Dispersed phase Multicomponent Diffusion

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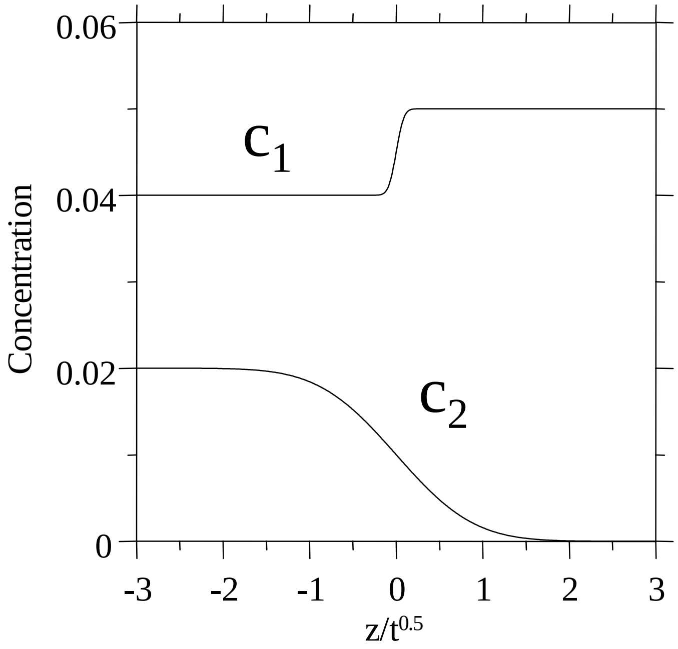
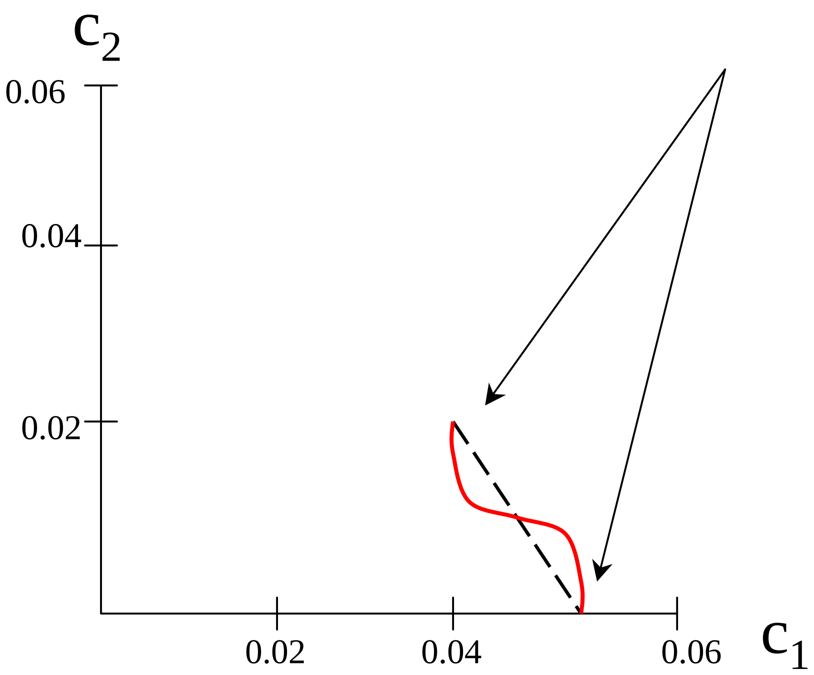
- What is a diffusion path?
- Assume planar interfaces ⇒ Compute Diffusion Path ⇒ Virtual path ⇒ Unstable Planar interface (Constitutional supersaturation) ⇒ Multiphase layers
- Examples from work of Clark and Rhines
- Examples of internal oxidation/ppt.
- Model of Morall et al. Diffusion paths in α / $\alpha+\beta$ diffusion couples
- What does DICTRA do? Example: Transient Liquid Phase Bonding

What is a Diffusion Path?

If c_2 is fast diffuser



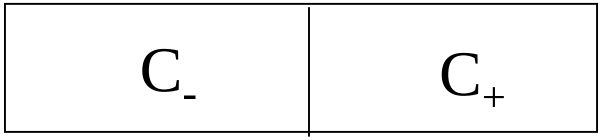
Path near ends is constant c_1

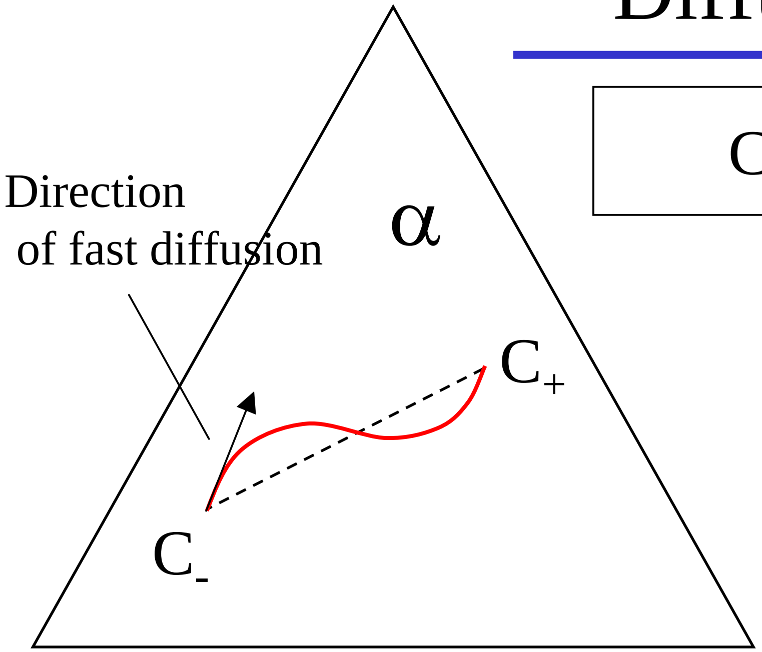


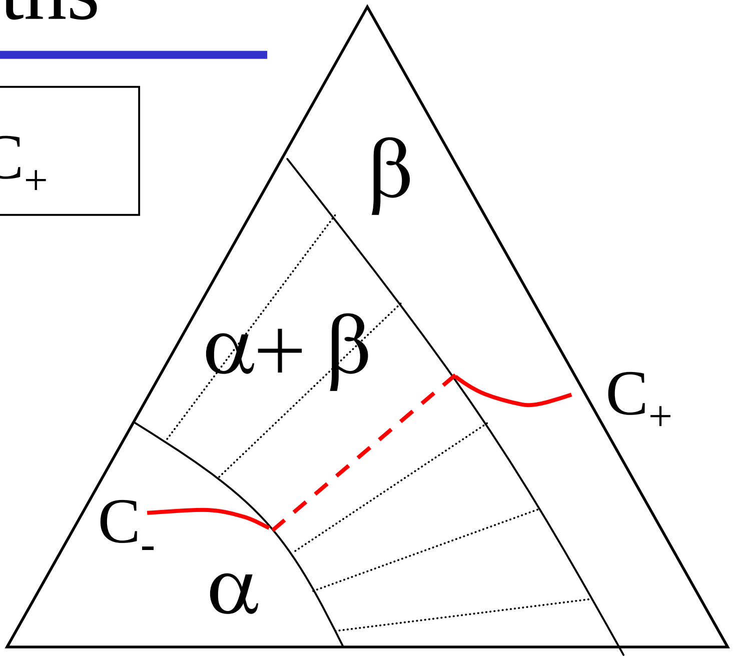
Diffusion paths in single phase ternary alloy are S-shaped.

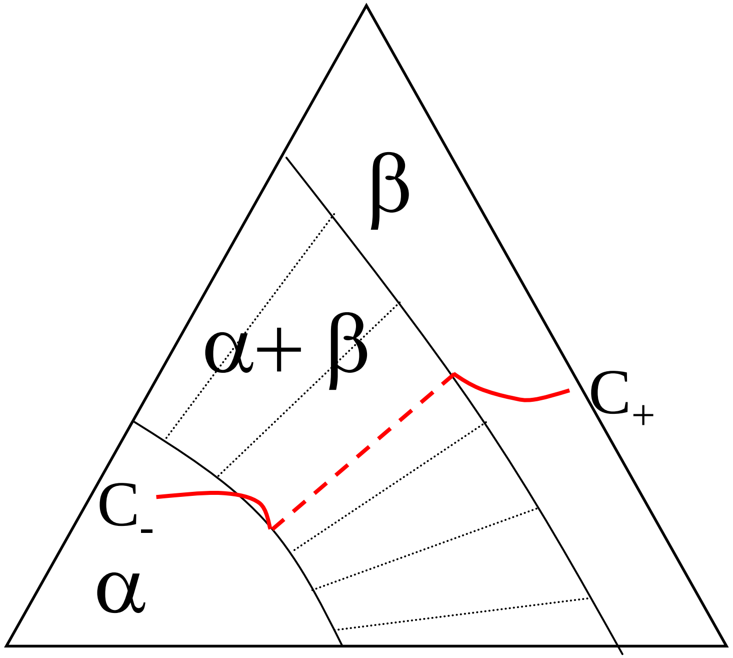
Even with no off-diagonal diffusion coefficients

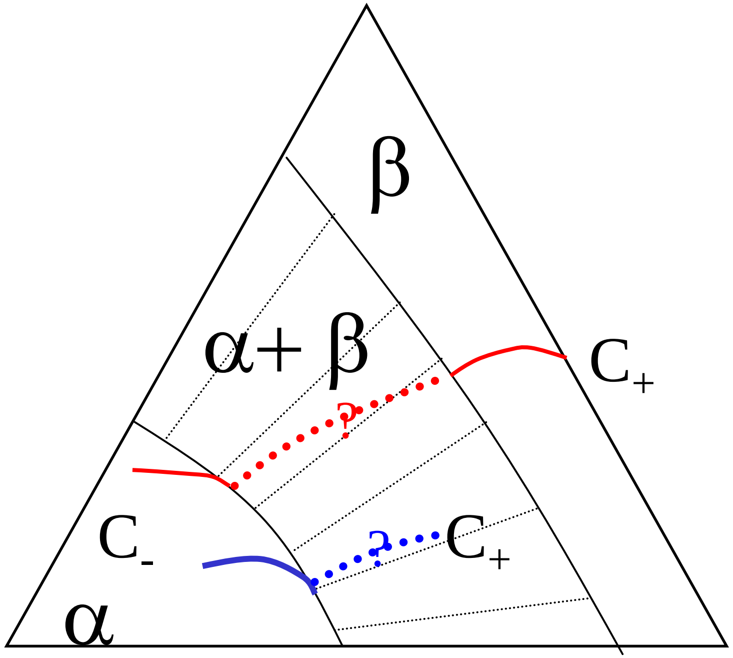
Diffusion Paths











J.B. Clark & F.H. Rhines Trans. ASM 51(1959) 199

Al-Mg-Zn

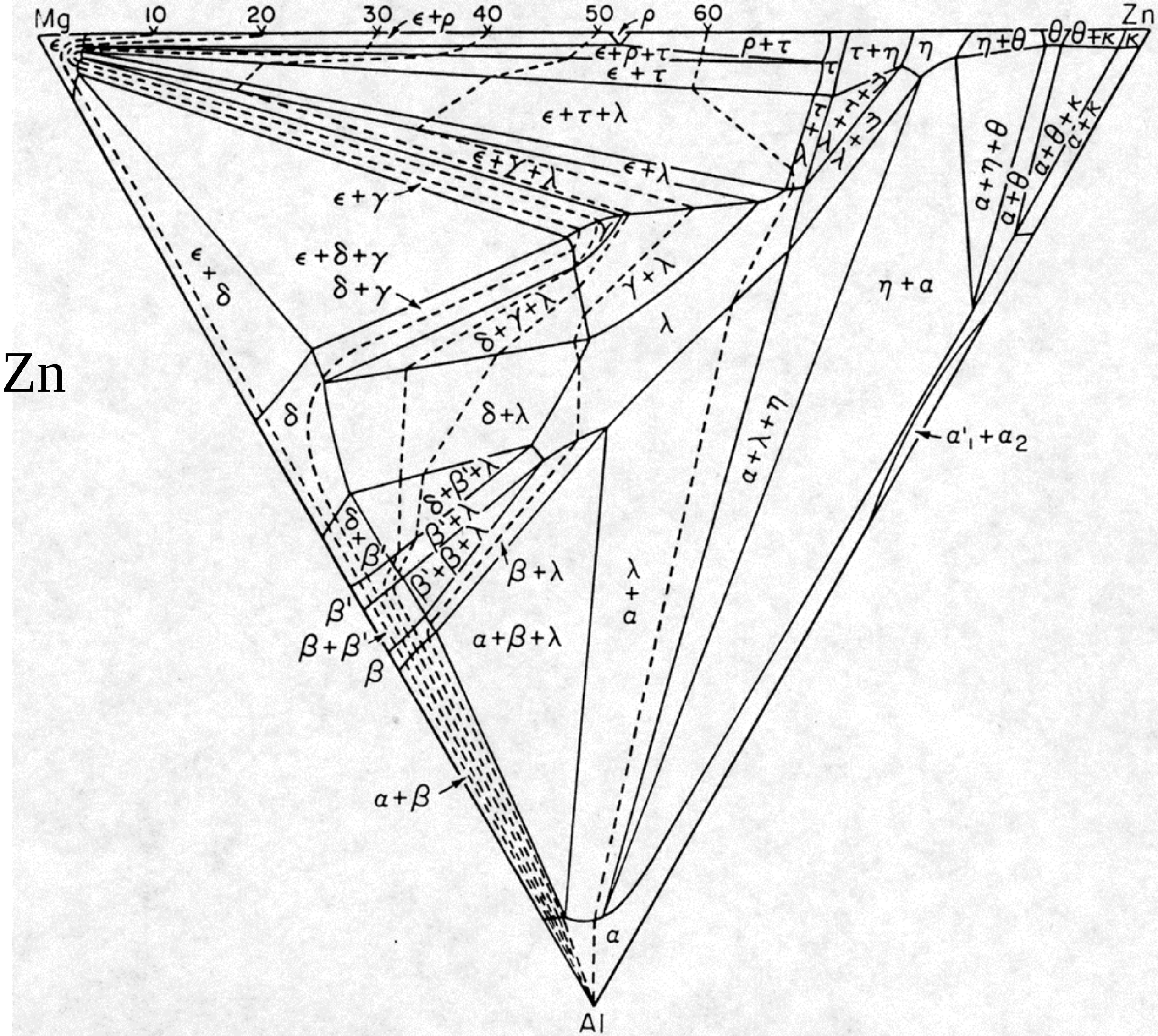


Fig. 1—The Redetermined 335 °C (635 °F) Isotherm of the Al-Mg-Zn Phase Diagram Showing the Paths of Composition in the Diffusion Zones of the Al-Mg-Zn Couples. The

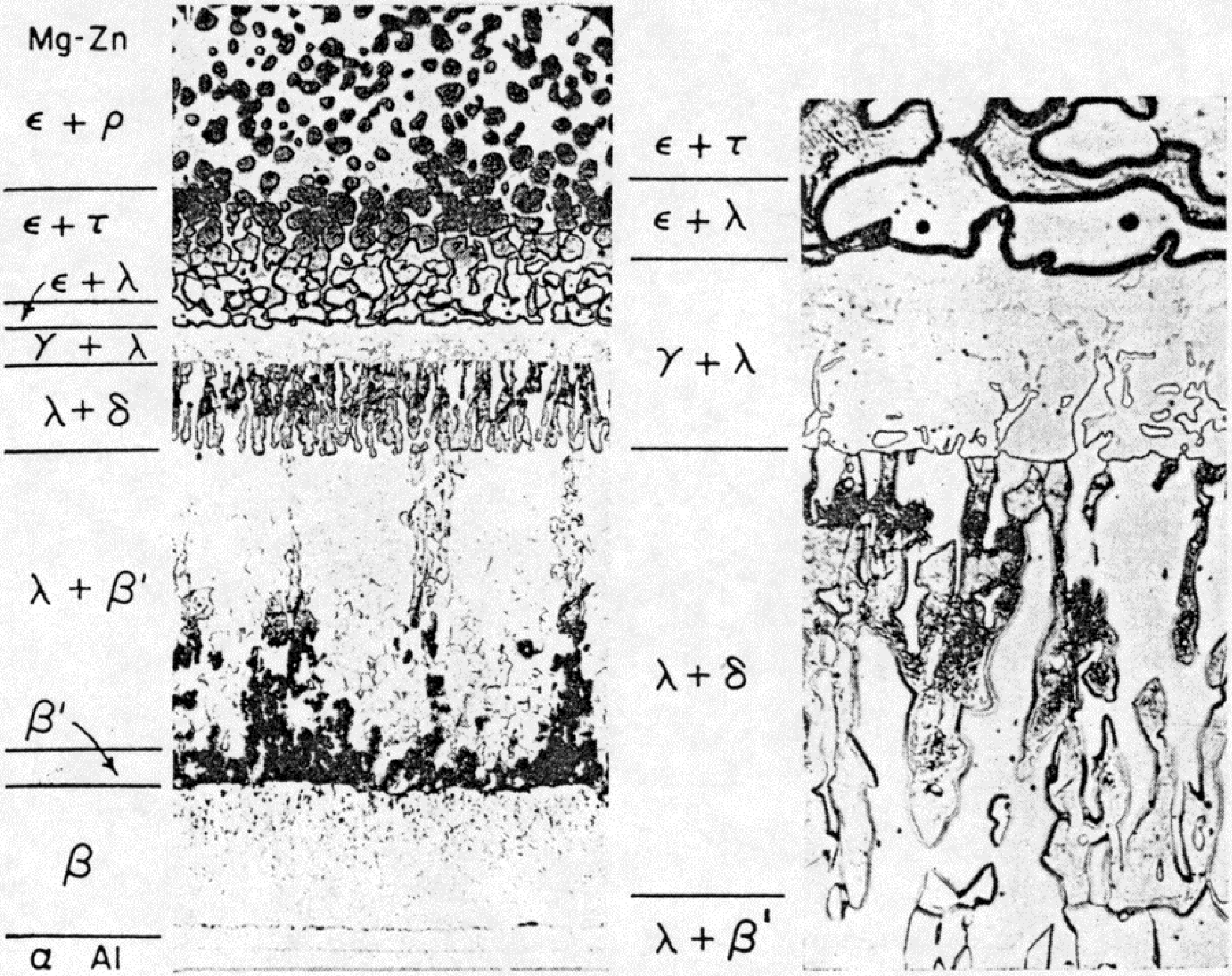
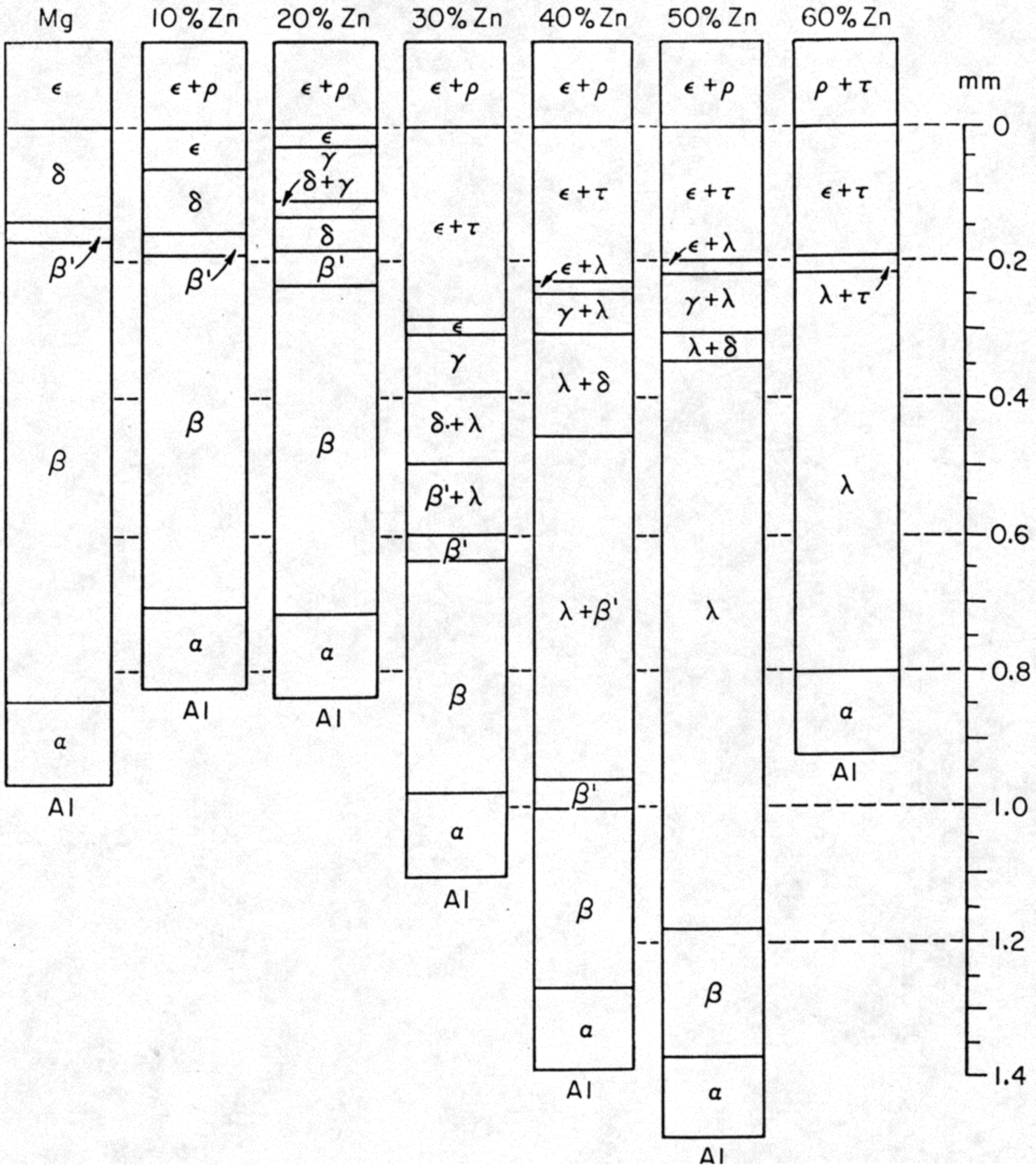
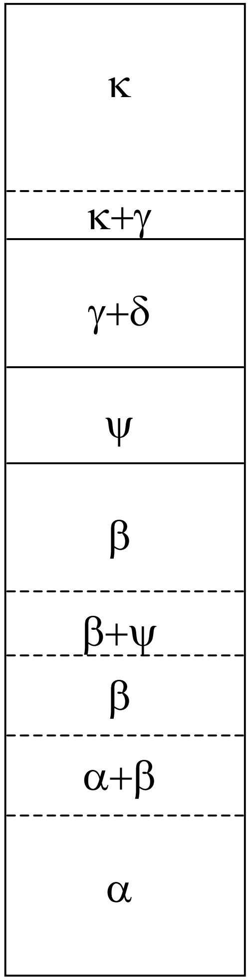


Fig. 6—The Diffusion Layer Structure of a 40% Zn 60% Mg Alloy/100% Al Couple After 1000 Hours at 335 °C (635 °F). Micrograph at left glycol etchant, × 65; micrograph at right, × 325. HCl-HF etchant.


Mg
10% Zn
20% Zn
30% Zn
40% Zn
50% Zn
60% Zn
ε
δ
β'
β
α
Al
ε+ρ
ε
δ
β'
β
α
Al
ε+ρ
ε
γ
δ+γ
δ
β'
β
α
Al
ε+ρ
ε+τ
ε
γ
δ+λ
β'+λ
β'
β
α
Al
ε+ρ
ε+τ
ε+λ
γ+λ
λ+δ
λ+β'
β'
β
α
Al
ε+ρ
ε+τ
ε+λ
γ+λ
λ+δ
λ
β
α
Al
ρ+τ
ε+τ
λ+τ
λ
α
Al
mm
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

J. B Clark, Trans. AIME 227(1963) 1250



κ

κ+γ

γ+δ

ψ

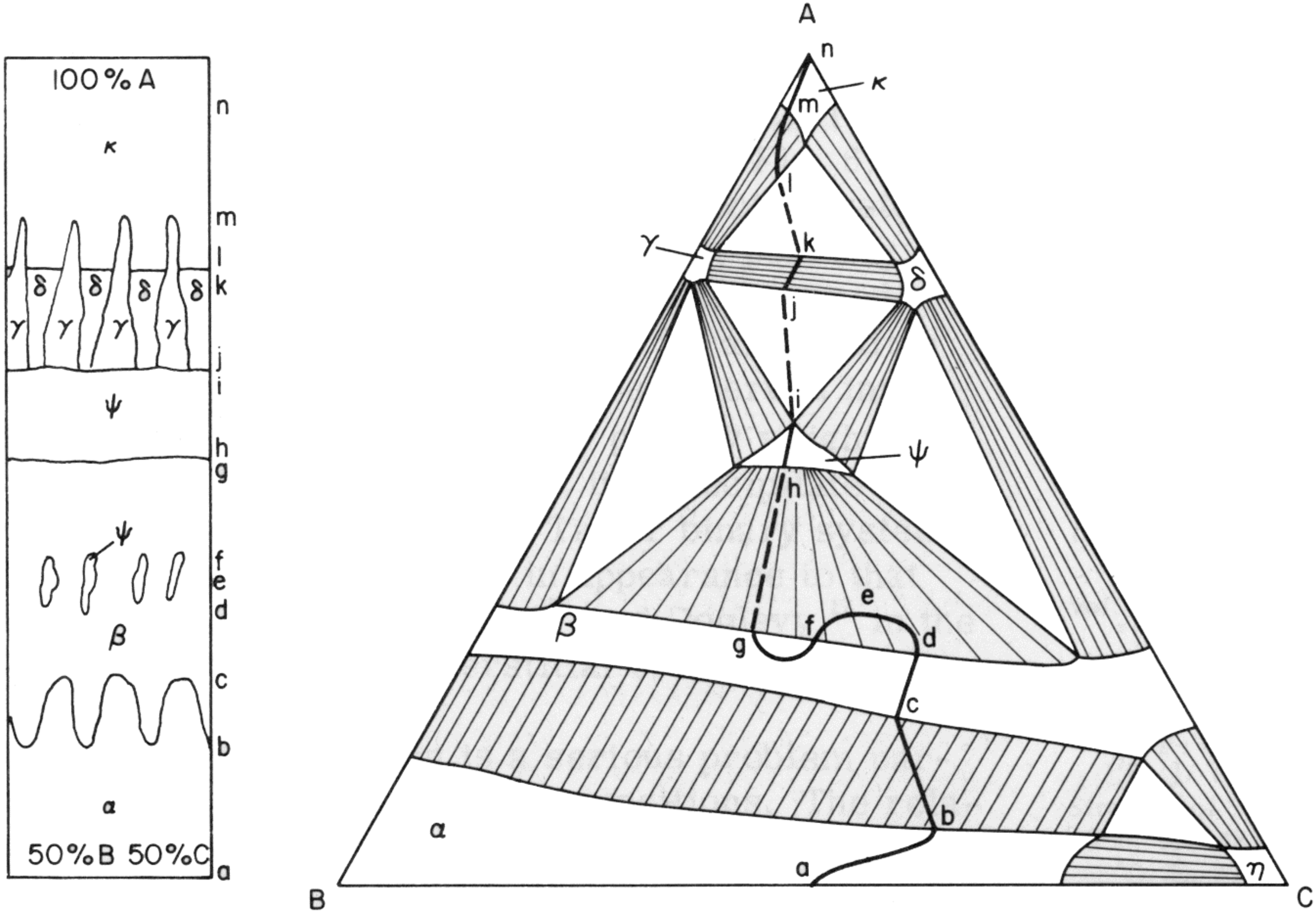
β

β+ψ

β

α+β

α



Example of Internal Oxidation to Mixed Oxidation
from: Birks & Meier Intro. to High Temperature Oxidation of Metals

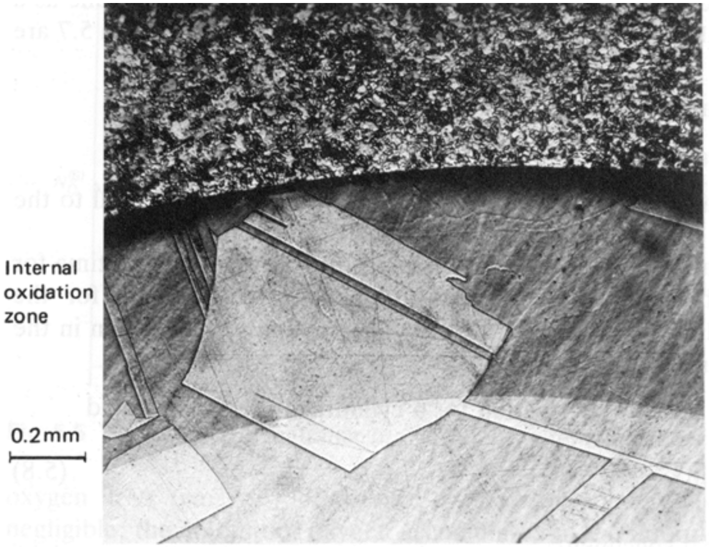


Fig. 5.6 Microstructure of a Cu–O.47 wt% Ti alloy internally oxidised at 800 °C for 97 hours

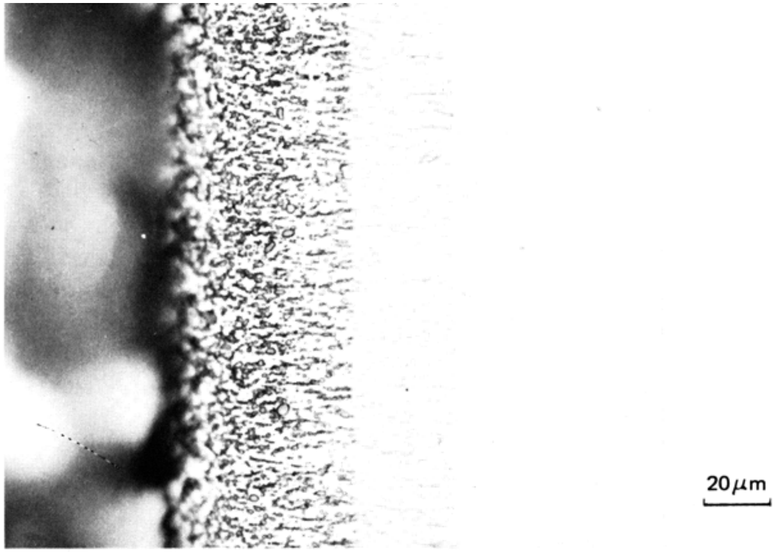


Fig. 5.8 Co–5 wt% Ti alloy internally oxidised for 528 hours at 900 °C. Unetched

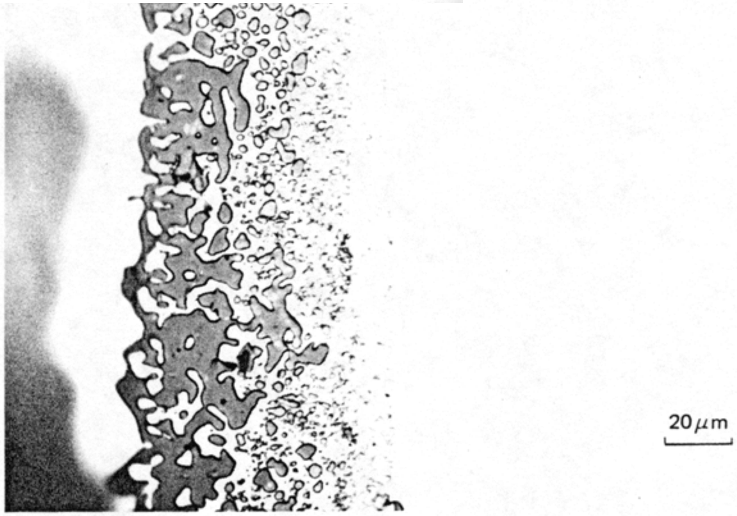


Fig. 5.11 Transition from internal to external oxidation in Co–7.5 wt% Ti alloy internally oxidised for 528 hours at 900 °C. Unetched

Model of J. Morall for Diffusion in Multiphase Region

- Define average concentrations of two phase (α+β) mixture

$$\frac{\partial \overline{C}_1}{\partial t} = -\frac{\partial \overline{J}_1}{\partial z} \quad \& \quad \frac{\partial \overline{C}_2}{\partial t} = -\frac{\partial \overline{J}_2}{\partial z}$$

- Assume flux in (α + β) mixture depends only on concentrations of α phase

$$\begin{cases} \overline{J}_1 = -D_{11}\dfrac{\partial c_1^\alpha}{\partial z} - D_{12}\dfrac{\partial c_2^\alpha}{\partial z} \\ \overline{J}_2 = -D_{21}\dfrac{\partial c_1^\alpha}{\partial z} - D_{22}\dfrac{\partial c_2^\alpha}{\partial z} \end{cases}$$

- Phase diagram tie lines give relationships (neglect Gibbs-Thomson Effect)

$$\begin{cases} c_1^\alpha = g(\overline{C}_1, \overline{C}_2) \\ c_2^\alpha = h(\overline{C}_1, \overline{C}_2) \end{cases}$$

- Chain rule gives →

$$\begin{cases} \bar{J}_1 = -\underline{\left[D_{11} \dfrac{\partial c_1^\alpha}{\partial \overline{C}_1} + D_{12} \dfrac{\partial c_2^\alpha}{\partial \overline{C}_1} \right]} \dfrac{\partial \overline{C}_1}{\partial z} - \underline{\left[D_{11} \dfrac{\partial c_1^\alpha}{\partial \overline{C}_2} + D_{12} \dfrac{\partial c_2^\alpha}{\partial \overline{C}_2} \right]} \dfrac{\partial \overline{C}_2}{\partial z} \\ \bar{J}_2 = -\underline{\left[D_{21} \dfrac{\partial c_1^\alpha}{\partial \overline{C}_1} + D_{22} \dfrac{\partial c_2^\alpha}{\partial \overline{C}_1} \right]} \dfrac{\partial \overline{C}_1}{\partial z} - \underline{\left[D_{21} \dfrac{\partial c_1^\alpha}{\partial \overline{C}_2} + D_{22} \dfrac{\partial c_2^\alpha}{\partial \overline{C}_2} \right]} \dfrac{\partial \overline{C}_2}{\partial z} \end{cases}$$

- These matrix of these four D’s have a zero determinant
- One eigen value is zero and the eigen vector is // to tie-lines
- Other eigen value is non-zero
- Diffusion path in two phase region *jumps* along tie-lines with ‘zig-zags’ at angle to tie-lines

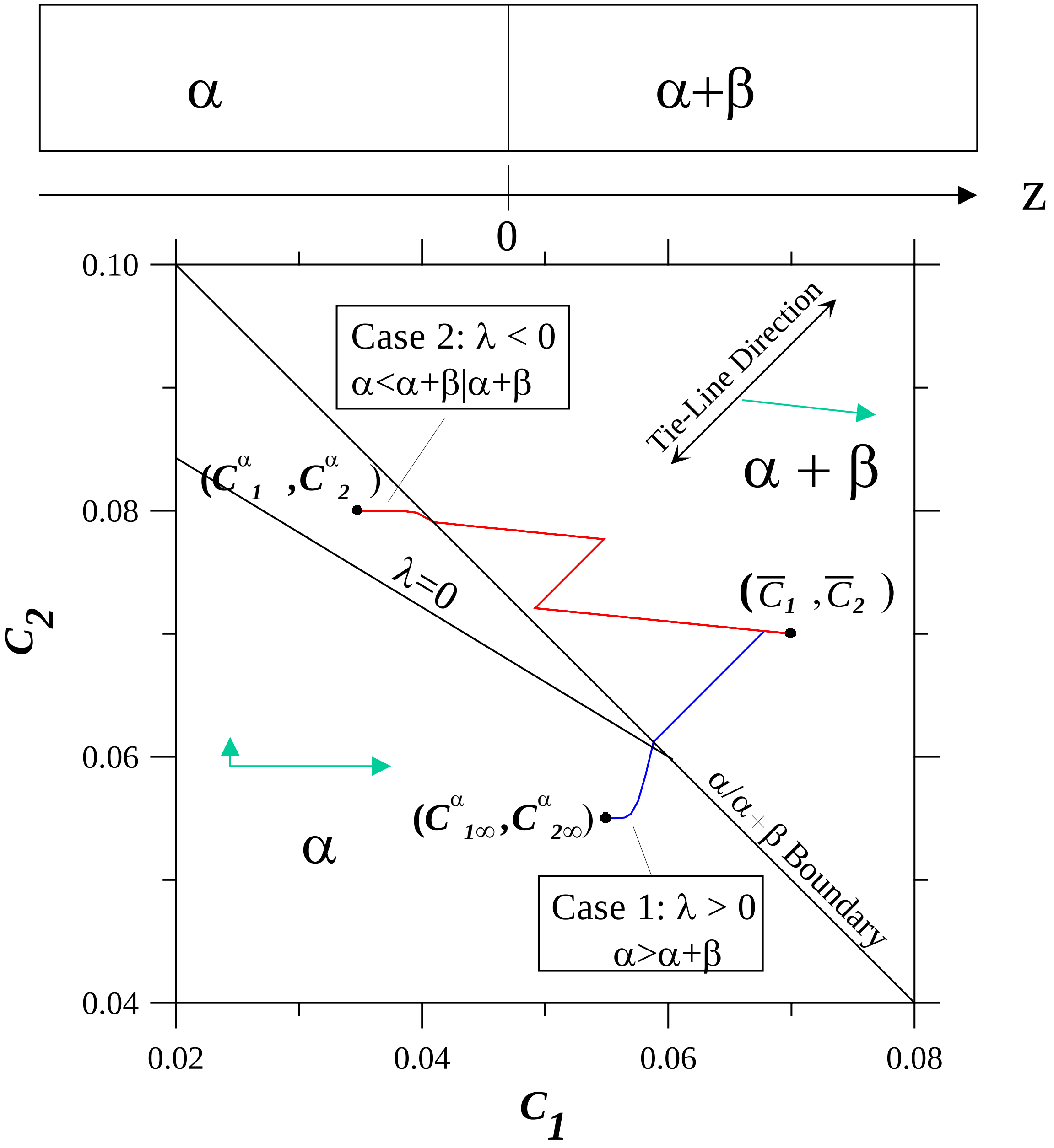
- If four D’s can be assumed constant→ error function solutions for ‘eigen concentrations
    - Interface position, $Z=\lambda t^{1/2}$,
    - One “error’ function solution is step function at z = 0
    - Other is ‘normal’

- Boettinger et al. Acta Mat.48 (2000) 481.
    - Proof about direction of $\alpha/(\alpha+\beta)$ ‘interfaces’& phase fraction jumps
    - Determined ‘Microstructure Map’ for $\alpha/(\alpha+\beta)$ diffusion couples

In α phase

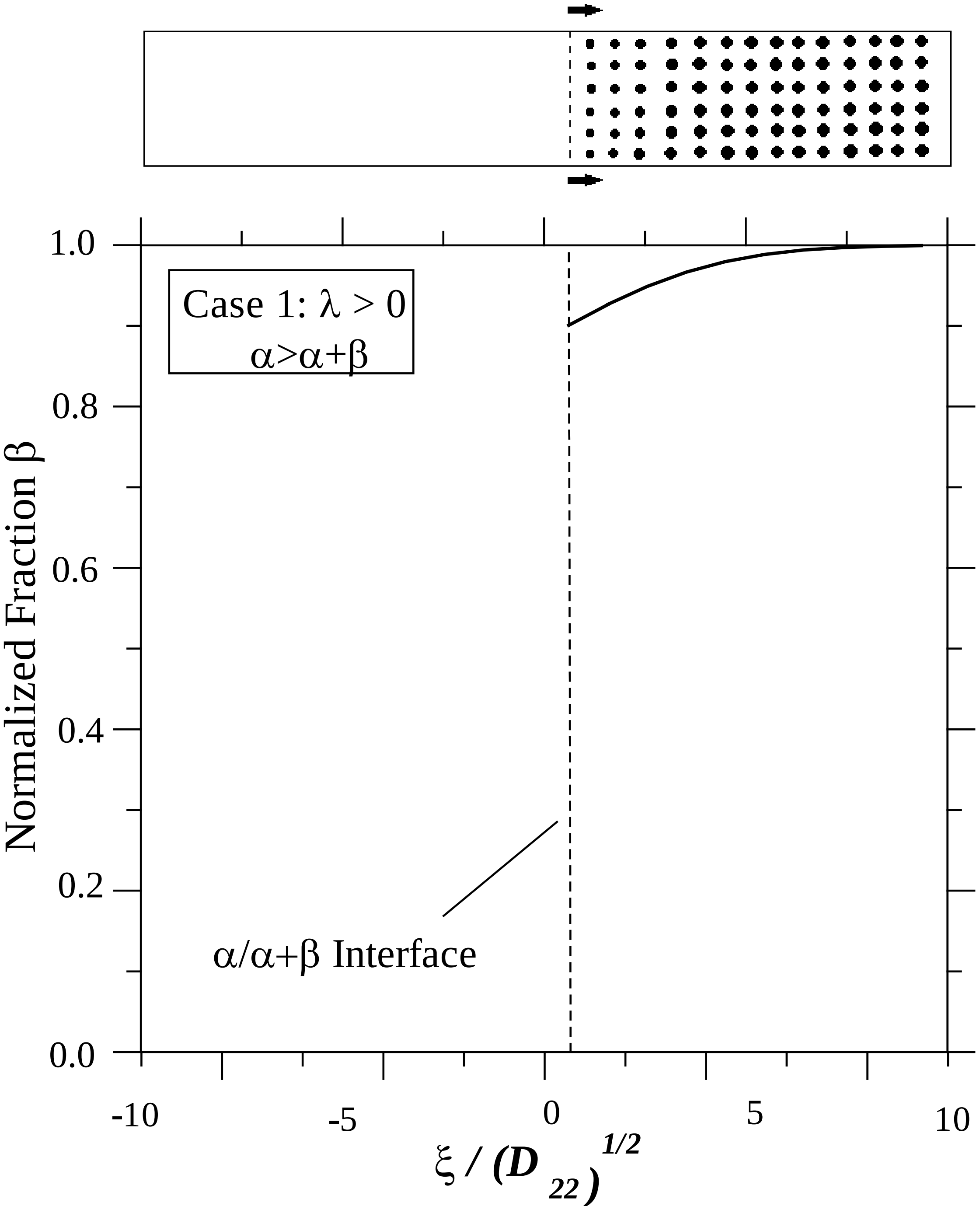
$D_{11}=10\ D_{22}$

$D_{12}= D_{21}=0$

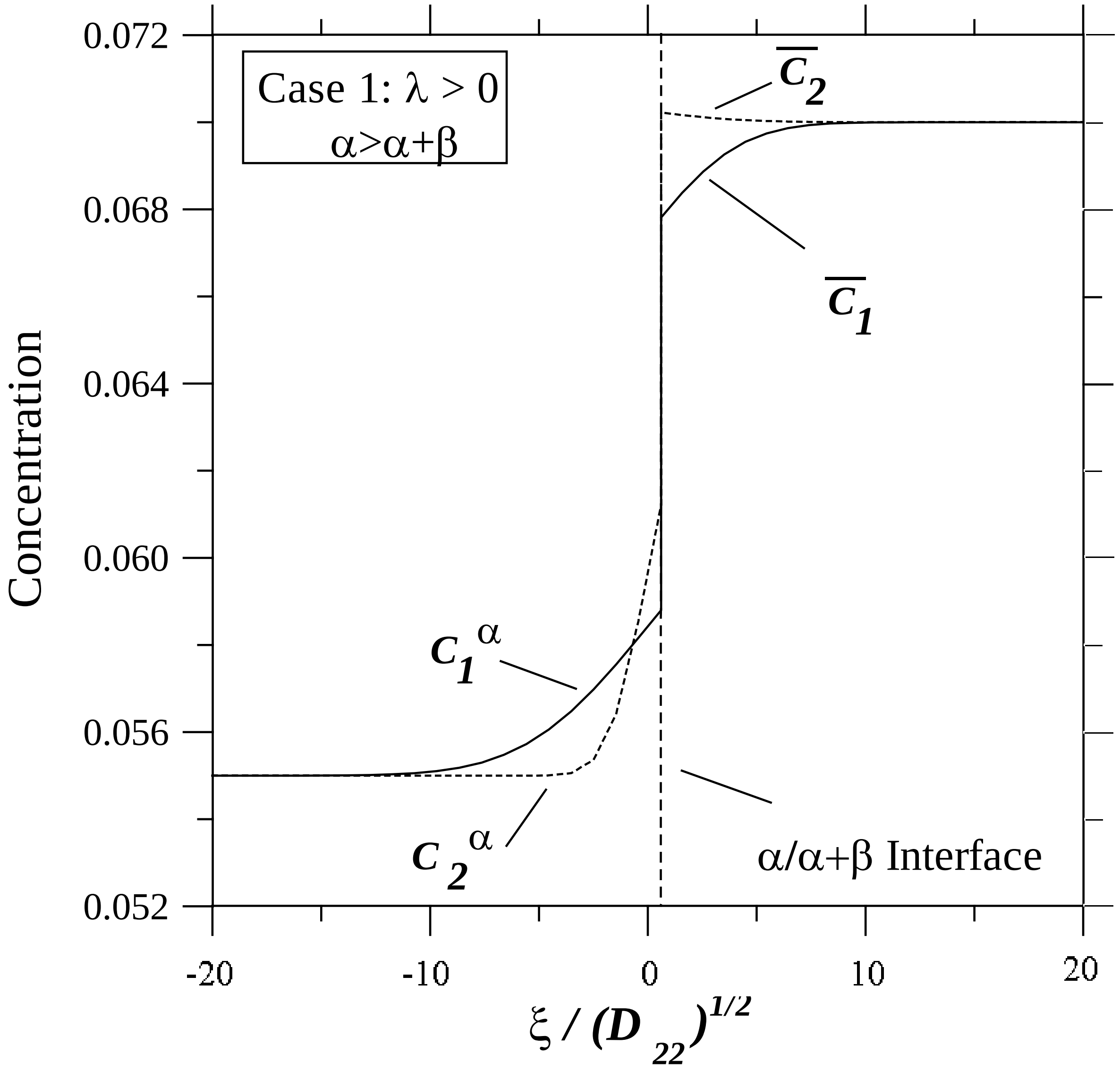


eigen vectors

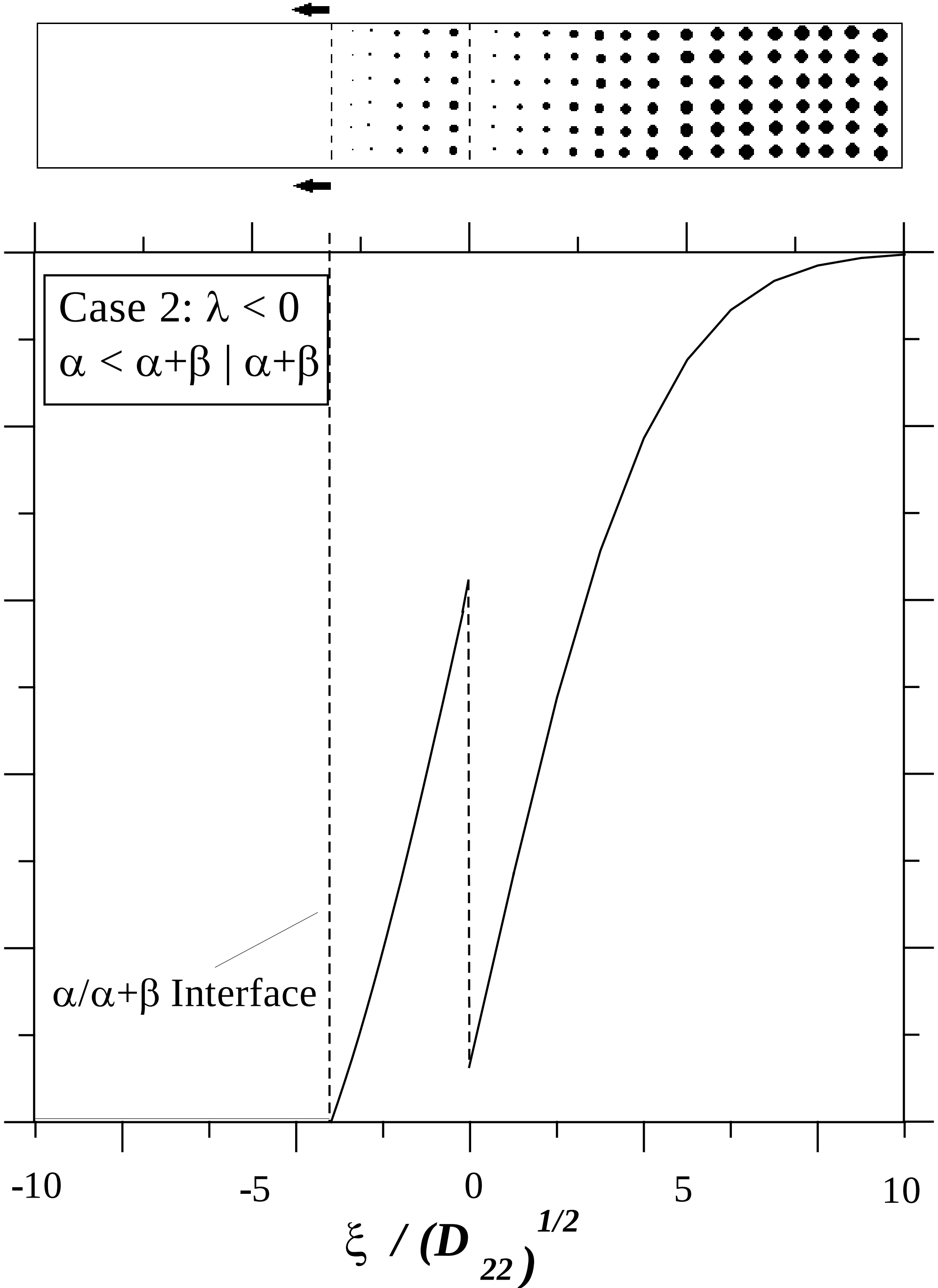
$\alpha>\alpha+\beta$



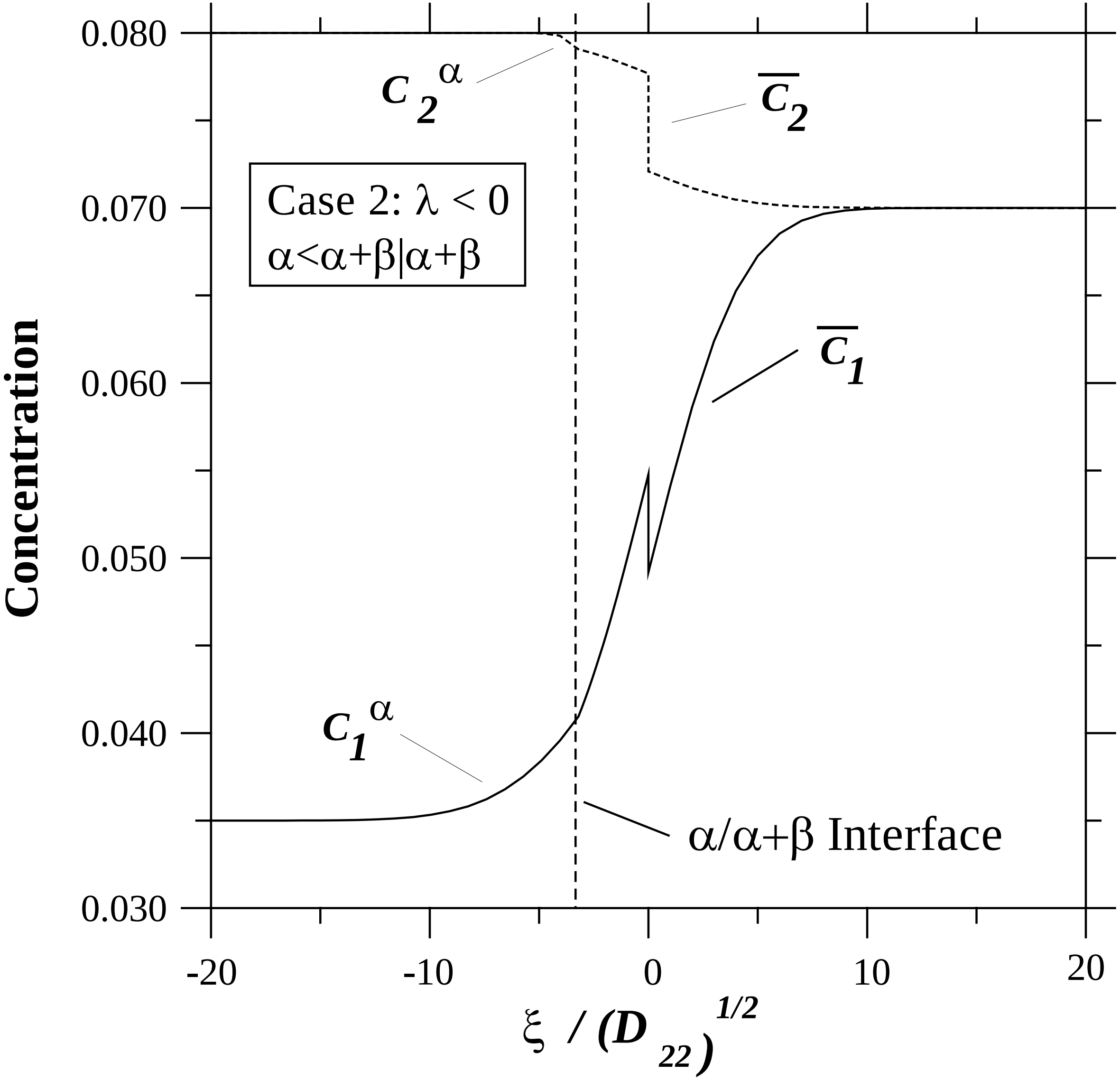
$\alpha > \alpha + \beta$



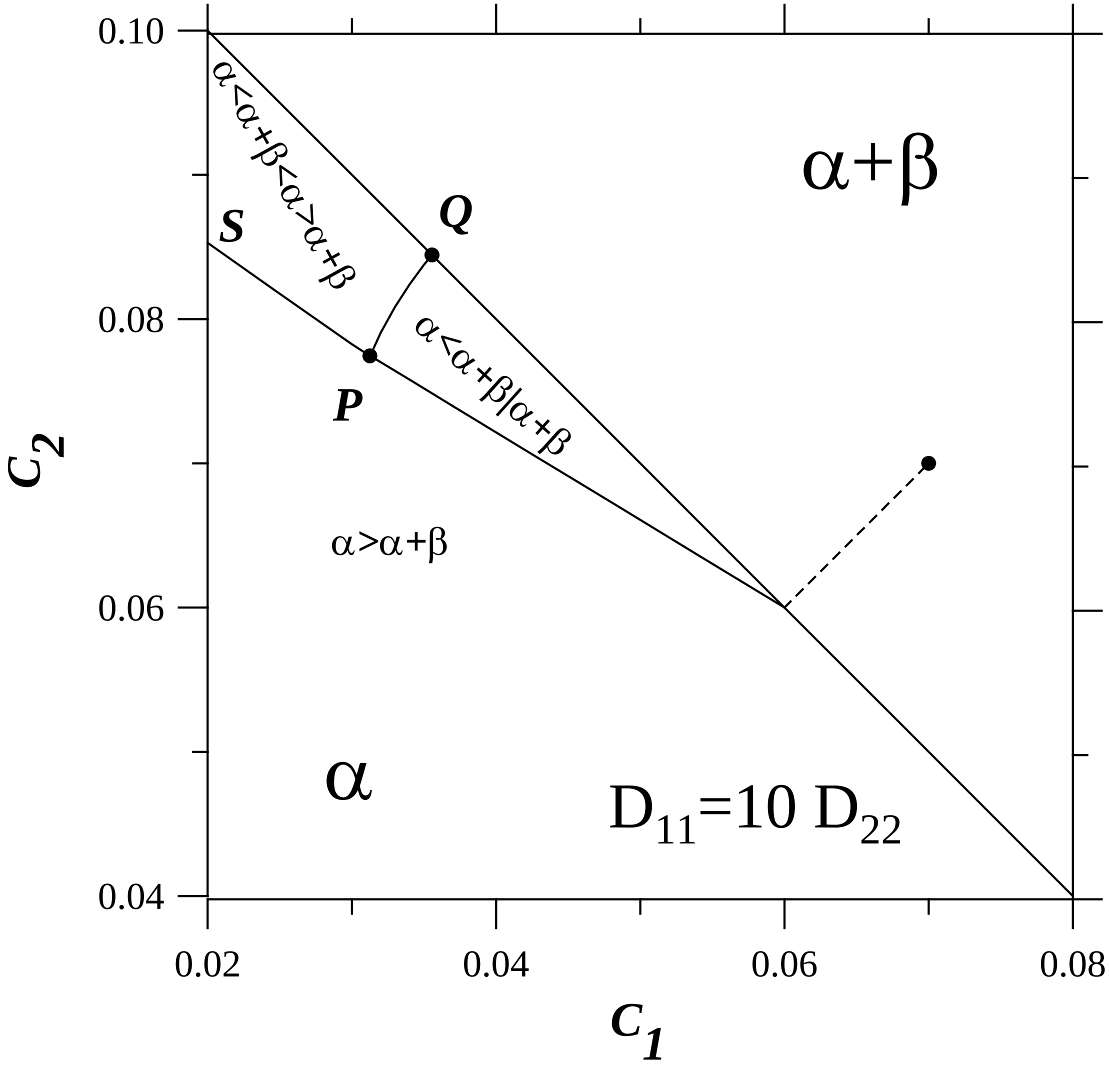
$\alpha < \alpha+\beta \mid \alpha+\beta$



$\alpha < \alpha+\beta \mid \alpha+\beta$



Diffusion Microstructures Predicted as α phase end point is varied



Boettinger, Campbell, Coriell & McFadden, Acta Mat, (2000)

H. Amy Chen (PhD Thesis w/ J. E. Morral, U. Conn, 2000)

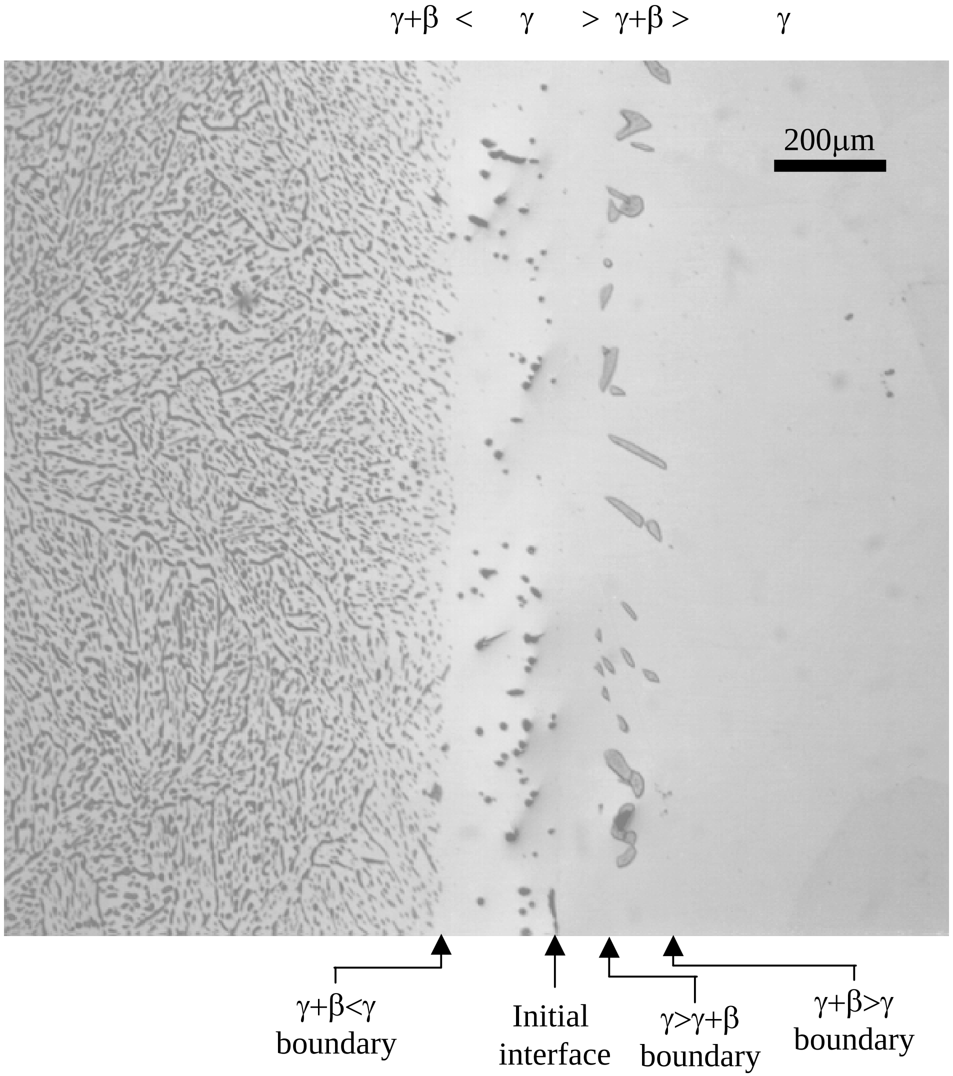
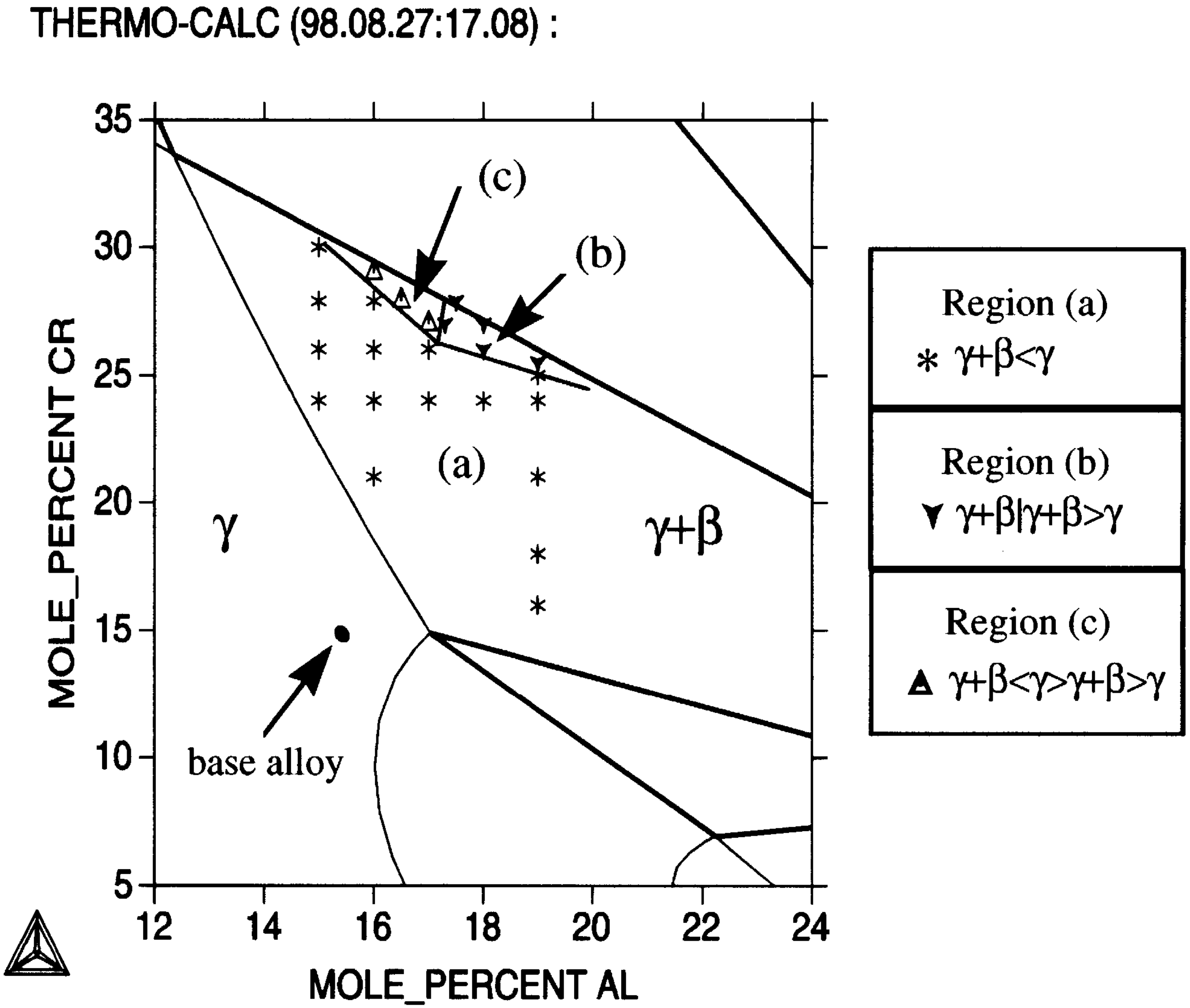


Figure 6.7 Type (c) interdiffusion microstructure

H. Amy Chen (PhD Thesis w/ J. E. Morral, U. Conn, 2000)



H. Amy Chen (PhD Thesis w/ J. E. Morral, U. Conn, 2000)

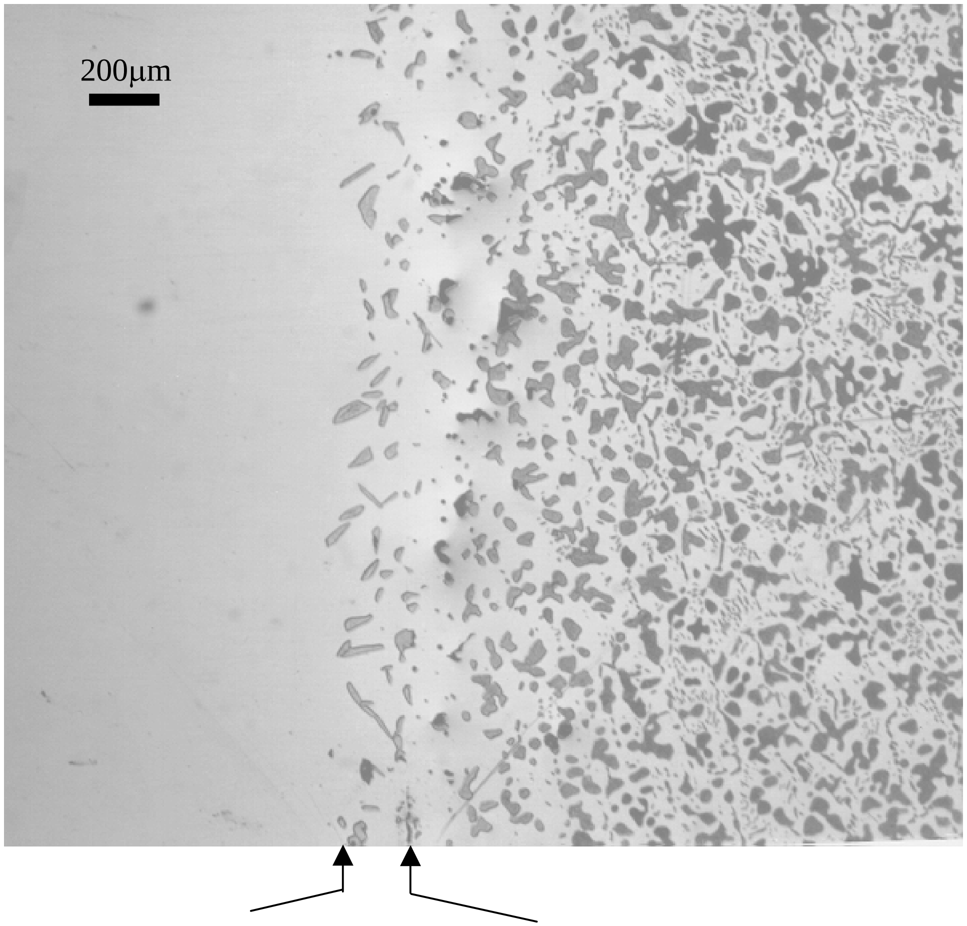
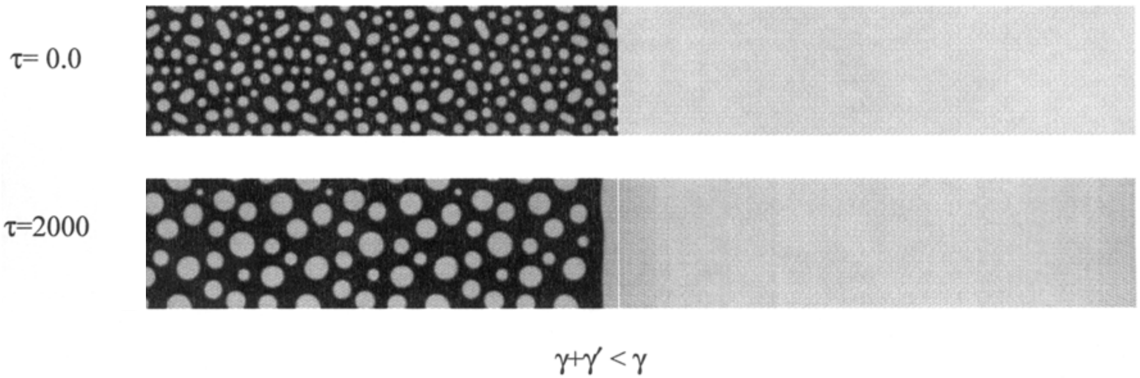


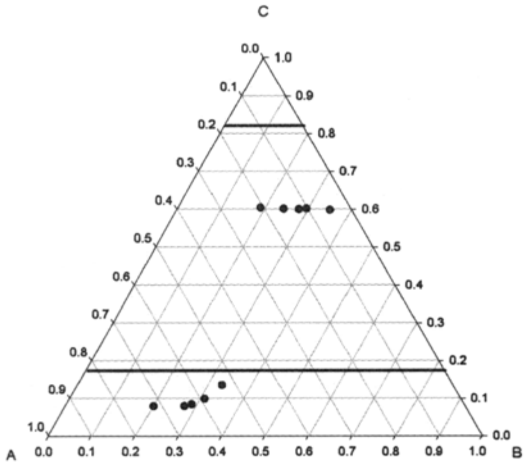
Figure 6.6 Type (b) interdiffusion microstructure

Simulations of Mutiphase Diffusion Couples

K. Wu, Y. Wang, (OSU) & J. E. Morall, (U. Conn) (2001)



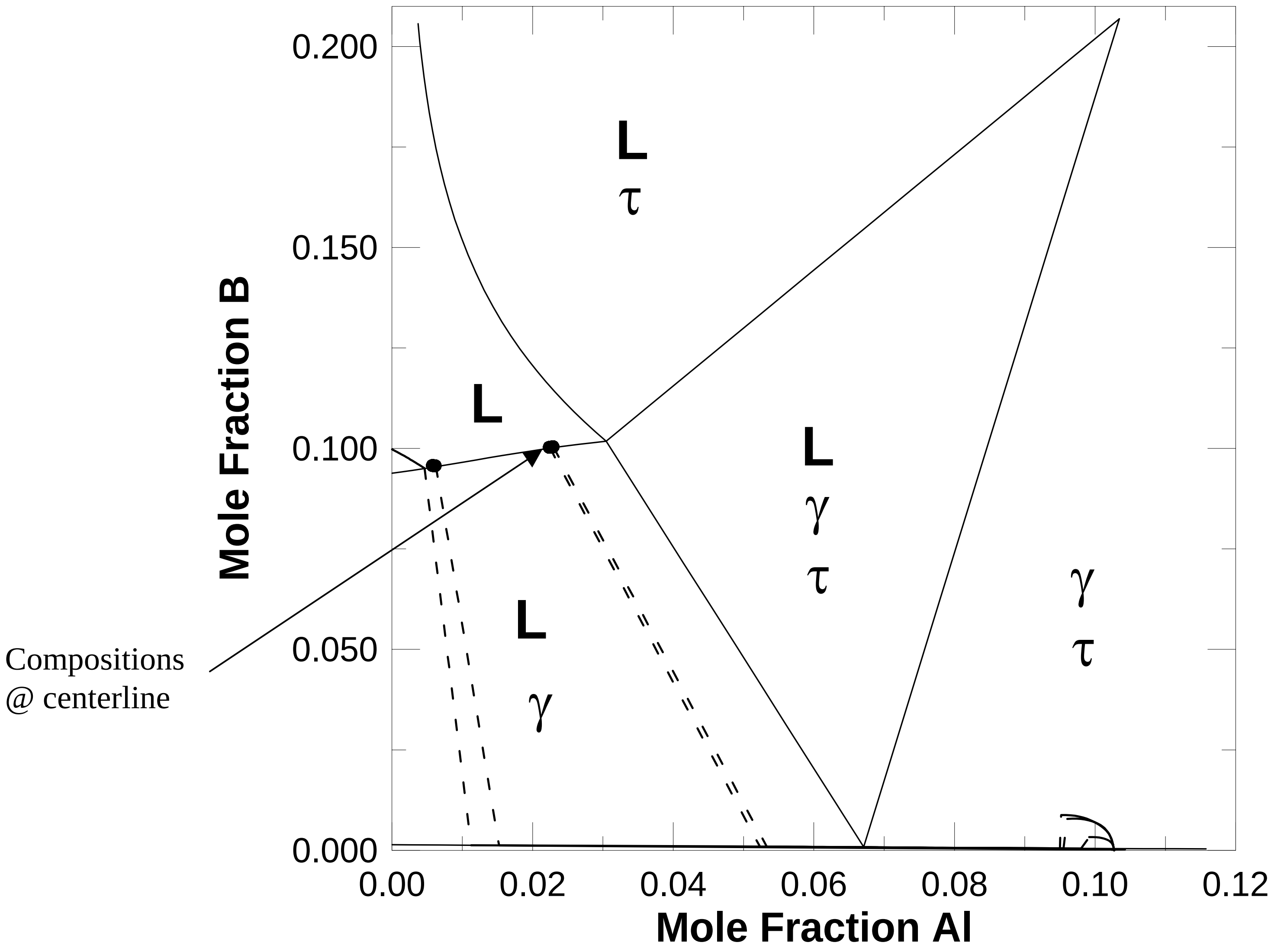
(a)



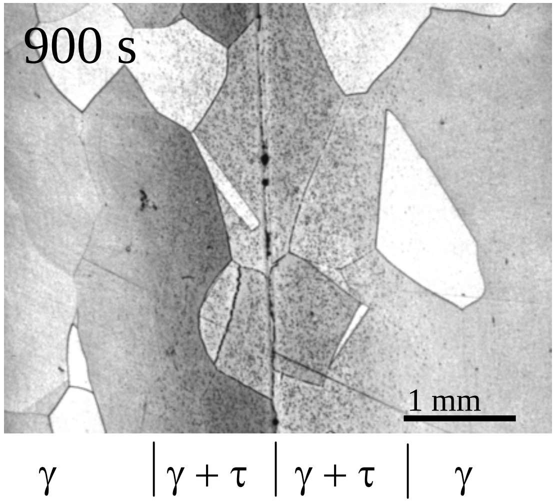
(b)

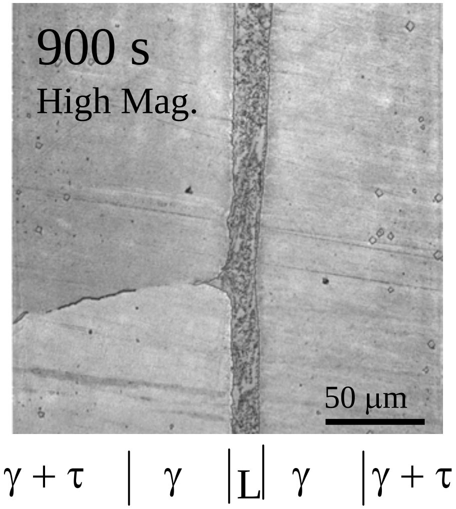
Figure 3. (a) Microstructural evolution during interdiffusion in a ternary $\gamma+\gamma'/\gamma$ couple of different continuous matrix phases. The atomic mobilities used in the simulation are $\beta_B=5.0$, $\beta_C=1.0$ and $\beta_A=5.0$. (b) The corresponding diffusion path.

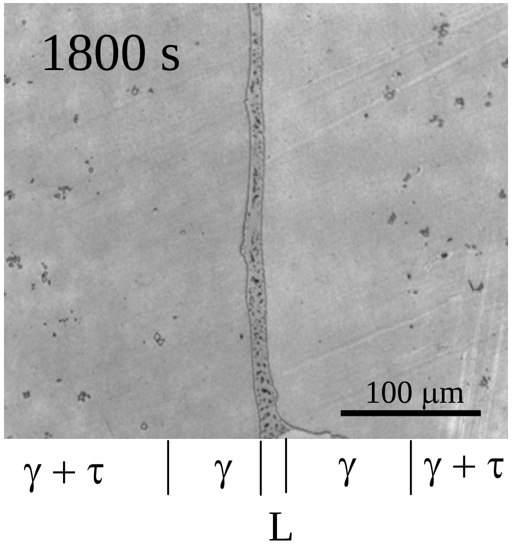
Example: Transient Liquid Phase Bonding

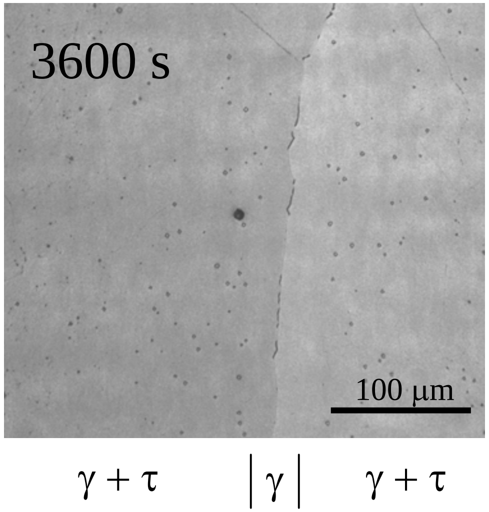

Mole Fraction B
0.200
0.150
0.100
0.050
0.000
0.00
0.02
0.04
0.06
0.08
0.10
0.12
Mole Fraction Al
L τ
L
L γ τ
L γ
γ τ
Compositions
@ centerline

Microstructures

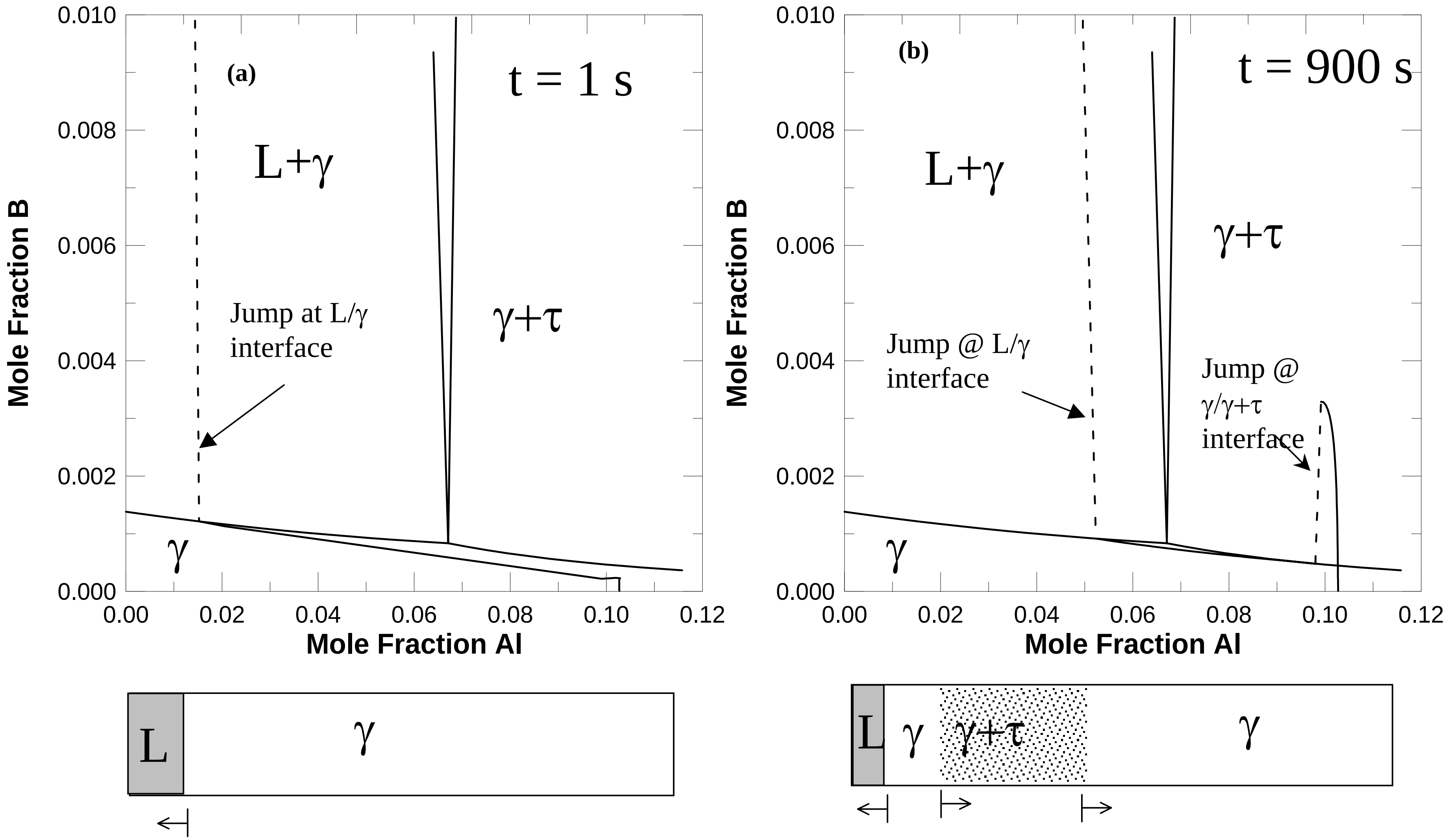




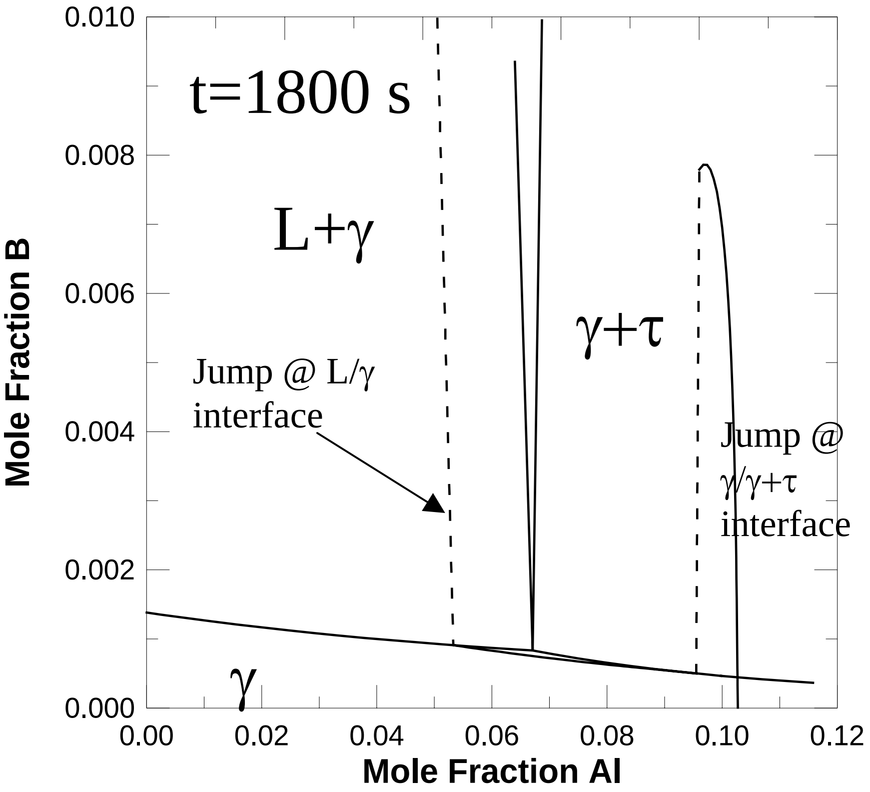


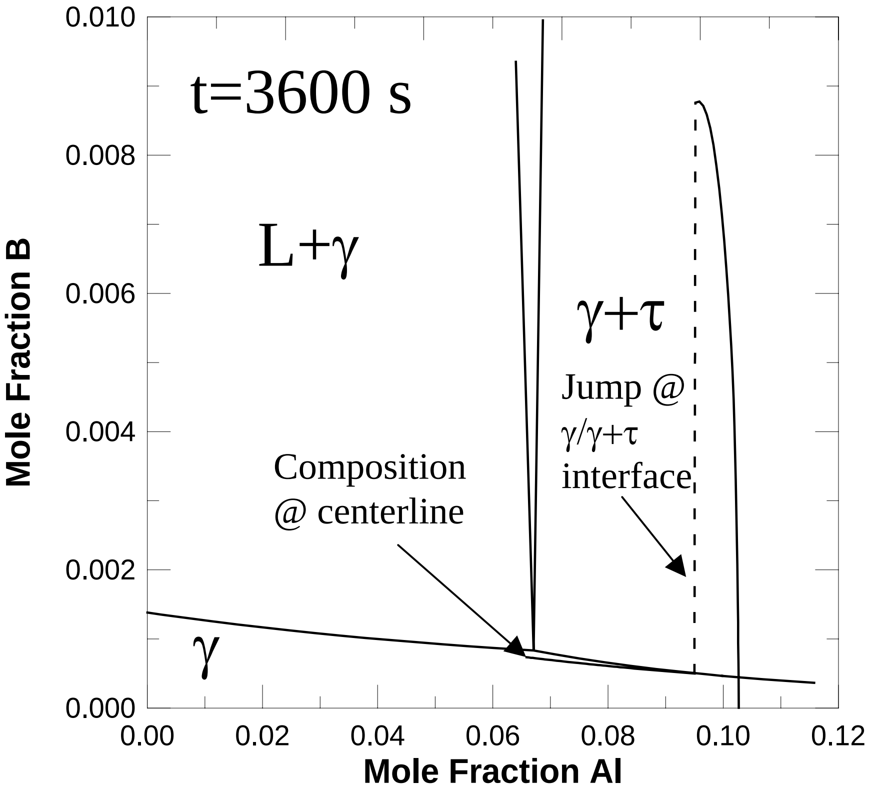


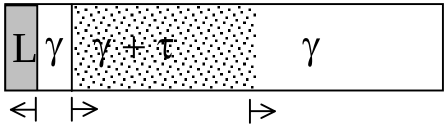
Calculated Diffusion Paths During TLP Bonding

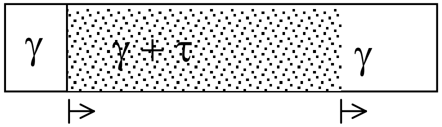


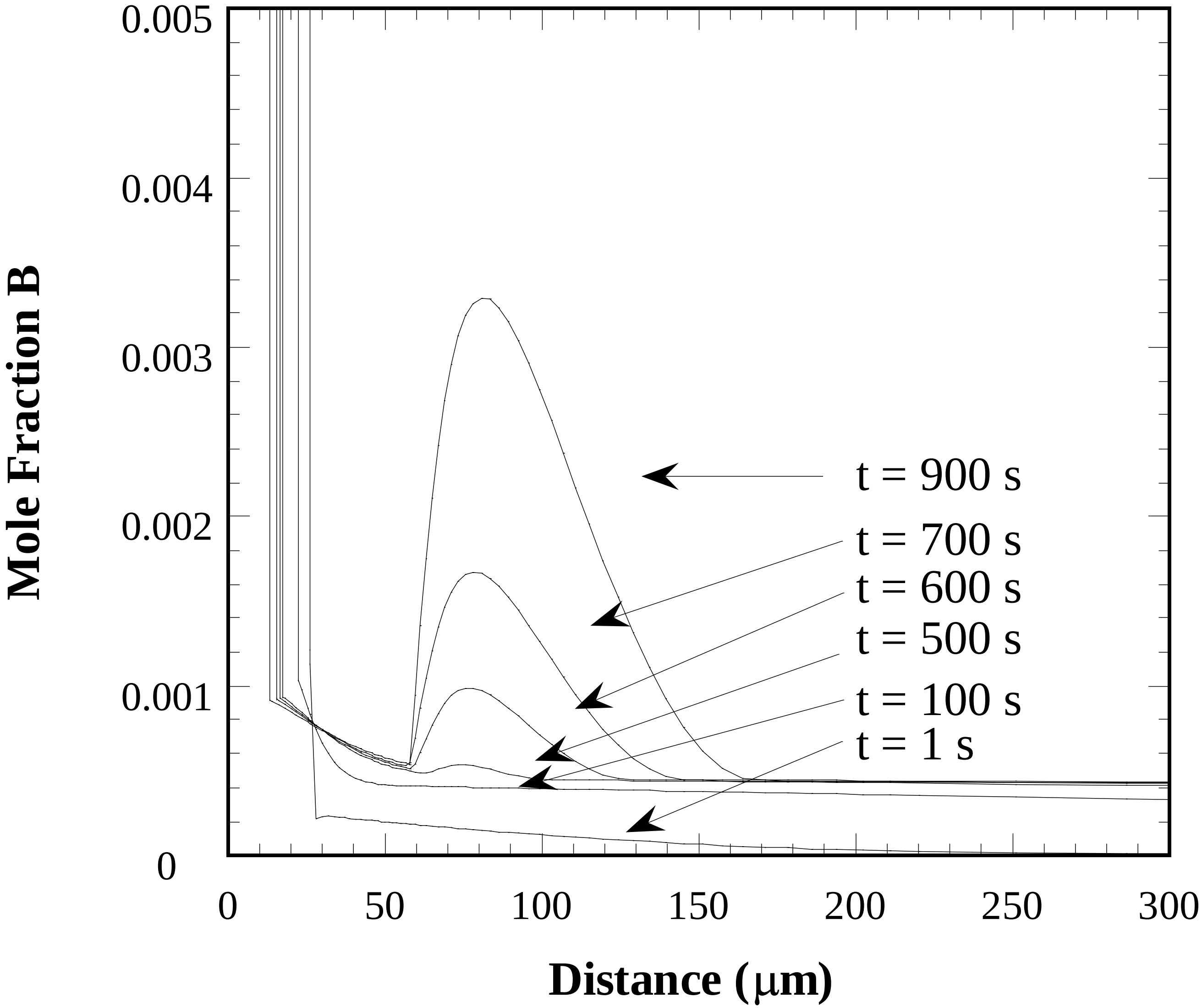
Calculated Diffusion Paths During TLP Bonding (Cont.)










Mole Fraction B
0.005
0.004
0.003
0.002
0.001
0
0
50
100
150
200
250
300
Distance (μm)
t = 900 s
t = 700 s
t = 600 s
t = 500 s
t = 100 s
t = 1 s

Conclusions

- Elementary aspectds of diffusion through multiphase microstructure regions can be modeled.
- Many challeges remain!