary systems based on the framework presented.

Bi-rich, Sn-Bi with Cu or Ni were shown to be promising formulations for TLPB. Previous studies involving eutectic Sn-Bi with Cu, identified a persistent, liquid-forming reaction at approximately 200°C (D’Hondt and Corbin 2006). This is the result of a class II invariant reaction between Cu₆Sn₅ and the Bi phase to liquid. It was shown that increasing the Bi composition and processing above 200°C allows the direct formation of Cu₃Sn. The melting temperature of the resulting bond is then increased to that of the Bi phase which precipitates as a solid as Sn is consumed by the formation of IMC. Processing regime maps were introduced as a method of categorizing the conditions under which specific phase(s) form. Intermetallic growth measurements were performed using solid-liquid diffusion couples using Cu substrates with a Sn-Bi liquid (80wt. % Bi) in a tube furnace at 235°C and 260°C. Direct formation of Cu₃Sn was found to occur more rapidly than the formation of Cu₆Sn₅ in pure Cu-Sn couples where Cu₆Sn₅ and Cu₃Sn form as layers. However, the total IMC growth in literature was faster when both
phases form than the direct formation of Cu₃Sn. Despite slower rates, Bi-rich compositions will isothermally solidify more rapidly due to lower total amount of Sn in the low-melting temperature component that must form for isothermal solidification to complete. A surface plot indicating the projected Sn consumption time as a function of bondline thickness and composition based on the rate of Cu₃Sn formation with Sn80Bi (wt. %) was presented as a process map for 235°C and 260°C. This advantage was further demonstrated in pre-soldered Cu-Sn80Bi-Cu, planar assemblies a bondline of approximately 10 to 20µm. Samples were thermally processed using DSC to accurately control the time temperature profile. The resulting heat flow signals indicated complete conversion of the Sn-Bi to Cu₃Sn and solid Bi with an isothermal hold as short as 20 minutes at 210°C. A matrix of cross-sections was presented showing similar microstructural morphology across conditions. Penetration of Bi between the Cu and Cu₃Sn layers was observed when processed at 260°C and 300°C, but this Bi layer was not observed at 210°C. This suggests a method to avoid this layer if it proves to be detrimental to mechanical strength.

Ongoing development will be needed to create commercial solutions based on the thermodynamic and kinetic insights from this work. Most importantly, mechanical and thermal performance will need to be tested. Several design variables have been identified that may be used to optimize bonding outcomes. Increased bondline thickness can be achieved by using a particle-based TLPB formulation where the high-melting temperature component is included in a paste as particles. Planar configurations were utilized in this work to reduce the number of variables and focus on demonstrating the thermodynamic advantages of a Bi-rich composition in Sn-Bi. Controlled porosity may also be designed into bonds to accommodate stresses caused by thermal expansion coefficient mismatches between bonded components. However, the inclusion of flux and binding agents in paste formulations will require detailed control of thermal processing profiles to regulate the resulting density and pore size. This task is complicated by the variation in thermal mass of the components that will be bonded. After demonstrating control of these aspects of a paste-based formula, die shear testing at room temperature and elevated operating temperature ranges is suggested as next step. Ideal particle sizes and distributions must be identified. Accelerated thermal cycling of bonds is also suggesting as a means of estimating the reliability of these bonding materials. Due to the brittle nature of the IMC phases in these systems, proven mechanical reliability will be necessary to gain industry adoption of TLPB.
REFERENCES


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