Phase Transformation of Materials

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Chapter 4. Solidification

4.3 Alloy solidification

4.3.1 Solidification of single-phase alloys

4.3.2 Eutectic solidification

No Diffusion on Solid, Diffusional Mixing in the Liquid

local equil. at S/L interface

no stirring→ diffusion

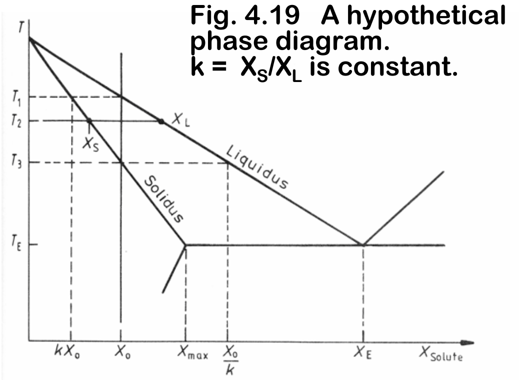
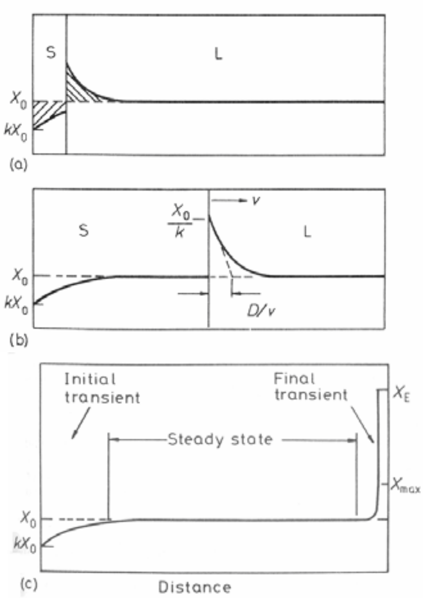


Fig. 4.19 A hypothetical phase diagram.
k = X_S/X_L is constant.

Consider the solidification during cooling under the conditions no diffusion on solid and diffusional mixing in the Liquid.

What would be the composition profile at $T_2 < T_{S/L} < T_3$?
What would be the steady state profile at T_3?
What would be the composition profile at T_E and below?

No Diffusion on Solid, Diffusional Mixing in the Liquid



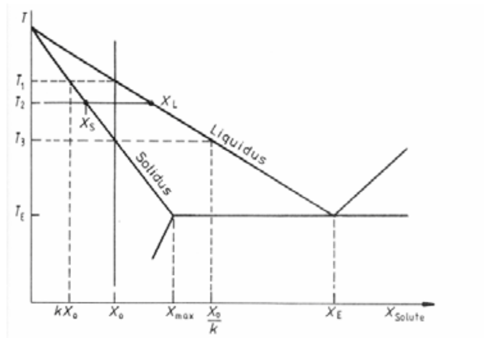


Fig. 4.22 Planar front solidification of alloy X_0 in Fig. 4.19 assuming no diffusion in solid and no stirring in the liquid.

(a) Composition profile when S/L temperature is between T_2 and T_3 in Fig. 4.19.

(b) Steady-state at T_3. The composition solidifying equals the composition of liquid far ahead of the solid (X_0).

(c) Composition profile at T_E and below, showing the final transient.

No Diffusion on Solid, Diffusional Mixing in the Liquid

During steady-state growth

Rate at which solute diffuses down the concentration gradient = Rate at which solute is rejected from the solidifying liquid

Set up the equation.

$$J = -D\frac{\partial X_L}{\partial x} = v\left(X_L - X_S\right)$$

Solve this equation.

$$X_S = X_o \text{ for all } x \geq 0$$

$$\frac{dX_L}{X_L - X_o} = -\frac{v}{D}dx$$

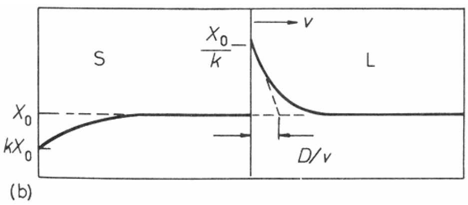
$$\ln\left(X_L - X_o\right) = -\frac{v}{D}x + c$$

$$x = 0; X_L = X_o / k$$

$$c = \ln\left(\frac{X_o}{k} - X_o\right)$$

$$\ln\frac{X_L - X_o}{X_o\left(\frac{1}{k} - 1\right)} = -\frac{v}{D}x$$

$$X_L - X_o = X_o\left(\frac{1-k}{k}\right)e^{-\frac{vx}{D}}$$

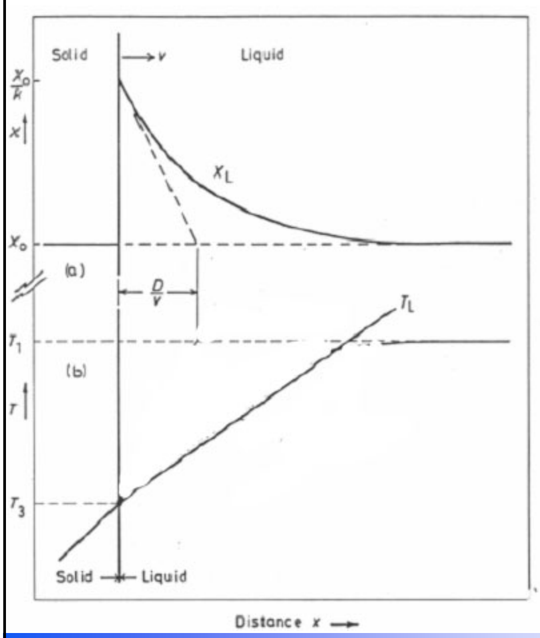


$$X_L = X_O[1 + \frac{1-k}{k}\exp(-\frac{x}{(D/v)})]$$

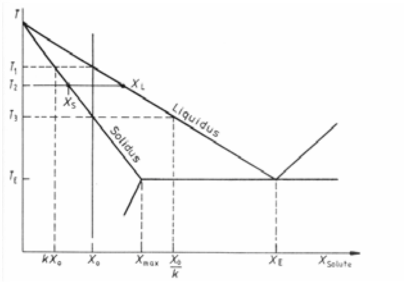
- The concentration gradient in liquid in contact with the solid :

$$J = -D\frac{\partial X_L}{\partial x} = v\left(X_L - X_S\right)$$

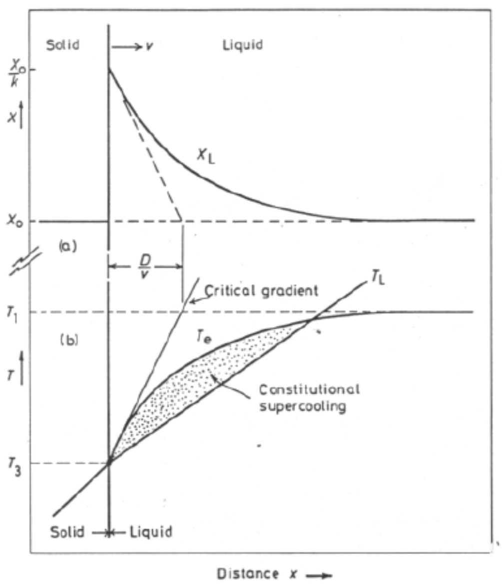
$$J = -DX_L' = v\left(X_L - X_S\right) \qquad X_L' = -\frac{X_L - X_S}{D/v}$$



What would be T_e along the concentration profile ahead of the growth front during steady-state solidification?



Constitutional Supercooling



Condition for a stable planar interface

$$T_L' > (T_1 - T_3)/(D/v)$$

$$T_L'/v > (T_1 - T_3)/D$$

Fig. 4.23 The origin of constitutional supercooling ahead of a planar solidification front. (a) Composition profile across the solid/liquid interface during steady-state solidification. The dashed line shows dX_L/dx at the S/L interface. (b) The temperature of the liquid ahead of the solidification front follows line T_L. The equilibrium liquidus temperature for the liquid adjacent to the interface varies as Te. Constitutional supercooling arises when T_L lies under the critical gradient.

Cellular and Dendritic Solidification

- **Constitutional supercooling** :

  At the interface, $T_L = T_e$ (not T_E) = T_3.

- **Criterion for the planar interface** :

  $T_L'/v > (T_1 - T_3)/D$: the protrusion melts back.
  $T_1 - T_3$: Equilibrium freezing range of alloy
  Large range promotes protrusions.

- **Dendrites**

  Development of secondary arms and tertiary arms: <100>

  Solute effect : low k enlarges $T_1 - T_3$
  Promotes dendrites.

  Cooling rate effect : Fast cooling makes lateral diffusion of the rejected solutes difficult and promotes cell formation of smaller cell spacing.

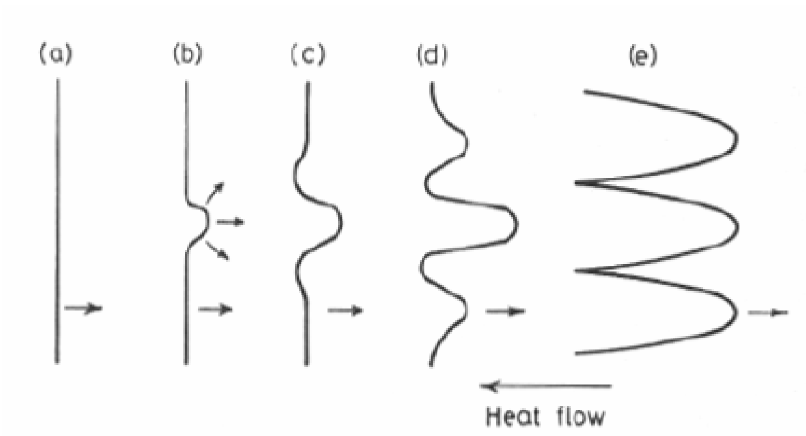
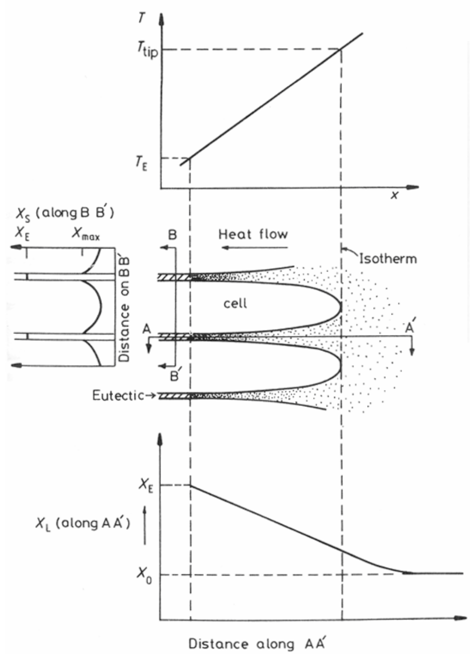


Fig. 4.24 The breakdown of an initially planar solidification front into cells



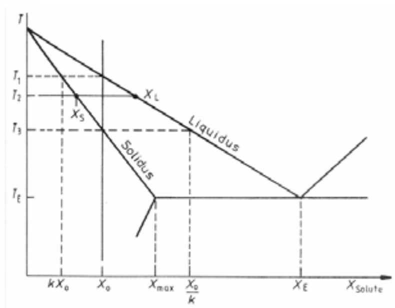


Fig. 4.25 Temperature and solute distributions associated with cellular solidification.
Note that solute enrichment in the liquid between the cells, and coring in the cells with eutectic in the cell walls.

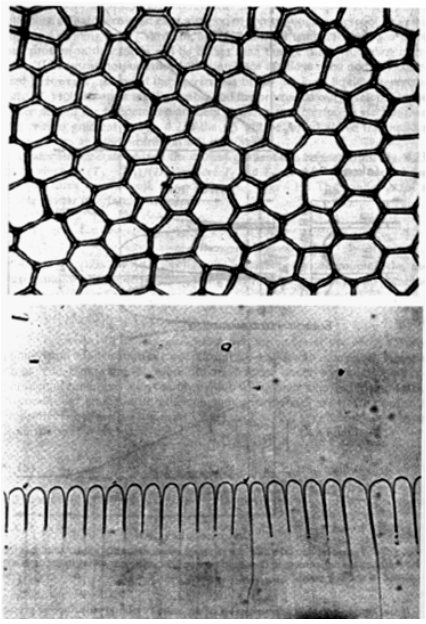


Fig. 4.26 Cellular microstructures. (a) A decanted interface of a cellularly solidified Pb-Sn alloy (x 120) (after J.W. Rutter in *Liquid Metals and Solidification*, American Society for Metals, 1958, p. 243). (b) Longitudinal view of cells in carbon tetrabromide (x 100) (after K.A. Jackson and J.D. Hunt, *Acta Metallurgica* 13 (1965) 1212).

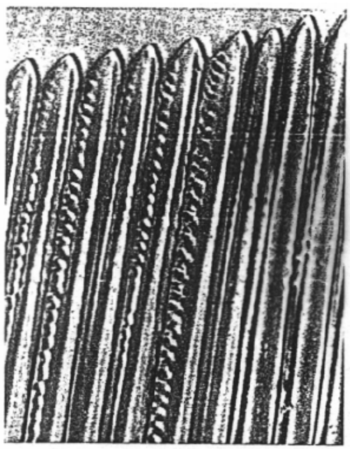


Fig. 4.27 Cellular dendrites in carbon tetrabromide.
(After L.R. Morris and W.C. Winegard, *Journal of Crystal Growth* 6 (1969) 61.)

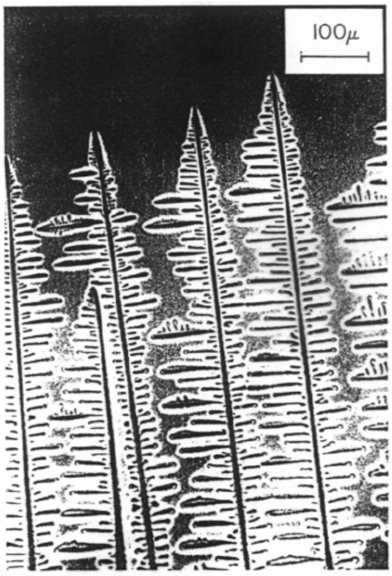
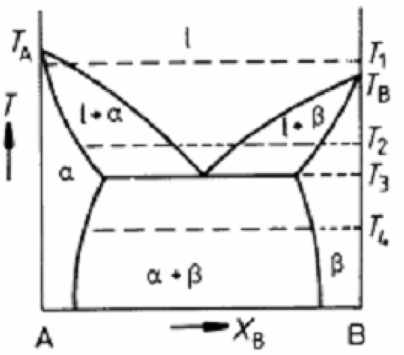
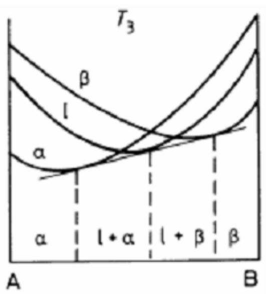
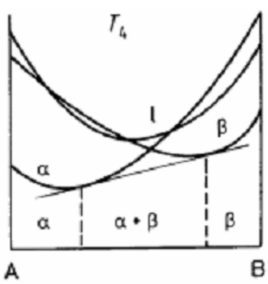


Fig. 4.28 Columnar dendrites in a transparent organic alloy. (After K.A. Jackson in Solidification, American Society for Metals, 1971, p. 121.)

4.3.2 Eutectic Solidification (Thermodynamics)







Plot the diagram of Gibbs free energy vs. composition at T_3 and T_4.

What is the driving force for the eutectic reaction ($L \rightarrow \alpha + \beta$) at T_4 at C_{eut}?

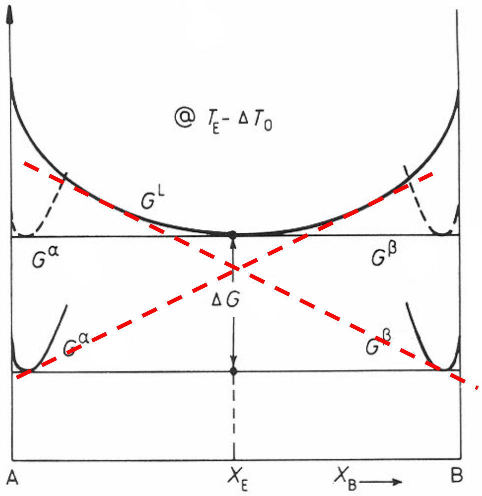
What is the driving force for nucleation of α and β?

Eutectic Solidification (Kinetics)

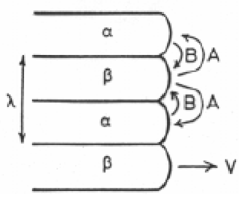
If α is nucleated from liquid and starts to grow, what would be the composition at the interface of α/L determined?

→ rough interface
→ local equilibrium

How about at β/L?
Nature's choice?



interlamella spacing →



What would be a role of the curvature at the tip?

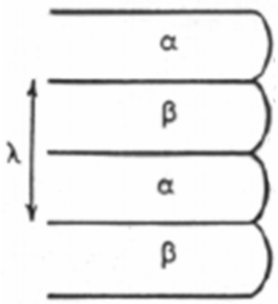
→ Gibbs-Thomson Effect

Eutectic Solidification

How many α/β interfaces per unit length? $\rightarrow 1/\lambda \times 2$

For an interlamellar spacing, λ, there is a total of ($2/\lambda$) m^2 of α/β interface per m^3 of eutectic.

$$\Delta G = \Delta\mu \cong \frac{L\Delta T}{T_m} \qquad \rightarrow \Delta G = \Delta\mu = \frac{2\gamma}{\lambda} \times V_m$$



$$\Delta G(\infty) = \Delta\mu = \frac{\Delta H\,\Delta T_0}{T_E}$$

$$\Delta G(\lambda) = ? \quad = -\Delta G(\infty) + \frac{2\gamma V_m}{\lambda}$$

What would be the minimum λ?

$$\Delta G(\infty) = \frac{2\gamma V_m}{\lambda} \qquad \lambda^* = -\frac{2T_E \gamma V_m}{\Delta H\,\Delta T_0}$$

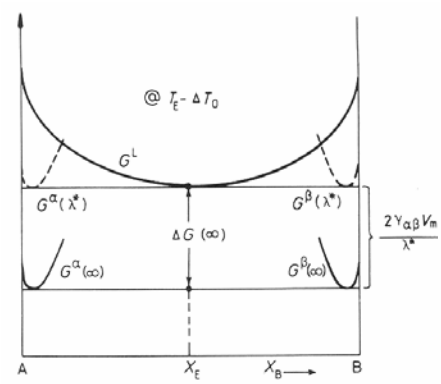
Critical spacing, $\lambda^* : \Delta G(\lambda^*) = 0$

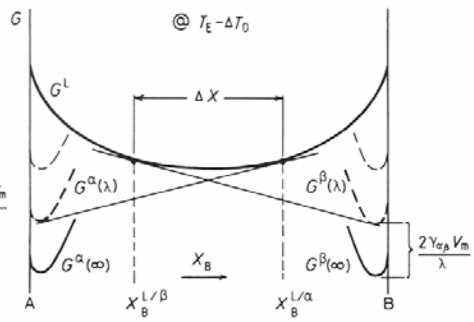
$$cf)\ r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \left(\frac{2\gamma_{SL} T_m}{L_V}\right)\frac{1}{\Delta T}$$

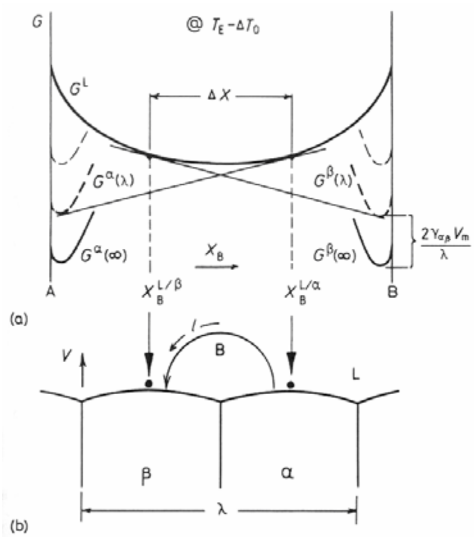
L_v : latent heat per unit volume

$$\lambda^* = -\frac{2T_E\gamma V_m}{\Delta H \Delta T_0} \rightarrow \textit{identical to critical radius}$$

Gibbs-Thomson effect in a ΔG-composition diagram?







Corresponding location at phase diagram?

Fig. 4.33 (a) Molar free energy diagram at (T_E - ΔT_0) for the case $\lambda^* < \lambda < \infty$, showing the composition difference available to drive diffusion through the liquid (ΔX). (b) Model used to calculate the growth rate.

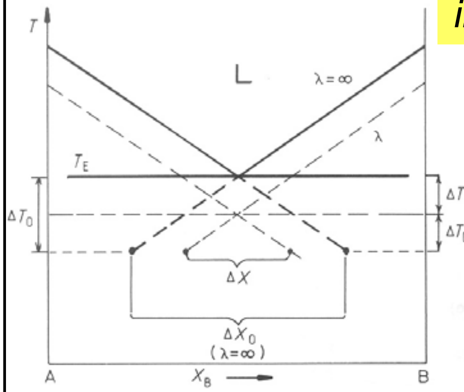
$$\Delta T_0 = \Delta T_r + \Delta T_D$$

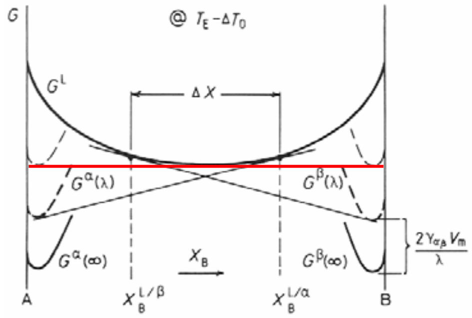
$$\Delta G_{total} = \Delta G_r + \Delta G_D$$

$$\Delta G_r = \frac{2\gamma_{\alpha\gamma} V_m}{\lambda}$$

→ free energy dissipated in forming α/β interfaces

ΔG_D → free energy dissipated in diffusion





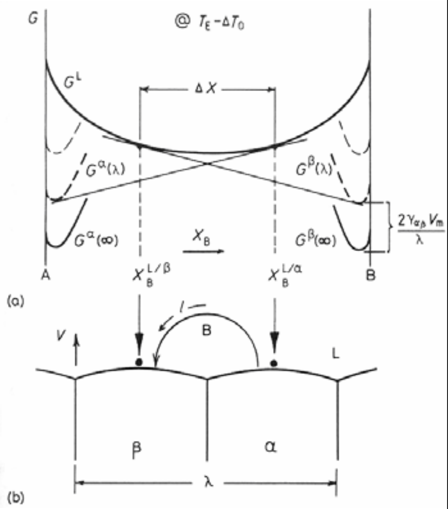
Nature's choice of lamellar spacing

$$v = \frac{J}{c} = \frac{1}{c}\left(-D\frac{dc}{dl}\right) = k_1 D\frac{\Delta X}{\lambda}$$

$$\Delta X = \Delta X_0\left(1-\frac{\lambda^*}{\lambda}\right) \propto \Delta T_0\left(1-\frac{\lambda^*}{\lambda}\right)$$

$$v = k_2 D\frac{\Delta T_0}{\lambda}\left(1-\frac{\lambda^*}{\lambda}\right)$$

Maximum growth rate at a fixed ΔT_0 $\rightarrow \lambda = 2\lambda^*$



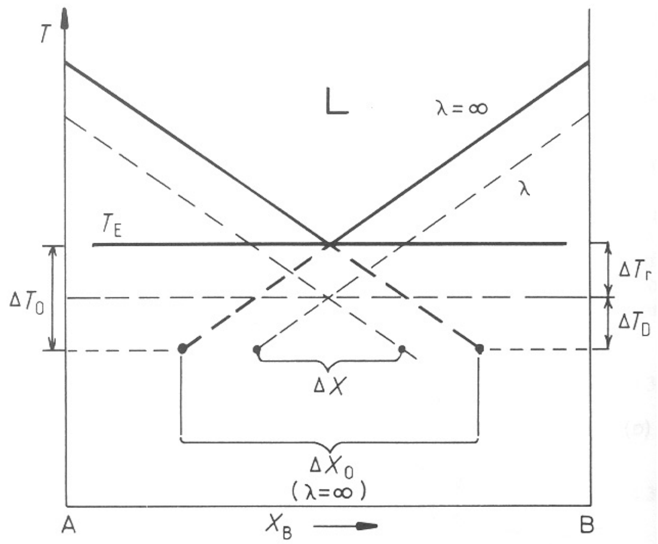


Fig. 4.34 Eutectic phase diagram showing the relationship between ΔX and ΔX_0 (exaggerated for clarity)

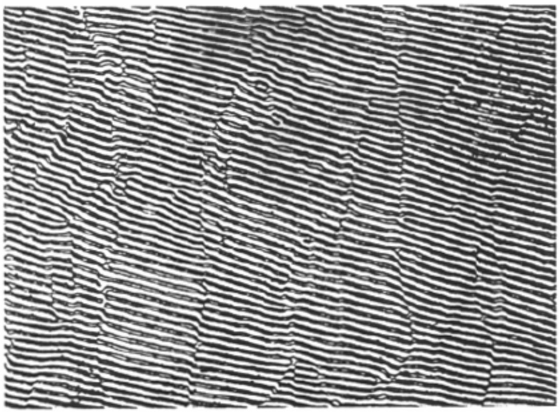


Fig. 4.29 Al-Cu Al_2 lamellar eutectic normal to the growth direction (x 680). (Courtesy of J. Strid, University of Lulea, Sweden.)

Fig. 4.30 Rod-like eutectic. Al_6Fe rods in Al matrix. Transverse section. Transmission electron micrograph (x 70000). (Courtesy of J. Strid, University of Lulea, Sweden.)