Estimation of Interface Temperature in Ultrasonic Joining of Aluminum and Copper Through Diffusivity Measurements

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Abstract

Ultrasonic metal welding (USW) is a rapid joining process that is widely used in automotive, electronics, semiconductor and other manufacturing industries. Despite the wide industrial acceptance, however, there is still a lack of complete understanding of the fundamental mechanisms of ultrasonic joining. This research addresses the effects of high strain rate plastic deformation on the diffusion in the materials subjected to ultrasonic joining and presents a new method for the estimation of the true joining temperature (the interface temperature) that is reached during ultrasonic joining at low to moderate nominal welding temperatures.

Specifically, sheet of commercial grade aluminum (Al 1100) and electrolytically deposited copper foil were ultrasonically joined at nominal temperatures ranging from room temperature to 413 K (140 °C). Significant diffusion of copper into the Al 1100 sheet was detected by energy-dispersive X-ray spectroscopy (EDS). Micro Knoop hardness measurements in the vicinity of the weld interface of both as-joined and heat treated specimens also revealed hardness changes characteristic of precipitation hardening which would not have occurred if there were no copper diffusion into aluminum.

Least-square fitting of the EDS data to a complementary error function yielded very high diffusivity ($D$) values of $1.54 \times 10^{-13}$ to $2.22 \times 10^{-13}$ m$^2$/s that are many orders of magnitude above the normal values at the nominal joining temperatures. This reflects the very high concentration of excess vacancies in the deforming aluminum. The experimental $D$ values, however, are still well below typical values of liquid diffusivity at/near the melting point by a factor of $10^4$. An analysis based on the mono-vacancy diffusion mechanism estimates the interface temperature to be about 390 - 410 K below the equilibrium melting point of aluminum. Thermodynamic calculations of the phase
stability for solid aluminum containing a large amount of excess vacancies also ruled out liquid formation at the predicted interface temperatures. Thus, solid-state joining has been confirmed for the ultrasonic joining of aluminum and copper at nominal joining temperatures up to 413 K (140 °C).
Publication by the Author

The author’s MS study in the Advanced Materials Processing Laboratory at Northeastern University produced the following publication.

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1. Introduction

1.1 Introduction of research project

Ultrasonic welding is a fabrication technology in which primarily metallic components are metallurgically bonded at room or moderately elevated temperatures which, in this study, ranged from 298 K to 413 K (25 °C - 140 °C). Ultrasonic welding emerged in response to the need to avoid complications arising from the melting in fusion welding, such as oxidation, thermal stresses and unwanted phase transformation. Having the ability to rapidly join materials without deleterious effects on material properties, ultrasonic joining potentially provides new ways of additive manufacturing with a wide range of structural, functional and reactive materials.

Although ultrasonic welding has been widely adapted in various areas of manufacturing, the fundamental mechanism(s) involved in the metallurgical bond formation are still not well understood. Possible mechanisms proposed so far include solid state bonding [5.5, 2.5, 5.7 - 5.13], local melting [5.8, 2.6] and mechanical interlocking [2.5, 5.10]. More recently, roles of excess vacancies in ultrasonic welding have been speculated [1.15, 2.14]. High strain rate deformation of a metal, as in ultrasonic welding, introduces large amounts of excess vacancies in the metal by the nonconservative motion of jogs on screw dislocations [1.1-1.3] and/or possibly by other mechanisms [1.4-1.7]. During the ultrasonic joining process, the interface temperature, $T_{int}$, between the materials being joined is very likely to rise above the nominal joining temperature, $T_{nom}$, due to frictional and adiabatic-deformation heating which must also enhance diffusivity. In order to investigate the joining mechanisms in ultrasonic joining,
it is imperative to know the actual value of $T_{int}$. Direct measurements with thermocouples [1.8-1.10] or infrared pyrometry, [1.11] however, have been difficult due to the transitional nature of the local heating over short process durations. Another recent research work with aluminum-zinc pairs [1.12] strongly indicated that deformation enhanced diffusion and structural changes might play important roles in high strain-rate metal joining. In this research, we investigated the effects of high strain-rate deformation on diffusion. We also developed a new method for the estimation of interface temperature in ultrasonic joining from diffusion data obtained on ultrasonically joined aluminum sheet and copper foil.

1.2 Previous study

Faryar Tavakoli-Dastjerdi, a former student in the Advanced Materials Processing Laboratory at Northeastern University, studied the effects of high strain-rate deformation on the diffusion of Cu into Al [1.13]. In his experiments, 1 mm thick 99.8% pure Al sheet, with and without 10 µm thick 99.8% pure Cu foil, kept at nominal temperatures 413K – 513 K (140 °C - 240 °C) under normal compression, was subjected to in-plane ultrasonic vibration. If the ultrasonic deformation enhanced the Cu diffusivity in the underlying Al sheet, it would cause precipitation hardening in the diffusion zone, increasing the subsurface hardness of the Al sheet specimen. Figure 1.1 shows the Knoop hardness determined at 3 µm from the surface of Al sheet for specimens subjected to 1 s of ultrasonic vibration under 120 MPa normal pressures with and without Cu foil on the Al surface, as a function of nominal processing temperature.
It is seen that the hardness of the specimens processed with Cu foil reached the maximized value of 268 HK at 433 K (160 °C) and then decreased at higher temperature, while the hardness of the specimens processed without Cu foil decreased monotonically with increasing temperature. The difference can be explained in terms of (1) solid solution hardening and (2) in-situ precipitation hardening, both of which may occur only if Cu diffuses into the Al sheet.

The diffusion of Cu into the Al was indeed confirmed by energy-dispersive X-ray spectroscopy (EDS), as seen in Figure 1.2 which shows the EDS profile of Cu concentration in the sub-surface region of an Al specimen processed with Cu foil at 523 K (250 °C) for 2 s.
Figure 1.2: EDS profile of copper diffusion in aluminum at 523 K in 2 s.

Tavakoli-Dastjerdi fitted the EDS data into an exponential function, which yielded a surface concentration value of 15.3 wt.%. The effective diffusion depth, \( x \), of Cu was then calculated as the distance from the surface at which Cu concentration is half the surface concentration. This procedure gave \( x = 0.73 \mu m \). The diffusivity of Cu in the aluminum subjected to ultrasonic deformation was then calculated with

\[
D = \frac{x^2}{t}
\]  

(1.1)

which at \( t = 2 \) s gives \( D = 0.26 \mu m^2/s \), a value four orders of magnitude higher than the normal diffusivity of copper in aluminum at 523 K (250 °C).
Such a high diffusivity may arise from a high vacancy concentration caused by high strain-rate ultrasonic deformation [1.14] as well as from high densities of other lattice defects, e.g., dislocations, that provide high diffusivity paths. A recent NMR study by Murty et. al. [1.14] in fact revealed vacancy mole fractions up to 0.1 in aluminum deforming under tension at a moderate strain rate of 0.55 s$^{-1}$ below about 310 K (37 °C).

In the presence of vacancies and dislocations in large amounts, substitutional diffusivity would increase by many orders of magnitude above thermal equilibrium values, causing diffusive penetration of Cu into Al, and probably in-situ precipitation of strengthening phases, such as $\theta'$ and G-P zones as well.

The present work was performed to further investigate the findings from the previous study through more systematic experiments and thorough characterization, with special interest in developing a method to estimate the actual temperature at the joining interface of Al sheet and Cu foil from diffusion data.

1.3 Objective

This research was conducted to further verify the enhanced diffusion in ultrasonic joining and also to develop a new method for the estimation of the interface temperature from the enhanced diffusion data taken from ultrasonically joined materials. The specific work performed in this research are:

- Controlled ultrasonic joining experiments of aluminum sheet with copper foil under systematically varied conditions
• Microhardness measurement of the aluminum sheet of joined specimens near the interface with the copper foil

• Determination of the extent of copper diffusion into the aluminum sheet by energy-dispersive X-ray fluorescence spectroscopy (EDS)

• Mathematical processing of the diffusion data to determine the enhanced diffusivity of copper in aluminum and estimation of the true joining temperature at the interface from the diffusion data

• Post-joining heat treatment of Al sheet - Cu foil specimens and microhardness measurement to further verify the prior copper diffusion into the aluminum sheet during ultrasonic joining
2. Literature Survey

2.1 Fundamentals of ultrasonic metal welding

Ultrasonic welding (USW) can rapidly join metals with metallurgical bonding at near room temperatures. Being a low-temperature joining process, USW is applicable to the joining of a wide range of materials without causing deleterious effects of high-temperature exposure, including oxidation, microstructural coarsening, residual stress and unwanted hardening. The bonding in ultrasonic metal welding occurs as the rapid, plastic deformation disrupts surface oxide films and contaminants, exposing clean metal surfaces that come together within atomic distances to metallurgically bond before new oxide films can form [2.1]. This makes USW a competitive means of joining, especially in the electronics and automotive industries.

In 1956, Jones et al. performed many experiments to ultrasonically weld metal foils and reported that USW was a solid state joining process in which the contacting force would cyclically displace the mating surfaces very rapidly to produce dynamic internal stress distributions sufficient to cause internal plastic flow at the weld interface [2.2]. In 1961, Jones et al. performed additional investigations of the process parameters involved in ultrasonic welding and determined the weldability of aluminum, copper, nickel and stainless steel [2.3]. Static loading of photoelastic slabs was used to investigate the resultant stress fields at the contact surface and within the materials. Evaluation of micrographs of the interface of welded 100-H14 aluminum sheets showed plastic flow, large displacement of the parent material in the weld zone and mixing of surface films with the displaced parent metal. No cast structures offering evidence of local melting
were detected by optical microscopy, and the welds were characterized as solid-state bonds.

In 1960, Weare et al. performed USW experiments that showed that the weld strength between aluminum foils was not affected by removing oxide film prior to welding [2.4]. In the latter work, aluminum foils were degreased using trichloroethylene followed by removal of heavy oxide film using both a NaOH solution and HNO₃ solution. Metallographic examination of the welds revealed no gross amounts of oxides in either the cleaned or non-cleaned aluminum foil welds.

In 1971, Joshi performed experiments to investigate the ultrasonic bonding mechanisms for soft, face-centered cubic (FCC) metals and reported that bond formation is due to a softening phenomenon followed by mechanical interlocking in dissimilar metals and atomic attraction for similar metals [2.5]. No localized melting was observed and the dissimilar bonds analyzed were found to be practically diffusionless and no intermetallic compounds were detected. Joshi also proposed that the ultrasonic softening involves plastic deformation accompanied by the creation of nonequilibrium concentrations of vacancies possibly through the nonconservative motion of jogs on dislocations.

In 1977, Kreye performed experiments to study the microstructure of ultrasonic welds using TEM and reportedly found evidence of melting phenomena [2.6]. Ultrasonic spot welds of 400 µm thick aluminum sheets resulted in a bond zone that was less than 1 µm thick. Within this bond zone, Kreye reportedly observed new grains with size between 0.05 to 0.2 µm. The new grains were considered to form by rapid cooling of the
melt that could be as small as a few hundred angstroms, and recrystallized grains formed after short time heating had a size of 3 µm [2.7]. Therefore, Kreye concluded that the formation of 0.05 to 0.2 µm grains at the interface are indicative of local melting followed by rapid re-solidification. Kreye speculated that the frictional heat generated at the interface during welding was sufficient to raise the temperature within the bond zone above the melting temperature. This conclusion was contrary to measured temperatures via thin thermocouples, but Kreye argued that the thermocouple only gave an average value over the bonding area.

In 1999, Gao developed a 2-D, quasi-static/dynamic, elasto-plastic mechanical analysis of the stress/strain field within ultrasonically joined aluminum foils using finite element analysis. The model described frictional boundary conditions at the foil/substrate interface which were identified experimentally via strain experiments [2.8]. The strain-time history at the loading edges of the weld areas was measured using strain gages mounted adjacent to the welding tip. Results showed that upon application of the ultrasonic vibration, the strain increased until it reached a maximum where the strain is kept constant until ultrasonic vibration was terminated. In 2001, Yadav expanded Gao’s mechanical model by addressing the thermomechanical process aspects, including the heat generation and transient-temperature profiles during welding [2.9]. Both thermocouple and infrared pyrometric temperature data were used to calibrate the models on tribological parameters [1.10]. Yadav’s model predicts that the initial increase in temperature during ultrasonic welding causes the coefficient of friction between the weld materials to decrease to a critical level, resulting in a constant strain at which point the temperature remains constant.
In 2004, DeVries performed ultrasonic metal welding experiments of aluminum alloys. Figure 2.1 shows the cross section of a typical weld interface from his work. The interface layer is approximately 50 µm and consists of very fine grain structure. Overall, the bonding within the interface layer is that of metallic bonding from nascent contact caused by the high strain rate plastic deformation. After 0.1 s, discrete regions of welded material (microweld or deformation islands) are separated by the unbounded surface, which disappear with welding times of 0.3 s to form a continuous interface layer as shown in Figure 2.1. There is a 10 - 15% reduction in thickness of the material during the ultrasonic welding.

Figure 2.1: Ultrasonic weld cross section of (a) the entire interface after 0.3 s, (b) deformation islands after 0.1 s and (c) high magnification of the continuous interface layer [1.11].
In 2006, Gunduz performed ultrasonic metal welding of aluminum to evaluate the necessary parameters to optimize bond formation. During the investigation, the effect of pre-heating the samples was analyzed and SEM images are shown in Figure 2.2(a) and (b) for samples initially at room temperature and pre-heated to 573 K (300 °C), respectively. The sample initially at room temperature showed a bond that displayed mechanical mixing and contained many voids. The sample pre-heated to 573 K (300 °C) showed a metallurgical bond with less voids in the central region surrounded by annular cracking. Also, the microhardness of the pre-heated sample was reportedly lower due to either dynamic recovery or recrystallization.

![Figure 2.2: Ultrasonic bond of aluminum at (a) room temperature and (b) pre-heated to 573 K (300 °C).](image)

2.2 Interface temperature measurements during ultrasonic welding of metal sheets

Ultrasonic welding is usually done at room temperature without preheating the work pieces. As such it is generally regarded as a solid-state joining process. However, it
is obvious that the actual temperature at the joining interface is higher than the nominal joining temperature because of the inherent frictional and adiabatic deformation heating involved. Moreover, the degree to which the interface temperature is elevated over the nominal temperature is not known due primarily to the transient nature of the temperature rise at the interface.

In 1998, Tsujino observed the temperature rise by measuring thermoelectromotive force between the layers of dissimilar metals welded using a 15 kHz ultrasonic butt-welding system [1.9]. However, this method does not apply to the measurement of the temperature rise between the same or similar metals as there is no thermoelectromotive force in such cases.

In 2005, Yadav investigated the thermomechanical effects on the transient heating during a single weld cycle under special welding conditions by infrared pyrometry to directly measure the interface temperature between layers of similar metals [1.10]. Basically, the initial increase in temperature during ultrasonic welding caused the coefficient of friction between the weld materials to decrease to a critical level, resulting in a constant strain beyond which point the temperature remained constant.

Both direct measurements of $T_{int}$ with thermocouples and infrared pyrometry, however, have been difficult due to the transient nature of the local heating over short process durations. This thesis presents a new method for the estimation of the interface temperature in ultrasonic joining.
2.3 High strain rate effects and excess vacancy formation

In 1950’s, Seeger et al. discovered that plastic deformation can produce vacancies in metals [2.10]. The excess vacancies are generated by the nonconservative motion of jogs on screw dislocations. Screw dislocations pinned by sessile jogs bend under stress until a critical stress is reached, after which the jogs climb non-conservatively, leaving vacancies or interstitials behind them [2.11].

In 1998, Murty performed in-situ nuclear magnetic resonance (NMR) experiments to investigate the strain, temperature and strain-rate relationship and strain-induced vacancy concentration in aluminum [1.14]. Experimental results correlated well with the Mecking-Estrin model based on both thermally and strain induced vacancy production [2.12]. Murty calculated the thermal equilibrium vacancy concentration using [2.13]:

\[
X_{v}^{eq} = 23 \exp \left( -\frac{0.66eV}{kT} \right)
\]  \hspace{1cm} (2.1)

Experimental results showed low and high temperature regimes for the strain induced vacancy production. The low-temperature excess vacancies concentration was temperature independent and increased linearly with plastic strain according to \(X_{v}^{\varepsilon}\)_{lowT} = 9.7\varepsilon\text{ where } 0.003\Gamma_{v}\varepsilon \ll \dot{\varepsilon}\text{, where } \Gamma_{v}\text{ is the jump frequency of vacancies and } \dot{\varepsilon}\text{ is the strain rate. The high temperature strain induced vacancy concentration decreases with increasing temperature due to in situ annealing and follows:}

\[
X_{v}^{\varepsilon}\]_{highT} = \frac{3.6 \times 10^{3}\dot{\varepsilon}}{\Gamma_{v}} \left[ 1 - c_{2}\exp(-43\varepsilon) \right]
\]  \hspace{1cm} (2.2)

where \(\Gamma_{v}\) and constant \(c_{2}\) are calculated, respectively, with:

\[
\Gamma_{v} = 2 \times 10^{14} \exp \left( -\frac{0.62eV}{kT} \right) \text{s}^{-1}
\]  \hspace{1cm} (2.3)
Murty et al.'s experiments were conducted using 2.7% strain at a 0.55 s\(^{-1}\) strain rate. The total vacancy concentration vs. temperature results are presented as an Arrhenius plot in Figure 2.3 along with calculations with Mecking-Estrin’s mechanical jog model at 0.0001 s\(^{-1}\) strain rate. It is seen that the transition temperature between the low and high temperature regions increases with increasing strain rate. The transition temperature that separates the low and high temperature regions is 553 K (280 °C) for the 0.55 s\(^{-1}\) strain rate. Below 553 K (280 °C) in the low temperature regime, strain-induced vacancies are dominant and increase linearly with plastic strain. Thermally generated vacancies dominate in the high temperature regime which Murty attributes to the annihilation of strain-induced “excess” vacancies via diffusion to sinks, primarily dislocations [1.14].

\[
c_2 = \frac{1}{1 - \left(\frac{c}{2\beta_o\rho_{eq}T_v}\right)\dot{\varepsilon}} \tag{2.4}
\]

![Figure 2.3: Total \(X_v\) vs. temperature.](image)
In 2004, Gunduz et al. studied the enhanced diffusion and phase transformations during ultrasonic welding of zinc and aluminum [2,14]. New phase diagrams of the Al-Zn system were calculated for different vacancy concentrations with a modified sub-regular solution model in which free energy curves of Al-Zn solutions under normal conditions were extracted from Thermo-Calc®. The experiments also showed evidence of enhanced diffusion which occurred due to strain induced excess vacancy formation during the ultrasonic welding of Al/Zn pairs. The enhanced diffusion was verified by calculations made in correlation with the EDS data which yielded a diffusivity five orders of magnitude higher than that of normal diffusivity at 513K (240 °C). During the high strain rate deformation in ultrasonic welding, which may go up to $10^5 \text{s}^{-1}$, vacancy concentration increased to about $7\times10^{-2}$, a value only slightly less than the reported physically possible maximum vacancy concentration of $\sim 10^{-1}$ [1.14]. The microstructure of the weld zone revealed formation of a featureless region, which had a constant Zn concentration of 80 at.%, while the Zn concentration in the fcc Al-Zn region exhibited an error-function profile with an effective diffusion depth of about 3.5 µm.
3. Experimental Procedure

Ultrasonic Joining experiments of aluminum sheet with copper foil were performed to investigate the diffusion of copper into aluminum during the high strain-rate plastic deformation of the mating surfaces of the Al sheet and the copper foil. This section describes the experimental equipment, the materials used, the ultrasonic joining experimental conditions, and energy-dispersive X-ray spectroscopy (EDS) used to determine the copper diffusion.

3.1 Ultrasonic welder

The ultrasonic welding unit used in this study was a CONDOR® ultrasonic welder manufactured by STAPLA Ultrasonics Corp, in Wilmington, MA. The operating frequency range of the weld head for metal welding is 20 KHz.

The control unit front panel, shown in Figure 3.1, includes push button switches and a large 80 character vacuum fluorescent display. The large green button on the right lower corner is the on/off button. The key switch located above the on/off button is used to select from the SETUP, TEACH and OPERATE modes. The TEACH mode is the most commonly used mode which allows the user to set various parameters, including duration, amplitude and welding energy, to optimize the welding process.

In order to make quality welds, the ultrasonic welder provides three weld modes namely: weld by time, weld by energy and weld by compaction. The weld by time mode
is the most commonly used mode in this study, as the user can set different vibration times in order to obtain different degrees of bonding.

![Control unit of the ultrasonic welder.](image)

**Figure 3.1:** Control unit of the ultrasonic welder.

The sonotrode, made of hardened high speed tool steel, has a 3680 µm x 3680 µm square tip with a 14 x 14 grid of square knurls that are 150 µm x 150 µm and spaced 10 µm apart as shown in Figure 3.2.

![Schematic diagrams of the sonotrode tip](image)

**Figure 3.2:** Schematic diagrams of the sonotrode tip
To conduct experiments at evaluated temperatures, a heater plate inserted with two custom-built heaters and a general purpose k-type thermocouple was designed and incorporated in this study. The drawing for the stainless steel heater plate is shown in Figure 3.3. The two heaters inserted in the heater plate were TUTCO high-temperature, 0.95 cm diameter, 5.1 cm length, 400 W stainless steel sheath cartridge heaters with stainless steel armored leads covering up to a maximum operating temperature of 1143 K. The k-type thermocouple is a custom-built SP series (# SP-GP-K-6) thermocouple with a general purpose probe, purchased from Omega Engineering Inc.

![Figure 3.3: Schematic of heater plate.](image)

### 3.2 Materials

The materials used in this study are (1) Al 1100 sheet 0.8 mm in thickness, shown in Table 1 and Figure 3.4, purchased from Alfa Aesar, and (2) electrolytic copper foil (99.9% pure), 75 µm in thickness, supplied by Fukuda Metal Foil and Powder Co. Ltd., Japan.
### Table 1: Chemical Composition of Aluminum 1100

#### Aluminum 1100 Chemical Composition (mass%)

<table>
<thead>
<tr>
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<th>Copper</th>
<th>Silicon + Iron</th>
<th>Manganese</th>
<th>Zinc</th>
<th>Remainder each</th>
<th>Remainder total</th>
</tr>
</thead>
<tbody>
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<td>99</td>
<td>0.05 max</td>
<td>0.95 max</td>
<td>0.05 max</td>
<td>0.1 max</td>
<td>0.05 max</td>
<td>0.15 max</td>
</tr>
</tbody>
</table>

**Figure 3.4:** Cross sectional SEM micrograph of as-received aluminum alloy 1100 sheet, cold rolled. Note metal flow around insoluble particles of FeAl$_3$ (black). The particles are remnants of scriptlike constituents in the ingot that have been fragmented by working.
The Al 1100 sheet was first polished mechanically with 800 grit emery paper in order to remove oxide on the surface. The Al 1100 sheet and the copper foil were then ultrasonically cleaned in an acetone bath three minutes to remove other surface contaminants using a Fisher Scientific FS 20D digital ultrasonic cleaner.

Pure aluminum (99.9%) was also tested in the beginning of this research. However, due to the low hardness of pure aluminum, the material deformed severely at low processing temperatures and we were not able to obtain successfully joined specimens at higher processing temperatures.

3.3 Ultrasonic sheet joining experiments

0.8 mm thick 1100 Al sheet and 75 µm thick electrolytic Cu foils were ultrasonically joined at different nominal temperatures, ranging from 298 K (25 °C) to 443 K (170 °C), on a Stapla Condor ultrasonic welder as schematically illustrated in Figure 3.5. Both the 1100 Al sheet and the Cu foil were cut into approximately 0.5 inch x 0.5 inch pieces. The 1100 Al sheet was first placed on the heater plate preheated to the set nominal joining temperature and then Cu foil was placed on top of the Al sheet. The Al 1100 sheet and the Cu foil were clamped under the sonotrode tip at a normal pressure of 56 MPa. A thermocouple was placed between the Al 1100 sheet and the Cu foil in order to monitor the nominal interface temperature before joining. As soon as the interface temperature reached the set nominal joining temperature (which took about 45 s), in-plane ultrasonic vibration was applied to the specimen through the sonotrode. The vibration frequency and amplitude were fixed at 20 kHz and 9 µm, respectively, for all
specimens. The vibration duration used in this study ranged from 0.75 s to 1.25 s. The specimen was removed from the welder and cooled in air immediately after the vibration was turned off.

The joined Cu-Al specimens were mounted in epoxy to expose their cross sections and ground with progressively finer emery paper ranging from 240 to 1200 grit sizes. The ground specimens were final-polished successively with 1 µm and 0.3 µm alumina suspensions. The specimens etched for 60 s with Keller’s reagent, were examined by optical microscopy and scanning electron microscopy (SEM) at an accelerating voltage of 10 kV.

Figure 3.5: Schematic of ultrasonic sheet joining setup.
3.4 Energy dispersive X-Ray spectroscopy

A Hitachi S-4800 SEM equipped with a Genesis Spectrum Energy-dispersive X-ray spectrometer was used at an acceleration voltage of 10 KV to analyze the Cu concentration in the Al subsurface regions of specimens subjected to ultrasonic vibration at 298 K (25 °C) – 413 K (140 °C) for 1.25 s under 56 MPa normal compressions.

3.4.1 Preparation of EDS specimens

The cross sections of the joined specimens were polished and etched with Keller’s reagent. The etched specimens were, each, placed on an aluminum specimen holding stub with double-stick adhesive tape. The mounted specimens were then coated with carbon by vacuum sputtering to provide the specimen surface with electrical conductivity. The specimen in the mount was electrically connected with the aluminum stub with silver paint to drain electrons from the specimen.

3.4.2 Interaction volume of Cu

In this study, the accelerating voltage was set at 10 KV to minimize the excitation volume and hence signal overlap at the Al-Cu interface. The interaction volume of electrons in EDS is the volume of the specimen in which electron-solid interactions occur. The interaction volume has a pear shape as shown in Figure 3.6 with the depth substantially greater than the width. Three factors affect the size and shape of the interaction volume,
(1) The atomic number of the material being examined. Materials with high atomic numbers slow down the electron projectile more effectively, therefore a high atomic number correlates to a small interaction volume.

(2) The energy of the incident electron beam. High energy electrons penetrate deeper into the specimen and create a larger interaction volume.

(3) The angle of incidence of the electron beam. A large incident angle leads to a small interaction volume.

![Schematic of electron interaction volume.](image)

**Figure 3.6:** Schematic of electron interaction volume.

The depth and width of the electron penetration are approximately given, respectively, by:
\[ x (\mu m) = \frac{0.1 E_0^{1.5}}{\rho} \]  

(3.1)

and:

\[ y (\mu m) = \frac{0.077 E_0^{1.5}}{\rho} \]  

(3.2)

where \( E_0 \) is the acceleration voltage (KeV) and \( \rho \) is the density (g/cm\(^3\)) of the materials.

In this study, the density was that of Al 1100 (2.71 g/cm\(^3\)) and the acceleration voltage was 10 KeV, so the depth of electron penetration is calculated to be \( x = 1.2 \mu m \) and the width of the excited volume is calculated to be 0.9 \( \mu m \). Based on this calculated width of the excited volume, it is deducted that the signal overlap at the Al-Cu joint interface would be significant only when the electron beam is positioned within 0.45 \( \mu m \) (half of the excited volume width) of the Al-Cu interface.
4. Microhardness Measurements of the Ultrasonically Joined Specimens

4.1 Hardness measurements procedure

As noticed in previous study [1.13], ultrasonic joining may enhance interdiffusion at the interfacial regions of the materials being joined. The enhanced diffusion is considered to result due to a high excess vacancy concentration caused by the non-conservative motion of jogs on screw dislocations during the high strain rate ultrasonic deformation imposed on the materials. In the present study, Knoop microhardness measurements were performed on the cross sections of ultrasonically joined Al 1100 sheet - Cu foil specimens using a Shimadzu HMV micro-hardness tester equipped with a Knoop microindentor. An indentation load of 98.07 mN and a loading time of 0.5 s were applied to all specimens.

4.2 Microhardness measurement results

Figure 4.1 shows the Knoop microhardness of the Al100-Cu specimens which were ultrasonically joined for 0.75 s at nominal joining temperatures of 393 - 413 K (120 - 140 °C) under a normal clamping pressure of 56 MPa. Micro-Knoop hardness measurements were performed in the aluminum side of cross sections of the heat treated specimens at distances of 3, 12 and 30 µm from the interface. At each distance, 5 to 10 measurements were made. The Knoop indentations were created with their long diagonals parallel to the weld interface. The width of the Knoop indentations created on the specimens was of about 6 µm. Therefore, the hardness values obtained at the distances of 3, 12 and 30 µm from the interface are regarded as the averages of the regions 0 - 6 µm, 9 - 15 µm and 27
- 33 µm from the interface, respectively. Also included in Figure 4.1 is the microhardness of Al 1100 specimens subjected to ultrasonic vibration under the same conditions as those for the Al100-Cu specimens, but without Cu foil overlay. We note that the microhardness near the interface, i.e., in the regions less than 12 µm from the interface, is higher than that of the specimens without Cu foil. We note also that the hardness of the Al 1100-Cu specimens at 30 µm from the interface is lower than those at the shorter distances from the interface and are comparable to that of the specimens without Cu foil. Therefore, the increased hardness near the interface in the Al100-Cu specimens must be attributed to the diffusion of Cu into the Al 1100 sheet.

Figure 4.1: Aluminum hardness at different distance from the interface versus temperature with 56 MPa pressure of sonotrode in 0.75 s of ultrasonic vibration.
Another important observation in Figure 4.1 is that the microhardness near the interface of the Al 1100-Cu specimens shows a maximum at the nominal joining temperature of 413 K (140 °C). This may be interpreted as an effect of in-situ precipitation hardening [1.13], in addition to that of solid solution hardening. Despite the short time of 0.75 s over which the specimens were subjected to ultrasonic deformation, the kinetics of precipitation might have been boosted in the presence of the excess vacancies that would increase diffusivity by many orders of magnitude [2.14], while dislocations and other crystalline defects created by the ultrasonic deformation could provide heterogeneous nucleation sites. Concurrently, dynamic recovery and strain hardening would compete with in situ precipitation hardening. The lower hardness values below 413 K (140 °C) suggest that the effect of in situ precipitation was not as pronounced as it was at 413 K (140 °C), while strain hardening and dynamic recovery were the main player. The decrease in hardness above 413 K (140 °C) may be attributed to over-aging and dynamic recovery (and possible dynamic recrystallization.)

Figure 4.2 shows the microhardness of Al 1100-Cu specimens ultrasonically joined with Cu foil for 1.25 s at nominal joining temperatures of 333 – 413 K (60 to 140 °C) under a normal pressure of 56 MPa. The measurements were made on the Al100 side 6 μm from the interface with the Cu foil. We note a peak at 353 K (80 °C). This is considered to reflect a higher rate of strain hardening than that of softening by dynamic recovery, while in situ precipitation was still insignificant. Above 353 K (80 °C), the microhardness dropped as softening offset strain hardening. Above 393 K (120 °C), microhardness increased as in situ precipitation hardening became more significant. We
note that the hardness 67 HK reached at 413 K (140 °C) is comparable to the peak hardness 69.4 HK in Figure 4.1. However, whether the hardness would peak at 413 K (140 °C) if the joining time is increased from 0.75 s to 1.25 s could not be determined since attempts to join Al 1100 sheet and Cu foil at higher temperatures caused the Al 1100 sheet to deform excessively, producing no joined specimens on which microhardness measurements would have been possible. We suspect that the excessive softening of the Al 1100 sheet above 413 K (140 °C) relates to the phenomena known as ultrasonic softening which some workers have reported (but without a clear understanding of underlining mechanisms) [5.5]. The ultrasonic softening might even involve melting due to strain-induced melting point depression, a hypothesis developed in our lab - Advanced Materials Processing Laboratory (AMPL) at Northeastern [2.14] although the latter has yet to be verified.

Figure 4.2: Aluminum hardness at 3 μm from the interface versus temperature with 56 MPa pressure of sonotrode in 1.25 s of ultrasonic vibration.
5. Estimation of the Interface Temperature in Ultrasonic Joining

5.1 Introduction

Ultrasonic joining is a rapid joining process in which parts/materials clamped under normal compression are metallurgically bonded by the application of local high-frequency vibration, usually in a fraction of a second. The process takes place at ambient conditions, without heating or a protective atmosphere [2.2]. Thus, it is widely adapted in electronics, auto and aerospace industries [5.1-5.3]. New applications have also evolved in ultrasonic additive manufacturing [5.4, 5.5] and more recently ultrasonic powder consolidation (UPC) [5.6].

Despite the wide industrial acceptance and potential for future innovations, however, understanding of the fundamental mechanism(s) of ultrasonic joining is still lacking. It is known that this process involves local, high plastic strains applied at high cyclic rates [2.2, 5.1-5.6]. Researchers have thus explored the consequences of such strains at an interface between two materials, including solid-state bonding [5.5, 2.5, 5.7-5.13], local melting [5.8, 2.6] and mechanical interlocking [2.5, 5.10]. One major debate is whether or not ultrasonic joining is truly solid state; if this is the case, the rapidity of bonding indicates greatly enhanced diffusivity, due to (i) increased vacancy concentration and/or (ii) increased temperature at the interface.

High strain-rate plastic deformation of a metal, as in ultrasonic joining, introduces large amounts of excess vacancies in the metal by the non-conservative motion of jogs on screw dislocations [1.1, 1.2, 1.3] and/or possibly by other mechanisms [1.4 - 1.7]. Vacancy mole fractions many orders of magnitude above the thermal equilibrium value
have been estimated by electron microscopy [1.4, 1.6], calorimetry [5.15], electrical resistivity measurements [5.15, 5.16], X-ray diffraction (XRD) [5.15] and nuclear magnetic resonance (NMR) [1.14]. Figure 5.1 shows a TEM micrograph of pure aluminum wire subjected to ultrasonic vibration for 1 s at 773 K (500 °C) nominal temperatures [5.16]. Numerous vacancy clusters and Frank loops about 3-10 nm and 20-30 nm in diameter, respectively, are found, attesting to the prior presence of excess vacancies in a very high concentration. The minimum value of prior mono-vacancy concentration can be assessed from the density of clusters and loops with

\[
X_v = \frac{(4/3)\pi r^3 n}{\theta} \quad \text{(clusters)} \quad \text{and} \quad X_v = \frac{\pi r^2 b n}{\theta} \quad \text{(loops)}
\]

where \( r \) is the radius of vacancy clusters, \( b \) is the Burgers vector, \( n \) is the number of clusters per unit TEM view area and \( \theta \) is the thickness of the TEM specimen. This gives \( X_v \sim 10^{-4} \) for the specimen in Figure 1. Other TEM studies [1.2, 1.3, 1.4, 1.6] also report \( X_v \sim 10^{-4} \). However, these \( X_v \) values do not include mono vacancies that annihilate at sinks, especially dislocations that should be present in high density in a deforming metal. Thus, the actual (in situ) value of \( X_v \) during ultrasonic deformation can be much higher than \( 10^{-4} \).
Figure 5.1: TEM image of Al wire subjected to ultrasonic deformation at 773 K (500 °C) [5.16].

The vacancy concentration in a deforming metal may reach high values even at lower strain rates as well, if temperature is sufficiently low. A recent in situ NMR study by Murty, et al. [1.14] reports that the mole fraction of vacancies ($X_V$) in pure aluminum deforming under tension at a strain rate of 0.55 s$^{-1}$ rises above the thermal equilibrium value below about 560 K (287 °C) and reaches a high plateau value of about 0.1 below about 310 K (37 °C) (Figure 5.2). The temperature at which $X_V$ hits the plateau value increases with increasing strain rate. At a strain rate of $10^5$ s$^{-1}$, estimated for the joining surfaces in ultrasonic joining [5.4], the model given in Ref. [1.14] predicts $X_V \approx 0.1$ below about 660 K (387 °C) (Figure 5.2). The high $X_V$ values in Figure 5.2 represent the steady state between the generation, annihilation and condensation of mono-vacancies.
during the deformation and hence are greater than those estimated off-line by TEM, although the very high plateau value of $X_v$ has not been confirmed by other workers.

Such a high value of mono vacancy concentration, whether it is 0.1 or less, translates into a large diffusivity several orders of magnitude over the normal value, giving rise to measurable diffusion distances in ultrasonically joined materials [5.18-5.19, 2.14], even during such short times.

The rise in $T_{\text{int}}$ above the nominal joining temperature $T_{\text{nom}}$ due to frictional and adiabatic-deformation heating must also enhance diffusivity. Direct measurements of $T_{\text{int}}$ with thermocouples [2.3, 1.9, 1.10] and infrared pyrometry [1.11], however, have been difficult due to the transitional nature of the local heating over short process durations. While these direct measurement methods may be further refined, indirect approaches can be taken to estimate the interface temperature based on the behavior of the materials being joined. The present work produced a new method for the estimation of the interface temperature in ultrasonic joining from diffusion data obtained on ultrasonically joined aluminum sheet and copper foil.
5.2 Estimation of diffusivity

Figure 5.3 shows profiles of Cu concentration at the interface for specimens joined at 298, 353, 373, 393 and 413 K (25, 80, 100, 120 and 140 °C) determined over a distance of 3 μm from the interface as shown in Figure 5.4. Each data point is an average of at least 5 measurements. Significant diffusion of Cu into the 1100Al is apparent for all four specimens. In EDS, the horizontal span of the excitation volume at an acceleration voltage of 10 kV is about 1 μm for aluminum [5.20] (see section 3.4). Therefore, the EDS data at 0.5 μm from the interface in Figure 5.3 were corrected for signal overlap by subtracting

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Figure 5.2: Excess vacancy concentrations at various strain rates calculated with Murty et al.'s model [1.14].
the background value (3.59 wt. %) obtained with the electroplated reference specimen. Table 1 shows the Cu concentrations with corrections of the data at 0.5 µm. The data at the larger distances do not require such corrections.

The magnitude of the Cu diffusivity in 1100 Al at the interface may be roughly estimated from the EDS data with the formula \( x = \sqrt{Dt} \) where \( x \) is the diffusion distance, \( D \) is the diffusivity and \( t \) is the vibration time. For instance, taking \( x \approx 0.5 \) µm and \( t = 1.25 \) s for the specimen joined at the nominal temperature of 413 K yields \( D = 2 \times 10^{-13} \) m²/s which is eight orders of magnitude higher than the value expected at 413 K (140 °C). The data from the other specimens joined at the lower nominal temperatures yield \( D \) values of the same order of magnitude. These large \( D \) values are indicative of the presence of excess vacancies created by the plastic deformation during ultrasonic joining.

Figure 5.3: Cu concentration profiles in the 1100 Al side of the diffusion couple vs. as determined by EDS. The data points are averages of at least 5 data point. The values at 0.5 µm are corrected in Table 2 for signal overlap.
To obtain more exact values of diffusivities, the EDS data in Table 2 were analyzed with a complementary error function, which, in the absence of simultaneous precipitation of a secondary phase in the diffusion couple (see Appendix), takes the form:

\[ C(z) = C_\infty + (C_S - C_\infty) \text{erfc}(z) \]  \hspace{1cm} (5.1)

where \( z = \frac{x}{2\sqrt{Dt}} \), \( C_\infty \) is the initial Cu concentration of the 1100 Al sheet (0.12 wt. %), and \( C_S \) is the Cu concentration at the interface. Since the 1100 Al sheet was joined with pure Cu foil, we expect \( C_S = \frac{100 - C_\infty}{2} \approx 50 \). To compare the \( \text{erfc} \) curve with the EDS profile on the same \( C - x \) plane, the \( \text{erfc} \) curve must be shifted towards the data points such that the points on the \( \text{erfc} \) curve \((C, x)\) are placed at \((C, 2\sqrt{Dt} \cdot z)\). In other words, the \( \text{erfc} \) curve \((C, kz)\) matches the data points when \( k = 2\sqrt{Dt} \). Thus, the value of \( D \) was determined by least-square fitting of the \( \text{erfc} \) curve to the EDS data using \( k \) as the
parameter (See Appendix A). This procedure yields $D$ values of $1.54 \times 10^{-13}$, $1.61 \times 10^{-13}$, $1.67 \times 10^{-13}$, $1.88 \times 10^{-13}$ and $2.22 \times 10^{-13}$ m$^2$/s for the nominal joining temperatures of 298, 353, 373, 393, and 413 K (25, 80, 100, 120 and 140 °C), respectively, which agree with the approximate values.

5.3 Estimation of Interface Temperature

5.3.1 Solid-state joining scenarios

A general formula of the substitutional diffusivity in the presence of excess monovacancies is $D = f \cdot D_v X_v$ where $X_v$ is the vacancy mole fraction, $D_v$ is the vacancy diffusivity and $f$ is the correlation factor of the substitutional atom jumps [5.21]. Thus, for a given interface temperature,
\[
\frac{D}{D_{\text{norm}}} = \frac{X_v}{X_{\text{eq}}}
\]  \ (5.2)

may hold [2.14] where \( D_{\text{norm}} \) is the normal diffusivity in the absence of excess vacancies and \( X_{\text{eq}} \) is the equilibrium mole fraction of thermal vacancies. For dilute Al-Cu solid solutions we may use [5.22]

\[
D_{\text{norm}} = 1.5 \times 10^{-5} \exp\left(-\frac{126,000}{RT_{\text{int}}}\right)
\]  \ (5.3)

where \( D_{\text{norm}} \) has the unit of m\(^2\)/s, \( R \) is the gas constant in J/Mol•K and \( T_{\text{int}} \) is in K. The value of \( X_{\text{eq}} \) may be approximated, on the basis of the low copper-vacancy binding energy [5.23], by the equilibrium vacancy mole fraction in pure aluminum which is given by [5.24]

\[
X_{\text{eq}} = 2.226 \exp\left(-\frac{59,820}{RT_{\text{int}}}\right)
\]  \ (5.4)

Solving Eq. (5.2) for \( T_{\text{int}} \) requires a value of \( X_v \). Although no established data are currently available, the actual value of vacancy concentration during rapid plastic deformation should exceed the values estimated off-line from the density of vacancy clusters and dislocation loops which do not account for vacancy annihilation at sinks, especially dislocations that have any edge component. The ratio of the vacancies that annihilate at sinks to those that condense into voids after the deformation may be roughly estimated by the relative time spans of vacancy annihilation and condensation. We may calculate the time for a vacancy to reach a nearby dislocation, \( \tau \), from the random walk
theory which gives $\tau = (\rho / 24)(X_v^{eq} / D_s)f$ where $\rho$ is the dislocation density and $D_s$ is the self-diffusivity. If we assume $\rho = 10^{14}$ to $10^{15}$ m/m$^3$ for solid aluminum being subjected to ultrasonic deformation, $\tau$ is in the range of 2 ~ 20 $\mu$s at 400 K (127 °C) and 40 ~ 400 $\mu$s at 500 K (227 °C). Even if the vacancy misses the first 10 nearest dislocations, it will hit a dislocation in about 0.02 ~ 0.2 s at 400 K (127 °C) and much sooner at 500 K (227 °C). Calculations at $\rho = 10^{13}$ increase the annihilation time only by a factor of 10. Conversely, the condensation of mono-vacancies into voids progresses typically over many seconds [5.25]. This suggests that most of the mono-vacancies present in the deforming aluminum would be lost to dislocations, leaving much fewer to condense into voids and dislocation loops. Thus, the actual mono-vacancy concentration during high strain-rate plastic deformation can be much greater than the reported off-line values of $10^{-4}$ by a factor as large as 1000.

The NMR data in Figure 5.5 [1.14] in fact indicate that the value of $X_v$ in aluminum deforming at a strain rate of 0.55 s$^{-1}$ reaches a very high plateau value of about 0.1 at deformation temperatures below about 310 K. At higher strain rates the plateau must extend to higher temperatures. Calculations with the model in Ref. [1.14], also shown in Figure 5.5, indicate that, at a strain rate of $10^5$ s$^{-1}$ estimated for ultrasonic joining [5.4], the plateau ($X_v = 0.1$) is reached at $T \leq 658$ K. Above 658 K (385 °C), $X_v$ transitions from the plateau value down toward $X_v^{eq}$, for which the same model gives

$$X_v = 1.85 \times 10^{-6} \exp \left( \frac{59,610}{RT_{int}} \right)$$

(5.5)
Figure 5.5: Excess vacancy concentrations at various strain rates calculated with Murty et al.'s model. The solid diamonds are NMR data [1.14].

The high plateau $X_V$ value in Figure 5.5 is even greater than the thermal equilibrium concentration at the melting point, which is $10^{-3}$ when calculated with Eq. (5.4). However, our thermodynamic calculations assuming ideal mixing of vacancies, Figure 5.7 suggest that solid aluminum may be more stable than liquid aluminum up to 536 K (263 °C) at $X_V = 0.1$ and up to 603 K (330 °C) at $X_V = 0.09$. At $X_V < 0.01$ solid aluminum is stable almost up to the equilibrium melting point (933 K). Thus, a steady-state value of $X_V$ defined between mono-vacancy generation, annihilation and condensation may sustain at very high value as long as temperature stays below the $X_V$-modified melting point. In a deforming metal in such a steady state, mono-vacancy diffusion may still govern the substitutional diffusion.
With the above justification, Eq. (5.2) may be solved for $T_{\text{int}}$ assuming $X_p = 0.1$ for the plateau region and Eq. (5.5) for the transition regions. The corresponding equations of $D$ (m$^2$/s) in the plateau and transition regions, respectively, are

$$\ln D = -14.21 - \frac{66,180}{RT_{\text{int}}} \quad \text{(plateau)} \quad (5.6)$$

and

$$\ln D = -25.11 - \frac{6,570}{RT_{\text{int}}} \quad \text{(transition)} \quad (5.7)$$

Figure 5.6 shows Arrhenius plots of $D$ calculated with Eqs. (5.6) and (5.7) together with the $D$ value of $2.22 \times 10^{-13}$ m$^2$/s determined for the specimen joined at the nominal temperature of 413 K. The plateau and transition regions are identified by their distinctly different slopes. We note that the calculated $D$ coincides with the experimental value ($2.22 \times 10^{-13}$ m$^2$/s) only in the plateau region, at 533 K, which translates into a moderate temperature increase $\Delta T$ of 120 K. At no temperature in the transition region above 658 K does the calculated $D$ match the experimental value.
Figure 5.6: Arrhenius plots of the copper diffusivity in aluminum calculated at a strain rate of $10^5 \text{s}^{-1}$ with Eq. (5.6) (plateau area), Eq. (5.7) (transition region), and Eq. (5.3) (normal conditions with no excess vacancies). The calculated $D$ coincides with the experimental value ($2.22 \times 10^{-13} \text{m}^2/\text{s}$) only in the plateau region, at 533 K (260 °C).

The above calculation was repeated for the other specimens. Table 3 lists the values of $D$, $T_{\text{int}}$, and $\Delta T$ estimated for the five nominal joining temperatures, 298, 353, 373, 393 and 413 K (25, 80, 100, 120 and 140 °C) together with those of $D^\text{norm}$ calculated at the respective values of $T_{\text{int}}$. We note that the estimated $T_{\text{int}}$ values are all well below 658 K (385 °C), and thus the use of the plateau value $X_{\nu} = 0.1$ in Eq. (5.2) remains valid (Figure 5.5). Also, the estimated interface temperatures are at least 400 K (127 °C) below the equilibrium melting point of aluminum (933 K) (660 °C), ruling out the occurrence of equilibrium melting in this scenario.
Figure 5.6 also shows an Arrhenius plot of $D^{\text{norm}}$ calculated with Eq. (5.3) which has a large negative slope because of the large combined activation energy for vacancy formation and motion. It is seen that $D^{\text{norm}}$ takes the experimental value ($2.22 \times 10^{-13} \text{ m}^2/\text{s}$) at 840.6 K (567.6 °C), which is still below the equilibrium melting point of aluminum. Such an interface condition, however, is not likely to occur in ultrasonic joining where excess vacancies may boost the diffusivity much above the normal values even just below the melting temperature.

Table 3: Interface Temperatures and Diffusivities Estimated for the Sheet Joining Experiments Performed at Nominal Process Temperatures of 298, 353, 373, 292 and 413 K.

<table>
<thead>
<tr>
<th>$T_{\text{nom}}$ (K)</th>
<th>$D_{T_{\text{int}}}^{\text{int}}$ (m$^2$/s)</th>
<th>$T_{\text{int}}$ (K)</th>
<th>$\Delta T$ (K)</th>
<th>$D_{T_{\text{int}}}^{\text{norm}}$ (m$^2$/s)</th>
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<tbody>
<tr>
<td>298</td>
<td>$1.54 \times 10^{-13}$</td>
<td>521</td>
<td>223</td>
<td>$3.49 \times 10^{-18}$</td>
</tr>
<tr>
<td>353</td>
<td>$1.61 \times 10^{-13}$</td>
<td>522</td>
<td>169</td>
<td>$3.69 \times 10^{-18}$</td>
</tr>
<tr>
<td>373</td>
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<td>523</td>
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<td>$3.90 \times 10^{-18}$</td>
</tr>
<tr>
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<td>$1.88 \times 10^{-13}$</td>
<td>527</td>
<td>134</td>
<td>$4.86 \times 10^{-18}$</td>
</tr>
<tr>
<td>413</td>
<td>$2.22 \times 10^{-13}$</td>
<td>533</td>
<td>120</td>
<td>$6.72 \times 10^{-18}$</td>
</tr>
</tbody>
</table>

5.3.2 Local melting scenario

Although the above observations rule out equilibrium melting at the joining interface, melting might still be possible thermodynamically. For completeness we refer to the normalized $X_v$- modified melting point of aluminum vs. $X_v$ in Figure 5.7 (for calculation of Fig 5.7, see Appendix - B) Significant melting point depression is predicted as $X_v$ exceeds 0.01, the reduced melting point being as low as 536 K (263 °C)
when calculated at the assumed plateau $X_v$ value of 0.1. Thus, melting might be possible if $T_{int}$ goes well above 500 K (227 °C) at a high plateau $X_v$ value approaching 0.1. To see if the high $D$ values determined with the EDS data could be elucidated on such a melting point depression, we take a typical liquid diffusivity value of $10^{-9}$ m$^2$/s for molten aluminum at the melting point (933 K) and assume activation energy of 20,000 J/Mol. Then, the liquid diffusivity value at 500 K (227 °C) is estimated to be $3 \times 10^{-10}$ m$^2$/s, which is three orders of magnitude larger than the values determined from the EDS data. Liquid diffusivity values of the order of $10^{-13}$ m$^2$/s would be observed only if melting occurred at ~ 220 K. But this is much below $T_{nom}$ and hence not possible. Even if the activation energy were as high as 30,000 J/Mol, the experimental $D$ value of $10^{-13}$ m$^2$/s requires that melting occur at ~ 330 K, which is still not possible for the same reason. Thus, it may be concluded that liquid could not have formed in the specimens joined in the present work, either at or below the equilibrium melting point.

![Figure 5.7: Normalized melting point of aluminum as a function of vacancy mole fraction calculated with a thermodynamic model.](image-url)
5.3.3 Effects of plateau $X_V$ and strain rate

The above calculations, done under the assumed conditions of $X_V = 0.1$ and strain rate of $10^5$ s$^{-1}$, strongly suggest that the specimens joined at the nominal temperatures of 298 to 413 K (25 to 140 °C) all experienced a similar $T_{int}$ about 400 K (127 °C) below the melting point of aluminum (Table 2) and that the joining involved no melting. To examine if this scenario remains plausible at lower values of plateau $X_V$ and strain rate $10^m$ s$^{-1}$, additional plots of diffusivity calculated with modified Eqs. (5.5) and (5.6):

\[
\ln D = -11.91 + \ln X_V - \frac{66.180}{RT_{int}} \quad \text{(plateau)} \quad (5.8)
\]

\[
\ln D = -25.18 - 2.303(5 - m) - \frac{6.570}{RT_{int}} \quad \text{(transition)} \quad (5.9)
\]

are shown in Figure 5.8. At a fixed strain rate of $10^5$ s$^{-1}$, decreasing plateau $X_V$ from 0.1 to 0.05 increases the $T_{int}$ of the specimen joined at $T_{nom}$ of 413 K from 533 K (point a in Figure 5.7) to 559 K (286 °C) (point b). At $X_V = 0.01$, $T_{int}$ is further increased to 630 K (357 °C) (point c). Decreasing the strain rate widens the transition region and also shifts it to lower temperatures. However, at a fixed plateau $X_V$ value of 0.1, a decrease in strain rate from $10^5$ s$^{-1}$ to $10^4$ s$^{-1}$ would not change $T_{int}$ from 533 K (260 °C) (point a), the value predicted at $10^5$ s$^{-1}$. Further decreases in strain rate would increase $T_{int}$ towards 840.6 K (567.6 °C) (point d), the temperature at which the normal diffusivity calculated with Eq. (5.3) and the diffusivity calculated with Eq. (5.9) both match the experimental value, 2.22
x $10^{-13}$ m$^2$/s. This happens when $m = 3.66$ or at a strain rate of $4.57 \times 10^3$ s$^{-1}$. Below this critical strain rate, no conditions exist that yield the observed high experimental $D$ value of $2.22 \times 10^{-13}$ m$^2$/s. This indicates that the local strain rate at the interface in the specimen joined at the nominal temperature of 413 K (140 °C) was at least $4.57 \times 10^3$ s$^{-1}$. Similar, but somewhat lower critical strain rates and corresponding $T_{int}$ are predicted for the specimens joined nominally at 353 - 393 K (80 - 120 °C).

![Figure 5.8: Arrhenius plots of the copper diffusivity in aluminum calculated with Eq. (8) for different $X_v$ values and Eq. (9) for different strain rates.](image-url)
5.3.4 Interface temperature vs. nominal joining temperature

Figure 5.9 plots the values of $T_{\text{int}}$ and temperature rise $\Delta T$ estimated at $X_V = 0.1$ and 0.05 (plateau values) and a fixed strain rate of $10^5 \text{ s}^{-1}$ against $T_{\text{nom}}$. As illustrated in Figure 5.8, higher values of $T_{\text{int}}$ and $\Delta T$ are predicted for lower plateau values of $X_V$. Regardless of the plateau $X_V$ values, $\Delta T$ decreases almost linearly with nominal temperature while $X_V$ increases only slightly over the investigated $T_{\text{nom}}$ range of 298 K to 423 K (25 to 150 °C). This suggests that in the ultrasonic joining of aluminum, $T_{\text{int}}$ will stay at a nearly constant value regardless of the $T_{\text{nom}}$ up to about 400 K (127 °C). This most probably explains why ultrasonic joining is an effective room-temperature joining process, as established in industrial practice. Moreover, the $T_{\text{int}}$ values estimated for room temperature joining compare well with the infrared-camera data reported by de Vries (~490 K) [1.11] and the thermocouple measurements reported by Tsujino, et al. (508 K) [33] and Jones, et al. (473 - 588 K) (200 - 315 °C) [2.3], which are also shown in Figure 5.9. This implies that the value of $X_V$ might actually go up close to 0.1, the NMR value reported by Murty, et al. [1.14]. Finally, we deduce that the $T_{\text{int}}$ - $T_{\text{nom}}$ plot at higher nominal joining temperatures should have a slope that approaches unity, i.e., that of $T_{\text{int}} = T_{\text{nom}}$. The broken curves in Figure 5.9 are such high-temperature extrapolations of $T_{\text{int}}$ and $\Delta T$ that are expected at higher nominal temperatures in the absence of local melting.
Figure 5.9: $T_{\text{int}}$ and $\Delta T$ against nominal joining temperature estimated at $X_v = 0.1$ and 0.05 and a fixed strain rate of $105 \text{ s}^{-1}$. The broken curves above 413 K (140 °C) are extrapolations drawn with the expectation that $T_{\text{int}}$ curves will have a slope that approaches unity, i.e., that of $T_{\text{int}} = T_{\text{nom}}$. 
6. Post-Joining Heat Treatment

6.1 Objective

The Aluminum 1100 - copper specimens ultrasonically joined at a nominal joining temperature of 413 K (140 °C) for 1.25 s were heat treated at 383 - 413 K (110 - 140 °C) to observe changes in hardness in the Al 1100 near the joining interface where EDS had detected significant Cu diffusion, Figure 5.3. It was thought that during the post-joining heat treatment the hardness would decrease due to recovery and would increase by the precipitation of strengthening phases, such as the GP zones and the $\theta'$ and $\theta^*$ phases, which would attest to the presence of Cu in the aluminum and hence the prior Cu diffusion. It was also expected that these hardness changes would occur over a much longer period than in ultrasonic joining as the excess vacancies present during the ultrasonic joining had all annihilated into dislocations with any edge component even before the heat treatment [5.17], causing the diffusivity to decrease to its normal level. Therefore, in order for significant additional precipitation hardening to be detected at 383 – 413 K (110 - 140 °C), aging times up to 24 hours were investigated.

Interpretation of hardness measurement results, however, is not straightforward since additional diffusion of Cu into 1100 Al from the welded Cu foil might occur over the course of the long heat treatment, giving rise to additional precipitation hardening over that caused by the copper introduced during the prior ultrasonic joining. Therefore, the possible additional Cu diffusion during the post-joining heat treatment is also discussed in this section.
6.2 Procedure

Al 1100 - Cu samples, ultrasonically joined at 413 K (140 °C) for 1.25 s under 56 MPa normal pressure were heat treated at 383 K, 398 K and 413 K (110, 125 and 140 °C) for various times up to 24 hours in a Lindberg/Blue M box (air) furnace, model number BF51694C. The specimen joined at 413 K (140 °C) was chosen for this experiment since it had the highest as-joined hardness of 67 HK (Figure 4.1). Micro-Knoop hardness measurements were performed in the aluminum side of cross sections of the heat treated specimens at distances of 3, 12 and 24 µm from the interface. An indentation load of 98.07 mN and a loading time of 0.5 s were applied to all specimens. The Knoop indentations were created with their long diagonals parallel to the weld interface. The width of the Knoop indentations created on the specimens was of about 6 µm. Therefore, the hardness values obtained at the distances of 3, 12 and 24 µm from the interface are regarded as the averages of the regions 0 - 6 µm, 9 - 15 µm and 21 - 27 µm from the interface, respectively.

6.3 Results of hardness measurements

Figure 6.1 shows the changes in Knoop hardness of the Al 1100 - Cu specimens ultrasonically joined for 1.25 s at 413 K (140 °C) under 56 MPa normal pressures during the post-joining heat treatments at 383 K, 398 K and 413 K (110, 125 and 140 °C). All the measurements in Figure 6.1 were made at points in the Al 1100, 3 µm from the interface.
At all three heat treatment temperatures, the hardness dropped during the initial two hours. This harness decrease was caused by elimination and rearrangement of dislocations (i.e., static recovery) in the ultrasonically deformed material. At 383 K (110 °C), the recovery rate was slow and only a slight decrease in hardness occurred. At 398 K (125 °C), the recovery rate increased while the precipitation hardening rate still remained low, causing the hardness to drop sharply. At 413 K (140 °C), precipitation hardening became significant and largely offset the effect of recovery.
After about 2 hours, recovery subsided while precipitation hardening continued. The rate of hardness increase was higher at 398 K (125 °C) than at 413 K (140 °C), and it was lowest at 383 K (110 °C). At 398 K (125 °C) and 413 K (140 °C), hardness reached similar peak values of about 70 - 72 HK at 12 hours and decreased at longer times. The rate of hardness decrease after 12 hours was higher at 413 K (140 °C) than at 398 K (125 °C), indicating faster overaging at 413 K (140 °C). The hardness of the specimens heat treated at the lowest temperature of 383 K (110 °C) kept increasing slowly to values comparable to those at 398 K (125 °C) but reached no peak over the 24 hours of holding.

The above hardness changes are consistent with the characteristics of precipitation hardening, and therefore provide indirect evidence of the presence of Cu in the Al 1100 which must have been brought in by the diffusion from the Cu foil, i.e., from no other sources could the Cu come. That the Cu present in the Al came from the Cu foil by diffusion is more clearly seen in Figure 6.2 which shows the hardness changes of the specimens ultrasonically joined for 1.25 s at 413 K (140 °C) under 56 MPa during post-joining heat treatment at 413 K (140 °C) at 3, 19 and 22 µm from the interface with the Cu foil. We first note that the hardness before the heat treatment, i.e., at time zero, decreases with increasing distance from the interface. This is primarily because regions closer to the interface get more strain hardening from the ultrasonic deformation than at positions away from the interface. Solution strengthening due to the Cu diffusion may have also contributed to the hardness near the interface. The regions closer to the interface experienced higher rates of softening by recovery over the initial 2 hours, as also seen in Figure 6.2. More importantly, subsequent hardening (due to precipitation) is significant only in regions very close to the interface, i.e., at 3 µm, while the hardness
remained virtually constant around 53 - 54 HK at 22 µm. These features can be understood only on the basis of Cu diffusion from the Cu foil.

![Hardness vs Aging Time](image)

**Figure 6.2:** Hardness of the Al 1100 - Cu specimens ultrasonically joined for 1.25 s at 413 K (140 °C) under 56 MPa normal pressures at different distance from the interface versus aging time for 0, 2, 5, 12, 24 hours during the post-joining heat treatments at 413 K (140 °C).

6.4 Simulation of additional Cu diffusion during heat treatment experiments

The hardness data in Figures 6.1 and 6.2 provide further evidence for the diffusion of Cu from the Cu foil into the Al 1100 sheet in addition to the EDS data in Figure 5.3 of Chapter 5. However, since the specimens were heat treated with the Cu foil joined to the
Al 1100 sheet, the hardness data in Figures 6.1 and 6.2 may reflect not only the Cu diffusion during joining but also possible additional Cu diffusion from the Cu foil during the post-joining heat treatment. Prolonged holding at a post-joining heat treatment temperature may also extend the diffusion depth, which was about 3 \( \mu \text{m} \) in the as-joined specimens (See Figure 5.3 in Chapter 5). A discussion is therefore provided in this section to facilitate a better interpretation of the hardness data in Figures 6.1 and 6.2 for the ultimate purpose of assessing the extent of prior Cu diffusion that took place when the Al 1100 sheet and Cu foil were ultrasonically joined at the nominal temperatures of 289 K - 413 K (25 °C - 140 °C).

The biggest difference between the Cu diffusion during ultrasonic joining and post-joining heat treatment is that the diffusivity in the latter is no longer boosted by the strain-induced excess vacancies that were present during the ultrasonic joining. This brings down the copper diffusivity by many orders of magnitude in the post-joining heat treatment. At such reduced (normal) diffusivity, short-range diffusional processes such as the precipitation of G-P zones, \( \theta \), \( \theta' \), and \( \theta'' \), in the supersaturated diffusion zone may proceed substantially before the Cu in the diffusion zone is carried away into the deeper bulk of the aluminum by long range diffusion. Therefore, two extreme conditions are considered here as the lower and upper bounds of the additional Cu diffusion from the Cu foil to the Al 1100 sheet.

**Lower bound case:** First we qualitatively discuss the case where no additional Cu enters the Al and precipitation precedes the long-range Cu diffusion toward the far field. The initial supersaturation for the precipitation in the diffusion zone is represented by the
Cu concentration profile as determined by EDS which is fitted to a complementary error function,

\[ C(z) = C_\infty + (C_s - C_\infty) \text{erfc} \left( \frac{x}{2 \sqrt{Dt}} \right) \]  \hspace{1cm} (6.1)

where \( C_\infty \) is the Cu concentration of the 1100 Al sheet (0.15 wt.%), \( C_s \) is the Cu concentration at the interface (50.075%), and \( D \) is the enhanced diffusivity during ultrasonic joining and \( t \) is the ultrasonic joining time (1.25 s). To keep the discussion simple, consider only the equilibrium intermetallic phases, \( \theta \) and \( \eta_2 \), as the precipitating phases, Figure 6.3. Figure 6.4 schematically illustrates where in the diffusion zone these phases may form together with the initial profile of Cu concentration. We see that the initial diffusion zone is transformed to three regions, namely a two phase region of \( \eta_2 \) and \( \theta \) just next to the interface followed by a two phase region of \( \theta \) and \( \alpha \) (solid solution of Cu in Al) and a single-phase \( \alpha \) region that extends into the deeper bulk of the Al. The \( \eta_2 + \theta \) region occurs at the interface where Cu concentration exceeds 33.3 at.%. In the \( \theta + \alpha \) region next to the \( \theta + \eta_2 \) region, Cu concentration ranges from 33.3 at.% to the equilibrium solubility of Cu in Al at the heat treatment temperature (\( C_{Cu}^{\alpha+\theta} \) in Figure 6.4).
The depths of the three regions depend on the local Cu concentration which changes with time as the overall transport of Cu toward the far-field takes place. Figure 6.5 shows schematically (a) the Gibbs free energy curves of the $\alpha$, $\theta$ and $\eta_2$ phases and (b) the profile of the chemical potential of Cu across the diffusion zone. It is clear that the overall transport of Cu will bring Cu toward the far field, decreasing the depths of the $\theta + \eta_2$ region, and ultimately that of the $\theta + \alpha$ region as well. However, this is a slow process which is most probably limited by the diffusion of Cu in the $\alpha$ region where $d\mu_{Cu}/dx < 0$. Therefore, in this scenario, the supersaturation in the diffusion zone is consumed mostly by the precipitation of the secondary phases ($\theta$ and $\eta_2$) while the overall transport of Cu toward the far field is sluggish.
Figure 6.4: Concentration profile and phase evolution in the diffusion zone

Figure 6.5: (a) Free energy – composition diagram for $\alpha$, $\theta$ and $\eta_2$ at a post-joining heat treatment temperature.
Figure 6.5: (b) Profile of chemical potential of Cu in the diffusion zone.

**Upper bound case:** Consider also the case where no precipitation occurs in the diffusion zone as additional Cu enters the Al. Such a scenario is not realistic and is considered only as an extreme opposite to the lower bound case where precipitation precedes the overall transport of Cu. The problem then reduces to solving the diffusion equation for a semi-infinite medium

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{6.2}
\]

where \(x\) is distance from the interface and \(D\) is the normal diffusivity, with the boundary conditions
\[ C = C_s, \; x = 0, \; t > 0 \]

\[ C = C_\infty, \; x = 4.5, \; t > 0 \]

and the initial condition given by Eq. (6.1).

Eq. (6.2) was solved for the specimen ultrasonically joined at 413 K (140 °C) and heat treated for 5 and 24 hours. The initial profile was calculated with the enhanced diffusivity, \(2.22 \times 10^{-13} \; \text{m}^2/\text{s}\) (Table 2) in section 5.2, and a joining time of 1.25 s. Appendix D shows the MatLab\textsuperscript{©} code used for the calculations. Figures 6.6 and 6.7 show (a) the Cu concentration at different positions and times, (b) the initial and final Cu concentration profiles and (c) the % increase in Cu concentration at different positions and times, calculated over a distance of 4.5 µm from the interface for specimens heat treated for 5 and 24 hours, respectively. The increase in Cu concentration due to additional diffusion from the Cu foil is best examined from Figures 6.6(b) and 6.7(b) where the initial and final concentration profiles are shown for holding times of 5 hours and 24 hours, respectively. The additional amount of Cu gained in the Al 1100 due to the diffusion from the Cu foil during the heat treatment is the area between the two profiles, \(S_t\), (shown dark). Thus, the percent increase is calculated with

\[
Y = \frac{S_t}{S_t + S_0} \times 100\% \quad (6.3)
\]

where \(S_0\) is the area under the initial profile which represents the amount of copper diffusion that had occurred during the ultrasonic joining process. This yields \(Y = 17\%\) for the heat treatment time of 5 hours and 42\% for 24 hours. These values, however, are the upper bound values obtained for the scenario in which the precipitation of secondary phases, i.e., G-P zones, \(\theta^*, \theta', \theta\) and \(\eta_2\), is suppressed while allowing the diffusion of
Cu in \(\alpha\) to proceed at concentrations above the equilibrium solubility \(C_{Cu}^{\alpha/\theta}\), which would not happen.

The events that actually happened in the specimens during the post-joining heat treatment must lie between the two extreme scenarios. Although we do not know the exact amount of Cu gained in the Al 1100 during the post-joining heat treatment, its contribution to the precipitation hardening during the heat treatment must not exceed the extent that is possible at the upper bound value of Cu gain, 42% at 24 hours. Since the precipitation of secondary phases in Al-Cu alloys occurs over much shorter diffusion distances than the overall Cu transport in Al, it can hardly be suppressed. Therefore, we believe that the actual events during the heat treatment were better approximated by the lower bound scenario in which the precipitation hardening during the heat treatment is caused entirely by the Cu that enters the Al during ultrasonic joining. Hence, the hardening observed during the post-joining heat treatment, Figures 6.1 and 6.2, is likely due to the prior Cu diffusion into the Al during ultrasonic joining.
Figure 6.6: (a) Cu concentration in the diffusion zone of an ultrasonically joined and post-joining heat treated specimen calculated over a distance of 4.5 µm from the interface. The specimen was joined at 413 K (140 °C nominal temperature) and heat treated at 413 K (140 °C) for 5 hours. (a) C(x, t) surface at 5 hours. (b) The initial and final profiles. (c) Increase in Cu concentration due to additional Cu diffusion from Cu foil.
Figure 6.7: (a) Cu concentration in the diffusion zone of an ultrasonically joined and post-joining heat treated specimen calculated over a distance of 4.5 µm from the interface. The specimen was joined at 413 K (140 °C nominal temperature) and heat treated at 413 K (140 °C) for 24 hours. (a) $C(x, t)$ surface at 25 hours. (b) The initial and final profiles. (c) Increase in Cu concentration due to additional Cu diffusion from Cu foil.
7. Conclusions

1. Ultrasonic joining of Al 1100 sheet to copper foil at nominal joining temperatures of 298 - 414 K for 0.75 - 1.25 s caused significant copper diffusion into 1100 aluminum. EDS determined diffusion distances of up to 3 μm into the Al 1100 sheet.

2. Micro Koop hardness measurements in the vicinity of the joining interface revealed hardening above the bulk value which peaked at 413 K (140 °C), a characteristic of the precipitation hardening in Al-Cu alloys. This provides additional evidence of Cu diffusion during ultrasonic joining.

3. Post-joining heat treatment of joined specimens at 383 K (110 °C) to 413 K (140 °C) caused the hardness in the vicinity of the interface to decrease initially and increase thereafter. The initial softening and subsequent hardening are due to recovery and the precipitation of strengthening phases, respectively. This provides further evidence for the prior diffusion of copper into Al 1100.

4. The EDS diffusion data, through least square fitting to a complementary error function, translate into $D$ values of $1.54 \times 10^{-13}$ to $2.22 \times 10^{-13}$ m²/s that are much higher than the normal values ($D^{\text{norm}}$).

5. The experimental $D$ values are still well below typical values of liquid diffusivity at/near the melting point by a factor of $10^4$. Comparable liquid diffusivity values are calculated only at temperatures below the nominal joining temperatures, indicating that melting was not involved in the ultrasonic sheet joining experiments.

6. The estimated $D$ values reflect high excess vacancy mole fractions ($X_v$) caused by the ultrasonic deformation in the joining surfaces which may have been many orders
of magnitude above the thermal equilibrium values ($X^e_v$) and might have even reached a plateau value as high as 0.1.

7. If the plateau $X_v$ value were actually 0.1, the corresponding values of interface temperature ($T_{int}$) for specimens joined at nominal temperatures of 298 - 413 K, estimated from the substitutional diffusion equation $D / D^{norm} = X_v / X_v^{eq}$, would range from 521 K to 533 K, about 400 K below the equilibrium melting point of aluminum. Higher interface temperatures of 545 - 559 K are predicted if $X_v = 0.05$.

Thermodynamic calculations verify the stability of solid aluminum with excess vacancies over liquid aluminum at the calculated interface temperatures.

8. The estimated interface temperatures are nearly constant (not a strong function of nominal joining temperature) up to about 373 K, which may explain the effectiveness of ultrasonic joining even at room temperature.

9. The interface temperatures estimated with NMR data and our diffusion data fall in the range of direct measurements by infrared pyrometry and thermocouple measurements.
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APPENDIX A: Least square fitting of EDS profile

Since the diffusion couples are made of 1100 Al and pure copper, \( C(z) = C_\infty + (C_S - C_\infty) \text{erfc}(z) \) should represent the concentration profile across the interface. Strictly, however, the use of the complementary error function requires that both sides of the diffusion couple form solid solutions with full miscibility so that the concentration profile is a continuous curve with a mid value of \( C(0) = (100 + C_\infty)/2 \approx 50\% \). This is certainly not the case for equilibrium states of the Al-Cu alloy system. Nonetheless, it may be assumed that rapid diffusion in the presence of a high concentration of excess vacancies may substantially precede the precipitation of intermetallic, at least over the duration of ultrasonic vibration (1.25 s).

The complementary error function then allows estimating the diffusivity from the EDS data by least-square fitting. In the present analysis, the \text{erfc} \ curve is shifted towards the data points such that the points on the \text{erfc} \ curve \((C, z)\) are placed at \((C, kz)\) so that the matching of the \text{erfc} \ curve with the data points is best when \( k = 2\sqrt{Dt} \). For \( n \) data points \((C_i, x_i)\), this condition is found by minimizing \( S \) given by:

\[
S = \sum_{i=1}^{n} [z(C_i) \cdot k - x_i]^2
\]

(A-1)

where \( z(C_i) \) is the value of \( z \) at which \( C_i = C_\infty + (C_S - C_\infty) \text{erfc}(z) \). Solving \( dS/dk = 0 \) or

\[
k = \frac{\sum_{i=1}^{n} x_i z(C_i)}{\sum_{i=1}^{n} z(C_i)}
\]

(A-2)

for \( k \) yields the value of \( D \) from \( D = (k/2)^2/t \).
APPENDIX B: Melting point depression

High stain rate plastic deformation of metals introduces a large amount of excess vacancies in additions to the thermal vacancies [1.1 - 1.3]. The excess vacancies may affect the thermodynamic stability of the metal that contains them as well as the substitutional diffusion as seen in 5.2. Excess vacancies affect the thermodynamic stability since their inclusion in the lattice of the solid metal increases the Gibbs free energy of the solid [2.14]. Such an increase in $G$ may be large enough to put the $G$ of the vacancy-containing solid above that of the liquid phase, thereby making it possible for the solid to transform to liquid below the equilibrium melting point [2.14]. The degree to which such melting point depression may occur depends on the vacancy concentration $X_v$, and can be assessed from the following simple thermodynamic calculation:

The free energy of a solid metal containing vacancies, $G_s(X_v)$, is given by

$$G_s(X_v) = G_{sp} + n_v g_v - T \Delta S$$

(B-1)

where $G_{sp}$ is the free energy per mole of a perfect solid without vacancies, $n_v$ is the number of vacancies per mole of solid, $g_v$ is the free energy of a vacancy and $\Delta S$ is the change in entropy associated with introducing the vacancies in the solid. Eq. (B-1) may be rewritten with $G_s$, the free energy of the solid containing thermal vacancies as

$$G_s(X_v) = G_s + n_v g_v - T \Delta S$$

(B-2)
which is justified since \( G_{sp} \approx G_s \). In the present work, the values of \( G_s \) extracted from THERMOCALC\textsuperscript{©} at different temperatures were curve-fitted to obtain

\[
G_s = -0.0179 T^2 - 24.487 T + 647.75 \text{ (J/mole)}
\]

(B-3)

Assuming random (ideal) mixing of vacancies in the solid, Eq. (B-2) can be further rewritten as

\[
G_s(X_v) = G_S + \frac{X_v G_v + RT[X_v \ln X_v + (1 - X_v) \ln (1 - X_v)]}{1 - X_v}
\]

(B-4)

where \( G_v \) is the free energy per mole of vacancies in the solid. \( G_v \), which is equal to \( N_a g_v \) where \( N_a \) is Avogadro’s number, is obtained from the equation of the equilibrium concentration of thermal vacancies in pure aluminum [5.24].

\[
X_v^{eq} = 2.226 \exp \left(-\frac{59,820}{RT_{eq}}\right)
\]

(B-5)

which gives

\[
G_v = 59820 - 6.653 T
\]

(B-6)

The melting point of aluminum at a vacancy concentration \( X_v \) then is calculated from

\[
G s (X_v) = G_L
\]

(B-7)

where \( G s (X_v) \) is given by Eq. (B-4) and \( G_L \) may be extracted from THERMOCALC\textsuperscript{©} which gives
\[ G_L = -0.0176 T^2 - 36.617 T + 11707 \text{ (J/mole)} \]  

(B-8)

Eq. (B-7) when written with Eqs. (B-3), (B-6) and (B-8), is rewritten as

\[ -0.0003T_m^2 + 12.13T_m - 11059.25 + \frac{X_v(59820 - 6.653T_m) + RT[X_v\ln X_v + (1-X_v)\ln(1-X_v)]}{1-X_v} = 0 \]  

(B-9)

Solving Eq. (B-9) for \( T_m \) at various values of \( X_v \) yields the plot of normalized melting point, \( T_m/T_m^{eq} \), for pure aluminum shown in Figure 5.6

Significant melting point depression is predicted as \( X_v \) exceeds 0.1, as seen in Figure 5.6. The reduced melting point being as low as 496 K (223 °C) when calculated at \( X_v = 0.1 \). The strain-induced melting point depression is only a hypothesis at present, but may play an important role in high strain-rate plastic deformation which is known to produce vacancies in a very high concentration, possibly above 0.01 [1.14]. It is of particular interest to investigate if local melting occurs in ultrasonic joining in which an elevated temperature is experienced at the joining interface.
APPENDIX C: The melting point depression calculation

```matlab
clc
clear
s=0.8*1.380658e-23*6.0221367e23;
h=0.62*1.602177e-19*6.0221367e23;
syms T
syms x
y1=-0.0003*T^2+[12.13+1/(1-x)*(-x*s+8.314462*(x*log(x)+(1-x)*log(1-x))))]*T-11059.25+x/(1-x)*h;
x=1e-5:1e-3:0.101;
for ii=1:101
    y2(1,ii)=subs(y1,x(ii));
end
for ii=1:101
    y3=vpa(solve(y2(ii),T));
    y(ii)=y3(1);
end
plot(x,y/933)
```

APPENDIX D: Simulation of additional Cu diffusion during post-Joining heat treatment experiments

function main

clc;
clear all;
close all;

C0 = 0.15;
C1 = 50.075;
D = 6.72e-6;
Dc = 0.222;

% total time
t_total = 86400;

t0 = 1.25;
% x = linspace(0,3,20);
% x0 = C0+(C1-C0)*erfc(x./(2*sqrt(Dc*t0)));

% space interval
x = linspace(0,4.5,30);

% time interval: 0 ~ t_total
% t = linspace(0,t_total,t_total*10);

m = 0;

sol = pdepe(m,@pdex1pde,@pdex1ic,@pdex1bc,x,t);

% Ctr(:,step) = sol(:,size(t,2),1);

u = sol(:,:,1);

% write solution u to file C.txt
fid = fopen('C.txt','w');
for i= 1:size(u,1)
    for j= 1:size(u,2)
        fprintf(fid,'%e	',u(i,j));
    end
    fprintf(fid,'\n');
end
fclose(fid);
figure;

index = 1:size(t,2)/50:size(t,2);

surf(x,t(index),u(index,:))
xlabel('Distance x')
ylabel('Time t')
zlabel('C')

figure;

du = zeros(size(u));
for tt = 1:size(t,2)
    du(tt,:) = abs(u(tt,:)-u(1,:));
end

surf(x,t(index),du(index,:))
xlabel('Distance x')
ylabel('Time t')
zlabel('C - C0')

mm = 0;
%------------------------------------------------
function [c,f,s] = pdex1pde(x,t,u,DuDx)
    c = 1/D;
    f = DuDx;
    s = 0;
end

function u0 = pdex1ic(x)
    u0 = C0+(C1-C0)*(1-erf(x./(2*sqrt(Dc*t0))));
end

function [pl,ql,pr,qr] = pdex1bc(xl,ul,xr,ur,t)
    CC0 = 50.075;
    CC1 = 0.15;
    pl = ul-CC0;
    ql = 0;
    pr = ur-CC1;
    qr = 0;
end