

Modeling of the Dynamics of Transient Liquid Films in Ternary Systems

Hatem S. Zurob, Jinichiro Nakano, and Gary R. Purdy

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The presence of a concentration gradient across a thin liquid film leads to the phenomenon of isothermal liquid film migration (LFM). In most cases, the concentration gradient is due to coherency stresses, and the migration of the liquid film results in the relaxation of these stresses. It is also possible to envisage cases in which LFM occurs as a result of chemical solubility differences between stable and metastable phases. Both situations are examined in this contribution with special emphasis on the effect of adding a second solute element to the liquid phase. The kinetics of LFM is examined as a function of the initial liquid concentration and the ratio of the solute diffusion coefficients in a model coherency-driven ternary system. The growth of the Γ_2 inside δ particles in the Zn-Fe-Al system is presented as a possible example of chemically driven LFM.

Keywords coherency strains, liquid film migration, solidification, ternary effects

1. Introduction

The study of the kinetic behavior of nonequilibrium thin liquid films, introduced to and constrained by a solid environment, has developed into a research subfield in its own right. In part, this is due to a technological drive to design and optimize transient-liquid-phase bonding and sintering processes. In all cases of interest, the liquid films are not initially in full equilibrium with their solid environment; this causes the films to respond by growing, or shrinking, or, in certain interesting cases, migrating.

The behavior of liquid films in binary systems has been extensively modeled and studied experimentally. In the simplest cases of isothermal transient liquid-phase bonding and sintering, for example, the liquid is supposed to quickly come to a local equilibrium with the surrounding solid, to remain homogeneous, and to change its volume (e.g., by melting some of the solid). In a later stage, the liquid and solid phases are assumed to maintain local equilibrium compositions, such that diffusion profiles are developed in the solid. A slow isothermal solidification ensues, controlled by the rate of solute diffusion in the solid phases, until the

liquid is exhausted. A final stage involves the homogenization of the region, again by solid-state diffusion.^[1]

In the picture described above, the liquid films are supposed to remain fixed in space, and to thicken or shrink as the solute is added to or removed from them. An interesting variation on this behavior was first reported by Yoon and Huppmann,^[2] in their studies of the sintering of compacts of tungsten spheres that had been infiltrated by liquid nickel. They presented clear metallographic evidence for the migration of nickel-rich liquid films, such that they advanced into the pure tungsten, leaving in their wake an equilibrium solid solution of nickel in tungsten. In a subsequent series of studies of liquid film migration (LFM),^[3-5] Yoon and his colleagues demonstrated that the migration was associated with different (equilibrium) solute compositions on either side of the liquid films, and that the different equilibria were determined by the states of stress at the leading and trailing edges of the films. For planar films, the trailing edge will be relaxed while the leading edge will be subject to a biaxial strain resulting from a thin, coherent gradient of misfitting solute in the retreating parent solid.^[6-8] This situation is illustrated schematically in Fig. 1. Consideration of the solute balance indicates that these migrating films are also transient; they must shrink as their supply of solute is transferred to the growing phase.^[9] The LFM occurring subsequent to the liquation of grain boundary precipitates was studied by Barker and Purdy.^[10] In that case, the effects of interface curvature were shown to be significant, resulting in the cessation of migration when the liquid lenses had bowed to a certain curvature. However, to the authors' knowledge, no detailed experimental studies of the kinetics of motion of the films have been reported.

The requirement for sustained LFM under local equilibrium conditions is then simply that a concentration gradient be maintained across the film. This can also occur in the dissolution of a metastable phase into the liquid film, followed by precipitation from the liquid of a more stable solid. This three-phase (metastable phase-liquid-stable phase) form of LFM can be considered to be driven solely by chemical forces.

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Hatem S. Zurob, Jinichiro Nakano, and Gary R. Purdy, Department of Materials Science and Engineering, McMaster University, 1280 Main Street West, Hamilton, ON, Canada L8S 4L7. Contact e-mail: zurobh@mcmaster.ca.

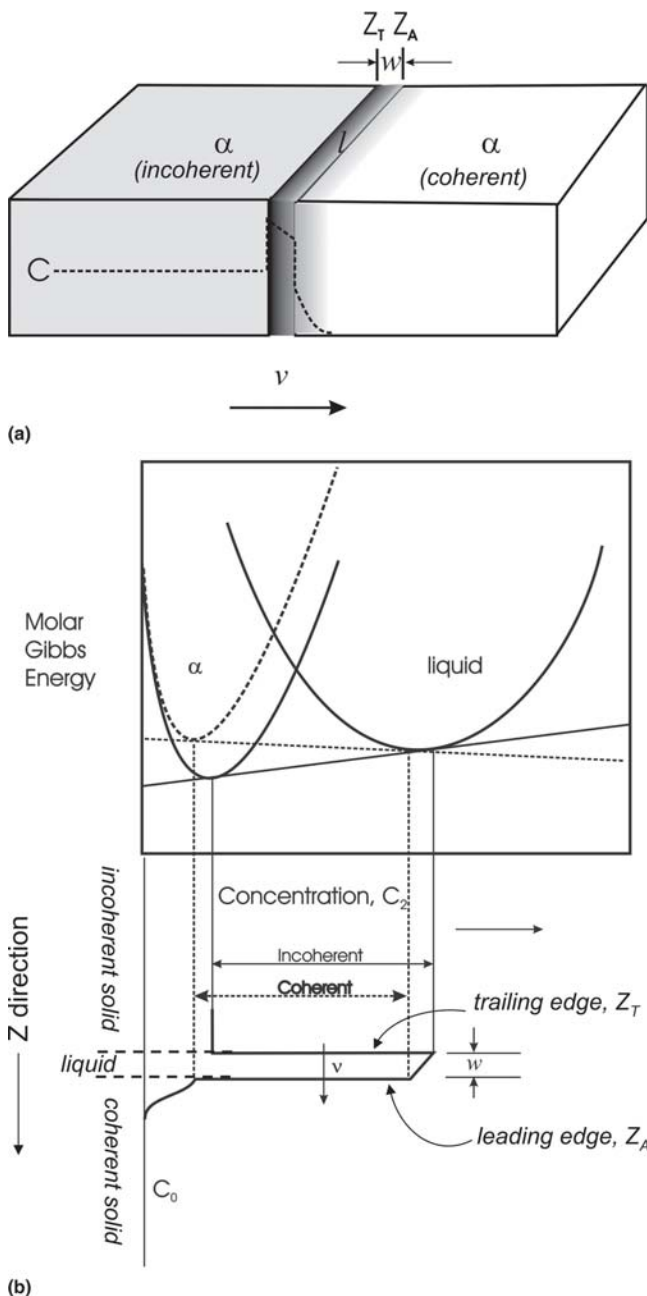


Fig. 1 (a) Schematic illustration of coherency-driven LFM. In this example, the liquid film migrates from left to right, and in the process the coherent solid is replaced by an incoherent solid. (b) Free-energy curves for a binary system in which coherency drives LFM. The corresponding solute concentrations in the liquid as well as the coherent and incoherent solids are shown.

The extension of these concepts to three-component (and higher order) systems is rather straightforward: a major consequence of the addition of a third component is that the local equilibrium interfacial concentrations are no longer fixed but are capable of changing isothermally as required by two solute balances, coupled through the phase boundaries and tie-lines of a ternary isotherm. The case of transient (static) liquid phase bonding in ternary systems was

analyzed by Sinclair et al.,^[11] who demonstrated that the local equilibrium interfacial tie-line will shift with time, and that the kinetics of final solidification were in general determined by the solute with the slowest rate of diffusion in the solid phase. In that analysis, the full ternary diffusion matrix (for the solid phases) was used to describe the solidification process. Purdy et al.^[12] subsequently used a full thermodynamic database to simultaneously compute and track the relevant phase equilibria and diffusion coefficients in their modeling study of the isothermal solidification and homogenization of multicomponent copper-based alloys.

A second consequence of the extension to three-component systems lies in the fact that it is always possible to choose a vector in a ternary isothermal section that corresponds to zero misfit strain. It has been shown experimentally^[7,8] that LFM associated with coherency strains is suppressed when the initial compositions of liquid and solid are chosen such that the net coherency strain associated with the two solute gradients is negligible.

In this contribution, the authors focus on modeling the kinetics of LFM in three-component systems for cases where the films migrate in response to elastic energy differences (section 2.1), and in response to chemical forces (section 2.2). In the first case, a simple model system is used to demonstrate the effects of ternary additions; in the second, the replacement via LFM of the metastable δ phase by a more stable Γ_2 phase in the well-characterized iron (Fe)-zinc (Zn)-aluminum (Al) system is examined.

2. Modeling of the Dynamic Response of Liquid Films

2.1 Response to Coherency Stresses

In this section, a hypothetical ternary system is used to illustrate the migration and solidification of liquid films in the presence of two solutes. The thermodynamics of this model system is described in section 2.1.1. This is followed by a description of the kinetics of film migration in section 2.1.2.

2.1.1 Thermodynamics of the Model Ternary System 0-1-2. In the following, 0 represents a solvent, while 1 and 2 are solutes. The model system was chosen rather arbitrarily to facilitate the elaboration of the different factors that enter the dynamics of liquid film motion, and to permit the examination of the effects of additions of small amounts of a second solute. The incoherent solid and liquid solutions are taken as ideal, an assumption that leads to constant incoherent distribution coefficients $k_i^{\alpha/L} = (C_i^{\alpha}/C_i^L)$ ($i = 1, 2$), linear phase boundaries on the isothermal section, and constant characteristic linear expansion coefficients with composition change $\eta_i = (d \ln a / dC_i)$, where a is the lattice parameter of the solid solution α . The liquid films will be assumed to be planar, so that capillarity can be neglected.

The liquid free energy curve is given by:

$$G^L = (1 - C_1 - C_2)\Delta H_L \left(1 - \frac{T}{T_L}\right) + RT(C_1 \ln(C_1) + C_2 \ln(C_2) + (1 - C_1 - C_2)\ln(1 - C_1 - C_2)) \dots \quad (\text{Eq 1})$$

where, $\Delta H_L = 15$ kJ/mole and $T_L = 700$ K. The free energy of the incoherent solid phase is given by:

$$G_T^S = -C_1 \Delta H_1 \left(1 - \frac{T}{T_1}\right) - C_2 \Delta H_2 \left(1 - \frac{T}{T_2}\right) + RT(C_1 \ln(C_1) + C_2 \ln(C_2) + (1 - C_1 - C_2) \ln(1 - C_1 - C_2)) \dots \quad (\text{Eq 2})$$

where $\Delta H_1 = 10$ kJ/mole and $\Delta H_2 = 20$ kJ/mole, while $T_1 = 300$ K and $T_2 = 500$ K. As for the free energy of the coherent solid, it is given by:

$$G_A^S = G_T^S + YV_m(\eta_1 C_1 + \eta_2 C_2) \dots \quad (\text{Eq 3})$$

where, $Y = 50$ GPa, $V_m = 10^{-5}$ m³/mole, and η_1 and η_2 are equal to 0.02 and -0.08 , respectively. These values were chosen to produce a system in which the factors that influence the dynamics of liquid film motion can be conveniently studied.

The coherent and incoherent isothermal phase equilibria computed on the basis of the above equations are shown in Fig. 2(a). The zero-strain direction is also depicted as a vector beginning in the α -phase region. This vector also defines the direction of the tie-line corresponding to zero strain. For an initial solid consisting of pure element 0 and for a particular choice of the composition of the initial ternary liquid, placed in contact with the above solid, Fig. 2(b) shows the two solute profiles and their relation to the coherent and incoherent equilibria. As discussed in the next section, the two solute mass balances can be satisfied through the selection of a pair of tie-lines, one coherent and one incoherent. These tie-lines lead to a self-consistent set of concentration differences across the liquid film.

2.1.2 Kinetics of Liquid Film Migration. In the following, the diagonal diffusion coefficients in the liquid phase D_i were taken as constant for a given simulation. Preliminary investigations showed that the contributions of the off-diagonal terms in the diffusion matrix were generally negligible. However, for the case of chemically driven LFM considered here, these terms, estimated on the assumption that the cross terms in the mobility matrix $[L_{ik}]$ are zero, were nonnegligible and were included.

To establish a baseline for the study, planar LFM in the binary 0-2 system was modeled first. The liquid alloy is introduced into a matrix of initially pure solvent 0. The films and the adjacent solids are assumed to attain and maintain fixed local equilibrium compositions at the trailing (incoherent) and leading (coherent) edges. If the authors denote the positions of the trailing and advancing sides of the liquid film by Z_T and Z_A , respectively, and if the width of the liquid film is denoted by w , then:

$$Z_A = Z_T + w \dots \quad (\text{Eq 4})$$

The position of the trailing interface can then be expressed as:

$$Z_T = \int v_T dt \dots \quad (\text{Eq 5})$$

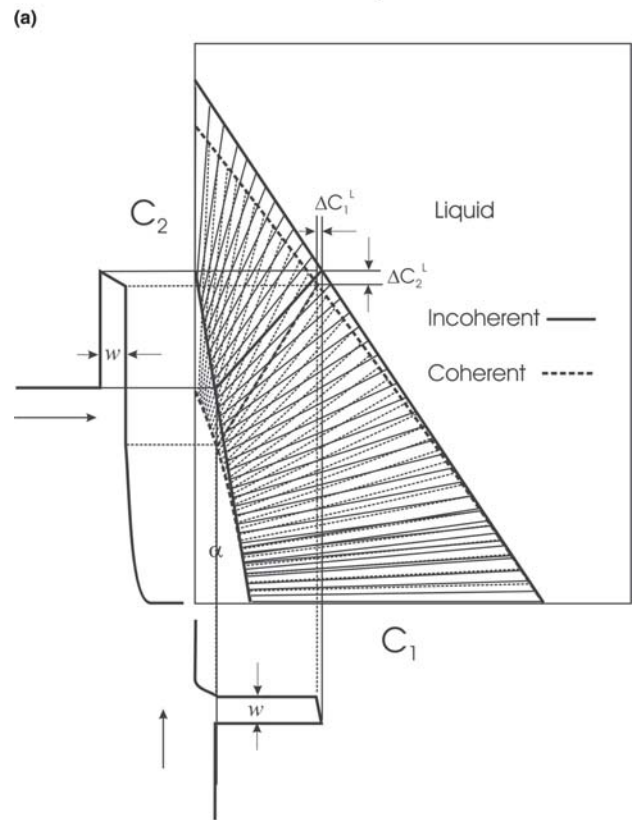
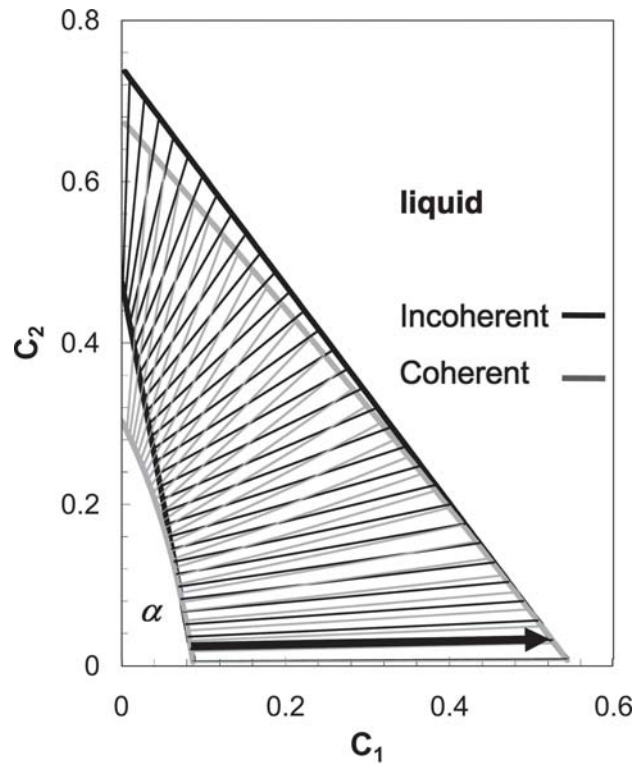


Fig. 2 (a) Hypothetical phase-diagram of a ternary (0-1-2) system in which coherency-driven LFM takes place. The tie-lines will migrate towards the zero-strain misfit-tie-line, which is highlighted on the diagram. (b) The concentration profiles of solutes 1 and 2 are related to the ternary phase diagram.

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where v_T is the speed of the trailing interface. Using the Zener approximation and following the notations shown in Fig. 1, the speed of the trailing interface can be expressed as:

$$v_T = \frac{D^L(C_T^L - C_A^L)}{w(C_T^L - C_T^S)} \dots \quad (\text{Eq 6})$$

The time evolution of Z_A , Z_T , v_T , and w is solved for, stepwise, using Eq 4 to 6 along with the following mass balance:

$$-\Delta w(C_T^L + C_A^L)/2 = \Delta Z_T C_T^S - \Delta Z_A C_A^S \dots \quad (\text{Eq 7})$$

The response of the binary system is shown in Fig. 3, using normalized time, width, and velocity. The films are predicted to accelerate continuously as they lose solute to the growing phase, thereby becoming thinner and supporting a larger concentration gradient. In the present case, limited film migration is expected to take place prior to the complete solidification of the film. This is to be expected given the large value of the partition coefficient used ($k\alpha^L = 0.646$) in the present system.

The extension to the ternary case is relatively straightforward. The Gibbs energy functions (Eq 1–3) are solved explicitly at each iterative step. If the concentration of one of the solutes at the coherent interface is defined, then the equations for G^L and G_A^S , along with the tangent plane construction, can be used to solve for $C_{1A}^L, C_{1A}^S, C_{2A}^L$ and C_{2A}^S . The concentrations at the trailing interface can be found using the equations for G^L and G_T^S , along with the tangent plane construction and the requirement of matching flux:

$$\frac{D_{11}^L(C_{1T}^L - C_{1A}^L) + D_{12}^L(C_{2T}^L - C_{2A}^L)}{(C_{1T}^L - C_{1T}^S)} = \frac{D_{22}^L(C_{2T}^L - C_{2A}^L) + D_{21}^L(C_{1T}^L - C_{1A}^L)}{(C_{2T}^L - C_{2T}^S)} \dots \quad (\text{Eq 8})$$

Finally Z_A , Z_T , v_T , and w can be solved for using Eq 4 and 5 and the mass balances for solutes 1 and 2 (Eq 7 used once for each solute). The results of these calculations are presented in section 3 and discussed in section 4.

2.2 Response of Liquid Films to Chemical Driving Forces

The authors next consider the system Fe-Al-Zn, for which, it has been reported^[13] that droplets, formed in the process of hot-dip galvanizing, transform from their initial phase structure, δ , to an equilibrium phase, Γ_2 , via the migration of an intermediary liquid film. An example is shown in Fig. 4.^[14] The primary motivation for LFM is then the reduction in Gibbs energy accompanying the replacement of a metastable phase by a more stable one.

In this case, a recently developed thermodynamic database^[15,16] permits the calculation of metastable and stable equilibria in the Fe-Zn and Fe-Al-Zn systems. For the process to occur to the extent reported, it is essential that the initial δ phase be strongly supersaturated with respect to Al.

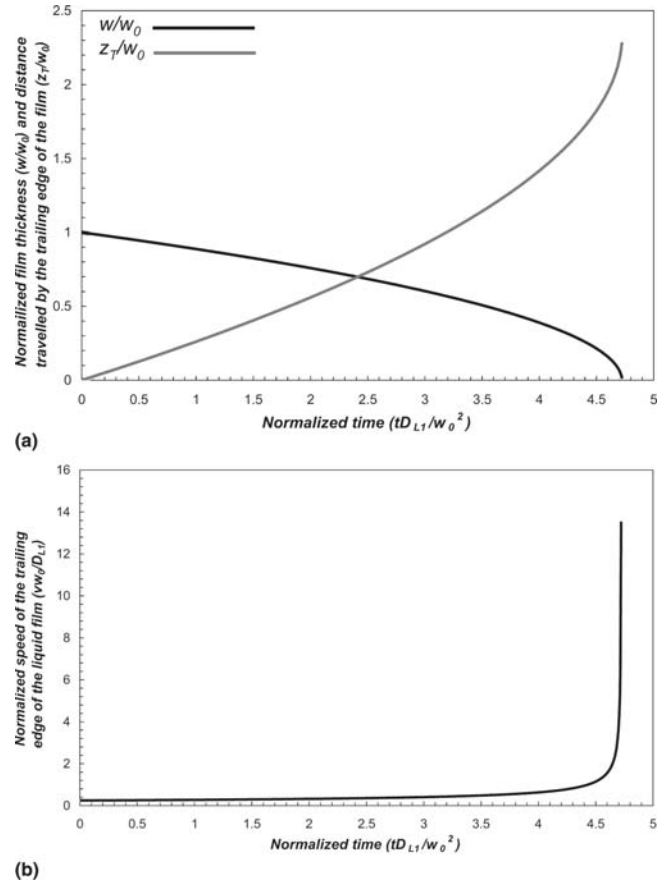


Fig. 3 (a) LFM and (b) liquid film velocity in the binary (0-2) system for an initial condition of $C_A^L = 0.6774$

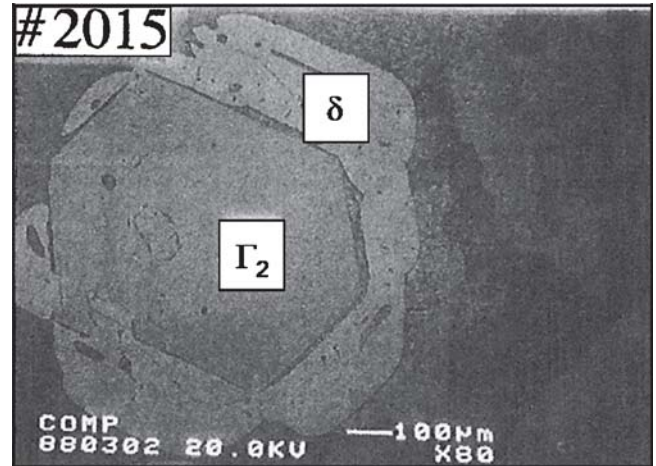
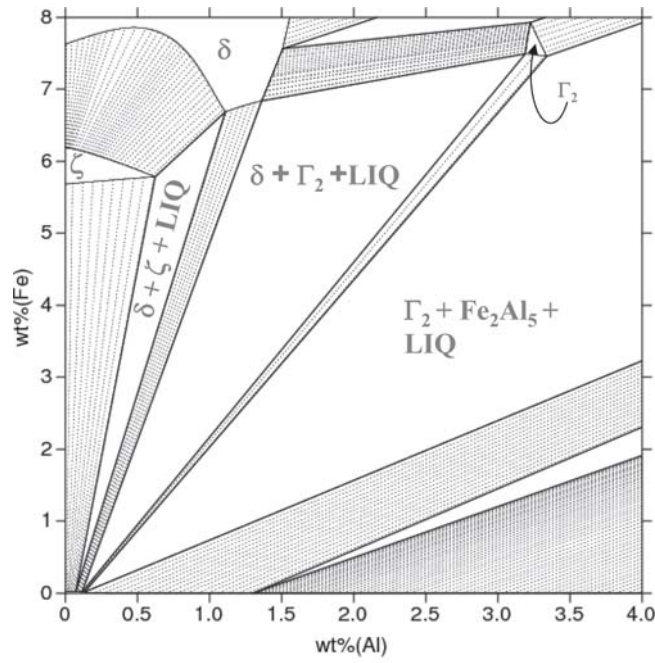
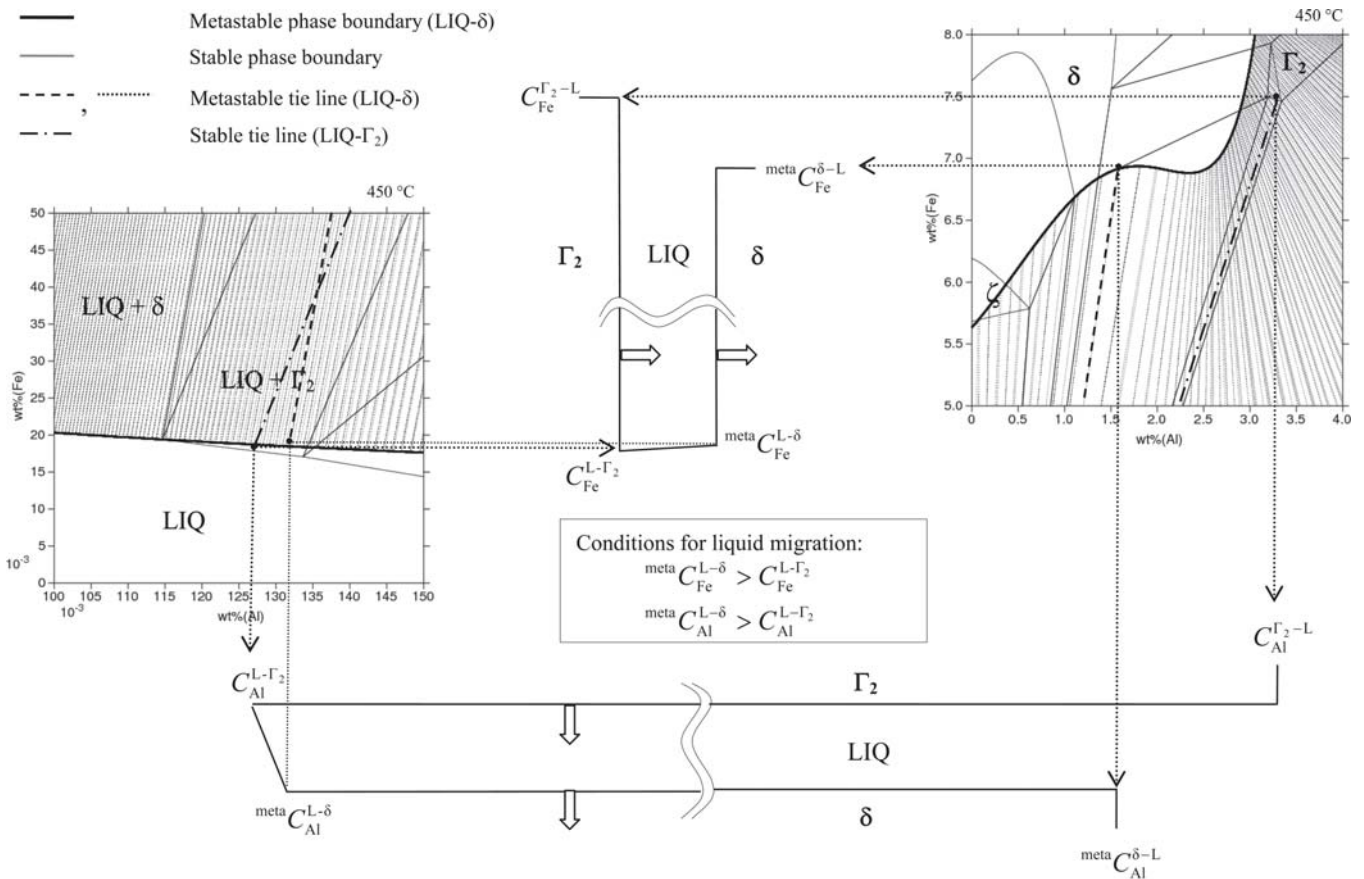


Fig. 4 Example of the transformation of the metastable δ phase to the equilibrium Γ_2 phase via the migration of an intermediary liquid film.^[14]

Figure 5(a), shows the equilibrium isothermal section of the Fe-Al-Zn ternary at 450 °C, while Fig. 5(b) shows the metastable equilibrium, which is considered to drive the migration of the liquid and the growth of the Γ_2 phase at the expense of the δ phase.



(a)



(b)

Fig. 5 (a) Stable equilibrium phase diagram of Zn-Fe-Al at 450 °C. (b) Solute concentrations leading to the formation of the Γ_2 phase from the metastable δ phase via the migration of the supersaturated liquid at 450 °C.

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The authors are not yet in a position to understand the detailed sequence of isothermal events that lead to the formation of the highly supersaturated liquid from which the Γ_2 phase nucleates. It is likely that the early formation of δ from the liquid follows metastable tie-lines at the interface resulting in appreciable supersaturation of the particle with Al (and Fe). The Al is subsequently rejected from δ and is dissolved into the liquid while keeping the metastable local equilibrium at the interface. The stable Γ_2 phase starts to nucleate in the supersaturated liquid by accepting Al, creating a new interface. Γ_2 then grows through the interfacial motion (i.e., LFM), which is driven by the concentration difference between the interfaces in the liquid. Supersaturation at the external interface of the δ particle should be moderated by immediate replenishment from the surrounding liquid. Γ_2 may therefore only nucleate in the liquid trapped inside the δ phase.

The concentrations at both interfaces change as the Γ_2 phase continues to grow inside the δ particle. Each concentration approaches an equilibrium value, which in turn slows down the interfacial motion. The growth of Γ_2 and the shrinkage of δ will eventually cease when the local system reaches the three-phase equilibrium (liquid, δ , and Γ_2).

Under the assumption of local equilibrium, transient concentrations and positions of the interface, for instance, can be estimated by utilizing the same mathematical arguments presented in section 2.1. In the present case, the front of the liquid film will be in contact with the δ phase, while the trailing face will be in contact with the Γ_2 phase. Coherency is assumed to have no influence in this case. An example of the predicted film migration kinetics is presented in the following section.

3. Modeling Results

The most convenient way of displaying the results of the present modeling is in terms of graphic representations that make use of normalized or dimensionless axes. The authors start by presenting the results on coherency-driven film migration; the effect of the initial liquid composition on the kinetics of film migration is shown in Fig. 6. The results for the binary 0-2 system are recovered when the concentration of solute 1 is low. However, as the initial concentration of solute 1 in the liquid increases, one starts to observe effects that are unique to the ternary or multicomponent system. Figure 6(a) clearly shows that the liquid film will stabilize, meaning that its thickness will become essentially constant and its migration rate will become very slow. When such conditions are reached, the solidification of the liquid film will change from being controlled by diffusion in the liquid phase to being controlled by solid state diffusion, as discussed in the study by Sinclair et al.^[11]

The effect of the ratio of the diffusion coefficients of the two solutes in the liquid on the kinetics of film migration is shown in Fig. 7(a). A maximum initial solidification rate is expected for a well-defined value of D_2/D_1 , which is in this case slightly smaller than 1. This point is further illustrated in terms of Fig. 7(b), which shows the solute concentration gradient across the liquid film; the kinetics of film migration

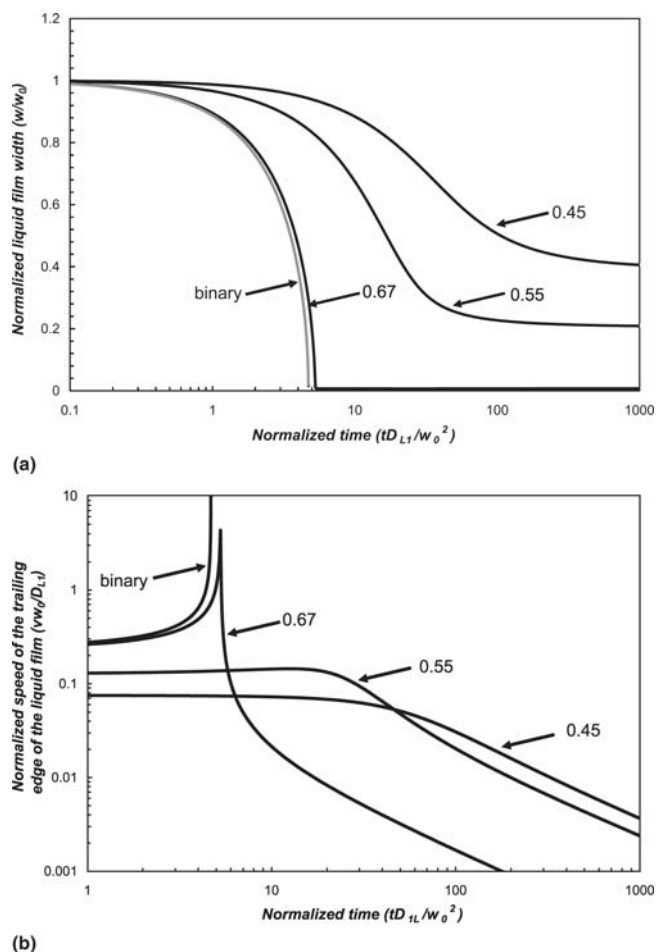
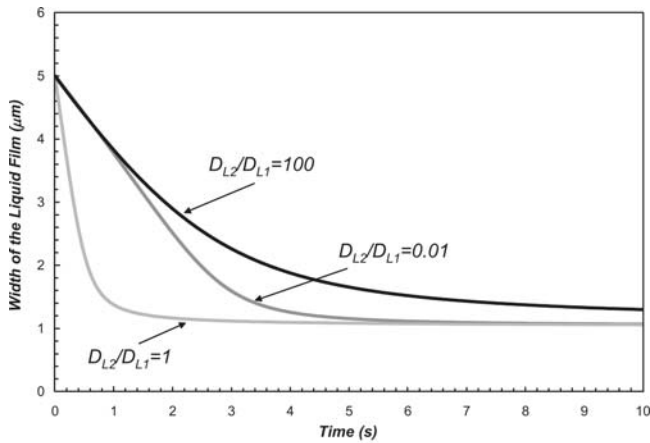


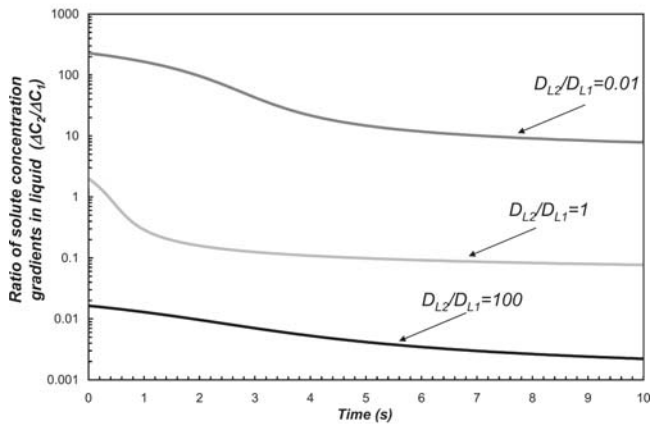
Fig. 6 Effect of initial concentration on (a) the time-evolution of the width of the liquid film and (b) the migration velocity of the trailing edge of the film in a hypothetical coherency-driven (0-1-2) system

is controlled by solute 2 when $D_2/D_1 \ll 1$, the reverse is true for large values of D_2/D_1 , and mixed control is observed when $D_1 \sim D_2$.

We next turn our attention to chemically driven LFM. In a baseline study of a binary Fe-Zn system, in which a metastable δ phase was dissolved in the liquid phase and replaced by a more stable ζ precipitate, the results obtained were fully equivalent to the binary coherency-driven LFM example of Fig. 3. In the present ternary case, in which a metastable δ is replaced by Γ_2 , the results are expressed in terms of real time, width, and velocity (Fig. 8). It is clear from these results that significant growth of Γ_2 can occur based on the proposed mechanism. It should be pointed out, however, that a high supersaturation of the δ phase is essential for the observation of significant Γ_2 growth. This point becomes evident by comparing Fig. 8(b), which shows the liquid film velocity, and Fig. 8(c), which shows the concentrations of the Al and Fe in the δ and Γ_2 phases; when supersaturation of the δ phase is small, the velocity becomes negligible, and no appreciable growth of the Γ_2 phase is expected.



(a)



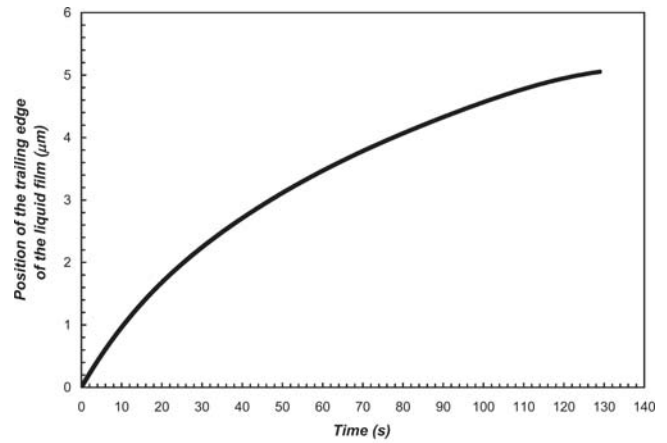
(b)

Fig. 7 Effect of the ratio of the diffusion coefficients on the (a) time evolution of the width of the liquid film and (b) the concentration gradient of solutes 1 and 2 across it. In this example, the width of the liquid film thickness was taken to be 5 μm, and the initial concentration was $C_2^{LA} = 0.55$. The ratio of the diffusion coefficients was varied while maintaining $\sqrt{D_{L1}D_{L2}} = 10^{-9}m^2/s$.

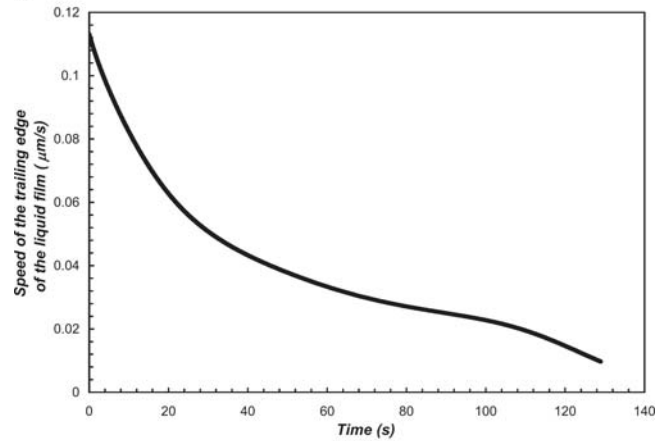
4. Discussion

The main thrust of this work has been to explore the likely results of adding a second solute, a third component, to the mix. This is particularly appropriate in a contribution to a symposium honoring Professor Mysore Dayananda, whose contributions to our understanding of the behavior of multicomponent systems are many and significant.

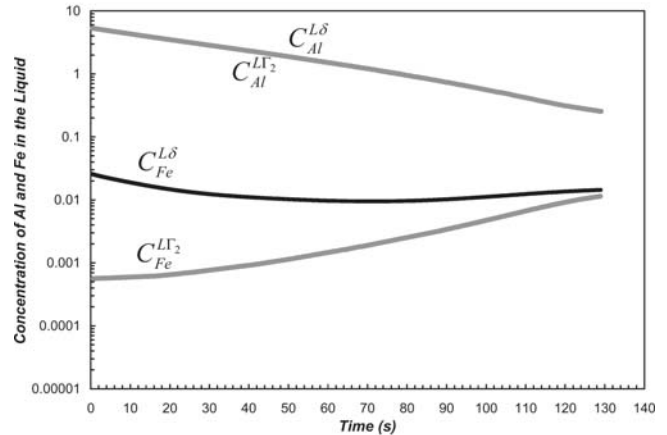
The phenomena discussed here have several features in common: all involve migrating coupled pairs of planar solid-liquid interfaces in isothermal systems; all depend on the rate of diffusion of the solute across the thin liquid film for their migration; and, in all cases, the driving concentration gradient is considered to be established between different local equilibrium compositions in the liquid on either side of the film. These phenomena could be considered to fall into a wider class of migrating liquid or amorphous films, which would include, for example, the case of a liquid film in a binary system that is subject to a thermal gradient,



(a)



(b)



(c)

Fig. 8 Time evolution of the (a) position, (b) velocity, and (c) concentrations within a liquid film during the $\delta \rightarrow \Gamma_2$ transformation. In this example, we used $w_0 = 5 \mu m$, $D_{Fe}^L = 1 \times 10^{-10} m^2/s = D_{Al}^L$ and $C_{Al}^{L\delta} = 0.054$.

or that of a liquid film that is subject to curvature. The field is rich with possibilities.

Besides the requirement that the solubilities on either side of the liquid film be different, it is also of interest to consider those conditions that will most naturally lead to an

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appropriate initial geometry. It is probably no accident that the first reports of coherency-induced LFM concerned the sintering of a dense array of (initially) spherical particles of a solid refractory metal, infiltrated with a second, liquid, metal.^[2-5] Similarly, the report of the replacement of a metastable initial phase by a more stable product by means of a “dissolution-reprecipitation” reaction,^[13] referred to a situation where a rather high volume fraction of the parent phase had precipitated from a liquid metal solution.

However, there is no reason that the conditions for LFM cannot be deliberately established to facilitate the study of the kinetics of migration. As noted in the introduction, the experimental study of this important subject has been limited largely to the observation of the existence or nonexistence of the phenomenon and has not dealt in depth with the kind of behavior discussed here.

For coherency-driven LFM, the present results indicate that the addition of small amounts of a third element (labeled “2” in this case) to a binary system (0-1) can have a profound influence on the kinetics of migration. For the case studied, this is related to a tendency of the instantaneous interfacial tie-line to shift so as to approach the direction of zero strain, and therefore to decelerate the film relative to the binary case. In the limit when the film reaches that zero-strain condition, motion will cease. The route to further solidification will then lie in the depletion of the solute in the film by solid-state diffusion in the leading grain, in analogy with the more symmetrical case discussed by Sinclair et al.^[11] The amount of ternary addition needed to bring this about is predicted to be on the order of 1% in this example, although this estimate may be dependent to some extent on the detailed structure of the numerical methods used.

5. Conclusions

- The conditions for isothermal LFM are: the establishment and maintenance of a concentration difference across the liquid film, due, in the cases considered here, to either coherency stresses in the parent phase or chemical solubility differences between metastable and stable phases; and an appropriate initial geometry.
- The effects of adding a second solute to the liquid phase result from the additional degree of freedom in the choice of instantaneous local equilibrium compositions on either side of the liquid film. In general, and in contrast to the binary case, these compositions will not be constant, but will change with time. In the case of coherency-driven LFM, the interfacial tie-lines will shift in the direction of zero strain. When and if the

associated tie-line is attained, the migration of the film will stop.

Acknowledgments

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