

# Analytical modeling of isothermal solidification during transient liquid phase (TLP) bonding

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Transient liquid phase (TLP) bonding has been employed in a range of applications, since it produces joints that have microstructural and hence mechanical properties similar to those properties of the base materials. However, the process generally takes long operational time (from hours to days) since it is controlled by the solute diffusion in solids. Therefore, quantitative prediction of the process kinetics, especially the completion times for different stages (namely heating, dissolution, isothermal solidification and homogenization) in TLP-bonding is very desirable. For those who are interested in the process descriptions and applications in different industries, and the kinetic modeling in general (both analytical and numerical), two detailed reviews [1, 2] are suggested. Examples of the use of numerical and analytical models in determining optimum joining conditions (e.g., bonding temperature and filler metal composition) can be also found in Refs. [1–3]. This communication will focus on the analytical solutions for the isothermal solidification stage during TLP-bonding. Although numerical methods provide more accurate prediction of the process kinetics during TLP-bonding [2, 3], there is still interest in a quick estimation of the kinetics for certain stages, especially for the isothermal solidification stage. The completion time required for the isothermal solidification stage is generally much longer than the completion time for the previous stages and therefore, a reasonably good estimation of the completion time for isothermal solidification may be used as an approximation for the whole process [1, 2]. This readily explains why much research has been carried out on this particular aspect of the TLP-bonding process.

When the isothermal solidification stage starts, the liquid phase is at its maximum width ( $W_{max}$ ). The solute build-up in the solid (base metal) is small (Fig. 1) and is, generally, ignored in the analytical modeling of the isothermal solidification stage [2]. The liquid zone shrinks as a result of solute diffusion into the base metal until the joint completely solidifies. It has been pointed out that solute distribution in the liquid can be considered uniform during almost all the isothermal solidification stage [3, 4]; therefore, solute diffusion in the liquid can be ignored. In addition, the base metal can be assumed to be semi-infinite because solute diffusion in the solid is relatively slow. These assumptions make the analytical modeling possible for the isothermal solidification stage [2, 3].

There are many analytical solutions proposed to predict the completion time for isothermal solidification

(e.g., Refs [5–12]); however, a close examination of these solutions indicates almost all of them can be classified into two categories. One type has treated the system as two semi-infinite phases with a coupled diffusion-controlled moving solid/liquid interface (Fig. 1), which will be called “two-phase” solutions in this work. The other type has treated the system as a single semi-infinite phase (the base metal) with a constant solute concentration ( $C_{\alpha L}$ ) at the surface of the base metal (Fig. 1), which will be called “single-phase” solutions. This treatment effectively eliminates the trouble of dealing with the liquid phase or, more importantly, dealing with the MIGRATING solid/liquid interface. Both types of solutions are used extensively in practice. We will examine the derivation procedures of these two types of solutions to study the difference between them.

A typical example of the “single-phase” solutions can be found in a paper by Tuah-Poku *et al.* [12] in a study on TLP-bonding of a Ag/Cu/Ag sandwich joint, which can be also derived from the classical solutions for Fick’s equation (e.g., solutions for semi-infinite media in Ref. [13]). An error function solution is first employed to describe the solute distribution in the semi-infinite base metal with a surface on which the solute

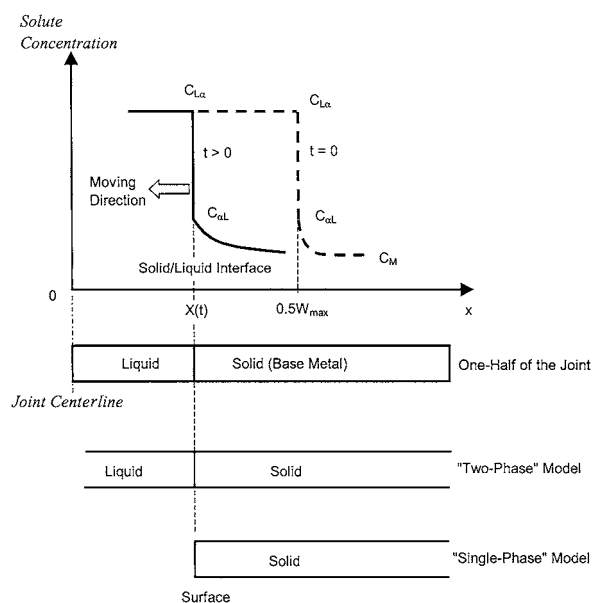


Figure 1 Schematic showing solute distribution during the isothermal solidification stage in TLP-bonding, and the two analytical models used to simulate the process.

concentration was maintained at  $C_{\alpha L}$  (Fig. 1)

$$C(x, t) = C_{\alpha L} + (C_M - C_{\alpha L}) \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right), \quad (1)$$

where  $C_{\alpha L}$  is the solute concentration at the surface,  $C_M$  is the initial solute concentration in the base metal,  $D$  is the solute diffusivity in the base metal and  $t$  is the solidification time. The total solute amount  $M$  that has entered the base metal at time  $t$  can be calculated from the relation

$$M(t) = 2(C_{\alpha L} - C_M) \sqrt{\frac{Dt}{\pi}}. \quad (2)$$

If the amount of solute diffused into the base metal during the heating and dissolution stages is ignored, the total amount of solute diffused into the base metal when the isothermal solidification is complete equals the original solute content of the filler metal, i.e.

$$C_F W_0 = 4(C_{\alpha L} - C_M) \sqrt{\frac{Dt}{\pi}} \quad (3)$$

where  $C_F$  is the original solute concentration in the filler metal and  $W_0$  is the initial width of the filler metal. The completion time for isothermal solidification can therefore be calculated using the relation

$$t = \frac{\pi}{16D} \left( \frac{C_F W_0}{C_{\alpha L} - C_M} \right)^2, \quad (4)$$

Similar treatments of this problem have been reported by others (e.g., Ikawa *et al.* [5], Nakao *et al.* [6] and Onzawa *et al.* [7]).

A typical example of the “two-phase” solutions was presented by Lesoult [8]. His derivation is similar to that described by Danckwerts [14], in which a general solution for unsteady state linear heat conduction or diffusion is given. A general error function solution is assumed in the solid phase (Fig. 1)

$$C(x, t) = a_1 + a_2 \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right), \quad (5)$$

where  $a_1$  and  $a_2$  are constants determined by the specific boundary conditions. When  $x \rightarrow \infty$

$$C(\infty, t) = a_1 + a_2 = C_M, \quad (6)$$

and at the moving solid/liquid interface, i.e.,  $x = X(t)$

$$C(X(t), t) = a_1 + a_2 \operatorname{erf}\left(\frac{X(t)}{\sqrt{4Dt}}\right) = C_{\alpha L}, \quad (7)$$

where  $C_{\alpha L}$  is the solute concentration of the solid phase at the interface (Fig. 1). Since Equation 7 has to be satisfied for all values of  $t$ ,  $X(t)$  must be proportional to  $t^{1/2}$ , i.e.,

$$X(t) = k\sqrt{4Dt}, \quad (8)$$

where  $k$  is a constant. The mass balance at the interface produces the relation

$$(C_{L\alpha} - C_{\alpha L}) \frac{dX(t)}{dt} = D \left( \frac{\partial C(x, t)}{\partial x} \right)_{x=X(t)} \quad (9)$$

where  $C_{L\alpha}$  is the solute concentration of the liquid phase at the moving solid/liquid interface. Solving Equations 5–9 produces

$$\frac{k(1 + \operatorname{erf}(k))\sqrt{\pi}}{\exp(-k^2)} = \frac{C_{\alpha L} - C_M}{C_{L\alpha} - C_{\alpha L}}. \quad (10)$$

Similar solutions were also derived by others (e.g., Sakamoto *et al.* [9], and Ramirez and Liu [10]). The completion time for isothermal solidification during TLP bonding, from Equation 8, can be calculated using the relation

$$t = \frac{W_{\max}^2}{16k^2D}, \quad (11)$$

where  $W_{\max}$  is the maximum liquid width calculated using the mass balance method [12].

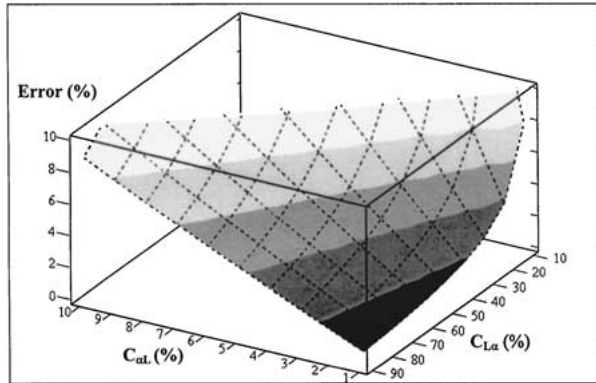
A study on numerical modeling of the TLP-bonding process has been pointed out that Equation 11 provides a good approximation for the completion time for the isothermal solidification stage [3]. However, no work has been done previously to study the prediction accuracy of Equation 4 although the equation is also used extensively in practice. From the above discussion, it may be postulated that the “single-phase” solution will be less accurate because more assumptions are involved in deriving Equation 4. This suspicion is further strengthened by an examination of a published paper [12], in which the estimation of the completion time required for isothermal solidification using the “single-phase” solution to be about 1200 h; however, the actual experimental result was about 200 h. While other solidification mechanisms and experimental errors were suggested for the discrepancy [1, 12, 15], it is believed that part of the discrepancy might be due to the error when using Equation 4. On the other hand, the “single-phase” solution has an advantage over the “two-phase” solution because the latter requires a numerical solution of Equation 10. Therefore, it is important to quantify the estimation error that may be caused when using the “single-phase” solution compared to the “two-phase” solution, and to provide a general guideline for the use of the solutions. In the present work, a graphical analysis is used to study the estimation error when using Equation 4 to approximate Equation 11. A discussion of the fundamental reason for the differences between these two solutions is also provided.

The error caused by using Equation 4 to approximate Equation 11 can be calculated by

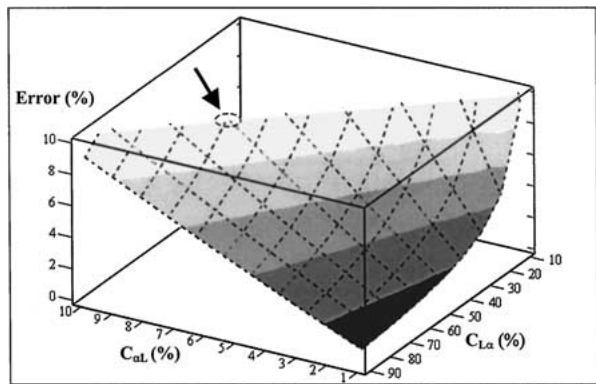
$$\begin{aligned} \text{Error} &= \frac{\frac{\pi}{16D} \left( \frac{C_{L\alpha} W_{\max}}{C_{\alpha L} - C_M} \right)^2 - \frac{W_{\max}^2}{16k^2D}}{\frac{W_{\max}^2}{16k^2D}} \\ &= \left\{ \pi k^2 \left( \frac{C_{L\alpha}}{C_{\alpha L} - C_M} \right)^2 - 1 \right\} \times 100\%. \quad (12) \end{aligned}$$

Since  $k$  is a function of  $C_{L\alpha}$ ,  $C_{\alpha L}$  and  $C_M$ , and has to be solved numerically using Equation 10, there is no simple way to illustrate the effect of variables ( $C_{L\alpha}$ ,  $C_{\alpha L}$  and  $C_M$ ) on the difference. For example, increasing  $C_{L\alpha}$  will reduce the value of  $k$  [8] and, hence, reduce the error calculated using Equation 12; however, reducing  $C_{L\alpha}$  will also increase the value of the term  $C_{L\alpha}/(C_{L\alpha}-C_{\alpha L})$  in Equation 12 and, hence, increase the error. Therefore, it is impossible to judge from this analysis how reducing  $C_{L\alpha}$  would influence the difference between two equations.

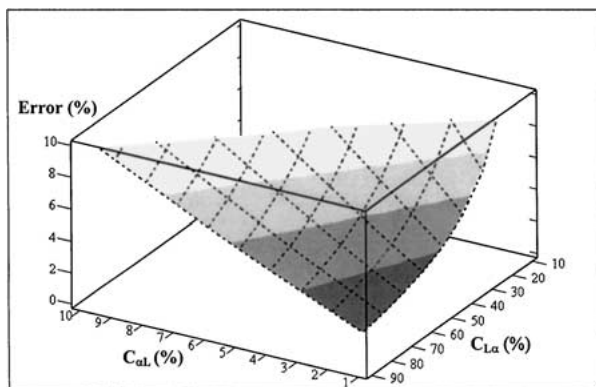
To study the effect of  $C_{L\alpha}$ ,  $C_{\alpha L}$  and  $C_M$ , Equation 12 is solved and plotted in Fig. 2 using MathCad® (com-



(a)  $C_M = 0$



(b)  $C_M = 0.1$



(c)  $C_M = 1.0$

Figure 2 The effect of solute concentrations ( $C_{\alpha L}$  and  $C_{L\alpha}$ ) on the estimation error calculated by Equation 13: (a) when  $C_M = 0$ ; (b) when  $C_M = 0.1$  (the error will be above 10% if  $C_{\alpha L}$  is above 8% when  $C_{L\alpha}$  is at 60% as pointed by an arrow); and (c) when  $C_M = 1.0$ . The concentration gridlines and the difference contours were indicated in the surface plots.

mercial mathematics software). It becomes clear in Fig. 2 that the possible error caused when using Equation 4 is influenced by all variables: decreasing  $C_{\alpha L}$  and  $C_M$ , and increasing  $C_{L\alpha}$  reduces the error. It follows that the Equation 4 is only a good approximation of Equation 11 when  $C_M$  and  $C_{\alpha L}$  are very small and  $C_{L\alpha}$  is relatively large. Plots like those concentration gridlines in Fig. 2 can be used to evaluate the estimation error when using Equation 4 to approximate Equation 11 for a certain metallurgical system, or to determine if Equation 4 could be used to approximate Equation 11 if a certain error level is allowed. For example, when an error of 10% is allowed, the “single-phase” solution can be used only if  $C_{\alpha L}$  is below 8% when  $C_{L\alpha}$  is at 60% and  $C_M$  is at 0.1% (Fig. 2(b)); or the error will be above 10% if  $C_{\alpha L}$  is above 8% at when  $C_{L\alpha}$  is at 60% and  $C_M$  is at 0.1%.

In the study on TLP-bonding of Ag/Cu/Ag, the completion time required for isothermal solidification estimated by Equation 4 was about 1200 h [12]; however, the actual completion time by experimentation was about 200 h. The reason for this large discrepancy was considered to be due to the non-planar solid/liquid interface (e.g., the solidification process was influenced by ledge-type migration and grain boundary grooving, both are likely to speed up the advancement of the solid/liquid interface) [12]. It is very clear from the present work that, at least, part of the discrepancy might come from the error when using Equation 4. With the data of  $C_{\alpha L} = 8\%$ ,  $C_{L\alpha} = 18\%$  and  $C_M = 0$  [12], the difference between Equations 4 and 11 is about fifty percent (Fig. 3). In other words, Equation 4 overestimates the completion time required for isothermal solidification by fifty percent, which can be also seen by solving Equations 4 and 11 directly with the data of  $C_{\alpha L} = 8\%$ ,  $C_{L\alpha} = 18\%$  and  $C_M = 0$ ,  $W_{\max} = 79 \times 10^{-4}$  cm and  $D = 4.6 \times 10^{-10}$  cm<sup>2</sup>/s [11], which results in by 1156 h Equation 4 and 770 h by Equation 11. Therefore, the use of Equation 11 can reduce the estimation error from 1200 h versus 200 h to 770 h versus 200 h. In this connection, a faster solidification rate has been observed due to the presence of base metal grain boundaries, and has also been suggested due to the squeezed out liquid metal during the process [1, 15],

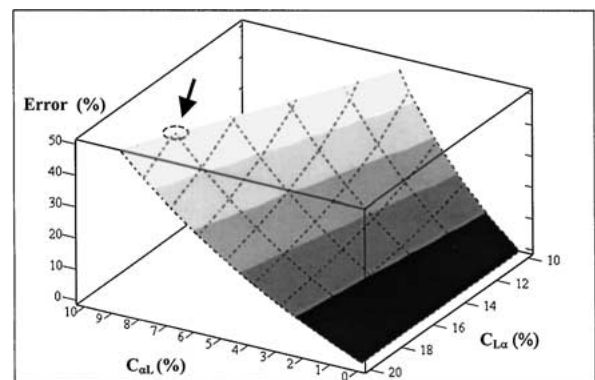


Figure 3 The error caused by using Equation 4 is about 50% (pointed by an arrow) for  $C_{\alpha L} = 8\%$ ,  $C_{L\alpha} = 18\%$ , and  $C_M = 0$ . The concentration gridlines and the difference contours were indicated in the surface plots.

which will also contribute to the difference between experimental data and calculated results.

Comparing the derivation procedures for Equations 4 and 11 can provide some insight into the differences between the two equations. The “two-phase” solution has employed Equation 9 to describe the mass balance at the solid/liquid and a general error function to describe the solute distribution in the solid. On the other hand, the “single-phase” solution has replaced the solid/liquid interface with a stationary surface with a constant concentration  $C_{\alpha L}$ , and assumed that the solute distribution is given by Equation 1 (which is only exact for a stationary interface). Since the liquid/solid interface migrates during TLP bonding, it is possible to determine when this assumption on a stationary surface can be applied. Solving Equations 5–7, we obtain

$$C(x, t) = C_M - \frac{C_M - C_{\alpha L}}{1 - \operatorname{erf}(k)} + \frac{C_M - C_{\alpha L}}{1 - \operatorname{erf}(k)} \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right), \quad (13)$$

for the solute distribution in the solid in the “two-phase” model, where  $k$  is the factor related to the solution distribution in Equation 10. When  $k \rightarrow 0$ ,  $\operatorname{erf}(k) \rightarrow 0$  and  $1 - \operatorname{erf}(k) \rightarrow 1$ , Equation 13 becomes

$$C(x, t) = C_{\alpha L} + (C_M - C_{\alpha L}) \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right). \quad (14)$$

This is identical to Equation 1. Therefore the difference between Equations 4 and 11 comes from the assumption used to derive Equation 4 that the interface is stationary. The analysis of Fig. 2 indicates Equation 4 is a good approximation of Equation 11 when  $C_M$  and  $C_{\alpha L}$  are very small and  $C_{L\alpha}$  is relatively large. It is interesting to note that a relatively small  $C_M$  and  $C_{\alpha L}$  compared with  $C_{L\alpha}$  will result in a very small  $k$  [8] and hence a very slow solidification rate judging from Equation 8; therefore, the migrating solid/liquid interface can be approximated by a “stationary” interface. The numerical method used in the present work (i.e.,

the graphical presentations of Fig. 2) provide an easy way to quantify the conditions, in terms of  $C_{L\alpha}$ ,  $C_{\alpha L}$  and  $C_M$ , under which the “single-phase” solution can be used to approximate the “two-phase” solution.

In summary, the estimation error of Equation 4 (one of the two popular analytical solutions) for the completion time required for isothermal solidification during TLP-bonding is analyzed. This work indicates that the overestimation of Equation 4 can be very large depending on the solute concentrations at the moving interface and initial solute concentration in the base material. This estimation error comes from the assumptions used to derive Equation 4 that the solid/liquid interface is stationary.

## References

1. W. D. MACDONALD and T. W. EAGAR, *Annu. Rev. Mater. Sci.* **22** (1992) 23.
2. Y. ZHOU, W. F. GALE and T. H. NORTH, *Inter. Mater. Rev.* **50** (5) (1995) 181.
3. Y. ZHOU and T. H. NORTH, *Z. Metallkd.* **85** (11) (1994) 775.
4. H. NAKAGAWA, C. H. LEE and T. H. NORTH, *Metall. Trans.* **22A** (1991) 543.
5. H. IKAWA and Y. NAKAO, *Trans. Jpn. Weld. Soc.* **10** (1) (1979) 24.
6. Y. NAKAO, K. NISHIMOTO, K. SHINOZAKI and C. Y. KANG, *ibid.* **20** (1989) 60.
7. T. ONZAWA, A. SUZAMURA and J. H. KIM, *J. Jpn. Weld. Soc.* **8** (4) (1990) 74.
8. G. LESOULT, cited in Ref. 12 (1976).
9. A. SAKAMOTO, C. FUJIWARA, T. HATTORI and S. SAKAI, *Weld. J.* **68** (1989) 63.
10. J. E. RAMIREZ and S. LIU, *ibid.* **71** (1992) 365s.
11. S. LIU, D. L. OLSON, G. P. MARTIN and G. R. EDWARDS, *ibid.* **70** (1991) 207s.
12. I. TUAH-POKU, M. DOLLAR and T. B. MASSALSKI, *Metall. Trans. A* **19A** (1988) 675.
13. J. CRANK, “Mathematics of Diffusion,” 2nd ed. Oxford University Press, New York, 1975.
14. P. V. DANCKWERTS, *Trans. Faraday Soc.* **46** (1950) 701.
15. K. SAIDA, Y. ZHOU and T. H. NORTH, *J. Mater. Sci.* **28** (1993) 6427.

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