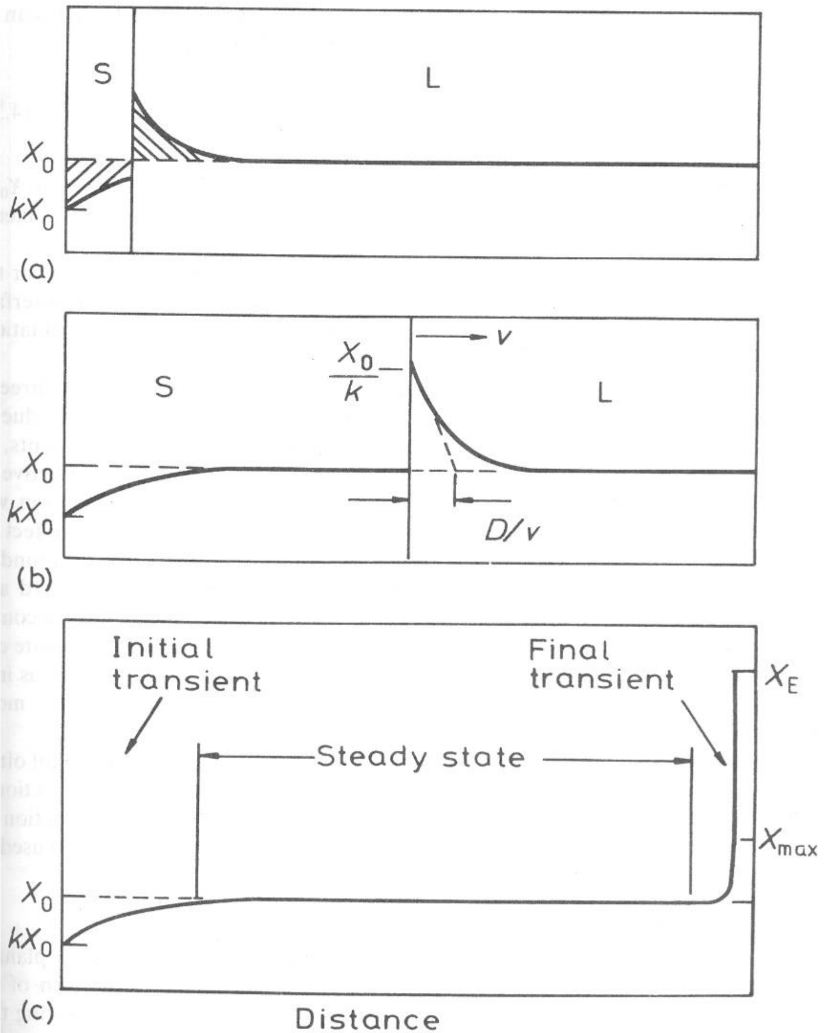
4.3 Alloy Solidification

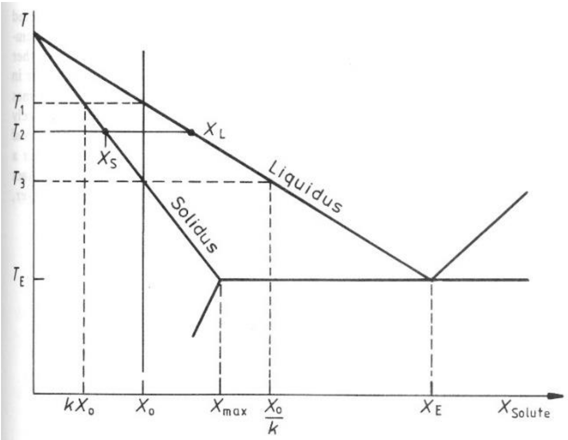
3. No diffusion in solid, diffusional mixing in the liquid

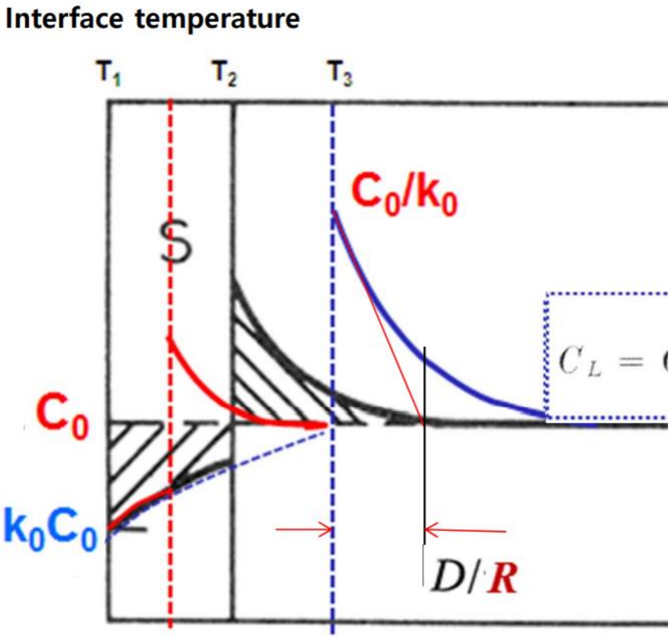


- ✓ Solute rejected from solid → diffuse into liquid with limitation
- ✓ Rapid build up solute in front of the solid → rapid increase in the composition of solid forming (initial transient)
- ✓ If it solidifies at a constant rate, v, then a steady state is finally obtained at T_3
- ✓ liquid : X_0/k , solid : X_0

4.3 Alloy Solidification (diff. mixing in liq.)

I. Initial transient

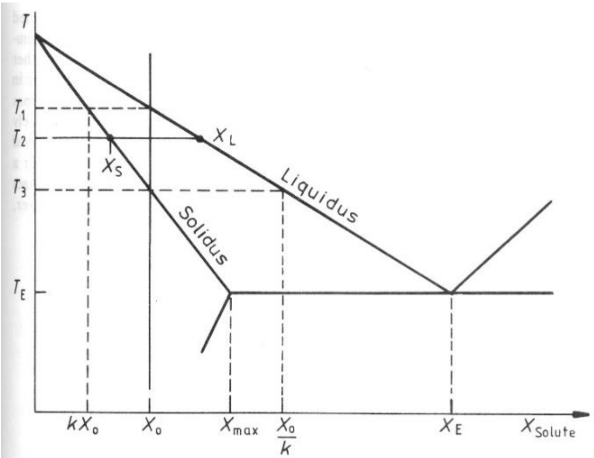


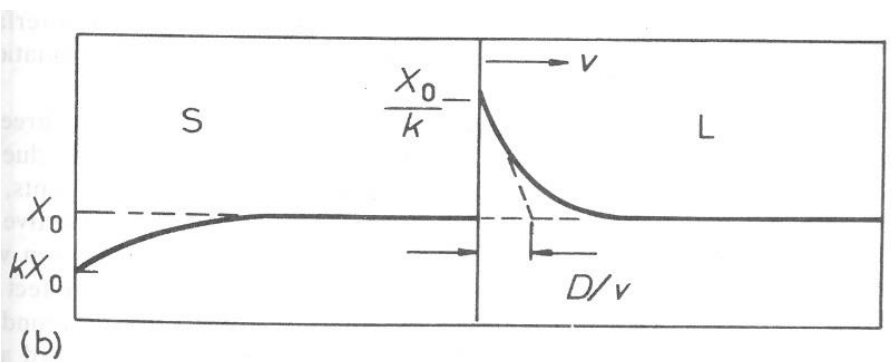


- ✓ $T_1 < T < T_3$
- ✓ First solid: kX_o
- ✓ Solute rejected from solid → diffuse into liquid with limitation
- ✓ Rapid build up solute in front of the solid → rapid increase in the composition of solid forming (initial transient)
- ✓ Solute rejected from solid to liquid, and increase the liquid concentration
- ✓ Two shaded areas are equal
- ✓

4.3 Alloy Solidification (diff. mixing in liq.)

II. Steady State

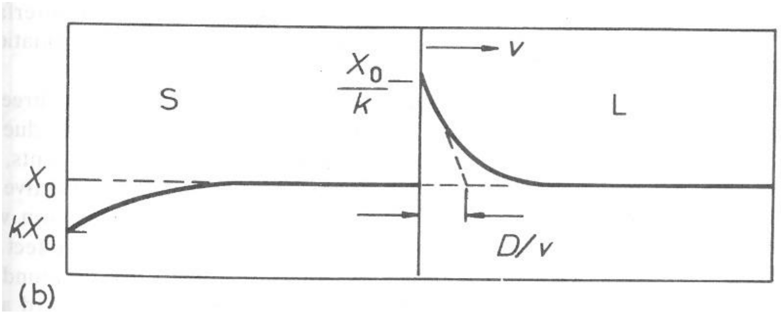




- ✓ $T = T_3$
- ✓ If it solidifies at a constant rate, v, then a steady state is finally obtained at T_3
- ✓ liquid : X_0/k , solid : X_0
- ✓ Rate of solute diffuses down (away from the interfaces)
 = Rate of solute is rejected from the solidifying liquids

$$-D\frac{dC_L}{dX} = v(C_L - C_S)$$

4.3 Alloy Solidification (diff. mixing in liq.)



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

$$(x=0, \qquad X_L = \frac{X_0}{k}) \qquad (\; X_O = X_S\;)$$

Slope of the curve at $x = 0$

$$\left.\frac{dX_L}{dx}\right|_{x=0} = \frac{1-k}{k}X_0\left[-\frac{1}{D/v}\right]\exp\left(-\frac{x}{D/v}\right)\Big|_{x=0}$$

$$= -\left(\frac{X_L - X_O}{d}\right) = \frac{1-k}{k}X_0\left[-\frac{1}{D/v}\right]$$

$$\therefore d = D/v$$

Characteristic distance:
excess conc. falls to 1/e

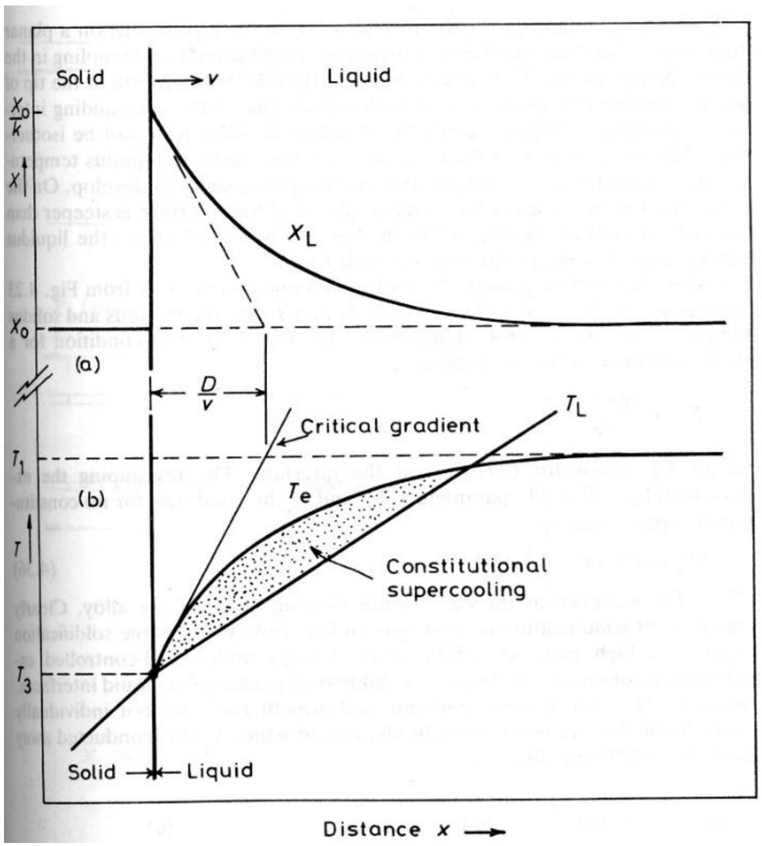
$x = D/v \rightarrow \exp(-1) \rightarrow 1/e$

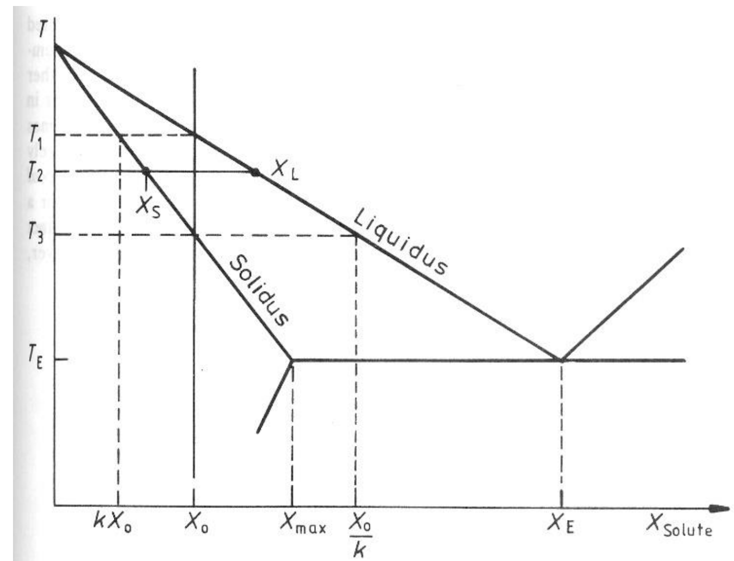
III. Finial transient

If solid/liquid interface in within $\sim D/v$ of the end of the bar
$\rightarrow$ compressed to final transient (eutectic formation)

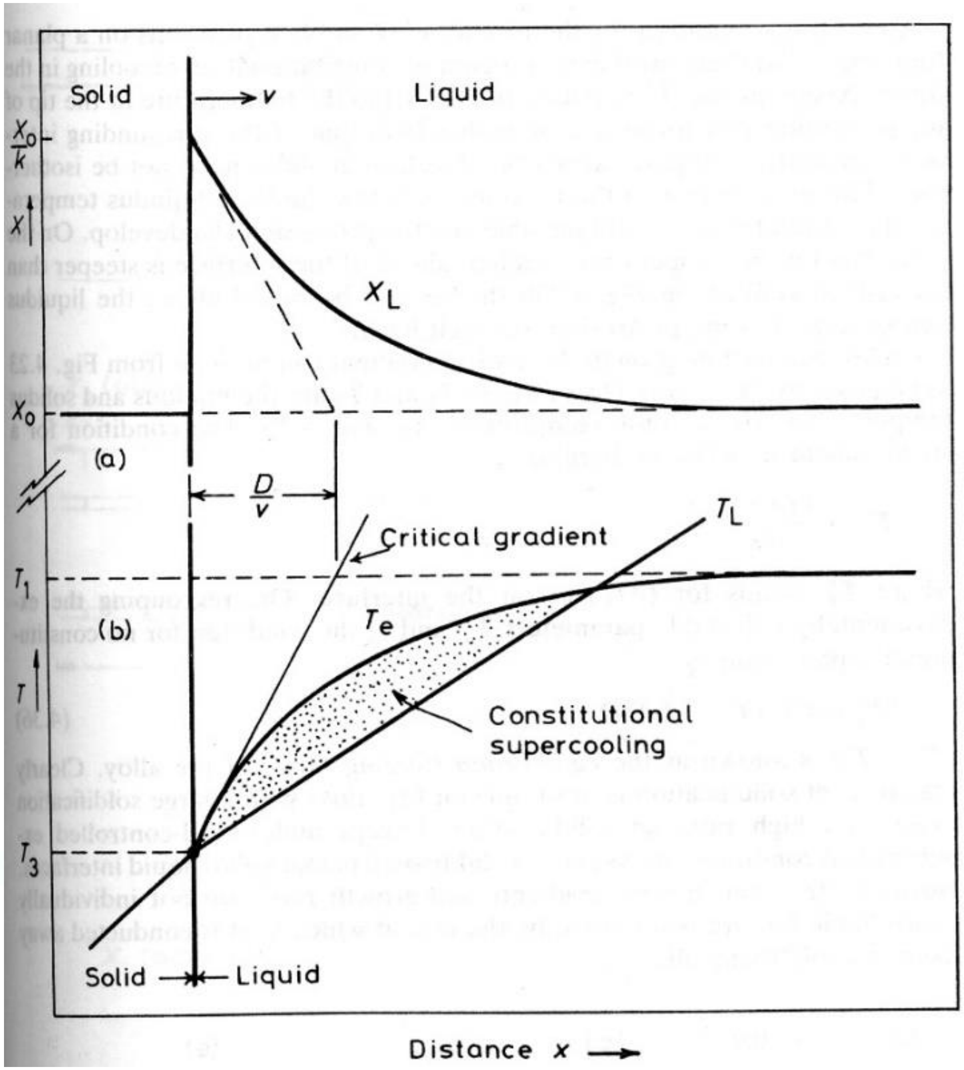
4.3 Cellular and dendritic solidification

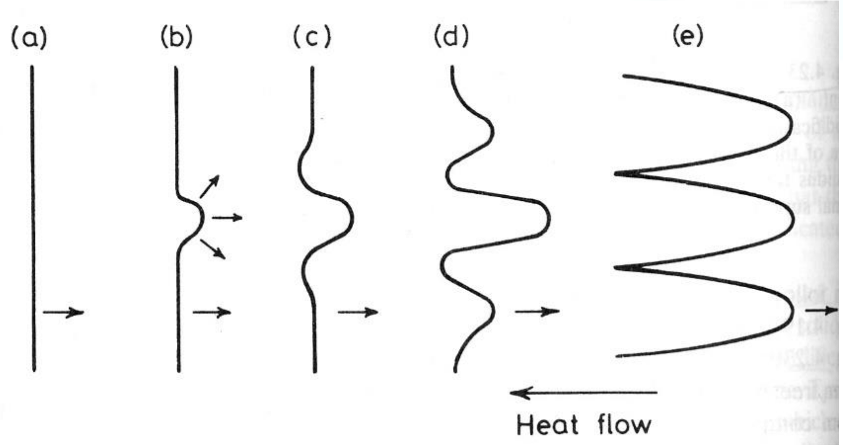
Solute diffusion into the liquid during solidification in alloy
~ similar to the conduction of latent heat in pure metal
→ possible to break up the planar front into dendrites.
→ complicated by the possible temp. gradient in the liquid.





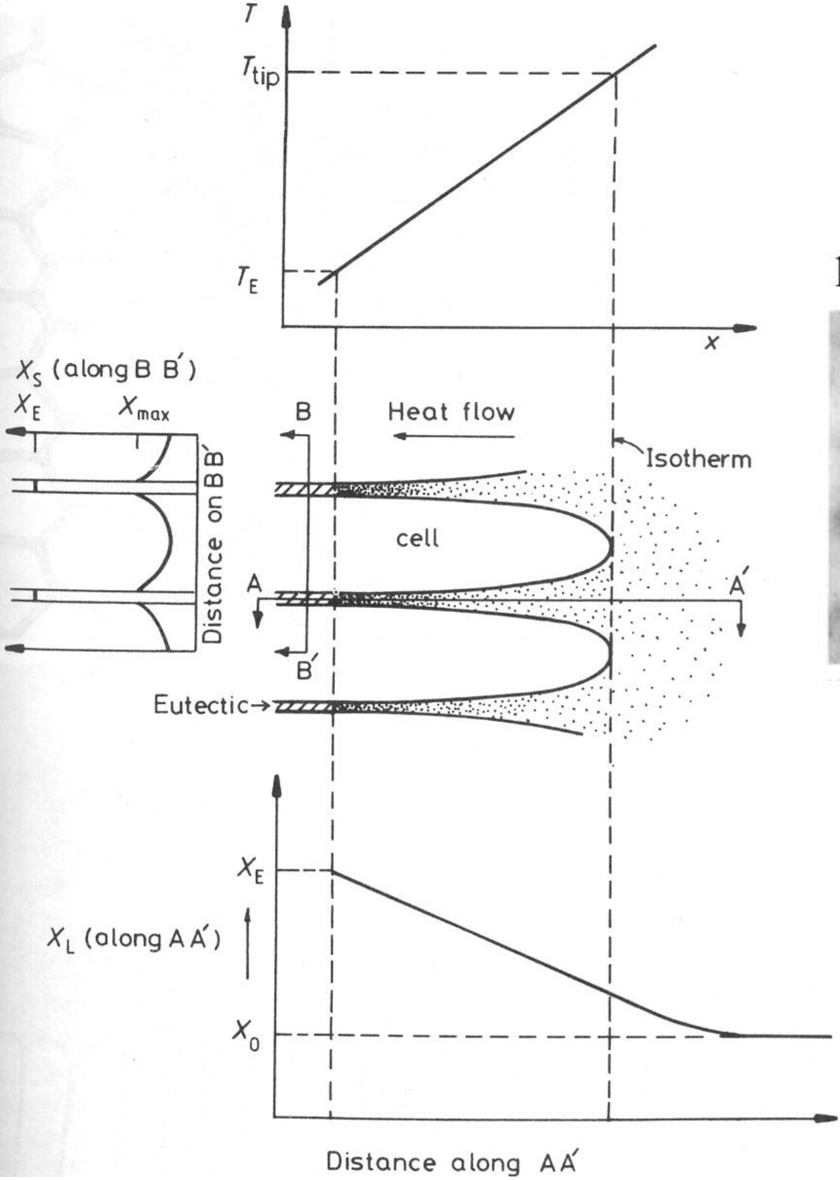
4.3 Cellular and dendritic solidification

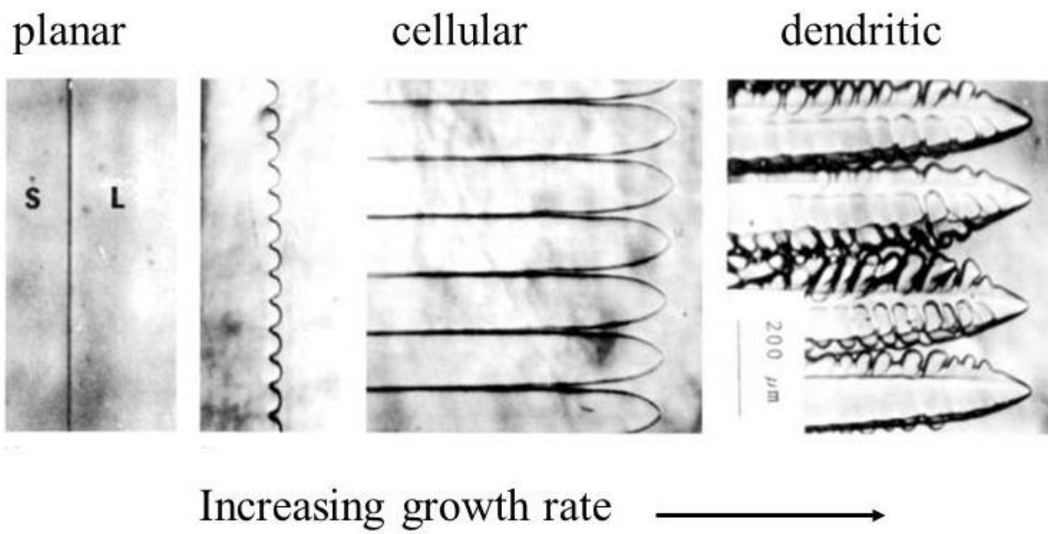




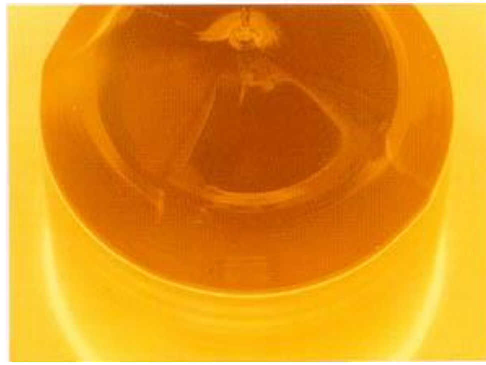
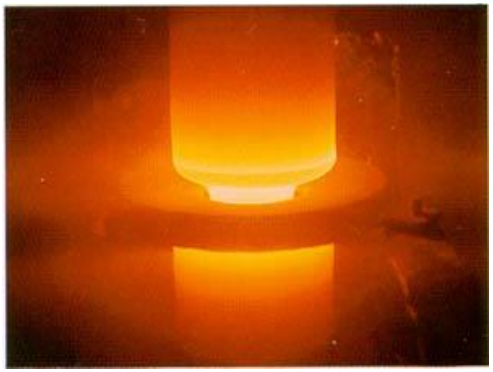
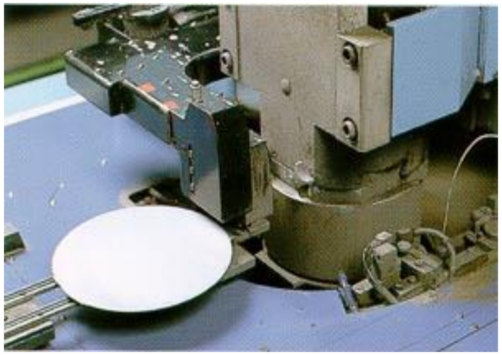
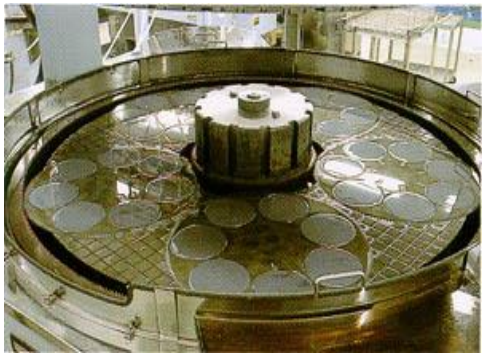
$$\left.\frac{dX_L}{dX}\right|_{X=0} = \frac{T_1 - T_2}{D/v}$$

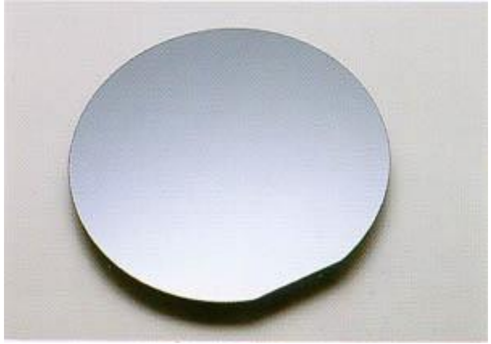
4.3 Cellular and dendritic solidification





Wafer Production

Poly-Si rod	CZ Growth	FZ Growth
Slicing	Lapping	Polishing
Cleaning	Wafer	

Dopant Behavior During Crystal Growth

- Dopants are added to the melt to provide a controlled N or P doping level in the wafers.

- However, the dopant incorporation process is complicated by dopant segregation.

Dopant	k_O
As	0.3
Bi	7×10^{-4}
C	0.07
Li	10^{-2}
O	0.5
P	0.35
Sb	0.023
Al	2.8×10^{-3}
Ga	8×10^{-3}
B	0.8
Au	2.5×10^{-5}

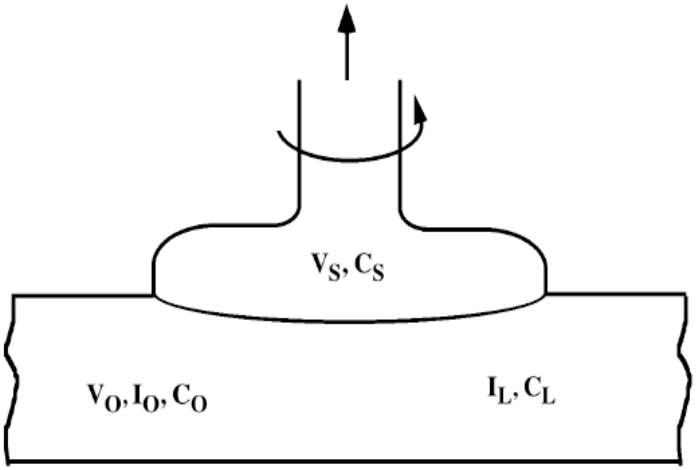
$$k_O = \frac{C_S}{C_L} \qquad (11)$$

- Most k_0 values are <1 which means the impurity prefers to stay in the liquid.

- Thus as the crystal is pulled, N_S will increase.

Dopant Behavior During Crystal Growth

- If during growth, an additional volume dV freezes, the impurities incorporated into dV are given by



$$dI = -k_O C_L dV = -k_O \frac{I_L}{V_O - V_S} dV \quad (12)$$

$$\therefore \int_{I_O}^{I_L} \frac{dI}{I_L} = -k_O \int_0^{V_S} \frac{dV}{V_O - V_S} \quad (13)$$

$$\therefore I_L = I_O \left(1 - \frac{V_S}{V_O}\right)^{k_O} \quad (14)$$

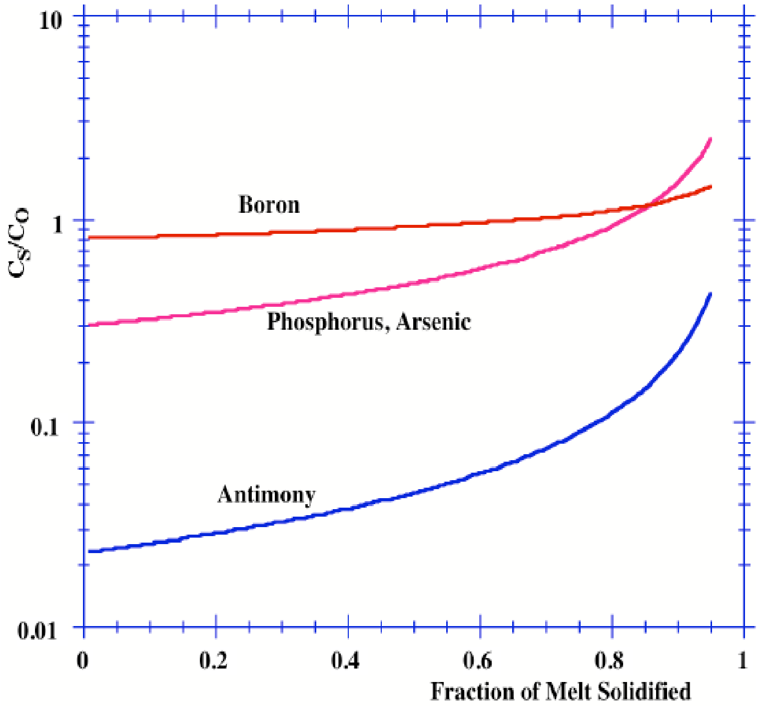
- We are really interested in the impurity level in the crystal (C_S), so that

$$C_S = \frac{dI_L}{dV_S} \quad (15)$$

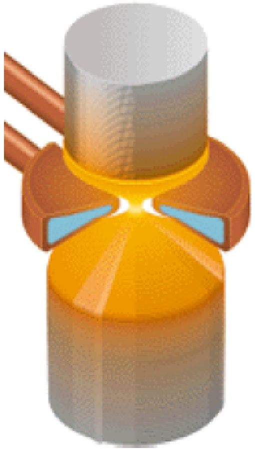
$$\therefore C_S = C_O k_O (1-f)^{k_O - 1} \quad (16)$$

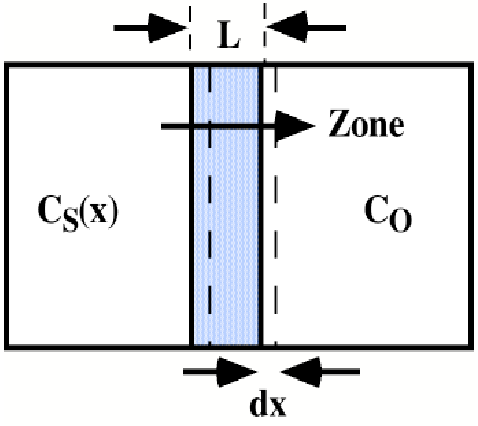
where f is the fraction of the melt frozen.

Dopant Behavior During Crystal Growth



- Plot of Eq. (16).
- Note the relatively flat profile produced by boron with a k_S close to 1.
- Dopants with $k_S << 1$ produce much more variation in doping concentration along the crystal.





- In the float zone process, dopants and other impurities tend to stay in the liquid and therefore refining can be accomplished, especially with multiple passes
- See the text for models of this process.