ANALYSIS OF CONCENTRATION DEPENDENT INTERDIFFUSION COEFFICIENT DURING TLP BONDING OF COPPER WITH GERMANIUM POWDER

By

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ABSTRACT

Transient liquid phase (TLP) bonding has evolved to be an attractive technique for joining difficult-to-weld structural materials. In this study, copper (Cu) substrates are TLP bonded with germanium (Ge) powder to examine the effects of holding time and bonding temperature on the process kinetics. Deviation from parabolic behavior is observed when the width of the isothermal solidification (ISW) is plotted against $\sqrt{t}$, which is in contrast to what is generally expected. To explain this deviation, a newly developed analytical method is used to calculate the concentration-dependent interdiffusion coefficient, $D = F(C)$ at different holding times and bonding temperatures. In contrast to the common assumption that $D = F(C)$ is an isothermally constant material parameter, the results show that it changes with time, which is attributable to diffusion-induced stress/strain, and this can explain the observed deviation from parabolic behavior.

Furthermore, it is observed that for all time durations, the rate of isothermal solidification as well as the concentration-averaged diffusivity, $D_{ave}$, reduces as temperature increases from 960°C to 1040°C. This observation contradicts what is expected based on the classical Arrhenius relationship where diffusivity increases with temperature. The anomalous behavior observed in this work is attributable to the fact that diffusion coefficient largely increases with concentration and, the concentration range of Ge in Cu reduces with increases in temperature above the Cu-Ge eutectic temperature. In contrast, Arrhenius relationship does not consider the dependence of diffusivity on solute concentration at a given temperature and how the concentration range changes with temperature. Therefore, contrary to general expectations, this study shows that diffusivity can indeed decrease with an increase in temperature during TLP bonding and this can cause prolongation of the time required to complete the process. The experimentally observed reduction in the calculated diffusivity values with increases in temperature during TLP bonding is being reported for the first time in the present work.
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List of Abbreviations and Symbols

HAZ – Heat Affected Zone
TLP – Transient Liquid Phase
MPD – Melting Point Depressant
IS – Isothermal Solidification
ISW – Isothermal Solidification Width
$D$ – Diffusion coefficient
$D = F(C)$ – Concentration dependent diffusion coefficient
$D_{ave}$ – Concentration-averaged interdiffusion coefficient
$C$ – Concentration
$x$ – Distance
$\phi$ – Isothermal solidification rate constant
$K$ – Constant value
$Y$ – Isothermal solidification width
$C_{\alpha L}$ – Solute concentration (at equilibrium) in the solid phase
$C_{L \alpha}$ – Solute concentration (at equilibrium) in the liquid phase
$s$ – Interface position
$W_{max}$ – Maximum dissolution width
$W_0$ – Initial thickness of the filler alloy
$t_f$ – Time required to complete isothermal solidification
$R_D$ – Ratio of diffusion coefficient
$R_K$ – Ratio of constant value, $K$
OM – Optical Microscopy
SEM – Scanning Electron Microscope
EDS – Energy Dispersive Spectrometer
EDM – Electro-Discharge Machine
MATLAB – Matrix Laboratory
BM – Boltzmann-Matano
SF – Sauer-Freise
1 INTRODUCTION

1.1 Background Information

Joining is an important process used in various industries: oil and gas, automotive, aerospace and power generation amongst others. The process primarily involves assembling individual parts into a larger yet complex assembly. Individual parts meet at the joint and during service, applied forces are distributed between these parts [1]. Static and dynamic loadings induce stress in mechanical structures and reduce their load bearing capacity, which may lead to structural damage and/or deformation. This highlights the need for a viable method to repair or maintain such structures. This also addresses the need to efficiently assemble complex structures and repair damaged parts through joining, especially in engineering structures where complex components are constantly subjected to different environments. Therefore, optimum structural performance requires continuous maintenance and structural assemblies should be made with the highest standards and techniques [2].

Traditional joining techniques are grouped into three known categories: mechanical, chemical, and physical bonding [3]. Among these three types of joining techniques, the most used methods are fusion welding, non-fusion welding, and cold welding.

Fusion welding involves the melting and solidifying of materials to be joined via a localized heat application. Superalloys are typically joined through fusion welding techniques, but this is not recommended for nickel (Ni)-based superalloys due to the significant amount of aluminum (Al) and titanium (Ti). The heat affected zone (HAZ) of these materials is prone to cracking during welding and strain age cracking in post weld heat treatment [4] [5]. Also, the deformation of a component could be found in its HAZ when a concentrated heat source is used which produces thermal gradients. As such, fusion welded joints have poor mechanical
properties (e.g., fatigue resistance) as compared to the base alloys. Non-metals cannot be fusion welded to metals and the use of heat on surfaces with complex geometries is not feasible, hence rendering the process ineffective [6].

Non-fusion welds are formed at a joint through chemical bonding. The process is carried out by heating the component pieces to a semi-molten state, then applying pressure to induce plastic deformation to bond the component at the joint interface [7] [8]. Finally, cold welds are formed by the intermolecular bonding of metal pieces which have large plastic deformation. As a solid-state joining method, cold welding is done by applying a significant amount of pressure onto metal components at room temperature [8]. Fusion welding is mostly used in the power generation, aerospace, biomedical and automotive industries due to their use of advanced materials, like superalloys. Cold welding and non-fusion welding are used with ductile materials.

Aside from these three methods of joining, brazing is a suitable alternative process for joining materials which involves the use of a filler metal between two base materials, and melts at temperatures above 450 °C. The selected temperature is within the liquidus temperature of the filler metal and solidus temperature of the base material, i.e., the temperature is high enough to melt the filler metal but not the base material. The molten filler metal wets and spreads across the joint of the base material, then solidifies upon cooling to form a bond. Brazing is very different from welding, as the process comprises melting and recrystallizing when heat or pressure is applied, or even both. This process is widely used in joint designs with complex geometries like heat exchangers. Many brazing fillers have been investigated, such as alloys or pure metals, with the common ones being Ni, copper (Cu), cobalt (Co), Al and silver (Ag) to braze metals such as austenitic and Ni-coated stainless steels (SSs) for adequate joint strength.
However, the formation of deleterious eutectic microconstituents (also known as deleterious microconstituents or eutectics) during cooling, which are harmful to the mechanical properties of the joint, remains a major drawback to the use of brazing [9]. As such, Duvall et al. [4] developed a novel joining method called transient liquid phase (TLP) bonding, which involves the merits of brazing, including the formation of eutectic-free joints via the diffusion of interlayer solutes into the base metal. These advantages have made TLP bonding an attractive joining method in many industries as the process does not cause any damage to the structural integrity of the components [4].

TLP bonding involves inserting a filler alloy (also known as the interlayer material) between a pair of substrates to form a sandwich assembly that is heated to the desired bonding temperature for a given holding time. This process allows the liquified joint region to isothermally solidify. Prior to heating up the filler alloy to the chosen bonding temperature, where the eutectic reaction between the interlayer and base metals forms a liquid at equilibrium due to the base metal dissolution, the interlayer material is expected to melt rapidly due to the presence of melting point depressants (MPDs). Subsequently, isothermal solidification is initiated due to the continuous diffusion of MPD solutes from the liquified joint region to the solid base metal at the bonding temperature. This process continues until the liquid is completely consumed. The isothermal solidification stage however prolongs the entire bonding process because insufficient bonding time could result in poor mechanical and physical properties in the joint region due to the presence of deleterious microconstituents. However, the efficiency of this joining process is dependent on the processing parameters, such as the bonding temperature, holding time, interlayer and base metal thickness, diffusion coefficient of the MPD elements and chemical compositions of the interlayer material. Thus, ensuring that the parameters are appropriate and can reduce the time needed to complete the entire bonding process [10] and reduce labor costs [11].
1.2 Knowledge Gap

TLP bonding is a diffusion-controlled process that produces a strong joint. The effectiveness of a TLP bonding process largely depends on the complete isothermal solidification of the liquid formed in the joint during heating. Complete isothermal solidification eliminates the formation of deleterious microconstituents, which can be detrimental to the mechanical properties of the joint. The isothermal solidification process is controlled by the diffusion of solutes from the liquid in the joint into the substrate. The extent of isothermal solidification is significantly affected by two major parameters: holding time and bonding temperature. Numerous investigations have been carried out to study the effects of holding time and bonding temperature on achieving complete isothermal solidification during TLP bonding.

The kinetics of an isothermal solidification process is generally expected to follow a linear relationship, where the lateral displacement of the solid/liquid interface is proportional to the square-root of time as shown in [12]. However, a contradictory finding, where a linear relationship did not hold, has been reported in the literature [5] and [13]. Additionally, the bonding temperature plays a major role in determining the rate of isothermal solidification. An increase in temperature is generally expected to increase the rate of isothermal solidification and decrease the time required to complete isothermal solidification, $t_f$. This is because solute diffusivity is generally expected to increase with an increase in temperature. Nevertheless, it has been reportedly observed that the rate of isothermal solidification decreases with increase in bonding temperature [14]. Recent studies [11] and [15] have shown that to fully understand the effects of time and temperature during TLP bonding, it is important to also study how these two parameters affect the concentration-dependent interdiffusion coefficient, $D = F(C)$. To properly compute $D = F(C)$, a method that incorporates the solute concentration profile present in the material prior to the actual diffusion process needs to be
used. This is because during most sample preparation processes, solute does diffuse into the material prior to the actual diffusion process. Unfortunately, conventional analytical methods that are used to compute $D = F(C)$, such as the Boltzmann-Matano (BM), Sauer Freise (SF) and Wagner methods do not consider the initial solute concentration profile present in the material prior to diffusion, and this can significantly reduce the accuracy of these methods. Fortunately, a new analytical method that addresses the key shortcoming of the conventional methods by incorporating the initial solute concentration profile in the computation of $D = F(C)$ has been recently developed by Olaye and Ojo [16] and this new method will be used in the present work.

1.3 Research Objectives

The objectives of this study are outlined as follows:

- To perform TLP bonding experiments on a Cu|Ge|Cu binary system to study the dependency of isothermal solidification on holding time and bonding temperature,

- To use a newly developed analytical method that incorporates initial solute concentration profile [16] to calculate $D = F(C)$ during the TLP bonding process and use the results to analyse the observed dependence of isothermal solidification on both the holding time and bonding temperature.

1.4 Major Findings

The experimental findings from the TLP bonding of Cu|Ge|Cu samples show a deviation from parabolic behavior when the isothermal solidification width is plotted against $\sqrt{t}$. Numerous studies reported in the literature have suggested reasons for the deviation from parabolic behavior during TLP bonding but these are generally inadequate. Hence, to understand the deviation from the normally expected behavior, as observed in the present work, $D = F(C)$ is
evaluated between different holding times and bonding temperatures using a newly developed analytical method [16]. It is observed that $D = F(C)$ varies with time at a constant temperature, which is in contrast to the general assumption in the literature that it is isothermally constant. The isothermal time variation of the $D = F(C)$ is attributable to the influence of diffusion-induced stress during the bonding process, which would explain the deviation from parabolic behaviour.

Furthermore, the experimental findings show that the isothermal solidification rate constant, $\varnothing$ decreases when the temperature is increased from 960ºC to 1040ºC, contrary to what is commonly expected. This anomaly is supported by the observation that isothermal solidification process was completed after 45hrs at 960ºC while a holding time of 65hrs was insufficient to achieve complete isothermal solidification at 1040ºC. Calculation of concentration-averaged interdiffusion coefficient ($D_{ave}$) shows that the $D_{ave}$ decreases as the bonding temperature is increased from 960ºC to 1040ºC. This is in contrast to what is generally expected based on the Arrhenius relationship, where diffusivity is normally expected to increase with increase in temperature. The observed reduction in the $D_{ave}$ with increase in temperature is a key factor that causes the anomalous reduction in the $\varnothing$ with increase in temperature. The major reason why the variation of $D_{ave}$ differs from what is normally expected based on the classical Arrhenius equation is that the Arrhenius relationship does not consider the variation of diffusivity with solute concentration at a given temperature. In the present work, diffusivity largely increases with concentration at a constant temperature and the range of solute concentration in the solid reduces with increases in temperature, due to the decreases in the solubility of Ge in Cu with increases in temperature above the Cu-Ge eutectic temperature. These two factors concurrently are responsible for the anomalous reduction of $D_{ave}$ and $\varnothing$ with increases in temperature. This anomalous behavior in the trend of $D_{ave}$ with
temperature during TLP bonding is experimentally observed and reported for the first time in the present work.

1.5 Thesis Outline

This thesis is structured in the following order.

Chapter 1 provides introduction with background information, knowledge gap, objectives, and thesis outline.

Chapter 2 is a detailed literature review on brazing and TLP bonding techniques, the advantages and disadvantages of these techniques and their applicable applications. The chapter also provides a discussion on how different processing parameters such as bonding temperature, holding time, interlayer thickness, etc., affect the entire bonding process.

Chapter 3 contains details of the materials, equipment and experimental procedure used in this study. In addition, the steps and methods used to acquire and analyse the data are also discussed.

Chapter 4 is a discussion and analysis of the data obtained from energy dispersive spectrometer (EDS) line scans to examine the effects of holding time and bonding temperature on isothermal solidification kinetics. Further discussions are made to analyse the effects of holding time and bonding temperature on the variability of $D = F(C)$ by using different factors, such as diffusivity vs concentration (D vs C) plots, diffusion induced stress and $D_{ave}$ values. These are used to understand the anomalous behavior found during the TLP bonding process.

Chapter 5 provides a summary of the findings and conclusions. Recommendation for future work is also presented.
2 LITERATURE REVIEW

2.1 BRAZING

Archaeological discoveries have shown that brazing began as an art and not as a science many centuries ago, which make this method “one of the oldest technological discoveries of humankind with its origin traced back to the dawn of civilization” [17]. Earlier civilizations have documented to have understood brazing as an art of joining metals with pioneering applications in brazing gold and silver by using copper foils even before 3000 BC [18]. In the 20th century, brazing has evolved to extensive use in industries due to wide scale technological reinvention and practices that produced low temperature brazing alloys (silver brazing alloys). This advancement is made possible due to sophisticated experimental techniques like scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD), used in conjunction with numerical simulation to fully understand and optimize the scientific impact and metallurgical characteristics of materials used in brazing. However, brazing is still being continuously advanced [17] [19].

Brazing is a technique that joins similar or dissimilar metals and ceramics alike by using a molten filler metal, which flows into the joint. This procedure is carried out at temperatures above the melting point of the filler metal, typically > 450°C but lower than the melting point of the parts that are being joined i.e., the base metals. This technique is used when typical methods such as riveting, and welding are not promising. For example, in welding, high temperatures are used to melt and fuse the base metals together, which makes them susceptible to cracking and subsequently negatively affects reliability during service [20]. Brazing has undoubtedly become one of the most widely used methods in metal joining for industrial and commercial purposes due to its flexibility and the resultant joint with high integrity [19].
In short, a robust brazed joint is constructed by considering the following:

- The base and filler materials should have metallurgical compatibility, which is achieved when the molten filler metal wets the faying surfaces extensively, well enough for an optimal performance.
- The joint design should allow the even distribution of the molten filler metal through capillary action.
- The surface should be cleaned thoroughly by using a chemical or mechanical process to remove substances (e.g., grease, dirt, oxide films) that could inhibit the wetting and flow of the molten filler metal.
- Brazing can be carried out in a variety of atmospheres, including air, combusted fuel gas, ammonia, nitrogen, hydrogen, noble gases, inorganic vapors, and vacuum, with a variety of different heat sources such as furnaces, torches, and induction coils [20].

Brazing offers several advantages but also limitations, and brazing differs from welding due to its “non-fusion” process - the base metals to be joined are not melted, which makes this technique suitable for joining similar and dissimilar materials such as metals and ceramics. Other advantages of this technique include [20] [9] [21]:

- Cost effectiveness and processing of multiple batches,
- Distinctive material properties and retained characteristics,
- Remarkable stress distribution and heat transfer properties,
- Ability to join different materials e.g., metal to non-metals,
- Possibility of joining metals with varying thicknesses,
- Large and complex assemblies are easily fabricated, and
- Protection of metal coating and cladding is possible.
Some of the major limitations of brazing are [9] [22]:

- The formation of a joint with different phases that are deleterious to the properties of the joint,
- Joints that can barely withstand high service temperatures, and
- Frequent necessity of a flux to maintain and protect the brazing atmosphere.

2.1.1 Key Brazing Parameters

The formation of a robust brazed joint depends on the combination of filler and component materials as well as the processing conditions. It is therefore important to understand the metallurgical transformations that occur during the brazing process, some of which are discussed below. A key aspect of brazing is the extent and flow of the molten filler alloy into the joint which are influenced by several factors [19]:

- Joint dimensions,
- Surface condition of the components,
- Spreading properties of the filler alloy, and
- Alloying between the filler alloy and components.

2.1.2 Wetting and Contact Angle

Wetting is based on the classical model behavior of a liquid droplet on a solid with a flat surface (rigid and inert), where the liquid will spread accordingly over the surface of the solid until three surface tensions are balanced, i.e., between the liquid droplet and the solid substrate, between the liquid droplet and the atmosphere, and between the substrate and the atmosphere. These are shown in the wetting equation also known as the Young’s equation [19]:

\[ \gamma_{SL} = \gamma_{SV} - \gamma_{LV} \cos \theta \]
where, $\gamma_{SL}$, $\gamma_{LV}$ and $\gamma_{SV}$ are the surface tension between the solid and liquid, $\gamma_{LV}$ liquid and vapor, and $\gamma_{SV}$ solid and vapor, respectively, and $\theta$ is the contact angle of the liquid droplet and the solid surface. The equation shows that an imbalance in surface tension where $\theta < 90^\circ$ corresponds to $\gamma_{SV} > \gamma_{SL}$, facilitates the spreading of the liquid over the surface of the solid, and reduces the unwetted surface area [19].

The contact angle is a measure of the quality of wetting. Some wetting is said to occur when $90^\circ < \theta < 180^\circ$ but the liquid droplet will not spread on the contact surface. However, at $\theta < 90^\circ$, wetting and spreading of the liquid droplet are expected over an area defined by the contact angle, $\theta$. Rewriting the wetting equation in terms of $\cos\theta$, yields:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

Based on this equation, the spreading area is said to increase with a decreasing contact angle, i.e., wetting is increased when $\cos\theta$ increases (decreasing $\theta$). As $\theta$ approaches zero, $\cos\theta$ could also be maximized by:

- Increasing $\gamma_{SV}$ – cleaning the faying surfaces to remove contaminants.
- Decreasing $\gamma_{SL}$ – altering the material composition with temperature to control spreading.
- Decreasing $\gamma_{SL}$ – altering the atmospheric conditions; that is, reducing pressure at a constant temperature, typically through vacuum brazing.

Poor wetting of the faying surfaces results in the formation of low-quality joints which is not restricted to the surface condition of the base metals but also the filler metal composition. An example is with Al brazes; when used without an appropriate fluxing agent, foils or other preforms, poor wetting and spreading result over the faying surfaces. However, wetting can be
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Figure 2-1: “Surface tension forces acting when a liquid droplet wets a solid surface, using the classical model” [19]
significantly enhanced with additional elements added to the composition which would reduce the surface tension of the molten filler and destabilize the surface oxide layer. Also, to avoid changes in the bulk metallurgical characteristics, the concentration of the additional elements should be limited to 1% [19].

2.1.3 Substrate Material

For an optimum joint, the substrate/base materials should meet certain criteria as follows [19]:

- Can absorb and accommodate diffusing MPD solutes,
- The solidus temperature of the substrate should be considerably higher than the liquidus temperature of the filler alloy,
- At the bonding temperature, the substrate should have thermodynamic stability and high strength,
- A substrate with an initial concentration of MPD elements is likely to behave differently than a substrate without an initial concentration, and
- Secondary phases do not form around a joint with metal that is suitable for brazing [19].

2.1.4 Selection and Spreading of the Molten Filler Metal

Brazing filler metals are produced in various forms. These include wire, rings, and foil mechanically produced from ingots through a process that involves heating, rolling, passing back and forth through large rollers, hot rolling, coiling and then cold rolling. Foils can also be produced directly from a melt through, a process that involves forcing molten metal through a slot onto a fast spinning, water-cooled metal wheel. The result is a strip alloy with fine crystalline or amorphous microstructure, and improved strength and compatibility in comparison to similar alloys that are mechanically produced or produces through a casting process. For instance, silver-copper-titanium brazes are generally brittle in the ingot form but
highly ductile in the foil form due to the rapid solidification process. Brazes are also available as finely separated powders that can be mixed with a binder to form a paste used for screen printing substrates. Pastes and powders have a high surface area to braze volume ratio, which could result in high oxide fractions that inhibit the formation of a robust joint. However, this could be prevented with necessary precautions by using spherical granules with a smooth and clean surface [19].

The compatibility of a braze to a base metal is dependent on certain characteristics as follows:

- The braze liquidus temperature must be lower than the solidus temperature of the base material.
- The braze joint must be produced at a temperature that does not degrade properties of the base material. For example, the mechanical properties of many work-hardened and precipitation-hardened alloys are degraded at elevated temperatures that they cannot tolerate.
- The braze must provide good wetting to the faying surfaces for good adhesion with the formation of metallic bonds.
- The braze and base metal both should not have any constituents or impurities that might weaken or embrittle the braze joint.

A selection of brazes that contain Ni and chromium (Cr) have been developed to offer corrosion resistance to 316L SS in seawater and acidic environments. To do so, the Cr content is kept at 10-16% with a melting range of 1000-1100 ºC. The melting range is determined by the addition of other alloying elements like boron, molybdenum, and silicon. The target microstructure imparts corrosion resistance, which in this case is a Ni-Cr solid solution - formed as a result of extending the brazing cycle times to allow sufficient diffusion of elements into the base metals,
until their concentration is low at the joint to prevent growth of Cr borides and other deleterious phases at the braze joint [19].

While molten filler metals have unique spreading characteristics, many share a common aspect: on a perfectly clean, highly wettable substrate, spreading of the molten filler metal increases with increasing temperature. The spreading of the filler metal is greatly dependent on its elemental constituents and the composition of the substrate. Figure 2-2 shows the spreading characteristics of some of the Ag-based filler alloys on 316L SS, heated in a vacuum furnace for 5 min. The figure also shows the addition of palladium (Pd), which has a beneficial effect on wetting and spreading of the braze, despite widening of the melting range of the filler alloy. The varying behavior shown by Cu-based braze alloys is because 316L SS is sensitive to liquid metal embrittlement when brazed with Cu-based filler alloys [19].

2.1.5 Surface Preparation

Preparing the surface of a component before brazing is crucial to achieving high quality bonds. Oxide residue and other contaminants like grease/oil could inhibit the wetting and spreading of the molten filler metal. Oxides could also be trapped at the solid and liquid interface and act as a barrier of diffusion. An ideal brazing surface would include adequate surface roughness and wettability of the filler alloy, which should have low viscosity and spreadability to enhance the quality of the brazed joint [19].
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Figure 2-2: wettability index of silver-based brazes on 316L stainless steel [23]
Surface cleaning can be done either mechanically or chemically at different stages of assembly preparation. Mechanical cleaning involves brushing, blasting, or grinding to remove large areas of surface oxides and slightly roughen the faying surfaces. Chemical cleaning could involve spraying, immersing, and suspending the part in chemicals to remove oil/grease by using degreasing substances. Ultrasonic cleaning with alcohol is a common method used in chemical cleaning to completely remove foreign substances. Another method is fluoride cleaning, which is used to remove layers of oxide in narrow regions and thermal fatigue cracks by exposing the material to fluoride ions in a reducing atmosphere. However, adequate control and supervision are required to avoid excessive depletion while ensuring proper cleaning [9].

The roughness of the faying surfaces can have a significant effect on the wetting and spreading of the brazing alloy. There is an optimum requirement of surface roughness for each type of parent material to enhance wetting and spreading. An example is given by Okamoto et al. [24]; when brazing Al alloys with Al-12Si alloy in high vacuum environment without fluxes, optimal results in terms of the formation of the spreading filler have been obtained when the surface is grinded by using 400-600 grit size of silicon carbide papers. Brazing a rough machined surface inhibits the filler from spreading uniformly in all directions, which is detrimental to the integrity of the joint [19].

2.1.6 The Joint Gap

At the processing temperature, the joint gap influences the joint filling and mechanical properties of the resulting brazed joint: “the thinner a joint is, the greater its load bearing capability tends to be, until a limiting condition is reached when joint filling becomes unreliable” [19]. With increasing temperature, the contact angle, surface tension and viscosity are all reduced, which makes it possible for narrow joints to have good joint filling when the
temperature increases above the melting temperature of the filler metal. However, the spreading of the filler metal decreases with increasing temperature due to the interdiffusion between the filler metal and the base metals, thus leading to premature solidification even before the joint filling is completed. Accordingly, it is generally advisable to avoid exceeding the liquidus temperature of the braze by more than 50°C, especially where joints with less than 100μm width are required. In designing a joint gap, the escape route for vapor should be provided to prevent void formation through gas entrapments and concurrently, reducing agents (if any) should be able to gain access to the joint surface for effective results. The metallurgy of the components is also another aspect, where the base metal surface area has limited solubility in the molten filler – base metal surface dissolution can result in compound formation at the interface or alloying with the filler to change its composition and melting temperature [19].

**Dissolution of the filler alloy into the base metal:** In this stage, a larger amount of braze filler is required due to shrinkage as the reaction progresses. However, absorption of the filler is generally undesirable because its constituents will tend to penetrate the parent materials preferentially along the grain boundaries. This is detrimental to the mechanical properties of the joint, and sometimes causes liquid metal embrittlement (as shown in the case of Cu and 316L SS).

It is vital that enough filler alloy is supplied to fill the entire joint. Hydrostatic forces will promote the flow of low-viscosity filler metal out of the wide-gap joints. With insufficient filler alloy to fill the gap, voids will form and if too much filler alloy is used, the excess will spill out and form droplets on the surface of the component [19]. It is imperative to control the joint width during the bonding cycle because it influences the mechanical properties of the joint. That is, as the gap increases, the mechanical properties of the braze progressively decrease to
those of the bulk filler alloy. To maintain a precise joint width, spacers such as wires are used to limit the relative movement of the base metals in combination with compressive loading on the joint during the bonding cycle to overcome the hydrostatic forces that suspend the upper component [19].

2.1.7 Brazing Fluxes

Brazing fluxes are used to enhance the wetting of substrates by the molten filler metal. With properly cleaned faying surfaces, the flux should be effective enough to dissolve any leftover oxide layers/films after cleaning. Fluxes are also used to inhibit the volatility of high-vapor-pressure constituents found in the filler metal. They are usually applied as a coating to evenly protect the exposed surface of the assembly during brazing. Fluxes should be used on appropriate materials and at appropriate temperatures, which will also enable proper wetting between the faying surfaces, because of the viscosity and interfacial energy between the surfaces and the flux. Several chemical combinations have been used in fluxes, with the most common constituents being [9]:

- Water
- Wetting agents
- Fluoborates (sodium, potassium, etc.)
- Fluorides (sodium, potassium, etc.)
- Fused borax
- Elemental boron
- Alkalis (sodium hydroxide, potassium hydroxide)
- Borates (sodium, potassium, lithium, etc.)
- Chlorides
Some filler metals are considered self-fluxing because they contain deoxidizers like lithium and phosphorus as well as other elements with strong oxygen affinity. The filler metal oxidizes during brazing and are only self-fluxing when molten. The additional elements could eliminate the need for a protective atmosphere and prepared fluxes. However, a combination of self-fluxing fillers, protective atmosphere and/or prepared fluxes is ideal [9].

2.1.8 Brazing Atmosphere

Typically, gases like nitrogen, helium and argon are used to make the atmosphere inert by purging oxygen and other gaseous elements that could inhibit wetting and spreading of the molten filler metal by reacting with the faying surfaces [19]. A hydrogen atmosphere is often used to break down the oxide layers that form during bonding at high temperatures but is particularly less effective on metals that contain Al and Ti, like Ni-based superalloys. Metals such as zirconium (Zr), tantalum (Ta) and Ti are also prone to embrittlement in a hydrogen atmosphere. On the other hand, a nitrogen atmosphere is not suitable for metals and fillers that contain molybdenum, Zr and Ti, due to their susceptibility to nitriding. Brazing is done in a controlled gaseous atmosphere in a vacuum furnace or in partial vacuum conditions, which in turn facilitates post-bonding processes like cleaning and removing flux residues with ease. However, using a gaseous atmosphere has the major drawbacks of being costly due to the equipment and gas used, along with the rigorous maintenance and operating of the vacuum system [9]. The vacuum condition is frequently used as an inert and protective atmosphere for filler metal joining processes as opposed to a gaseous atmosphere because the vacuum condition allows for immediate measurement and control of the oxygen partial pressure. Another major advantage of a vacuum-based joining process is the enhancement of liquid spreading without the need to modify the contact angle. At constant temperatures, the pressure of the atmosphere is reduced, especially when excluding chemical fluxes is necessary.
However, there is a drawback of using this process which is that “it restricts access to the workpiece and the inadvisability of using fluxes or filler metals with volatile constituents, like cadmium that could vaporize and corrode the vacuum chamber or degrade its seals and contaminate pumping oils” [19].

2.1.9 Heating Methods

Heat must be transferred to the brazed joint effectively, to elevate the temperature of the filler metal beyond its melting point. The molten braze flows preferentially towards the region of higher temperature, hence, it is ideal for the faying surfaces and braze filler to reach the brazing temperature simultaneously. If the joint surfaces are maintained below the liquidus temperature of the braze, they will freeze and “ball-up” while in contact with the base metal. To prevent this, heating could be applied locally in the joint vicinity to heat the region to the desired temperature or diffuse heat which elevates the temperature of the entire assembly. Heating techniques commonly used for brazing based on these methods include [19] [9]:

- Torch brazing
- Furnace brazing
- Induction brazing
- Infrared brazing
- Dip brazing
- Resistance brazing
2.1.9.1 Torch Brazing

This is the oldest and most common method of heating joints by using a naked flame and gases like burning acetylene and propane in oxygen. These gases are inexpensive, widely available, easy to use and can be made oxidizing, reducing or neutral by adjusting the oxygen to gas ratio. Ideal for different production scales, a manual torch is used to heat the assembly joint in the presence of a flux to prevent oxidation at the braze joint. This heating method could be applied in three different ways: manually, where a skilled operator uses a handheld torch to supply heat; using a machine process that can be manual or automated, where the torch is automated and the assembly movement is controlled manually; and finally, automatically, which is a fully mechanized process with high production rates, where an operator only loads and unloads the assembly [19] [9].

2.1.9.2 Furnace Brazing

As the name suggests, furnace brazing uses a furnace as its heat source to heat components to the required brazing temperature. Heat is supplied either electrically or gas-fired and upon completing the heating cycle, the cooling of the joint is carried out in a separate chamber to create the braze. This method allows for production of large batches. Therefore, furnace brazing is the most economically viable and versatile of all the brazing methods. Brazed components are produced without aesthetic damage due to the protective atmosphere of the furnace, which could be a gaseous or vacuum environment [19] [9].
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Figure 2-3: Dual-tipped brazing torch (left), comparison of carburizing, neutral and oxidizing flames (right) [25]
2.1.9.3  Induction Brazing

Induction brazing uses induction heating to provide heat to braze assemblies via electromagnetic fields without flame or contact. The heating method is localized, repeatable and easily automated. The brazing process begins with heating the entire assembly to the required brazing temperature, in the presence of a flux to prevent oxidation at the joint and enhance wetting and spreading. Then, the filler metal is applied to the joint, which melts and flows through the entire joint through capillary action. This method is safe and prevents aesthetical damage to the assembly [26].

2.1.9.4  Dip Brazing

Dip brazing involves the immersion of a brazing assembly into a molten flux or metal bath maintained at an appropriate temperature. The surface of the molten metal bath is covered with flux. The molten filler flows into the joint via capillary action to fabricate robust, continuous, and leak-proof joints. Preheating the assembly is essential when brazing large components to avoid flux-freezing on cold or dry parts due to the risk of trapped humidity and the flux must be removed as quickly as possible after brazing. Dip brazing is highly effective for uniform and rapid heat applications through direct contact (used mostly for Al parts). Multiple joints in different assemblies could be bonded in a single dip, making the process cost and time efficient. The process is also commonly used in the electronics industry as an alternative to soldering [27] [9].
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https://ultraflexpower.com/induction-heating-applications/induction-brazing/#learn

Figure 2-4: Induction brazing of T-shaped copper tubes [26]
2.1.9.5 Infrared Brazing

Infrared brazing is a highly advantageous technique with low energy consumption and rapid thermal cycle. The technique is not dependent on vacuum conditions, it is inexpensive with operational ease and causes little or no deformation to the material properties. It is very similar to furnace brazing, with the main difference being the heat source for the brazing process. Heat is applied via different means (e.g., quartz lamps) that emit high levels of invisible infrared radiation, which could be concentrated on the part that is of concern by using reflectors. The brazing operation may be performed in a vacuum or inert gas environment and is usually completed in seconds due to very rapid heating [9].

2.1.9.6 Resistance Brazing

Resistance brazing is mostly used to join metals with high electrical conductivity to produce a relatively simple joint. In this brazing procedure, the assembly is arranged as part of an electric circuit, with the filler material inserted at the joint. The filler material could be in the paste form, a foil or even electroplated on the faying surfaces of the substrates. After a direct current is passed through the assembly, either the resistance of the base metals to electricity or a high-resistance electrode placed at the joint, generates the heat that melts the filler alloy. The use of self-fluxing filler materials (e.g., silicon-phosphorus alloys) is preferred in this brazing process as opposed to fluxes applied separately, because that can distort the close fit contact between the faying surfaces during the brazing process [9].

Other less common forms of brazing include [9]:

- Laser brazing,
- Exothermic brazing,
- Weld brazing, and
- Microwave brazing.
2.2 TRANSIENT LIQUID PHASE BONDING

Transient liquid phase (TLP) bonding is a highly graded technique that uses an interlayer material to join similar or dissimilar materials. The TLP bonding process has several other names and variants. In the sixteenth century, the process was termed *granulation* by ancient craftsmen who used Cu oxide paint as the interlayer to attach tiny gold balls to gold articles, like a vase [28]. Other terms that evolved are eutectic brazing, eutectic bonding, and diffusion brazing amongst others, but not until 1974 when a team of researchers associated with Pratt and Whitney (aerospace engine manufacturer) devised and copyrighted the term ‘transient liquid phase’ bonding, after a process patented by Duvall et al. [4]. The process is mostly referred to as diffusion brazing because it is a hybrid process that combines the flexibility of metallurgical simplicity and service temperature of diffusion bonding with the good joint filling and fillet formation of conventional brazing [19] [29] [28].

Like brazing, the TLP bonding process depends on filling the initial joint gap with a molten filler metal (interlayer), when heat is applied. During the heating stage, solid phases form because of the diffusion of the interlayer elements into the base/parent metals, which consequently results in isothermal solidification and elevates the melting temperature of the joint [19]; this distinguishes the TLP bonding process from brazing. Usually, the interlayer contains an MPD, which upon heating to the bonding temperature reacts quickly with the parent materials to form a liquid. When the temperature is kept constant at a level higher than the melting point of the interlayer, the MPD solutes will diffuse from the liquid phase into the base metals via solid state diffusion, which reduces the liquid phase and forms a solid phase until all the MPD solutes are removed. This results in the complete isothermal solidification of the joint when the solid/liquid interfaces meet, thus producing a homogeneous bond with properties comparable to those of the parent materials [30].
Over the years, TLP bonding has been used in many systems and structures, which include non-metals like alumina (Al$_2$O$_3$) [19] and metals like iron (Fe), Co, Ni, Ti, and Al based alloys [30]. The isothermal solidification process has made TLP a highly sought option in other applications such as joining metal matrix composites (MMCs) [29], semiconductors in microelectronics, single and poly crystals, as well as structural intermetallics [30]. TLP bonding is most beneficial in applications where robust joints are required but cannot be achieved through conventional joining methods, such as brazing and welding. An example is heat resistant alloys that are prone to hot cracking during welding or heat treatment after welding. This has made TLP a highly feasible method in joining metals for high temperature applications, especially in the manufacture and repair of turbine blades used in the aerospace and power generation industries [29]. Just like other joining/bonding methods, there are some merits and limitations with exploiting the TLP bonding process. However, note that some of these limitations could be prevented by optimizing the TLP bonding parameters, which will be addressed later in this chapter.

The merits of the TLP bonding process are as follows [19] [29] [30]:

- Due to homogeneity, the bond region has similar microstructural and mechanical properties as those of the parent materials.
- The joints of components produced from TLP bonding are serviceable at temperatures that are higher or equal to their bonding temperature.
- Unlike brazing, minimal surface preparation is needed and bonding can occur even in the presence of oxide films, and therefore TLP is not dependent on fluxes to prevent oxidation.
- TLP offers the possibility of uniform production on a large scale.
- TLP provides the means for uniform wetting and spreading of the molten filler even in joints that are not perfectly smooth or flat, which does not incur extra costs in post-bond processing.
- In comparison to brazing, there is minimal melting of the parent materials.
- Joints with a narrow width (<50 µm) and tolerance can be realized; such joints have exceptional mechanical properties and thermal conductivity.
- TLP prevents loss of strength and hardness due to over aging in susceptible materials especially at high temperatures.

The following are the limitations of the TLP bonding process [19] [29]:
- As a diffusion dependent process, a substantial amount of time is spent for preparation and completion usually in the order of hours or days, which has cost implications.
- Post-bond heat treatment is needed in age hardened alloys such as SS to enhance bond homogeneity.
- Precipitation of intermetallics at the joint interface during cooling that could inhibit solute diffusion and isothermal solidification and proliferate brittle phases that reduce the joint strength and ductility.

2.2.1 Process Setup

The TLP bonding process begins with an assemblage of the base materials in close contact to form a joint (at room temperature), after which an interlayer material that contains an MPD is placed in between the faying surfaces. The interlayer material can have different forms such as thin foil, fine powder or brazing paste and can be physical vapor deposited or even electroplated on the faying surfaces. The interlayer with a powdered form is sometimes placed outside the joint and allowed to flow into the joint through capillary action when molten. A certain amount
of pressure is needed to keep the assembly in place by preventing relative motion of the substrates and enhancing bonding by ensuring a close enough contact between the substrates and interlayer. The assembly is heated to form a liquid at the joint and held at a constant bonding temperature, which results in the isothermal solidification of the liquid due to solid state diffusion and the joint is homogenized at a given heat-treatment temperature. The assembly heating and bond homogenization processes are usually carried out in a chemically inert or gas-controlled atmosphere. The latter is the most likely option, and usually done in a vacuum furnace. The vacuum pressure of the furnace when heating the assembly is about 0.00015 μmHg, which is held constant until cooling is completed and the assembly is taken out for further processing [29] [30].

2.2.2 Kinetics of TLP Bonding

Several studies have described the kinetics of the TLP bonding process. According to the work of Duvall et al. [4], the TLP bonding process has three stages: dissolution, isothermal solidification, and homogenization. However, it was later reported that whilst heating the assembly, solid-state diffusion of MPD solutes can occur, which is dependent on the heating rate, diffusivity of the MPD elements and bonding temperature. Thus, a heating stage is included in the TLP bonding process due to solute loss during the heating process. This stage is also referred to as the melting stage where the interlayer melts and spreads across the faying surfaces. The four stages of TLP bonding as proposed by [31] and [32] are:

I. Heating/melting
II. Base metal dissolution
III. Isothermal solidification
IV. Homogenization
Figures 2-5 and 2-6 show these four stages and mechanisms of the TLP bonding process for a binary eutectic system where the solid and liquid phases at the interface are assumed to be in equilibrium. The initial thickness of the interlayer is represented by $W_0$ with an initial MPD concentration $C_F$. While A and B in Figure 2-6 represent the base metal and filler alloy respectively. The boundary conditions during the dissolution and isothermal solidification stages are given as:

$$\begin{cases} C = C_{l,α}, \quad x = s^+, \quad t > 0 \\ C = C_{α,L}, \quad x = s^-, \quad t > 0 \end{cases}$$

Where $C_{l,α}$ and $C_{α,L}$ are the liquidus and solidus concentrations at equilibrium respectively, which are adjacent to the interlayer while $s$ is the interface position and $t$ is the processing time [11].

### 2.2.2.1 Melting stage

The melting stage sets in when heat is applied to the assembly to a chosen bonding temperature, which is usually higher than the melting point of the interlayer to produce a completely molten matrix. However, the interlayer starts to melt when there is a eutectic reaction between the interlayer and the substrate materials. A completely molten interlayer is required for uniform wetting and spreading on the faying surfaces to produce a robust joint. At this stage, there could be diffusion of MPD solutes from the joint region to the base metals; this is dependent on factors such as the diffusivity of the MPD solutes, bonding temperature, and heating rate. A slow heating rate can cause significant amount of solute diffusion, which can then cause loss of the filler alloy after the process, especially in thin filler alloys with low solute concentration [33]. Therefore, using the proper heating rate and interlayer thickness are crucial for this stage.
Figure 2-5: Schematic of TLP bonding stages [11] [31]

Figure 2-6: Schematic of a binary eutectic phase diagram [11] [31]
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Figure 2-7: Cu-Ge binary phase diagram [34]
2.2.2.2 Dissolution and Widening Stage

Upon reaching the dissolution and widening stage, the assembly has been heated to a temperature above the eutectic temperature, completely melting the interlayer with continuous heating to attain the designated bonding temperature. On the other hand, interdiffusion of the molten interlayer and the substrate takes place, which changes the elemental concentration at the solid/liquid interface. Dissolution and widening of the liquid phase, which is inhomogeneous and supersaturated, continues at the joint and more MPD solutes diffuse into the substrate from the liquid interlayer. A melt-back is triggered to conserve mass because the liquid is not in equilibrium with the solid base. This continues until the liquid concentration reaches an equilibrium value of $C_{La}$ and the concentration of the solid adjacent to the liquid phase also equals $C_{al}$ [32]. As shown in the schematic illustration in Figure 2-8, the maximum dissolution width $W_{max}$ can also be attained at this stage. The extent to which dissolution occurs is dependent on the concentration of MPD solutes, initial interlayer thickness and solubility of the solutes in the substrate/base material [35].

2.2.2.3 Isothermal Solidification Stage

The third stage, i.e., isothermal solidification, begins when a constant bonding temperature is attained and the liquid zone reaches its maximum width, $W_{max}$ where MPD solutes from the molten interlayer diffuse into the solid base material at a rate controlled by the diffusivity of the MPD solutes, $D_s$. While diffusion occurs isothermally, the liquid region shrinks to conserve the mass of the fixed solid and liquid concentrations and the equilibrium solidus and liquidus concentrations stay fixed at $C_{al}$ and $C_{La}$ respectively (see Figure 2-9). Sufficient holding time is required for the completion of isothermal solidification until no liquid is found at the joint, then the bonding process could end, if required [28].
Figure 2-8: Schematic illustration of the dissolution and widening stage [11][29]
The kinetics of isothermal solidification is primarily controlled by solid-state diffusion and it is the most critical of all the stages because unlike preceding stages which occur rapidly and are completed in minutes, this stage is slower and mostly completed in hours or even days [28] [32]. Hence, a proper understanding of the process kinetics is necessary for this stage to be efficiently completed and to obtain optimal joint properties in the shortest possible time [10]. This can also help to eliminate high fabrication costs [11].

2.2.2.4 Homogenization

Homogenization is carried out to homogenize the bond at a pre-set time to smoothen the solute peak that was formed after isothermal solidification (see Figure 2-10) via solid state diffusion. This process is carried out by either extending the heating-time during bonding or applying a post-bond heat treatment at temperatures higher or below the bonding temperature. Lower temperatures are used for substrates with a temperature sensitive microstructure. The assembly is held at an elevated temperature until the solute peak reduces to an acceptable level through diffusion. Nevertheless, there is no standard for an acceptable solute peak level (as it varies with the material). The level should however be at a concentration where the harmful phases will not precipitate into the solid during cooling (i.e., at a lower concentration), because such precipitates have been found to degrade the mechanical properties of the joint. Adequate homogenization time yields a sufficiently high bond strength, with a joint microstructure that is comparable to that of the substrate material, with no concentration gradient. TLP bonding is said to be completed when the joint has a re-melting temperature higher than the initial melting temperature of the interlayer, but comparable to that of the substrate [29] [30].
Figure 2-9: Schematic illustration of the isothermal solidification stage [11] [29]
Figure 2-10: Schematic illustration of the homogenization stage [11] [29]
2.2.3 Selection of TLP Bonding Processing Parameters

The aim of utilizing the TLP bonding process is to produce high quality joints that are free from harmful materials in the shortest possible time and a cost-effective way. One of the key stages during TLP bonding is the completion of isothermal solidification, which takes the most time to produce the required microstructure and properties. To achieve this goal, key experimental parameters used in the TLP bonding process have been identified: the interlayer material, interlayer thickness, holding time and bonding temperature. These parameters undoubtedly have great influence on the resulting bond quality and must be duly optimized [10] [36].

2.2.3.1 Interlayer Material

The elemental composition of the interlayer material is crucial for determining the kinetics of the TLP bonding process and the quality of the produced joint. Cook et al. pointed out that the dissolution of a eutectic interlayer takes a shorter length of time as opposed to a pure metal interlayer [30]. The reason is that the eutectic interlayer melts upon reaching the eutectic temperature while pure metal melts linearly with time. One of the required properties of a suitable interlayer is its wettability and spreadability on the faying surfaces. Another is the addition of MPD solutes, which diffuse rapidly into the substrate material and most likely to form a solid solution phase [10] [30].

2.2.3.2 Interlayer Thickness

As pointed out in the previous section, achieving a robust bond requires a critical interlayer thickness. This parameter is also affected by other variables such as: “roughness of the faying surfaces, intermetallic formation, solid/liquid surface tension and applied clamping force” [30]. In the initial heating stage, the solutes begin to diffuse into the base metals because of the
melting interlayer. Depending on the diffusion and heating rate, if the interlayer thickness is not sufficient, the interlayer could shrink immensely or be completely consumed by solid-state diffusion before reaching the bonding temperature. In the case where it is too thick, more liquid is formed at the joint, thus prolonging the completion of isothermal solidification. Therefore, it is imperative that an appropriate interlayer is selected for a TLP bonding system [10] [30].

2.2.3.3 Holding Time

The holding time is an important parameter in TLP bonding and dependent on other factors (material system - diffusion coefficients, MPD solubility of a substrate, substrate microstructure) and parameters (bonding temperature and interlayer thickness). When a large volume of liquid forms at the joint during heating, sufficient holding time is required for complete isothermal solidification [30]. Upon cooling, the residual liquid at the joint forms brittle constituents also known as “eutectics”, which are detrimental to the mechanical properties of the joint. By and large, sufficient holding time in the TLP bonding process allows for complete consumption of the liquid and diffusion of the MPD solutes from the molten interlayer into the base materials.

2.2.3.4 Bonding Temperature

Determining the appropriate bonding temperature is crucial for optimal isothermal solidification conditions. As shown by the Arrhenius equation:

\[ D = D_0 \times \exp\left(\frac{-Q}{RT}\right) \]  \hspace{1cm} 2.2

The diffusion coefficient, \( D \) increases with increases in temperature, \( T \), which denotes that an increase in temperature will result in an increase in the rate of the isothermal solidification,
since it is governed by the diffusion rate of MPD solutes into the base materials. In the literature [37] and [38], reported an increase in isothermal solidification rate with increase in bonding temperature respectively while [39] and [40] reported the opposite, where the rate of isothermal solidification reduced with increase in bonding temperature, thereby increasing the time required for the completion of isothermal solidification, $t_f$.

2.2.4 Research Scope

TLP bonding has been widely recognized as an efficient and cost-effective method for repairing and joining components (particularly difficult to weld alloys) in many industries, such as: fan blades and nozzle guide vanes in aerospace structures [41], heat exchangers, heat shields and other gas turbine components [42]. To increase the use of TLP bonding in industrial applications, different models and techniques have been studied, especially to further understand and enhance the kinetics of the process. As indicated in the previous section, there are mixed findings in the literature on the influence of the holding time and bonding temperature on isothermal solidification behavior. Nevertheless, achieving complete isothermal solidification is crucial in TLP bonding to remove deleterious eutectic microconstituents that can have detrimental effects on the mechanical properties of the joint. Hence, this research has been structured to better understand the dependence of isothermal solidification behavior on holding time and bonding temperature by using a new analytical method to compute $D = F(C)$ during TLP bonding.
3 MATERIALS AND EXPERIMENTAL TECHNIQUES

3.1 Materials
Commercially pure copper is used as the substrate material in the present work and pure Ge powder is used as the filler material.

3.2 Sample Preparation
Pure Cu plates with dimensions 7mm x 12mm x 6mm were machined using electro-discharge machining (EDM), and a gap slot of 250 µm was produced in the middle of each test coupon. The test coupons were inserted in a hydrogen chloride-1-butanol solution (3M HCl) at a high temperature for 3 mins to clean and break up the oxide layers that formed on the coupons during EDM. The coupons were then ultrasonically bathed in an acetone solution for 15 mins to complete the cleaning process.

The sides and edges of the rectangular test coupons were coated with a Nicrobraz Stop-off to prevent spillage of the molten interlayer during bonding. The coating allows a reasonable amount of liquid in the joint with a planar geometry to be retained, which is crucial for the post-bond microstructural analysis. The design of the substrates was also modified to prevent relative movement of the substrates during bonding which could occur when the coupons are joined separately.

The interlayer material, pure Ge powder was applied in the joint by using a spatula, along with a series of vibrations made to ensure that the ~250µm gap width was filled with the alloy. Before inserting the filler alloy, the bottom and side openings of the substrate were tacked with ceramic-coated stainless-steel foils and Cu tape to retain the powder in the joint during the preparation process.
3.3 Experimental Setup

The test specimens were encapsulated in Vycor glass capsules that were evacuated to $10^{-6}$ torr (1.3 x $10^{-4}$ Pa) and subsequently back filled with argon. The encapsulated specimens were TLP bonded in a muffle furnace at 960ºC, 1010ºC and 1040ºC for holding times that ranged from 5 h to 65 h, respectively. The coated samples filled with Ge powder and wrapped with SS foils and Cu tape were mounted onto a metallic base, which will provide a flattened base support for the interlayer when it melts. This was carried out before enclosing the assembly in a Vycor glass tube to prevent material loss due to sublimation in the furnace.

3.4 Microscopic Evaluation

The bonded coupons were electro-discharge machined in the perpendicular direction. The sectioned samples were then mounted in bakelite by using a Buehler mounting press for ~6 mins. The mounted samples were grounded by using 600 to 1200 grit silicon-carbide (SiC) paper to even the surfaces; subsequent polishing was performed up to a 1 µm finishing by using a diamond suspension fluid. After a satisfactory polish, the samples were etched by swabbing with cotton using a ferric chloride ($\text{Fe}_3\text{Cl}_3$) solution (60 mL HCl+240 mL H$_2$O+ 20 g Fe$_3$Cl). The samples were then cleaned with water and dried in air before examined under an Inverted reflected light microscope (OM) fitted with a CLEMEX Vision 3.0 image analyzer to examine the joint microstructure for the presence of centerline eutectics and take images. Also, a JOEL 5900 scanning electron microscope fitted with an ultra-thin window Oxford EDS and connected to a calculator installed with INCA analysis software. The EDS was used to acquire the chemical composition data of the diffusing solutes and plot the concentration profiles [10] [43].
4 RESULTS AND DISCUSSION

4.1 Variation of Isothermal Solidification Width (ISW) with Time

Different methods have been used to determine the extent of isothermal solidification, with the most common method being a microstructural analysis [10] [14] [35].

The method used in this study, however, is similar to the approach that is previously used by researchers at the Massachusetts Institute of Technology (MIT) MacDonald and Eagar [44]. The method involves the following steps:

1. Acquisition of 5 experimental concentration profiles from the bonded pieces, starting from the region adjacent to the eutectic boundary into the substrate region.
2. An average concentration profile is computed from the 5 separate profiles.
3. The position of the Matano interface on the average concentration profile is computed using Equation 4.1
   \[ X_M = \frac{1}{(C_R - C_L)} \int_{C_L}^{C_R} X dC \]  
   where
   - \( X_M \) is the position of the Matano interface. The Matano interface is positioned such that the area of ‘A’ equals the area of ‘B’ [44] as shown in Figure 4-1.
   - \( C_R \) is the solidus concentration limits of Ge in Cu and \( C_L = 0 \), as shown in Figure 4-1.
4. Calculation of ISW using Equation 4.2
   \[ ISW = X_M - X_o \]  
   where
   - \( X_o \) is the position of the solidus concentration on the average concentration profile, as shown in Figure 4-1.
Figure 4-1: Average concentration profile of Cu-Ge diffusion couple (top) and the Matano and initial solid/liquid interfaces (bottom).
The extents of isothermal solidification after different holding times were computed and plotted against the $\sqrt{t}$ at the three temperatures used in this study. The results are presented in Figures 4-2, 4-3 and 4-4.

Isothermal solidification is a diffusion-controlled process and based on the analytical model for TLP bonding [31], plotting the ISW against $\sqrt{t}$ should show a linear relationship, also known as parabolic relationship. In contrast to what is commonly assumed, however, the results presented in Figures 4-2, 4-3 and 4-4 show that the parabolic relationship does not occur.

Various reasons have been given to explain for the deviation from parabolic behavior when the ISW is plotted against the square root of time, $\sqrt{t}$. A plethora of studies have experimentally observed and reported this phenomenon, however, adequate explanations as to its occurrence remain largely absent [45] [46] [47] [48]. The presence of two MPD elements with different solubilities and diffusivities, which are diffusing from the interlayer to the base metal has been suggested as the cause of deviation from linearity [49]. However, deviation was observed in the work of Ramirez and Liu [45], where a binary system with a single diffusing solute was used.

The formation of secondary phase precipitates in the base metal near the isothermal solidification zone (ISZ)/substrate boundary has been reported as a cause for the deviation of the isothermal solidification kinetics from the parabolic law [46]. Nevertheless, a study carried out by Tuah-Poku et al. [32] reported deviation from parabolic law, even though no secondary phase precipitates were formed during the isothermal solidification process.
Figure 4-2: Plot of isothermal solidification width against square root of time for samples bonded at 960°C
Figure 4-3: Plot of isothermal solidification width against square root of time for samples bonded at 1010°C
Figure 4-4: Plot of isothermal solidification width against square root of time for samples bonded at 1040°C
Grain growth has also been suggested in the literature as a reason for deviation from the parabolic law [47] [48]. Li et al. [48] indicated the formation of intermetallic composites (IMCs) in a solid/liquid interface instead of a solid solution phase affected the rate of the isothermal solidification process. At the initial stage of the solidification process, diffusion took place via grain boundaries but as the grains that contained IMCs become more coarse, volume-diffusion controlled the process, which led to deviation from parabolic behavior [10] [48]. According to [10] who used a single crystal and [50] who used a polycrystalline alloy, deviation from the parabolic law occurred and no grain growth could be observed in the findings of both studies, which contradicts the notion that grain growth is the main cause of deviation from the parabolic behavior [47] [48]. Therefore, none of the reasons/suggestions from the previous studies above can explain the cause of the deviation observed in the present work because the substrates are heat treated at a higher temperature to grow the grains before bonding and no IMCs formed or were detected during the microstructural analysis. Furthermore, only one solute was used, which prevents the formation of secondary phase precipitates.

Numerical studies, however, have shown that parabolic behavior can only be achieved when \( D = F(C) \) does not change with holding time [11]. In cases where \( D = F(C) \) changes with time, there will be a deviation from the parabolic relationship. To verify if this suggested concept is responsible for the deviation from parabolic relationship observed in the present work, it is necessary to compute the \( D = F(C) \) at various holding times.
4.2 Use of Concentration-Dependent Interdiffusion Coefficient to Explain the Variation of ISW with Time

\[ D = F(C) \] is calculated by using the newly developed analytical method by Olaye and Ojo [16], which is represented by Equation 4.3:

\[
D[C] = -\frac{1}{2t} \left( \frac{dx}{dC_i} + \frac{dx}{dC_f} \right) \left[ \left( \int_{C_R}^{C} (x_f - x_{Mf}) dC \right) - \left( \int_{C_R}^{C} (x_i - x_{Mi}) dC \right) \right]
\] 4.3

where

- \( x_{Mf} \) – is the Matano interface location at the final holding time,
- \( x_{Mi} \) – is the Matano interface location at the initial holding time,
- \( x_f \) – is the interface boundary location at the final holding time,
- \( x_i \) – is the interface boundary location at the initial holding time, and
- \( \frac{dx}{dC_i} \) and \( \frac{dx}{dC_f} \) – are the inverse gradients of the initial and final concentration profiles.

This method can be used to calculate the concentration-dependent interdiffusion coefficients in operation between two isothermal concentration profiles obtained at two different diffusion holding times. The approach involves several steps, which include:

1. Smoothing the experimental concentration profiles,
2. Averaging the concentration profiles into a single average profile for a given holding time and temperature,
3. Calculating the Matano interface position by using Equation 4.1,
4. Calculating \( D = F(C) \) with the newly developed method between two given holding times using Equation 4.3
5. Calculating \( D_{ave} \) using Equation 4.4
In this work, two approaches are used to determine if the calculated $D = F(C)$ changes with time, which include:

1. Plots of Diffusion Coefficient against Concentration ($D$ vs. $C$) with standard deviations at various time intervals,

2. Variation of concentration-average diffusivity, $D_{ave}$ with time.

The computed diffusion coefficients operative between different holding time intervals at the three temperatures used in the present work are plotted against concentration and are presented in Figures 4-5, 4-6 and 4-7. The D vs. C plots are presented for six (6) different holding time durations: (1) 5-25hrs, (2) 5-45hrs, (3) 5-65hrs, (4) 25-45hrs, (5) 25-65hrs, and (6) 45-65hrs. The results show that $D = F(C)$ changes with holding time at all bonding temperatures used in the TLP bonding of the Cu-Ge system, which differs from popular opinion in the literature that $D = F(C)$ is isothermally constant for a given system and does not change with holding time. It can be observed in the D vs. C plots that the error bars do not overlap in many regions, which is clearly an indication that $D = F(C)$ changes with time because the shape and position of the curves are different for different time intervals.
Figure 4-5: Plot of diffusion coefficient against concentration for different holding times at 960°C
Figure 4-6: Plots of diffusion coefficient against concentration for different holding times at 1010°C
Figure 4-7: Plots of diffusion coefficient against concentration for different holding times at 1040ºC
Furthermore, the computed concentration-averaged diffusivity, $D_{ave}$ values are listed and compared in Table 4-1. In the literature, 10–15% has been reported as an acceptable range when comparing diffusivity values determined by the B-M method [51]. Therefore, in this study, two calculated $D_{ave}$ values are considered different if the percentage difference between them is higher than 15%. The results presented in Table 4-1 show that the $D_{ave}$ values differ by more than 15% and up to 105%. This concurs with the results of D vs. C plots, that $D = F(C)$ indeed isothermally changes with time.

In the literature, it is generally assumed and expected that $D = F(C)$ does not change isothermally with time since it is considered to be an exclusively material constant. However, the mismatch in atomic size and intrinsic diffusivity between two different diffusing solute atoms combined with a concentration gradient generated during the interdiffusion of the solutes can induce stress/strain during diffusion [52] [53] [54]. Several studies have established this concept of diffusion induced stress/strain, which is comparable to how a thermal gradient generates thermally induced stress/strain. The magnitude of diffusion induced stress/strain has also been reported to change with time due to the generation and relaxation of stress/strain during the diffusion process. The equation for the resultant generation and relaxation of stress/strain during diffusion in a binary system is given as [54] [55] [56]:

$$\frac{dp}{dt} = -\left(\sum_{i=1}^{2} (V_i \nabla j_i) + \frac{3p}{4\eta} \right) \left( \frac{2E}{9(1-v)} \right)$$  \hspace{1cm} 4.5
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<th>5-45 (Hrs)</th>
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<th>45-65 (Hrs)</th>
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<th>5-25 vs 25-45</th>
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<th>5-25 vs 45-65</th>
<th>25-45 vs 45-65</th>
</tr>
</thead>
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<td>-</td>
<td>0.58</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>27</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>50</td>
<td>86</td>
<td>67</td>
<td>41</td>
<td>49</td>
</tr>
</tbody>
</table>

Table 4-1: Comparing $D_{ave}$ at different holding times using percentage difference
where

- $V$ – molar volume
- $J$ – atomic flux
- $E$ – Young’s modulus
- $p$ – diffusion induced stress/strain (without any external stress/strain)
- $\eta$ – shear viscosity
- $\nu$ – Poisson’s ratio

When the concentration profile changes, relaxation and generation of stress are influenced by the relative magnitude of the divergence of the atomic fluxes and the $\frac{3p}{4\eta}$ term. These conditions are shown in the following equations, when:

\[
\sum_{i=1}^{2} (V_i \nabla J_i) \gg \frac{3p}{4\eta} \text{ stress generation}
\]

\[
\sum_{i=1}^{2} (V_i \nabla J_i) \ll \frac{3p}{4\eta} \text{ stress relaxation}
\]

With the relaxed-stress condition, an analytical solution for time-dependent stress during diffusion is shown below [55]:

\[
p(t) = p_0 \exp \left( -\frac{Et}{6(1-\nu)\eta} \right) \quad \text{4.6}
\]

Thus, the resultant stress changes with holding time during diffusion. There is a general agreement that diffusivity can be influenced by the presence of stress/strain in a crystal lattice. According to Beke et al. [52], the intrinsic diffusion coefficient has been reported to change exponentially with the generated stress in a system during diffusion. An equation that shows the dependence of the intrinsic diffusion coefficient on stress is:

\[
D_i(p(t), T) = D_{i0} \exp \left( -\frac{p(t)V_i}{RT} \right) \quad \text{4.7}
\]
Equation 4.7 shows that intrinsic diffusivity can be expected to change with time since diffusion induced stress changes with time. There are reports in the literature where the concept of diffusion induced stress/strain has been experimentally confirmed [52] [56] [57] [51], including an observation that \( D = F(C) \) changed with time during the diffusion process [57]. Belova and Murch [58] in their theoretical work on non-equilibrium concentration of vacancies during interdiffusion, also indicate that it is possible for \( D = F(C) \) to isothermally change with time during a diffusion process.

Thus, the varying \( D = F(C) \) with time observed in the present work could be attributed to diffusion induced stress/strain due to the generation and relaxation of stress/strain during diffusion [55]. Accordingly, the time variation of \( D = F(C) \) can explain the deviation from parabolic behavior that is observed in the present work during the TLP bonding of Cu with Ge.

### 4.3 Effect of Temperature on Isothermal Solidification Rate

TLP bonding temperature is an important parameter to achieving complete isothermal solidification needed to eliminate residual liquid that forms deleterious microconstituents that are harmful to the mechanical properties of the joint [35]. During TLP bonding, the temperature is a key factor that controls the kinetics of the isothermal solidification process. Generally, the rate of isothermal solidification increases with increase in temperature. Plots of the ISW against bonding temperature for different holding times are shown in Figures 4-8, 4-9 and 4-10.
Figure 4-8: Plot of isothermal solidification width against temperature for samples bonded for 5hrs
Figure 4-9: Plot of isothermal solidification width against temperature for samples bonded for 25hrs.
Figure 4-10: Plot of isothermal solidification width against temperature for samples bonded for 45hrs
The plots show that as the bonding temperature increases from 960ºC to 1040ºC, the extent of isothermal solidification produced within any given time duration reduces and this is observed for all the time durations used. These results indicate that the rate of isothermal solidification generally reduces with increases in temperature, which is the opposite of what is normally expected.

To further verify this anomaly, it was observed that isothermal solidification was completed after 65hrs at 960ºC. However, after 65hrs at 1040ºC, residual liquid was still found in the joint, which is labelled ‘A’ in Figure 4-12.

**Region A** is made up of microconstituents formed as a result of incomplete isothermal solidification of the molten liquid phase, that is, when adequate time is not given for the solutes to diffuse completely into the substrate. This then results in the formation of deleterious microconstituents during cooling from the bonding temperature [10]. **Region B** is the isothermally solidified zone, which consists of a Cu-rich solid solution phase. This region is formed due to compositional changes in the liquid phase induced by the diffusion of solutes from the interlayer into the base metal while the bond assembly is held at a constant bonding temperature [10]. **Region C** is the Cu base metal, also known as the substrate. The solutes diffusing from the liquid interlayer are consumed by the solid matrix of the substrate, which drives isothermal solidification. Hence, the completion of the TLP bonding process is very much dependent on the interaction between the Cu base metal and the diffusing Ge solutes [10].
Figure 4-11: Optical Microscopy image of joint microstructure showing complete isothermal solidification after bonding at 960ºC for 65hrs
Figure 4-12: Optical Microscopy image of joint microstructure showing the eutectic region after bonding at 1040°C for 65hrs.
The experimental data derived from the Cu-Ge binary system show that $\phi$ decreases with increasing bonding temperatures, which is an anomalous behavior. To understand this anomalous behavior, there is a need to understand how $D = F(C)$ changes with temperature because $\phi$ is greatly influenced by the nature of $D = F(C)$.

Since TLP bonding is diffusion-controlled, it is generally expected that diffusivity, $D$ will increase with increases in temperature in accordance with the Arrhenius equation (Equation 2.2). Hence, it is commonly assumed that the isothermal solidification rate constant, $\phi$ will always increase with increases in temperature due to increases in diffusivity. The $D$ vs. $C$ plots at a given holding time for the three different temperatures: 960°C, 1010°C and 1040°C are presented in Figures 4-13, 4-14 and 4-15. The results show that the diffusivity generally reduces with increases in the bonding temperature, which is in contrast to what is generally predicted based on Arrhenius Equation. It should be noted that the expectation based on the Arrhenius Equation that, diffusivity exponentially increases with temperature does not incorporate the dependency of diffusion coefficient on concentration and how the concentration range in a material, changes with temperature. In the case of the present work, however, the following key factors are crucially relevant to the variation of diffusivity with temperature in the Cu-Ge system:

1. Diffusivity that is strongly dependent on concentration i.e., $D = F(C)$
2. Diffusivity, $D$ which largely increases with concentration,
3. Solubility/concentration range decreases with increases in temperature.

According to Equation 4.4 [15] used to compute $D_{ave}$, synergic effects of the above listed factors can cause the $D_{ave}$ to reduce with an increase in temperature as experimentally observed in the present work.
Furthermore, aside for $D_{ave}$, which is computed over a range of composition, a recent numerical study of diffusion induced stress/strain and its effects has showed a unique feature that can be produced by diffusion induced stress/strain when temperature is increased [59]. The study shows that, for a certain same range of concentration and within a given time duration, it is possible for diffusion induced stress/strain to cause the diffusion coefficient to reduce with an increase in temperature in violation of what is expected based on the Arrhenius relationship. It should be emphasized that this unique feature occurs for same range of solute concentration in contrast to what is discussed above for $D_{ave}$. A careful study of the D vs. C plots obtained in the present work, shows the occurrence of this unique feature, which is presented in Figure 4-15. It is observed that for the time duration of 25-45hrs and specifically for concentration range of $\sim$1.4 to $\sim$3.2 At %Ge, the diffusion coefficient reduced with an increase in temperature from 960ºC to 1040ºC. This unique feature confirms that diffusion induced stress/strain does occur during TLP bonding of Cu with Ge, which corroborates the finding and explanation provided for the observed deviation from parabolic behavior between ISW and holding time. Regarding the anomalous effect of temperature, four key factors are responsible for the reduction of isothermal solidification rate with temperature – (i) strong dependency of diffusivity on concentration, (ii) largely increase of diffusion coefficient with concentration, (iii) reduction of Ge solubility in Cu with increase in temperature, and (iv) diffusion-induced stress.

**It should be stated that experimentally observed reduction in diffusivity with increase in temperature during TLP bonding is reported for the first time in the present work.**
Figure 4-13: Plot of diffusion coefficient against concentration for 5-25hrs at 960°C, 1010°C and 1040°C.
Figure 4-14: Plot of diffusion coefficient against concentration for 5-45hrs at 960°C, 1010°C and 1040°C
Figure 4-15: Plot of diffusion coefficient against concentration for 25-45hrs at 960°C, 1010°C and 1040°C
5 SUMMARY, CONCLUSIONS AND RECOMMENDATION FOR FUTURE WORK

5.1 SUMMARY AND CONCLUSIONS

1. The experimental findings from the TLP bonding of Cu|Ge|Cu samples show a deviation from parabolic behavior when the isothermal solidification width is plotted against $\sqrt{t}$.

2. Concentration-dependent interdiffusion coefficient, $D = F(C)$ and concentration-averaged diffusivity, $D_{ave}$ values were calculated at different holding times and bonding temperatures using a newly developed analytical method that incorporates initial solute concentration profile.

3. This study shows that the deviation from parabolic behavior in the Cu-Ge system is due to the variation of $D = F(C)$ with holding time.

4. The variability of $D = F(C)$ with holding time could be attributed to diffusion induced stress/strain due to the generation and relaxation of stress/strain during diffusion.

5. The isothermal solidification rate constant, $\phi$ decreased as temperature increased from 960ºC to 1040ºC, which is an anomalous behaviour. This anomalous behaviour is supported by the observation that isothermal solidification was completed after 45 hrs of bonding at 960ºC, whereas even after 65hrs of bonding at 1040ºC, isothermal solidification was not completed.

6. Concentration-averaged diffusivity, $D_{ave}$ reduced with increases in temperature. This is in contrast to what is generally expected based on the Arrhenius relationship where diffusivity is expected to increase with increase in temperature. The variation from the expectation based on Arrhenius relationship is because Arrhenius relationship does not consider the dependence of diffusivity on solute concentration at a given temperature.

7. Increase in temperature can cause anomalous reduction in diffusivity due to the combination of the following factors:
a. Strong dependency of diffusivity on concentration,

b. Diffusivity largely increases with concentration at all temperatures.

c. The solubility of Ge in Cu also decreases with increases in temperature above the Cu-Ge eutectic temperature.

8. In addition, another type of anomalous reduction of diffusivity with increase in temperature, which is attributable to diffusion-induced stress/strain is observed in the present work. In this second type, aside of $D_{ave}$, which is the average diffusivity computed over the entire range of solute concentration, diffusivity at a specific concentration within a certain concentration range, reduces with increase in temperature.

9. Hence, contrary to general expectations, this study shows that diffusivity can decrease with increase in temperature during TLP bonding and this can explain the reduction in the rate of isothermal solidification and prolongation of isothermal solidification completion time, as observed in the present work. This experimentally observed behavior during TLP bonding is being reported for the first time in the present work.

5.2 RECOMMENDATION FOR FUTURE WORK

The effects of temperature and time on $D = F(C)$ during TLP bonding of other binary systems should be studied by using the new analytical method that is used in the present work.
REFERENCES


