MME 345

Lecture **B:04**

# Solidification and Crystallisation

## 3. Solidification of metals and alloys

Ref:

[1] A. Ohno, The Solidification of Metals, Chijin Shokan Co. Ltd., 1976

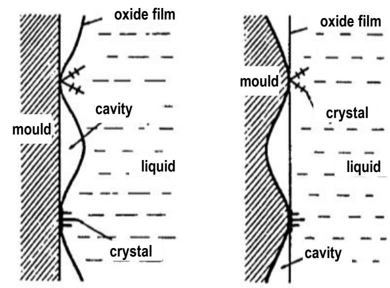
[2] P. Beeley, Foundry Technology, Butterworth-Heinemann, 2001

## Topics to discuss today ....

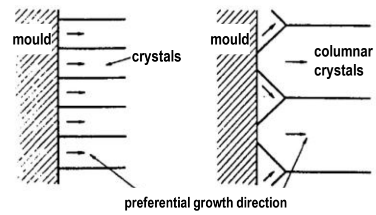
1. Solidification of pure metals
2. Depression of undercooling
3. Freezing of impure metals and alloys
4. The structure of casting

## Review of earlier class

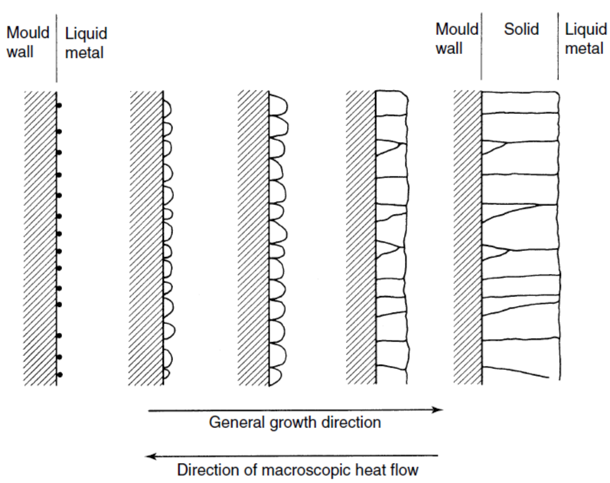
- Solid most readily nucleates heterogeneously on pre-existing surfaces having good metallic properties (i.e., wetted by the liquid).
- Since undercooling is the maximum at the mould wall, solid crystal is always nucleated randomly at the mould wall and form equiaxed chill zone.




- A nucleus makes contact with the pre-existing surface in many ways, causing different growth directions for different nucleus.
- Those nuclei having good contact with the mould wall will grow preferentially and form columnar crystals.





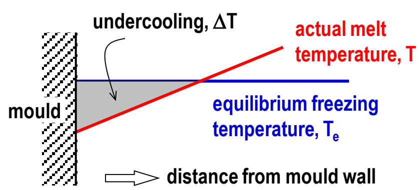




development of columnar grain structures

# 1. Solidification of pure metals

- Immediately after pouring of liquid metal into the mould, a temperature gradient or, **undercooling**, $\Delta T$, is developed in the melt adjacent to the mould wall

  this gradient decreases as time passes




undercooling ahead of the mould wall immediately after pouring

- For a mould with
  - **wider wall thickness,**
  - **low temperature, and**
  - **high thermal conductivity**

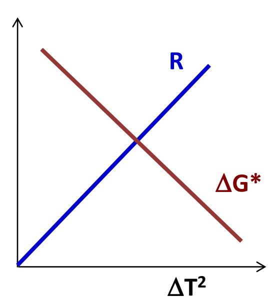
  the temperature gradient will be very steep in the liquid in front of the mould wall

- The largest amount of undercooling, $\Delta T$, is expected in the liquid at the mould surface

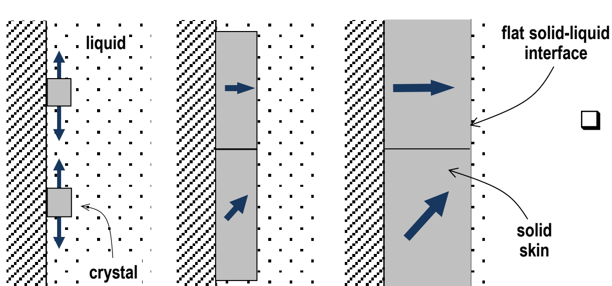


- The mean growth rate, **R**, of a nucleus is proportional to the square of the degree of undercooling:

$$\mathbf{R} \propto \Delta T^2$$




- So a crystal nucleated at the mould wall grow first **along the mould surface** until it comes in contact with adjacent crystals that are also growing along the mould surface.




crystal growth of a pure metal on the mould wall

- A **solid skin** is thus formed, which then grows perpendicular to the mould wall in a stable manner with a **smooth/flat solid/liquid interface**.
- This is called the **planer mode of solidification**.

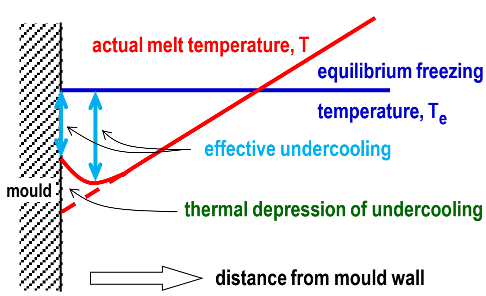
- A clean pure metal always solidifies in a **planer mode**.

- Such planer mode of solidification of pure metals can be altered when the liquid is contaminated due to the
  - absorption of gases
  - reaction between crucible/mould materials
  - presence of impurities or alloys



# 2. Depression of undercooling

- When crystal grows, **latent heat** is evolved due to liquid➔solid transformation
  - this may raise the actual temperature of nearby liquid and reduce or **depress** the degree of undercooling $\Delta T$ at the liquid-solid interface



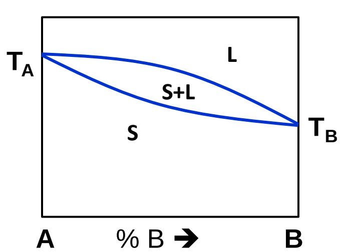

depression of undercooling
due to the evolution of latent heat

- Because of this thermal depression of undercooling, $\Delta T_{max}$ occurs, not at the solid-liquid interface, but at a distance from the mould wall inside the liquid.

- For impure metals and alloys, a **variation in composition** of liquid in contact of solid/liquid interface with that of the bulk liquid occurs because of the segregation of solute atoms.
  - the time of solidification may not be enough to homogenize the composition by diffusing solute atoms inside the liquid.

- This variation in composition of liquid ahead of the interface can also result a decrease in undercooling.
  - this is referred to as **compositional depression of undercooling.**
  - in some textbook, this compositional depression of undercooling is often termed as **constitutional supercooling**.



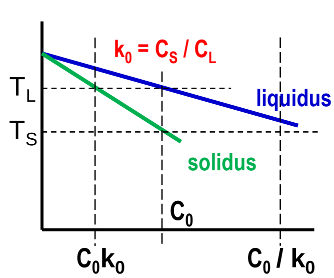



isomorphous phase diagram

$$k_0 = \text{equilibrium distribution coefficient}$$

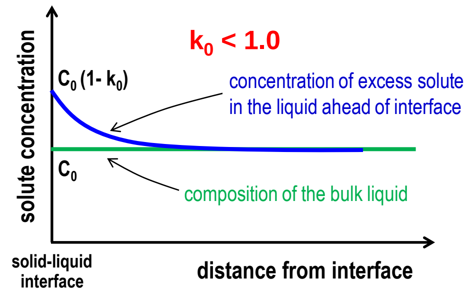
$$= \frac{\text{concentration of solute in solid, } C_S}{\text{concentration of solute in liquid, } C_L}$$

**$k_0 < 1$, when an addition of solute lowers the liquidus temperature of the solvent** (for $k_0 > 1$, the reverse is true)



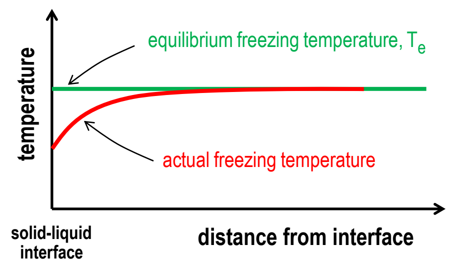

- When a liquid with solute concentration $\mathbf{C_0}$ is cooled to the temperature T, the first solid formed will contain solute of composition $\mathbf{C_0 k_0}$.
- As $k_0 < 1$, the solid contains a lesser amount of solute than the bulk.
- The excess solute $\mathbf{C_0(1 - k_0)}$ will be rejected or segregated at the advancing solid/liquid interface.

❑ If there is not enough time for solute diffusion, the solute concentration at the solid/liquid interface would be higher than in the remaining bulk.

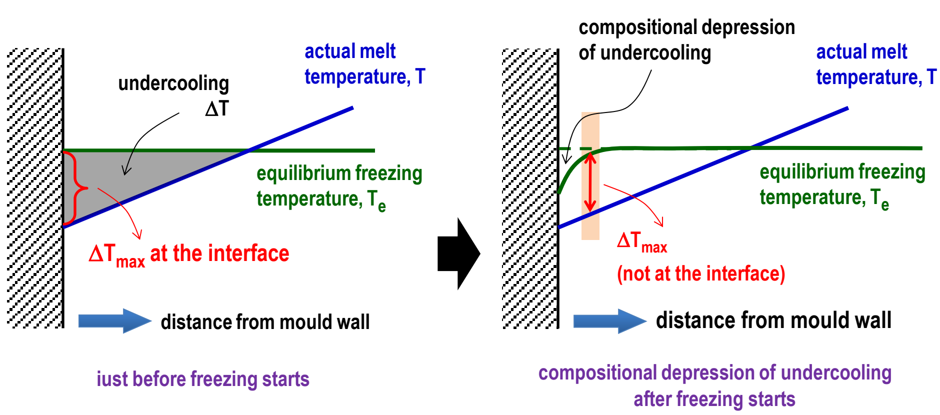



❑ This segregation of solute at the interface will cause a decrease in the equilibrium freezing point of the liquid at the interface.

**this effectively results a decrease in the degree of undercooling at the interface**





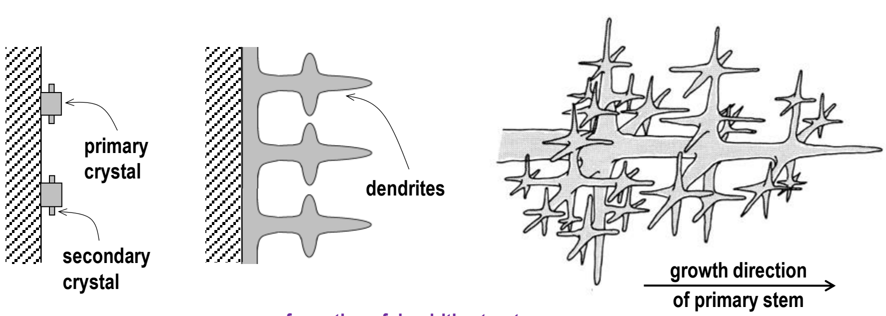
# Consequence of depression of undercooling

- Because of these thermal and/or compositional **depressions of undercooling** growth of crystal at the liquid/solid interface will be prevented.
- Freezing will now continue/initiate away from the interface inside a band of liquid where undercooling is the maximum.
- Interaction of temperature with compositional gradient in liquid is thus regarded as **the single most important factor** that influence the structure of a casting.

  Both grain and substructure depend upon this factor.



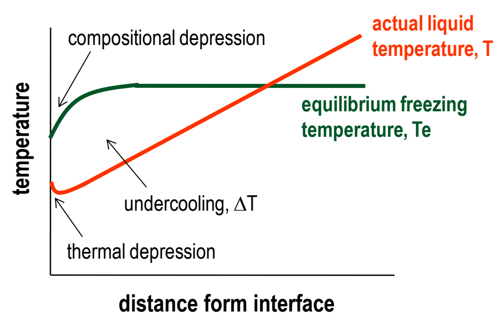
- When undercooling occurs in a band of liquid ahead of the interface, any protrusion / perturbation / bump at the face of primary crystal becomes stable and acts as the **centre for preferential growth**.
- These growth centres probe further into the zone of undercooling and developed as secondary arms of the primary crystals.
- Thus, a tree-like structures, call the **dendrites**, are formed. Solidification of this type is called **dendritic mode of solidification**.




formation of dendritic structures

# 3. Freezing of impure metals and alloy

- The undercooling at the solid/liquid interface for impure metals and alloys can be depressed by both thermal and compositional methods.




depression of undercooling in the liquid ahead of interface for impure metals and alloys

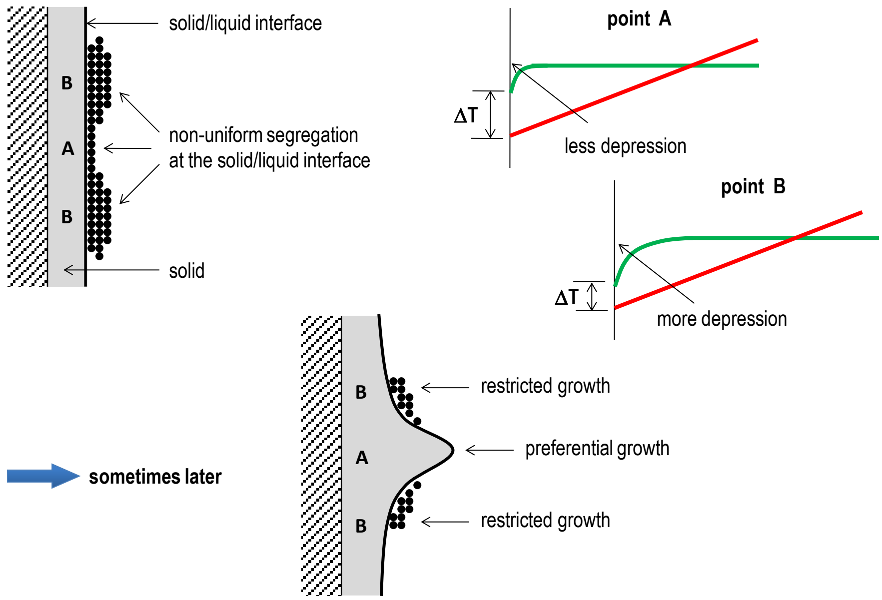
- Because of high heat conductivity of metals and alloys, thermal depression of undercooling is always smaller than the compositional depression of undercooling.
- In pure metals, compositional depression does not occur and thermal depression of undercooling is also very small. Thus, dendritic mode of solidification in pure metals is limited.
- Because of both types of depression, the growth morphologies of impure metals and alloys are complex.



- The rates of growth of crystals at the mould wall are different due to many factors (e.g., favourable growth direction, wettability, non-uniform mould wall, etc.)

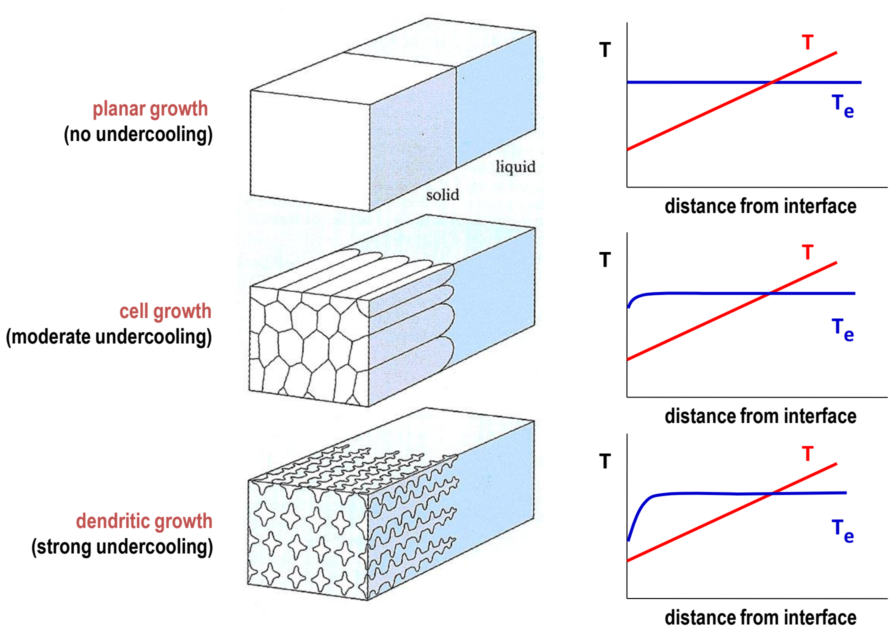
  rates of segregation of solute will also be different in different areas of the interface

- As a result, local areas of interface where segregation is the smallest (and thus ΔT is the largest) will grow preferentially.




preferential growth of solid / liquid interface due to differential solute segregation
and the resultant depression of undercooling






schematic illustration of a solid/liquid interface in the presence of solute

**To summarise :**

- A pure, clean melt always solidifies in planer mode.
- When a metal contains a small amount of solute, the projections that preferentially grow may develop in a non-equilibrium manner.
- As the solute concentration increases, the plain and smooth shape solid/liquid interface of pure metal will progressively develop into more extreme morphologies, termed node, cells and dendrites.



# 4. The Structure of Casting

- So we have seen that **metal composition** (characterized by particular distribution and diffusion coefficients for solute in liquid and solid phases, which establish the relative tendency to depression of undercooling) governs the basic mode of crystallisation.
- Besides solute concentration, the structure of solid/liquid interface is also influenced by the **freezing rate** and **convection in liquid** in the front of the interface.
  - **faster freezing rate ➔ decreases the diffusion time for segregated solutes**
  - **faster convection in liquid ➔ promotes atom movement**

- If the solid-liquid front moves forward by **d** to from a solute layer in time **t**, then the freezing rate **R = d/t**.
- Similar to all diffusion-controlled process, we then have:

$$d = (Dt)^{1/2}$$ D = diffusion coefficient of solute in the liquid

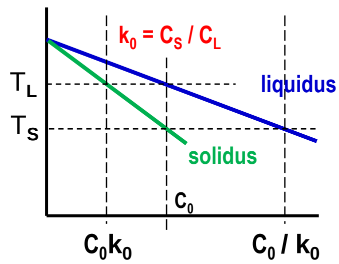
$$d = D/R$$

- Now the compositional depression of undercooling will occur when the temperature gradient, **G**, in the liquid at the front is:

$$G \le -\frac{T_L - T_S}{d}$$

$$G/R \le -(T_L - T_S)/D$$

$$G/R \le -\frac{m\,C_0\,(1-k)}{kD}$$



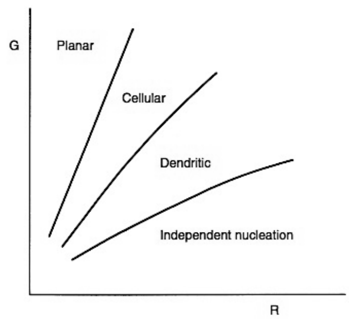

m = slope of liquidus line = $(T_L - T_S) / (C_0/k - C_0)$



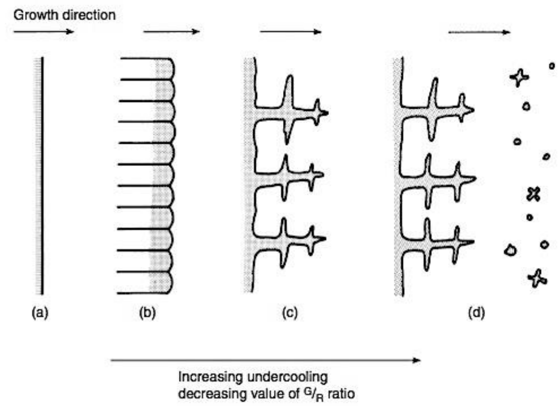
## Influence of G/R ratio

### which assesses the compositional depression of undercooling

- Progressive change in the parameter **G/R** from a high to a low value is accompanied by **successive transitions in the mode of crystallization** as the effect of undercooling becomes more pronounced.
  - **With a very high G/R ratio, columnar growth takes place with the advance of a plane interface, which first gives way to the cellular growth form as G/R ratio is decreased.**
  - **Further diminishing values of G/R bring about the cell-dendrite transition, with columnar growth now occurring on probes of solid some distance ahead of the main interface.**
  - **At still lower values of G/R, homogeneous independent nucleation in the undercooled zone brings about the growth of new grains in positions remote from the existing interface.**

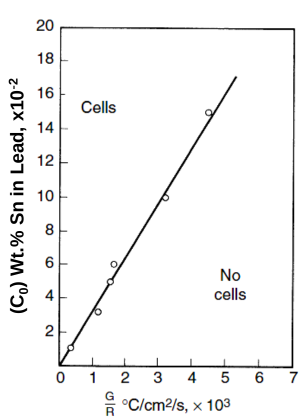



influence of temperature gradient *G* and freezing rate *R* on solidification morphology of a given alloy

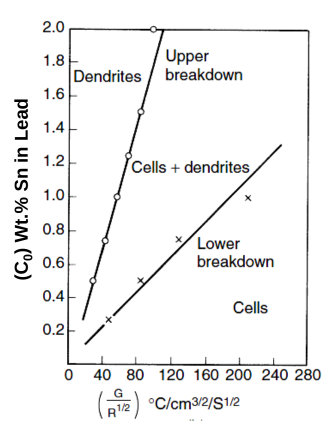


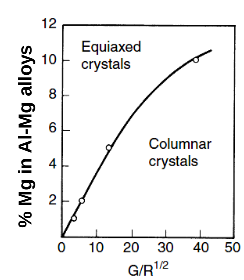

influence of undercooling on interface morphology and mode of growth: (a) planar interface, (b) cellular interface, (c) dendritic growth, (d) independent nucleation






linear relationship between G/R and $C_0$ for planer ➔ cellular transition




complex relationship between G/R and $C_0$ for cellular ➔ dendrite or columnar ➔ equiaxed transition

**Next Class**

MME **345**, Lecture **B:05**

## Solidification and Crystallisation

**4.** Formation of dendrites