Critical interlayer thickness for transient liquid phase bonding in the Cu–Sn system

N.S. Bosco, F.W. Zok *

Materials Department, University of California, Santa Barbara, CA 93106, USA

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Abstract

The study focuses on the critical interlayer thickness for averting pore formation during transient liquid phase (TLP) bonding in the Cu–Sn system. Such pores are a consequence of the growth and subsequent contact of Cu₆Sn₅ intermetallic grains on the two surfaces to be bonded, prior to the formation of the transient liquid phase. A criterion for the critical interlayer thickness is developed, based on the heights of the largest intermetallic grains. Experiments are performed to ascertain the growth kinetics and the morphology of the intermetallic as a function of heating rate. On this basis, TLP bonding experiments are designed and implemented to demonstrate the transition from pore-containing to pore-free bonds as the interlayer thickness exceeds the predicted critical value. The benefits of high heating rates on both the critical interlayer thickness and the bonding time needed to achieve a targeted terminal microstructure are illustrated.

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1. Introduction

Transient liquid phase (TLP) bonding has been used widely for attachment of metals [1–5], ceramics [6,7] and composites [8]. The process employs a low melting point interlayer between the base metals to be joined and relies on interdiffusion for isothermal solidification at the bonding temperature. The integrity of the resulting bonds is enhanced by the presence of the liquid phase during bonding, yet the bonds are able to withstand operation at temperatures above the bonding temperature once solidification is complete.

The present article focuses on the use of TLP bonding of Cu using Sn as the interlayer material. This system is motivated in part by the widespread use of Cu in high temperature electronic products, especially on ceramic substrates, and its potential as a device metallization layer. The choice of Sn as the interlayer material stems from its low melting point (232 °C) and its relatively high solubility in Cu: in excess of 10% above 350 °C.

Additionally, when the process is taken to completion to form a Cu solid solution through the entire bonded region, the solidus temperature of the bond can exceed 800 °C. This sets the limit on the upper use temperature of the bonded structure. Indeed, previous studies have shown that this system has potential for creating robust bonds and may offer an alternative to existing solders [4].

The specific objective of this work is to identify the critical interlayer thickness to produce pore-free bonds. The critical value arises in the following way. During heating to the bonding temperature, the interlayer material reacts with the base material through interdiffusion. For successful bonding, the thickness of the interlayer must exceed that which is consumed through solid state diffusion; otherwise, no liquid is formed at the bonding temperature. This sets a minimal requirement on the interlayer thickness. Furthermore, as demonstrated in the present study, the interaction between the two may lead to the formation of an intermetallic with a non-planar interface. A possible consequence is that the largest intermetallic grains on the opposing surfaces come into contact before the interlayer melts. As a
result, the two surfaces are constrained from approaching one another once the remaining interlayer material melts, setting up conditions for pore formation during subsequent melting, interdiffusion and solidification. This sets a higher minimal requirement on interlayer thickness, above that associated with a planar interface. Provided the critical thickness is exceeded, the subsequent isothermal solidification occurs by diffusion of the interlayer material into the base material. Consequently, the time to complete the bonding process and achieve a targeted microstructure is proportional to the square of the interlayer thickness. To minimize bonding time and temperature, thin interlayers are preferred. The implication is that an optimum exists, slightly above the critical value, to ensure robust bonds at minimum bonding time.

The article is organized in the following manner. First, some of the basic features of TLP bonding are reviewed. Next, as motivation for this study, results from preliminary bonding experiments, showing the formation of pores along the bond mid-plane, are presented. A mechanism for pore formation is proposed and a critical interlayer thickness for averting these pores is identified. The latter is dictated largely by the height of the largest intermetallic grains, formed upon heating to the bonding temperature. On this basis, experiments are conducted to determine the growth characteristics of this intermetallic and to ascertain the critical interlayer thickness. The results are then used to design critical experiments that demonstrate the transition from pore-containing to pore-free bonds as the critical thickness is exceeded. The mechanical properties of the latter bonds are addressed elsewhere [9]. Finally, an assessment is made of the related effects of heating rate and critical interlayer thickness on the time needed to achieve a Cu solid solution across the entire bonded region. It is demonstrated that significant reductions in bonding time can be achieved with increasing heating rate, because of the corresponding reductions in the required interlayer thickness.

2. Background on TLP bonding

The TLP bonding process is illustrated in Fig. 1 for a simple eutectic system [10]. Here the two substrates to be bonded are made of material A and the interlayer made of material B. The process can be divided into four stages: (i) Upon heating to the targeted bonding temperature, $T_B$, solid state interdiffusion occurs between the interlayer and the substrate. This reduces the amount of interlayer material available for subsequent melting. In extreme circumstances, wherein the initial interlayer thickness and/or the heating rate are very small, the interlayer material is completely consumed, precluding formation of a TLP at higher temperature. (ii) Upon reaching the bonding temperature (above the melting point, $T_B$), dissolution of the substrate causes widening of the liquid layer. Its maximum thickness is obtained when the composition of the entire liquid reaches the solubility limit, $C_L$. (iii) Further interdiffusion results in local isothermal solidification at the interface between the liquid and the solid substrate. This process is manifested in a reduction in the liguid layer thickness. It proceeds until all of the liquid is consumed and a solid joint is formed. (iv) Additional time at the bonding temperature leads to homogenization within the bonded region. That is, the peak solute concentration diminishes progressively with time, below the solubility limit, $C_L$, through further solid state diffusion [11]. This has the effect of raising the solidus temperature of the bond, gradually approaching the melting point of material A.

Although a similar sequence is obtained during TLP bonding in the Cu–Sn system, some additional features arise because of the formation of intermediate phases (Fig. 2). In the context of the present study, the most notable one is $\eta$(Cu$_6$Sn$_5$): a phase that persists up to 415 °C. Its growth in the solid state during heating proves to be the dominant factor in the critical interlayer thickness. Among the other phases, $\delta$(Cu$_{41}$Sn$_{11}$) is the most critical in determining the time needed to form a Cu-rich solid solution across the entire bond [12].
3. Preliminary bonding experiments

The motivation for this study came from a set of preliminary bonding experiments on Cu–Sn–Cu sandwich specimens. The conditions for these experiments were seemingly ideal for producing good bonds, yet they yielded extensive porosity along the bond mid-plane, as detailed below. Bonding was carried out in the following manner.

Copper substrates, 10 mm × 10 mm × 2.5 mm thick, were ground and polished to a 6 µm finish using a suspension of diamond paste. They were then degreased, pickled in a 5% HCl solution, rinsed in de-ionized water and blown dry. In preparation for bonding, two layers were deposited sequentially onto the substrates using a dual gun electron-beam deposition (EBD) system: a 25 µm layer of Cu, followed immediately by a 5 µm layer of Sn. Deleterious effects of oxidation of the Cu surfaces were minimized by keeping the samples in the chamber between deposition of the two layers and minimizing the intervening time. Substrate heating during deposition was mitigated by employing a water-cooled substrate mount. After removal from the EBD chamber, pairs of such samples were placed into contact along the Sn surfaces and bonded in a vacuum chamber. To prevent movement, a small weight, producing a compressive stress of about 0.001 MPa, was placed on top. The chamber pressure was maintained below 10⁻⁵ torr. The samples were heated at a rate of 5 K/min up to the targeted bonding temperature of 550 °C, held at this temperature for 2 h and subsequently cooled to ambient at approximately 5 K/min. The targeted terminal microstructure was a two-phase mixture of δ and (Cu), formed through the eutectoid reaction at 520 °C (Fig. 2). The bonded samples were then sectioned, polished and examined by both optical and scanning electron microscopy.

4. Proposed mechanism of pore formation

Typical cross-sections through these bonds are shown in Fig. 3. The most notable features are the pores that exist along the bond mid-plane. The lengths of the pores, measured parallel to the bond plane, varied from about 10 to 300 µm. SEM observations of fracture surfaces confirmed the presence of these pores (Fig. 4). In the latter case, they were manifested as rather smooth amorphous surfaces, clearly distinguishable from the cleavage facets passing through the bonded regions. Such pores are expected to compromise the mechanical integrity of the bonds, especially when present in the quantities seen in Fig. 3. A proposed mechanism for their formation is described below.
the \( \eta \)-phase. If all of the Sn is consumed in forming \( \eta \) before the melting point of Sn is reached, then no Sn is available for the formation of a TLP at higher temperatures, thereby precluding TLP bonding. This scenario represents the most extreme form of a bonding defect. In contrast, if some Sn remains once the melting point of Sn is reached, three possible scenarios can be obtained. These are illustrated in Fig. 5 and described below.

(i) If growth of the \( \eta \)-phase occurs in a planar manner, the remaining Sn melts and forms the requisite TLP. This scenario sets a lower limit on the thickness, \( 2h_{c} \), of the Sn layer needed to affect TLP bonding. From a mass balance, the critical thickness is:

\[
h_{c} = h_{\eta}C_{\eta}\left(\frac{\rho_{\eta}}{\rho_{\text{Sn}}}\right)^{2},
\]

where \( 2h_{\eta} \) is the total thickness of the \( \eta \)-phase when the melting point of Sn is reached, \( C_{\eta} \) is the mass fraction of Sn in the \( \eta \)-phase, and \( \rho_{\eta} \) and \( \rho_{\text{Sn}} \) are the mass densities of \( \eta \)-phase and Sn, respectively.

(ii) If growth of the \( \eta \)-phase occurs in a non-planar manner and the Sn layer thickness is only slightly greater than \( 2h_{c} \), then the two \( \eta \) layers contact one another at discrete points before the Sn melts. Upon further heating, the remaining Sn melts, but subsequent reaction with the Cu is constrained by the solid \( \eta \)-grains that span the two surfaces. Assuming that these contacts are rigid, the consumption of Sn through reaction with Cu leads to a net deficit of material within the confined volume, ultimately leading to void formation near the bond mid-plane. This scenario sets a higher requirement, \( 2h_{c}^{*} \), on the initial Sn layer thickness, given by

\[
h_{c}^{*} = h_{c}\Omega = h_{\eta}C_{\eta}\left(\frac{\rho_{\eta}}{\rho_{\text{Sn}}}\right)^{2}\Omega,
\]

where \( \Omega \) is a non-dimensional parameter that characterizes the degree of non-uniformity in the thickness of the \( \eta \)-phase. If the largest grains that make contact are of height \( H_{\eta}^{0} \), then, from geometry, \( \Omega \) is given by:

\[
\Omega = 1 + \left(\frac{H_{\eta}^{0} - h_{\eta}}{h_{c}}\right).
\]

In general, \( H_{\eta}^{0} > h_{\eta} \) and hence \( \Omega > 1 \). In the planar interface limit, \( H_{\eta}^{0} = h_{\eta} \) and hence \( \Omega = 1 \).

(iii) If growth of the \( \eta \) occurs in a non-planar manner and the Sn layer thickness is greater than \( 2h_{c}^{*} \), the Sn melts before the \( \eta \)-layers come into contact. Consequently, TLP bonding proceeds, unimpaired by the presence of the transient \( \eta \)-phase.

The subsequent experiments were conducted to ascertain the growth rate of the \( \eta \)-phase and, in turn, the critical Sn layer thickness for several heating rates. The results were then used to design additional bonding experiments in the regime in which pore-free bonds are predicted.

5. Solid state growth of \( \eta \)-phase

The critical Sn layer thickness was ascertained from experiments on solid state growth of the \( \eta \)-phase during heating. Samples for this part of the study were produced in essentially the same manner as that used for the bonding experiments. Notably, clean Cu substrates were coated with both Cu and Sn by EBD. For the growth experiments, the Sn layer was 20 \( \mu \)m thick, to ensure adequate supply during subsequent growth. Following deposition, individual coated samples were heated in a rapid thermal anneal furnace under flowing gas of Ar–5% H\(_2\). Three heating rates were employed: 2, 5, and 15 K/min. The samples were heated to a temperature of 228 °C, just below the melting point of Sn (232 °C), and cooled to ambient at a rate of 100 K/min. Following cooling, the specimens were cut with a low speed diamond saw perpendicular to the coated surfaces. One half of each specimen was mounted in epoxy, polished along the cutting plane and examined in both optical and scanning electron microscopes. Phase identification was made using energy dispersive spectroscopy (EDS) in the SEM. The other half of each pair was etched with a solution of 5% HCl in methanol. This etchant removes the unreacted Sn, thereby revealing the underlying intermetallic grain morphology. These surfaces were also examined in the SEM.

Representative micrographs from both the polished sections and the etched coated surfaces are shown in Figs. 6 and 7. The \( \eta \)-phase grows as a series of roughly hemispherical grains, thereby creating a scalloped
interface with the adjoining Sn. Furthermore, a thin uniform layer of ε-phase resides between the η-grains and the Cu substrate. Similar observations have been reported previously [13–17].

The grain morphology was characterized by three complementary parameters: (i) The average grain radius, \( \bar{R} \), in plan view of the coated surfaces was determined from a count of the number of grains per unit area. The results are plotted in Fig. 8 against the heating time: \( t_h = \frac{\Delta T}{T} \) with \( \Delta T \) being the temperature change (208 K) and \( T \) the heating rate. The grain radius follows a power law with time with an exponent of about 0.3. A similar scaling had been obtained in an earlier study, for isothermal exposures, and rationalized on the basis of a model for volume diffusion limited grain coarsening [17]. (ii) The average thickness \( h_\eta \) of the intermetallic layer was determined from area measurements on the polished sections using image analysis software. These results are also plotted in Fig. 8. (iii) The apparent heights \( H_\eta \) of the individual grains were measured from micrographs of the polished sections. At least 100 such measurements were made for each heating rate. The resulting distributions are shown in Fig. 9 and the average values plotted in Fig. 8.

Also shown in Figs. 8 and 9 are the expected results for the true average grain height and the distribution of
the apparent height, assuming: (i) that the grains are equi-sized hemispheres of radius $R$, and (ii) that the variation in apparent heights is due to the 2-dimensional nature of the imaging procedure. A rudimentary analysis of the apparent height of a randomly sectioned hemisphere yields a cumulative distribution function, $P(H_g)$, given by:

$$P(H_g) = 1 - \left[ 1 - \left( \frac{H_g}{R} \right) \right]^{1/2}$$

and an average apparent height of

$$H_g = \frac{\pi R}{4}.$$  \hspace{1cm} (5)

Interestingly, the distributions calculated by Eq. (4) appear to have similar shape to that of the measured distributions, especially at the low end. This suggests that a significant portion of the apparent breadth of the distribution is a consequence of stereology, rather than being a reflection of the real size distribution. Furthermore, the inferred average grain radius (from Eq. (5)) is essentially equivalent to the value obtained from the plan view measurements (Fig. 8). This result re-affirms the conclusion that the grains are approximately equi-sized hemispheres.

Despite these correlations, each of the height distributions clearly exhibits a flat “tail” at large values of $H_g$, deviating significantly from the shape predicted for equi-sized hemispheres. Indeed, these large grains are believed to be responsible for the bonding defects described in Sections 2 and 3. That is, during bonding, these grains make contact with one another on the opposing surfaces before the Sn melts. The subsequent analysis focuses on this part of the distribution and its effect on the critical interlayer thickness.

6. Critical bonding experiments

The predicted critical Sn layer thickness for averting pore formation was assessed through a small number of bonding experiments, using a heating rate of 5 K/min. Samples for bonding were produced in the manner described above, with Sn layer thicknesses of $h_{Sn} = 5$, 10 and 15 µm. Upon bonding, these samples produce total Sn layer thicknesses of $2h_{Sn} = 10$, 20 and 30 µm. The first of these ($2h_{Sn} = 10$ µm) lies in the lower part of the band that defines the critical thickness, $2h_c$, for the prescribed heating rate (corresponding to $\Delta T/T = 41$ min), but well above the limit for planar growth: $2h_c \approx 3$ µm.
Fortuitously, this interlayer thickness had been used in the preliminary bonding experiments, presented in Section 2. The latter two values \((2h_{\text{Sn}} = 20 \text{ and } 30 \mu m)\) were selected to lie above the critical thickness. Bonding was performed according to the procedure described in Section 3. The bonded samples were subsequently sectioned and polished. Micrographs of the polished sections are shown in Figs. 3 and 11. As noted earlier, the samples with either 20 or 30 \(\mu m\) Sn layers, there was no detectable porosity. The transition in bond quality is consistent with the predictions of critical thickness shown in Fig. 10 and provides preliminary validation of the proposed mechanism of pore formation. Furthermore, the presence of pores in samples with 10 \(\mu m\) layers confirms the notion that the critical thickness \(2h_c \approx 3 \mu m\) calculated on the basis of a planar interface is non-conservative. That is, the non-uniformity of the \(\eta\)-grains must be taken into account in the selection of the Sn layer thickness.

7. Implications for design of bonding schedule

The preceding results have been used to assess the related effects of heating rate and critical interlayer thickness on bonding time and temperature. The targeted terminal microstructure consists of a single phase Cu-rich solid solution throughout the entire bonded region. The time required to achieve the targeted state is assumed to be dictated by that associated with the consumption of the most Cu-rich intermediate phase: the \(\delta\)-phase, for \(350 ^\circ C < T < 520 \circ C\). This assumption is supported by an experimental study on phase evolution in Cu–Sn bonds [12]. That is, in the pertinent temperature regime, the time required to fully consume all other phases, including liquid Sn, \(\eta\) and \(\epsilon\), is at least an order of magnitude smaller than that for conversion of \(\delta\) to Cu solid solution. Additionally, to ensure adequate reserve of Sn for the formation of the TLP, the interlayer thickness is taken to be 50% greater than the critical value: \(2h_{\text{Sn}} = 1.5(2h_c^*)\), with \(h_c^*\) evaluated using the top 1% value for the critical \(\eta\)-grain height. The full analysis of the moving boundary problem is presented elsewhere [18]; only the key results for the time to completion are presented below.

Assuming the process to be diffusion-limited, the time \(t_c\) needed to consume a layer of \(\delta\)-phase of thickness \(2h_\delta\) in the formation of Cu solid solution is [18]:

\[
t_c = \frac{(2h_c)^2}{16K^2 D_0} \exp \left( \frac{Q}{RT} \right),
\]

where \(K\) is a non-dimensional parameter that depends on the solubility of Sn in Cu and the concentration of Sn in \(\delta\); \(D_0\) and \(Q\) are the interdiffusion constants for the Cu solid solution; \(R\) is the gas constant and \(T\) is absolute temperature. An upper bound on \(2h_\delta\) is obtained by assuming that all of the Sn is consumed in the formation of \(\delta\). A mass balance leads to:

\[
2h_\delta = \frac{2h_{\text{Sn}}}{C_\delta} \left( \frac{\rho_{\text{Sn}}}{\rho_\delta} \right)^2,
\]

where \(C_\delta\) is the mass fraction of Sn in \(\delta\), and \(\rho_\delta\) is the mass density of the \(\delta\)-phase. In turn, the dependence of \(h_c^*\) and hence \(h_{\text{Sn}}\) on heating rate is given by a power law of the form:

\[
2h_{\text{Sn}} = 1.5(2h_c^*) = 1.5k \left( \frac{\Delta T}{\bar{T}} \right)^n,
\]

where \(k\) and \(n\) are the constants that characterize the uppermost data set in Fig. 10. Combining Eqs. (6) and (8) yields:

\[
t_c = \frac{1}{D_0} \left( \frac{3k}{8C_\delta K} \right)^{\frac{1}{n}} \left( \frac{\rho_{\text{Sn}}}{\rho_\delta} \right)^4 \exp \left( \frac{Q}{RT} \right).
\]

The pertinent parameter values are summarized in Table 1.

Fig. 12 shows the predicted variation in \(t_c\) with heating rate, \(\bar{T}\), for three representative bonding temperatures: 400, 450 and 500 \(\circ C\). It demonstrates that a significant reduction in bonding time can be achieved through an increase in heating rate. Specifically, because \(t_c \propto \bar{T}^{-2n}\) (with \(n = 0.3\)), a tenfold increase in \(\bar{T}\) leads to a fourfold reduction in \(t_c\). This effect is expected to be significant in the implementation of TLP bonding.
8. Conclusions

Intermetallic formation during heating leads to a critical interlayer thickness for successful TLP bonding in the Cu–Sn system. The critical value is dictated by the largest intermetallic grains. Below this value, contact is made between the intermetallic grains before melting begins, leading to the formation of pores during the subsequent bonding process. For practical implementation, a thickness only slightly above the critical value is preferred, allowing for the formation of the intermetallic during heating whilst retaining some reserve for subsequent melting. The consequence of an excessively thick interlayer, relative to the critical value, is an increase in the time required to achieve a targeted microstructure. Significant reductions in both the critical interlayer thickness and the bonding time can be achieved through an increase in the heating rate en route to the bonding temperature.

Acknowledgements

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References


Table 1

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<td>$C_g$</td>
<td>60%</td>
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</tr>
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<tr>
<td>$n$</td>
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<td>Fig. 10</td>
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<tr>
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Fig. 12. Effects of heating rate on the bonding time needed for complete consumption of the intermetallics, leaving the Cu solid solution as the terminal phase. The initial interlayer thickness is taken to be $h_{Sn} = 1.5h^*_c$. 

Fig. 10. Table 1: Summary of property values