

Transient Liquid-Phase Bonding in Two-Phase Ternary Systems

C.W. SINCLAIR, G.R. PURDY, and J.E. MORRAL

The process of isothermal solidification during transient liquid-phase (TLP) bonding in a ternary system is analyzed. In the most usual situation, and in contrast to the binary case, the composition of the liquid is required to change continuously as solidification proceeds. If the solubilities and/or diffusion coefficients of the two solutes are very different, the solidification stage is clearly divided into two parabolic regimes, the first dominated by the “faster” solute and the second by the slower of the two. In extreme cases, full solidification may not be realized in experimentally accessible times.

I. INTRODUCTION

THE problem of transient liquid-phase (TLP) bonding (along with the allied one of liquid-phase sintering) has received considerable attention in recent years. The joining process holds high promise for the controlled bonding of base materials; it involves the isothermal disappearance of a liquid phase at a rate determined primarily by solid-state diffusion. The liquid results from the placement at the joint of a thin layer (interlayer) with a melting point lower than that of the material to be joined. In the simplest case, the base material is a pure component, and the interlayer a binary alloy containing the base material as a solvent and a solute that lowers its melting point. In a more general case, the base material and the interlayer will be made up of more than two components. For the most part, the literature makes only passing reference to the possible effect of a third component (a second solute) on the process of isothermal solidification.^[1] This contribution builds on a previous communication dealing with the extension to the three-component problem.^[2]

The experimental situation is reviewed, along with the analysis of the binary problem in a recent article by Zhou *et al.*^[3] The process is considered as a sequence of distinct stages: heating to the joining temperature, isothermal solidification, and homogenization. The usual treatment of the isothermal solidification stage is relatively simple, as illustrated in Figure 1, for the case of bonding a pure element using an interlayer containing a solute,^[1] which lowers the melting point of the solvent. For a given temperature, the compositions of the liquid and solid in equilibrium are fixed. Once the interlayer material melts, it is assumed rapidly to come to equilibrium with the solid base material. (This equilibration process will generally involve the growth of the liquid phase from its initial volume.) In the subsequent solidification stage, the solute is taken from the liquid by solid-state diffusion; consequently, the interlayer shrinks, and eventually disappears. Under the reasonable assumptions of local equilibrium at the solid-liquid interface, planar solid-liquid interfaces, complete mixing in the thin liquid

layer, and constant diffusion coefficient in the solid, the binary solidification problem lends itself to a straightforward analytical treatment. For the isothermal solidification stage, the result is a parabolic time dependence of the liquid-layer thickness w on the diffusion length (\sqrt{Dt}) of solute 1 in the solid α phase^[3]:

$$w \propto \sqrt{D_1^\alpha t} \quad [1]$$

If we consider the ternary extension of this most elementary analysis, we find that the isothermal-solidification problem takes on a new level of interest and complexity. Each solute will have a characteristic pair of diffusion coefficients and a solubility in the solid phase that varies with the concentration of the other solute. It will often be sufficient to ascribe a constant partition coefficient ($k^{\alpha/l} = G^\alpha = C^l$) to each solute, particularly if the liquid is sufficiently dilute that Henrian behavior is a reasonable approximation.

In Figure 2, we assume that the base material is pure solvent. The figure illustrates an initial condition, formed on melting back of a ternary interlayer until the uniform liquid composition lies on the liquidus surface. The tie-line (shown as a broken line) defines the composition of the solid solution in local equilibrium with this liquid. A diffusion path will develop in the solid solution; this path will be determined by the solid-state diffusion coefficients D_{ik}^α . It is clear on a moment's reflection that the initial interfacial tie-line, corresponding to an arbitrary initial liquid composition, will not in general support a self-consistent solution of the diffusional solidification problem in which the solid and liquid interfacial concentrations are constant in time. A mass balance can be written for each solute, and the simultaneous satisfaction of the two mass balances will require, in general, that the interfacial, local equilibrium concentrations change continually during the course of solidification.

A number of possible situations may develop, as follows.

- (1) The most usual case will involve the continual shifting of the instantaneous interfacial tie-line, in a manner dictated by the two mass balances. This process will continue until the final liquid solidifies, leaving a set of solute profiles in the solid, which will relax by diffusion on further isothermal treatment. The last liquid to solidify will have a composition that depends on the full solidification history of the material. This case will be examined in detail later. However at this point, we note that within this class of transformations, we can distinguish those cases:

C.W. SINCLAIR, Graduate Student, and G.R. PURDY, Professor, are with the Department of Materials Science and Engineering, McMaster University, Hamilton, ON, Canada L8S 4L7. J.E. MORRAL, Professor, is with the Metallurgy and Materials Engineering Department, Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3136.

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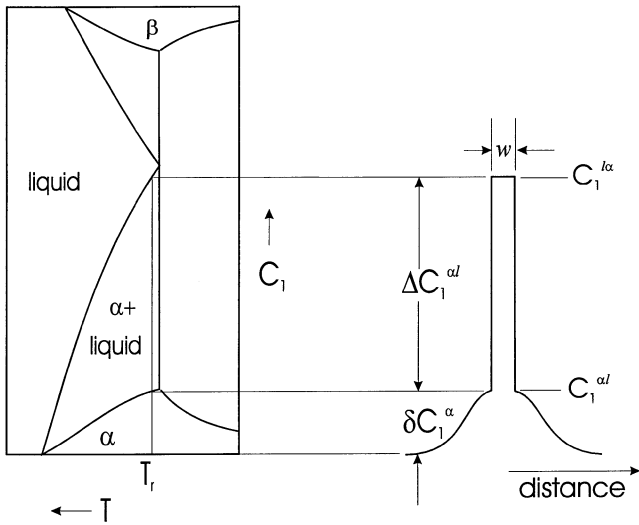


Fig. 1—Schematic illustration of the equilibrium condition between liquid interlayer and solid phase during isothermal solidification stage for a binary system. The interfacial concentrations are assumed constant and given by the local equilibrium conditions. The tie-line length is defined as $\Delta C_1^{al} = C_1^{l\alpha} - C_1^{al}$.

- (a) where the solubilities and solid-state diffusivities of the two solutes are similar; and
 - (b) where the solubility and/or the diffusivity of one of the solutes is much smaller than that of the other.
- (2) There is a special case of some interest, for which the liquid will solidify with constant composition equal to the initial composition formed on melting back. We will call this the *stationary case*. It can be understood as follows.

Referring to Figure 2, we write for each solute i :

$$\frac{dw}{dt} (\Delta C_i^{al}) = 2D_{ii}^{\alpha} \nabla C_i^{\alpha} \quad [2]$$

where w is the interlayer thickness. We have ignored diffusional interaction between solutes. If, as a further approximation, we assume the D_{ii}^{α} are constant, and that $\delta C_i^{\alpha} \ll \Delta C_i^{al}$, then the error function solutions for the concentration profiles apply, and

$$\nabla C_i^{\alpha} = \frac{\delta C_i^{\alpha}}{\sqrt{\pi D_{ii}^{\alpha} t}} \quad [3]$$

where δC_i^{α} is the concentration range of solute i in the base solid ($=C_i^{\alpha}$ in Figure 2, which is drawn for a pure solvent base material). D_{ii}^{α} is its diffusion coefficient in the solid. On equating velocities for the two solutes, 1 and 2, we obtain

$$\frac{\sqrt{D_{11}^{\alpha}} \delta C_1^{\alpha}}{\Delta C_1^{al}} = \frac{\sqrt{D_{22}^{\alpha}} \delta C_2^{\alpha}}{\Delta C_2^{al}} \quad [4]$$

which, in conjunction with the phase diagram, defines the stationary case for which interfacial concentrations will be constant throughout the isothermal solidification process. If in addition the phase diagram is characterized by constant solute distribution coefficients, then any initial composition on the liquidus surface will remain constant during the entire course of solidification.

- (3) A third case may be envisaged which involves the shifting of the interfacial tie-line until a particular liquid

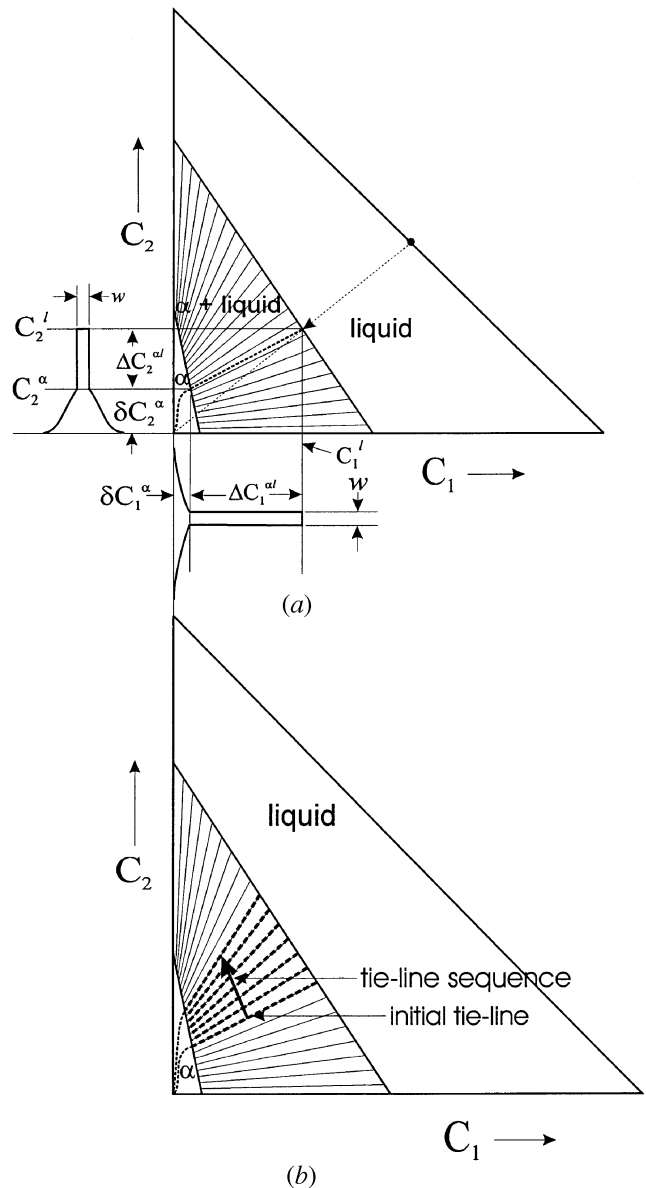


Fig. 2—In a ternary system, the initial liquid composition is arbitrary and set by the initial melting of the interlayer. (a) An early stage in the solidification process; the two mass balances for the two solutes (1 and 2) are represented by solute profiles. (b) A sequence of tie-lines, as determined by the requirement that the two mass balances be simultaneously satisfied.

composition is reached that will support a constant set of interfacial concentrations for the balance of the solidification step. We will call this liquid composition the *terminal liquid*, and the corresponding tie-line the *terminal tie-line*. Note, however, that this state is history dependent and that the condition given in Eq. [4] for the stationary tie-line is not relevant to this case.

A more rigorous treatment of the diffusion problem, which includes the full-diffusion matrix $[D^{\alpha}]$ and which allows for a base material that is also an alloy in the ternary system, is obtained as follows. The rate of change of the interlayer thickness is

$$\frac{\partial w}{\partial t} [\Delta C^{al}] = -2[D^{\alpha}] [\nabla C^{\alpha}] \quad [5]$$

Here, we have used the notation developed by Hopfe and Morral,^[4] in which column $[\]$ and row $(\)$ vectors are distinguished by differing parentheses. The concentration gradients in the α phase when $\delta C_i^\alpha \ll \Delta C_i^{\alpha l}$ are then given in terms of the square-root diffusivity^[5] as

$$[\nabla C^\alpha] = \frac{1}{\sqrt{\pi t}} [r^\alpha]^{-1} [\delta C^\alpha] \quad [6]$$

Equation [6] is based on the error-function solution to the diffusion equations and is exact in the limit where the ratio of w_0 to the diffusion distance approaches zero. Then

$$\begin{aligned} \frac{\partial w}{\partial t} [\Delta C^{\alpha l}] &= -\frac{2}{\sqrt{\pi t}} [D^\alpha][r^\alpha]^{-1} [\delta C^\alpha] \\ &= -\frac{2}{\sqrt{\pi t}} [r^\alpha] [\delta C^\alpha] \end{aligned} \quad [7]$$

Further, if we express the time dependence of the interlayer thickness w as $w = w_0 - \kappa\sqrt{t}$, we have

$$\kappa[\Delta C^{\alpha l}] = \frac{4}{\sqrt{\pi}} [r^\alpha] [\delta C^\alpha] \quad [8]$$

which relates the composition vector in the solid $[\delta C^\alpha]$ and the terminal tie-line $[\Delta C^{\alpha l}]$.

II. THE ISOTHERMAL SOLIDIFICATION PATH

We next inquire into the process of the evolution of the liquid composition from an arbitrarily set initial liquid composition. Clearly, if the two solutes have very different solid solubilities and diffusion coefficients in the solid state, then the interfacial tie-line will migrate along the two-phase region of the ternary isotherm toward the terminal compositions defined above in Eq. [8]. This shift of the local equilibrium tie-line with time is a consequence of the requirement that the two solute mass balances be simultaneously satisfied. If, for example, the solubility and solid-state diffusivity of component 1 yield the greater flux of this solute from the liquid layer, the solidification will proceed at a rate determined by component 1, and the slower diffusing solute, component 2, will be partitioned to the liquid. This is suggested by the schematic illustration of Figure 3, in which the solute flux of component 2 is taken as negligible.

The solution of this problem requires continual monitoring of interfacial concentrations in the solid and liquid phases; it is clearly suited to modelling using finite-difference methods. In Section III, we will describe two approaches: one involving simplified mass balances based on linear composition gradients in the solid phase in a manner first put forward by Zeners,^[6] and a second, in which the composition gradients in the solid are determined more completely. In both treatments, off-diagonal D_{ik} 's will be assumed negligible and the on-diagonal D 's constant.

III. COMPUTATIONAL METHODS

With the Gibbs isotherm defined by constant partition coefficients, the isothermal solidification of the liquid interlayer may be predicted *via* a simple mass balance. For this purpose, diffusion in the liquid layer was assumed to be rapid, such that there develops no gradient in the liquid. However, some means of modeling the diffusion profile in

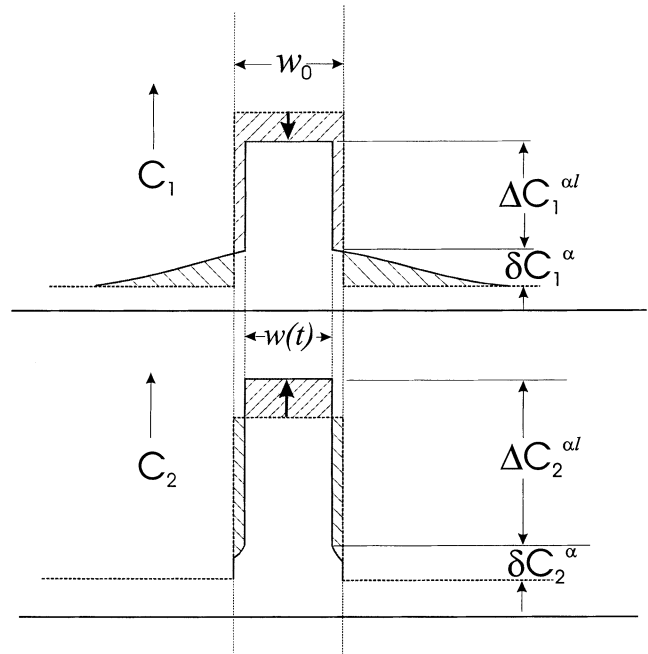


Fig. 3.—For the special case $D_{11} \gg D_{22}$, solute 1 will be removed from the liquid and solute 2 will be partitioned to the liquid, as indicated schematically here.

the solid must be made. To do this, two scenarios were examined. As a first approximation, the diffusion profile was assumed linear (*i.e.*, Zener's approximation). The concentration of the liquid (which may be completely defined by specifying the concentration of one component and invoking local equilibrium) could then be iterated along the two-phase boundary. The two mass balances (one for each solute) must be satisfied:

$$\begin{aligned} C_{j+1}^\alpha \sqrt{D^\alpha(t + \Delta t)} - C_j^\alpha \sqrt{D^\alpha t} \\ = C_j^L w - C_{j+1}^L (w + \Delta w) \end{aligned} \quad [9]$$

where the superscripts α and L refer to the solid and liquid, respectively. The subscript $j + 1$ refers to the current interfacial concentration, while the subscript j refers to the previous interfacial concentration. By iterating the concentration ($C_j^\alpha \rightarrow C_{j+1}^\alpha$), the change in the width of the interlayer ($2\Delta w$) and the increment in time needed to reach that width (Δt) may be found.

The advantage of the preceding scheme is its simplicity of implementation. However, the assumption of linear diffusion profiles is often an inaccurate one. For this reason, an explicit finite-difference approach was used to model more precisely the diffusion profiles in the solid. With this method, the flux in the solid phase at the interface at some time t may be written as

$$J_i = D_{ii}^\alpha \frac{\delta C_i^\alpha}{\Delta x} = D_{ii}^\alpha \frac{C_i^\alpha(x=0) - C_i^\alpha(x=\Delta x)}{\Delta x} \quad i = 1, 2 \quad [10]$$

where the interface is defined at $x = 0$ and Δx represents the distance step in the finite-difference algorithm. This flux must be balanced at the interface to conserve mass:

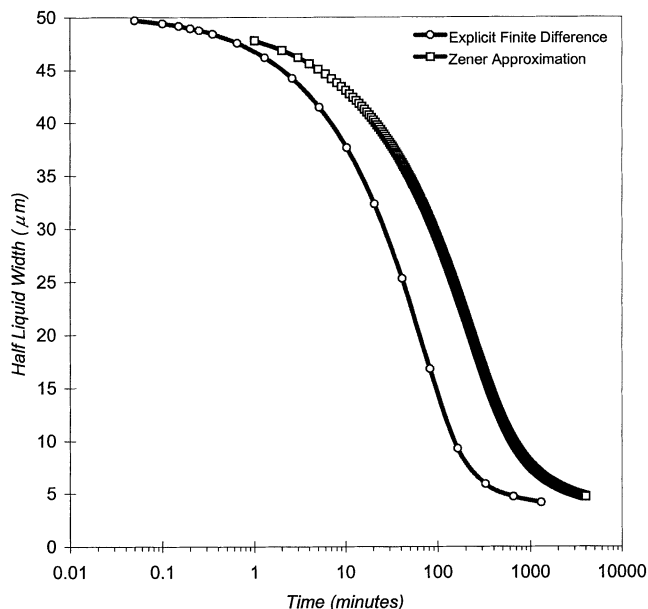


Fig. 4—Comparison of the results obtained for the isothermal solidification of the Al-Zn-Sn system modeled using the Zener approximation (Eq. [9]) and the explicit finite difference model (Eqs. [10] and [11]). Error in the finite difference algorithm is manifested as a slight underestimation of the solidification kinetics at short times.

$$J_i = \frac{\Delta w}{\Delta t} [C_i^L - C_i^S]_{t=t} + \frac{w + \Delta w}{\Delta t} [C_i^L]_{t=t} - \frac{w + \Delta w}{\Delta t} [C_i^L]_{t=t+\Delta t} \quad i = 1, 2 \quad [11]$$

The two resulting mass balances may be solved for the interfacial concentrations and change in liquid width ($2 \Delta w$) given time and distance increments Δt and Δx . Utilization of an explicit finite-difference routine to solve for the concentration profile in the solid results in a conditionally stable solution. For this problem, the solution is stable only for combinations of Δx and Δt such that

$$0 < \frac{D_{ij}^s \Delta t}{\Delta x^2} \leq 0.5 \quad i = 1, 2 \quad [12]$$

The results of these two computation methods are compared in Figure 4 for the Al-Zn-Sn system (aluminum solvent) at 500 °C. In this system, the diffusivity of tin in aluminum is two orders of magnitude lower than that for zinc.^[7] The Zener approximation underestimates the rate of solidification at all times (a numerical error in the finite-difference solution makes it appear that the kinetics are faster for the Zener approach at very short times). Figure 5 shows the results predicted by the finite-difference model for different concentrations of tin in the liquid at the beginning of the isothermal solidification stage. Figure 6 is a normalized representation of the width of the liquid layer vs time, using the normalization procedure suggested by Morral and Barkalov.^[8] Here the slight divergence of the curves at short times may be attributed to numerical error in the finite-difference method. Figure 7 shows the variation of the interfacial-equilibrium liquidus concentration of tin with the width of the layer. Figure 8 shows the effect of varying the diffusivity of the slow diffuser (in this case, simply by arbitrarily setting

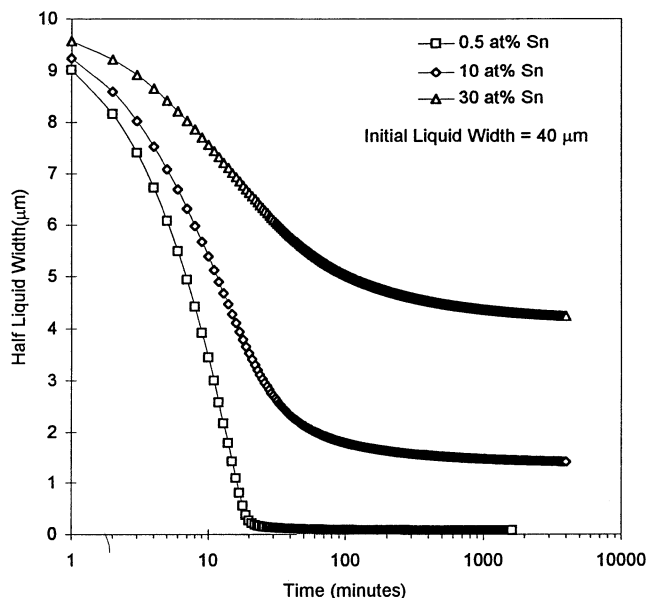


Fig. 5—Computed variation of liquid width with time for three different initial liquid compositions.

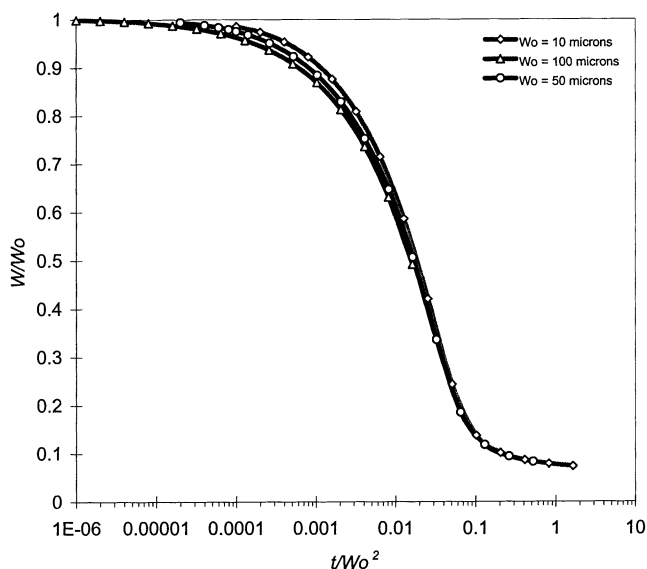


Fig. 6—Normalized plot of liquid width vs time for three different initial widths.

the diffusivity of tin a multiple of that of zinc) on the rate of solidification. Figure 9 is a series of computed zinc profiles in the base aluminum material for different times; the quantitative similarity to the error-function penetration curve at early times, and to the plane-source profile at later times is noted.

Figure 10 is a parabolic plot for a model system for which $D_{22} = 0.01 D_{11}$. This representation, perhaps more than any other, demonstrates the clear separation into two regimes, each dominated by the diffusion of a particular solute.

We have also used the finite-difference technique to verify that “stationary” kinetic states do exist; using Eq. [4] to estimate the ratio of solid-state diffusivities for the solutes, and under the assumption of constant solute-distribution

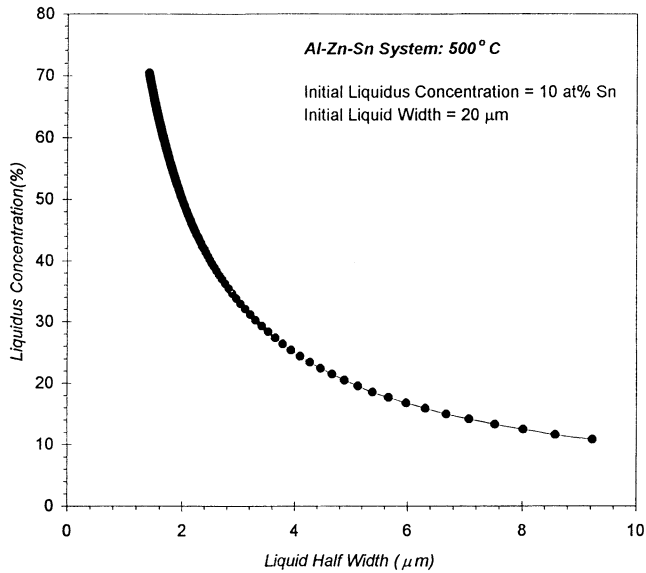


Fig. 7—Liquidus concentration as a function of width of the liquid layer.

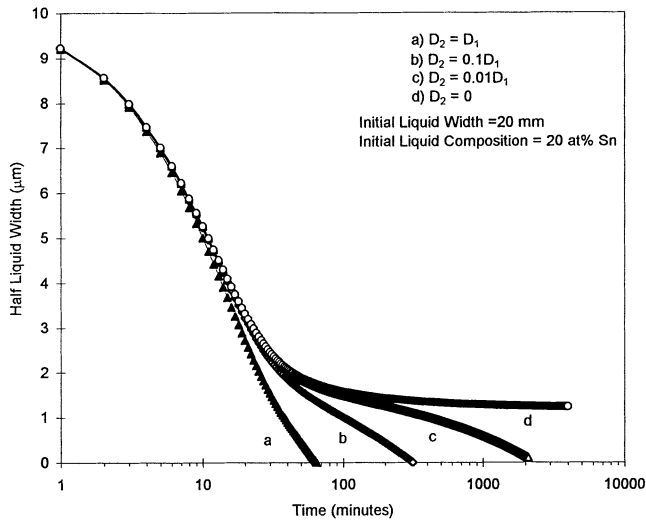


Fig. 8—Computed liquid width vs time for four different ratios of the solute diffusivities.

coefficients, we find that the liquid composition remains constant through the entire course of solidification.

IV. DISCUSSION

The results of the modeling demonstrate clearly the effect of a second solute on the process. Provided that the diffusivity and/or solubility of the two solutes differ markedly, one can expect to find two kinetic regimes, each regime controlled by a different solute. The model system Al-Zn-Sn has been chosen to demonstrate this behavior. A small amount of tin added to the interlayer would be expected effectively to arrest the isothermal solidification process and to prevent the complete bonding of the base material within conveniently accessible times.

We have tested this prediction with a few preliminary experiments in this system. In particular, it has been found that the tin to zinc concentration ratio in the liquid phase

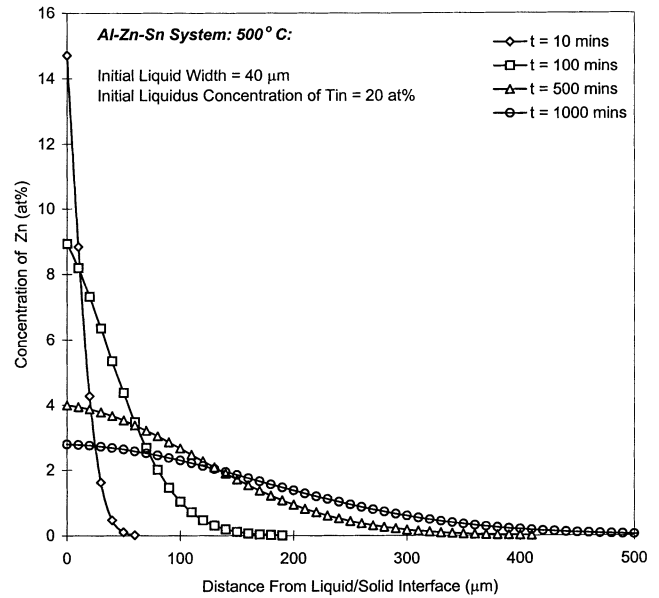


Fig. 9—Computed solid-state concentration profiles for Zn (the fast diffusing solute) in Al after various times.

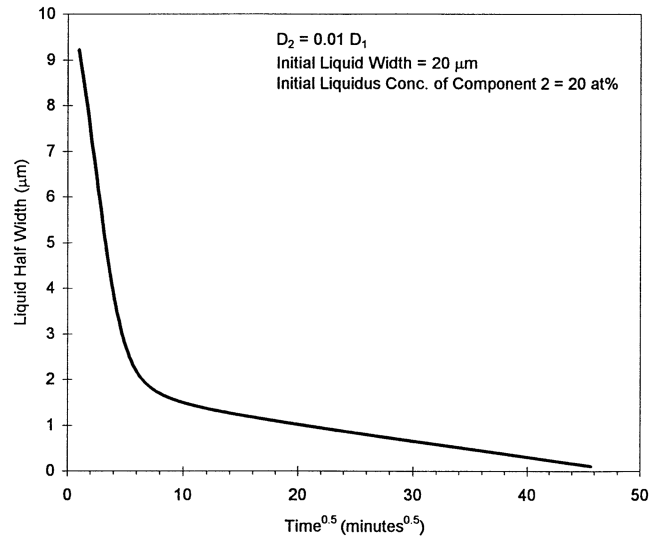


Fig. 10—Liquid width vs square root of time, showing the two kinetic regimes associated with the two solutes.

increases from 1:2 to approximately 7:1 on annealing a solid-liquid-solid couple for 3 days at 500 °C. During that time, the interlayer thickness decreased from 40 to 1 μm. The Sn to Zn ratios were determined by electron dispersive spectroscopy analysis on a fractured surface, and are, therefore, subject to considerable error; the trend is unmistakable however, and it is consistent with the results of the modeling.

There is further evidence for the effect of a second solute in the literature. Ramirez and Liu^[9] reported on extensive experiments in the nickel-boron system and noted that their results fell into two regimes, precisely as suggested by the current model. Boron was the fast-diffusing species in their experiments, and they assumed that they were dealing with a binary system. (Their base material was nickel of commercial purity.) They speculated that the lack of complete solidification was due to a departure from local equilibrium at

the final stages of the process. We suggest instead that a second solute, present as an impurity in the base material or the interlayer, may have been responsible for their observations.

Indeed, the complete isothermal solidification of interlayers may be the exception rather than the rule. Further experimental investigations are required to determine the maximum level of impurities (related to their solubilities in the solid and their diffusivities), that can be tolerated if complete transient-liquid-phase bonding is to be accomplished.

V. CONCLUSIONS

1. The modeling of the isothermal solidification stage of TLP bonding in ternary systems demonstrates a rich variety of responses. While the binary process is straightforward, and admits of a simple analytical treatment, the equivalent three-component problem profits from a numerical approach for its full exploration.
2. We have identified several cases of interest. One, termed stationary, corresponds to a constant liquid-interlayer composition throughout the full solidification process. This situation is characterized by a set of solute fluxes that compensates the set of solid-liquid concentration differences (Eq. [4]). If, in addition, the solute distribution coefficients are constant, any starting liquid concentration on the liquidus surface will remain unchanged throughout the solidification process. This is clearly a very special case, which will not in general be realized.
3. The more usual case involves the continual shift of the local equilibrium tie-line from the beginning to the end of solidification. This is the direct result of the simultaneous satisfaction of two coupled mass balances, and it can be

predicted using the modeling techniques described in this work. In the case, where the two solutes are removed from the liquid at very different rates (*e.g.*, Al-Zn-Sn), we find two distinct parabolic stages, each representing the result of the removal of one solute.

4. If the tie-line-shifting process is not interrupted by the complete solidification of the interlayer, we expect that the system may, under certain circumstances, reach a terminal tie-line, for which the liquid composition remains constant to a good approximation for the balance of the solidification. Again, the modeling methods described here can be used to identify these cases.

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