MME 345

Lecture **B:03**

Solidification and Crystallisation

2. Nucleation and growth of solids

Ref:

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

[2] J. Campbell, Castings, Butterworth-Heinemann, 1991

Topics to discuss today ….

1. Transition from liquid to solid
2. The concept of undercooling
3. Nucleation of solids
4. Growth of nucleated crystals

1. Transition from liquid to solid

- The nucleation process of solids is influenced to some extent by the structure and properties of the liquid
- During liquid to solid transition
  - Properties depending upon the distance of atoms (e.g. density, volume) change a little for liquids
  - Properties depending upon the order of atoms (e.g. fluidity/viscosity, thermal diffusivity) changes much
- This indicates that, liquids at the solidification temperature have structure fairly similar to solids with a short-range order

- Solids have more closely packed crystal lattice than liquids
  freezing in most metals is associated with ~ 3 - 5 % **volume contraction**

Metal	Crystal structure	Melting point (C)	Volume change on melting (%)
Aluminium	fcc	660	+ 6.00
Zinc	hcp	420	+ 4.20
Copper	fcc	1083	+ 4.15
Magnesium	hcp	650	+ 4.10
Iron	bcc	1537	+ 3.00
Tin	Tetragonal	232	+ 2.30
Bismuth	Rhombohedral	271	- 3.35

- FCC and HCP materials contract more than others
  because of their compact structures in the solid state.
- Few materials (bismuth, cast iron) expand while cooling.

- Freezing is also associated with a liberation of energy in the form of **latent heat of freezing, L**.

- This exerts a marked effect upon
  1. the rate and mode of solidification, and
  2. the crystal growth

- **L** depends upon the bond energy.

Metal	Specific heat (cal/g-deg C)	Latent heat of fusion (cal/g)
Lead	0.036	5.7
Tin	0.062	14.2
Zinc	0.115	26.3
Copper	0.118	48.9
Iron	0.176	65.0
Nickel	0.157	72.1
Magnesium	0.333	85.6
Aluminium	0.259	92.7

- During freezing, a **decrease in entropy** (~ **2–5** cal/deg/mol) is occurred due to the ordering of structure.

At S–L equilibrium,

$\Delta G = 0 = \Delta H - T\Delta S$

$\Delta S = \Delta H / T$

$$\Delta S = L / T_e$$

L = latent heat of freezing

T_e = Freezing temperature

Metal	Freezing temperature (K)	Latent heat of freezing (cal/mol)	Entropy change of freezing (cal/deg-mol)
Tin	505	1690	3.3
Lead	600	1150	1.9
Zinc	692	1740	2.5
Magnesium	923	2100	2.3
Aluminium	933	2500	2.7
Copper	1356	3100	2.3

Richards rule: $\Delta S^F = \Delta H^F/T^F \approx$ 9.0 J/mol-K = 2.15 cal/mol K

- Small values of ΔS indicates a small degree of ordering during freezing

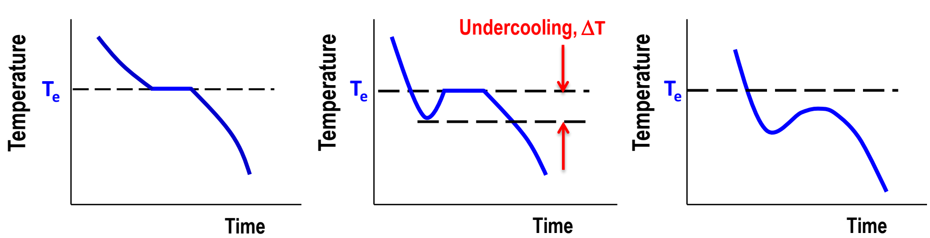
2. The concept of undercooling

- In most cases, transition during solidification is not easy. Solidification cannot begin at the equilibrium freezing temperature, T_e, during cooling of liquid.

- Undercooling, ΔT (= equilibrium freezing point – actual freezing point), occurs because metal experiences reluctance to convert into a solid despite cooling to a temperature below T_e.

  This is especially true for clean liquid in a clean container.

- Although pure metal solidifies at a constant temperature $\mathbf{T_e}$, the nature of cooling curve of metals depends on:
  1. cooling conditions,
  2. latent heat of freezing, and
  3. temperature, specific heat, and heat conductivity of liquid and mould material

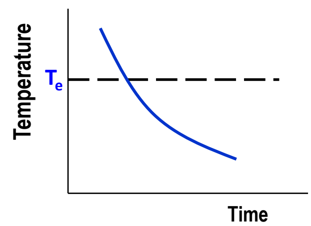


cooling curve of a pure metal | cooling curve of pure metal showing undercooling, ΔT | cooling curve of pure metal showing undercooling but the temperature didn't rise to T_e

- For pure metals and some alloys, undercooling can be very large

Metal	Equilibrium melting point (C)	Maximum undercooling (C)
Lead	327.6	80
Bismuth	271	90
Tin	232.1	118
Copper	1083.6	236
Iron	1536	295
Nickel	1453	319

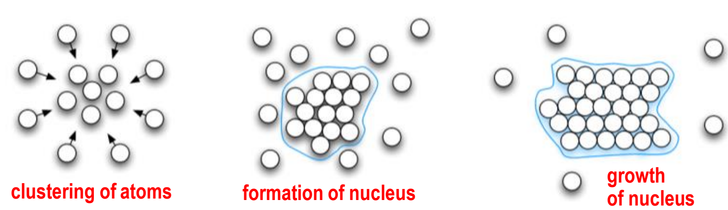
- For amorphous solids (e.g., glass), the liquid is so sluggish that undercooling and a sharp freezing point is never observed



Cooling curve of an amorphous metal

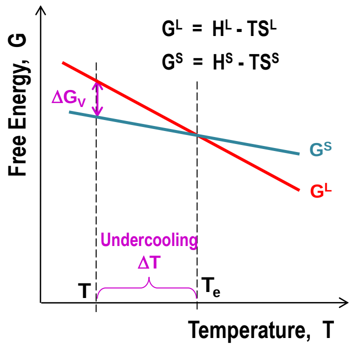
3. Nucleation of solids

- If and when the conversion from liquid to solid occurs, it is by a process first of **nucleation**, and then of **growth**.
- Nucleation is a process of aggregation of clusters of atoms representing the first appearance of the new phase.
  kinetic energies of several atoms of molten metal reaches a low enough value so that they form a short-range order, called a **nucleus**



- Growth means getting bigger
  as more heat is extracted, this newly formed nucleus continues to grow at the expense of liquid phase

The driving force for solidification



- ❐ Since $G^L > G^S$ below $\mathbf{T_e}$, as the temperature is decreased below T_e
  - the liquid phase becomes thermodynamically unstable, and
  - the urge for L ➔ S transformation is increased

- ❐ The driving force, ΔG_V, at T ($<T_e$):

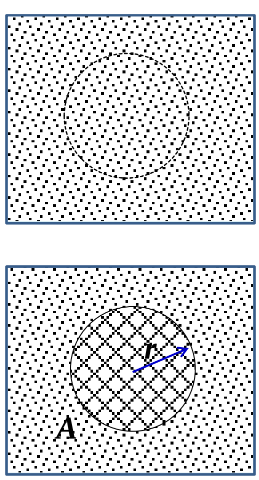
$$\Delta G_V = G^S - G^L = \Delta H - T\Delta S \approx \Delta H_e - T\Delta S_e$$
$$= T_e \Delta S_e - T\Delta S_e = \Delta S_e (T_e - T) = \Delta S_e \Delta T$$

$$\Delta G_V = \frac{L\,\Delta T}{T_e}$$

ΔG_V = Volume free energy
L = Latent heat = ΔH_e
$\Delta T = T_e - T$ = undercooling

The driving force for solidification is proportional to the undercooling provided that the latent heat and the entropy of fusion do not vary much with temperature.

Why liquid does not transform into solid immediately below T_e ?



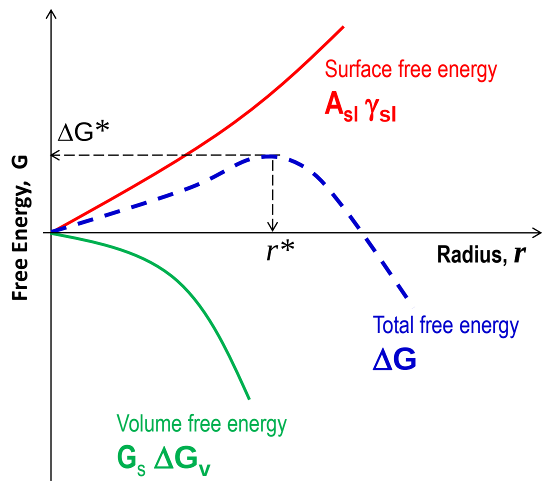
liquid – solid transformation

"Classical theory of nucleation" Volmer & Weber, 1925

- ❑ Solid begins to form as very small spherical nuclei throughout the bulk of the liquid.
- ❑ Thermodynamically, the formation of nuclei must result in a net negative Gibbs free energy change.
- ❑ The total free energy change for nucleation

$$\Delta G = G_{after} - G_{before} = V_s\, \Delta G_v + A_{sl}\, \gamma_{sl}$$

- Below T_e, volume free energy change, ΔG_V (= $L\Delta T/T_e$), is always –ve (since L is always negative)
- Energy required to create new surface γ_{sl} is always +ve.
- For a very small nucleus (~10^{-8} m), the **A/V** ratio is very high and, thus, the surface free energy, γ_{SL}, acts as a barrier to the formation of small nuclei.



free energy change associated with nucleation of a solid nucleus of radius r inside the liquid

r^* = critical radius

- the net energy change to grow the embryo increases first, reaching a maximum for the critical sized nucleus r^*, and then decreases

For $r < r^*$

- embryos that do not reach the critical value r^* require more energy to grow
- system can lower its free energy by dissolution of solid back into the melt
- **unstable nucleus**

For $r > r^*$

- free energy decreases if the solid grows further
- **stable nucleus**

- The actual nucleation process is not thought to occur by this large-scale type of fluctuations where ***n*** liquid atoms suddenly become solid.
- It is thought at a size distribution of small clusters of atoms exists in the liquid at any time and these clusters are considered potential nuclei.
- Due to thermal fluctuations these clusters continuously gain and lose atoms.
- A nucleation event occurs when one of these clusters continues to gain more atoms than it loses.

- For a spherical embryo of radius ***r***, the energy equation:

$$\Delta G = (4/3)\pi r^3 . \Delta G_v + 4\pi r^2 . \gamma_{sl}$$

the size of critical nucleus (obtained by **d(ΔG)/dr = 0**)

$$r^* = -\left(\frac{2\gamma_{sl} T_e}{L}\right) \frac{1}{\Delta T}$$

remembering that,
$\Delta G_V = L\Delta T / T_e$

and free energy requirement of the critical nucleus

$$\Delta G^* = \left(\frac{16\,\pi\,\gamma_{sl}^3\,T_e^2}{3\,L^2}\right) \frac{1}{\Delta T^2}$$

- For a cubic embryo of side ***a***, the energy equation is:

$$\Delta G = a^3 \Delta G_v + 6a^3\,\gamma_{sl}$$

$$a^* = -\frac{4\gamma_{sl}}{\Delta G_v} = -\left(\frac{4\gamma_{sl} T_e}{L}\right) \frac{1}{\Delta T}$$

$$\Delta G^* = \frac{32\,\gamma_{sl}^3}{\Delta G_v^2} = \left(\frac{32\,\gamma_{sl}^3 T_e^2}{L^2}\right) \frac{1}{\Delta T^2}$$

Problem

For a homogeneous nucleation, undercooling of the order of 230 °C is required for liquid copper. Determine the size of the critical radius of the spherical embryo and the energy change associated with the process. If the volume of one copper atom is about $1.16\text{x}10^{-23}$ cm^3, calculate the probable number of copper atoms required to form such embryo.

Given data: T_e = 1083 °C, γ_{sl} = 144 erg/cm^2, L = -1.88x10^{10} erg/cm^3.

For homogeneous nucleation of a spherical embryo, the critical radius

$$r^* = -2\,(\gamma_{sl}/L)\,(T_e/\Delta T) = -2 \times \frac{-144\ \text{erg/cm}^2}{1.88\text{x}10^{10}\ \text{erg/cm}^3} \times \frac{1356\ \text{K}}{230\ \text{K}} = 9.03\text{x}10^{-8}\ \text{cm}$$

Now the volume of the critical embryo

$$V = (4/3)\,\pi\, r^{*3} = (4/3)\,\pi\,(9.03\text{x}10^{-8}\ \text{cm})^3 = 3.08\text{x}10^{-21}\ \text{cm}^3$$

Thus, number of copper atoms required forming a critical embryo

$$n = 3.08\text{x}10^{-21} / 1.16\text{x}10^{-23} = 265.5$$

Thus about 266 atoms would be required.

3.1 Homogeneous nucleation

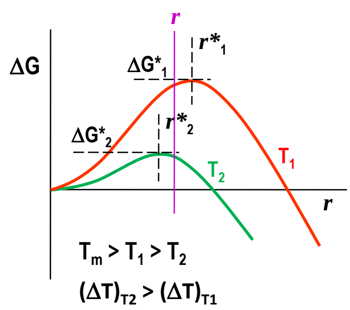
$$\Delta G = (4/3)\pi r^3 . \Delta G_v + 4\pi r^2 . \gamma_{sl}$$

$$r^* = -\left(\frac{2\gamma_{sl}T_e}{L}\right)\frac{1}{\Delta T} \quad ; \quad \Delta G^* = \left(\frac{16\,\pi\,\gamma_{sl}^3\,T_e^2}{3\,L^2}\right)\frac{1}{\Delta T^2}$$

- Solidification cannot begin at T_e during cooling of liquid since, for a very small nucleus, the A/V ratio is very high and, the surface factor acts as a barrier to the formation of stable nucleus.

- But with increasing undercooling (ΔT),
  (1) the driving force for nucleation, ΔG_v is increased and
  (2) the size of critical nucleus r* and critical total energy requirement ΔG^* are reduced.

- If some atoms form an embryo of size r (< r^*_1) at T_1, then according to the figure below its further growth will be discouraged and it will be dissolved back into the liquid.



$$r^* \propto \frac{1}{\Delta T}$$

$$\Delta G^* \propto \frac{1}{\Delta T^2}$$

effect of decreasing temperature on critical radius for nucleation and on free energy change for nucleation

- But if the **temperature is sufficiently low** (at T_2 for example), the size of that embryo (r) would be bigger than the critical size r^*_2 at that temperature (T_2) and its further growth will then be encouraged by a reduction in energy.

- Thus, at a certain low enough temperature, known as the **homogeneous nucleation temperature**, the driving force becomes too high and the size of nucleus exceeds the size of the critical nucleus.

- The nucleus becomes stable and the growth of nucleus enters into a runaway conditions and numerous of small randomly nucleated crystals begin to grow.

- This is called **homogeneous nucleation**.
  the homogeneous nucleation temperature can be as low as $0.2T_e$.

3.2 Heterogeneous nucleation

- Homogeneous solidification requires a large driving force to meet the surface energy demand.

$$r^* \propto \gamma_{sl} \ ; \qquad \Delta G^* \propto \gamma_{sl}^3$$

- Liquids undergoing solidification, thus, always attempt to reduce the surface energy barrier by having nucleation occur upon a pre-existing interface.

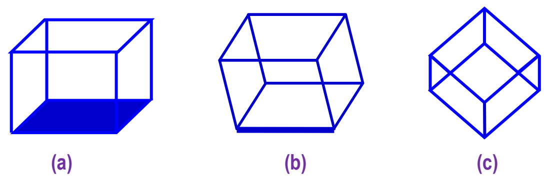
- During actual melting, some foreign particles (e.g. mould wall, liquid surface, inclusion/foreign particles, surface film) are always present in the liquid metal.
  - nucleation occurs preferentially on these pre-existing surfaces
  - the positive interfacial energy component in energy relation can, thus, be reduced or even eliminated

- Nucleation of solid on such pre-existing interface is called **heterogeneous nucleation.**
  - For a very favourable circumstance, heterogeneous nucleation can even be started at the equilibrium freezing temperature T_e.

- In practice, all nucleation takes place heterogeneously.

- Homogeneous nucleation is only observed when no heterogeneous nucleation sites are available in the liquid.
  - one way of doing it is to get rid of all foreign surfaces (including surface of container)
  - examples: magnetic levitation, float zone method, etc.

- Not all foreign particles in liquid are **favourable nucleating sites** for the formation of solid phase



a cubic nucleus can nucleate (a) on a plane, (b) along the edge, or (c) at a point

- In case (a), total surface energy to overcome

$$\gamma_{het} = 6a^2\gamma_{sl} - (a^2\gamma_{sl} + a^2\gamma_{fl}) + a^2\gamma_{sf}$$

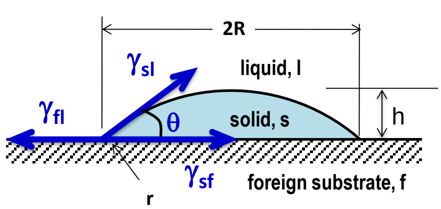
$$\gamma_{het} < \gamma_{hom} \; ; \quad \Delta G_{het} < \Delta G_{hom}$$

s = solid
l = liquid
f = foreign body

- But in case (c), change in surface energy component is negligible.

Thus, the more active the surface of foreign substrate, the smaller the value of γ and the easier will be the nucleation to occur heterogeneously.

- Again, consider the nucleation of a spherical cup shaped solid embryo on a flat substrate of an inclusion inside a liquid metal.



θ = contact angle between the embryo and the substrate
r = radius of the embryo; h = height of embryo
R = projected radius of the embryo on to the substrate

$$\gamma_{fl} - \gamma_{sf} = \gamma_{sl}\cos\theta$$

Volume of the embryo, $\mathbf{V_s}$

$= (1/3)\,\pi h^2 (3r - h)$ where $h = r(1-\cos\theta)$

$= (1/3)\,\pi r^3 (2 - 3\cos\theta + \cos^3\theta)$

Surface area of the embryo, $\mathbf{A_{sl}}$

$= 2\pi rh = 2\pi r^2 (1 - \cos\theta)$

Surface area of the embryo-substrate contact, $\mathbf{A_{sf}}$

$= \pi R^2$ where $R = r\sin\theta$

- The change in surface energy produced by formation of this nucleus

$$\Delta G_{surface} = A_{sl}\gamma_{sl} + A_{sf}\gamma_{sf} - A_{fl}\gamma_{fl} = (A_{sl} - \pi R^2\cos\theta)\,\gamma_{sl}$$

- Then the total free energy change due to the heterogeneous formation of this spherical nucleus is on top of the substrate is

$$\Delta G_{het} = \Delta G_{volume} + \Delta G_{surface} = V_s\,\Delta G_V + (A_{sl} - \pi R^2 \cos\theta)\,\gamma_{sl}$$

$$= (1/3)\,\pi r^3\,(2 - 3\cos\theta + \cos^3\theta)\,\Delta G_v$$

$$+\ 2\pi r^2\,(1 - \cos\theta)\,\gamma_{sl} - \pi r^2\,(1 - \cos^2\theta)\cos\theta\ \gamma_{sl}$$

$2\pi r^2 (1 - \cos\theta)\gamma_{sl}$ → surface area added at the new liquid-solid interface

$\pi r^2 (1 - \cos^2\theta)\cos\theta\ \gamma_{sl}$ → replacing substrate-liquid interface with solid-substrate interface

$$\Delta G_{het} = \frac{2 - 3\cos\theta + \cos^3\theta}{4}\left(\frac{4}{3}\pi r^3.\Delta G_V + 4\pi r^2.\gamma_{sl}\right)$$

$$\Delta G_{het} = f(\theta)\,.\,\Delta G_{hom}$$

Here $f(\theta) = \dfrac{2 - 3\cos\theta + \cos^3\theta}{4}$ is called the **shape factor**

Thermodynamic barriers

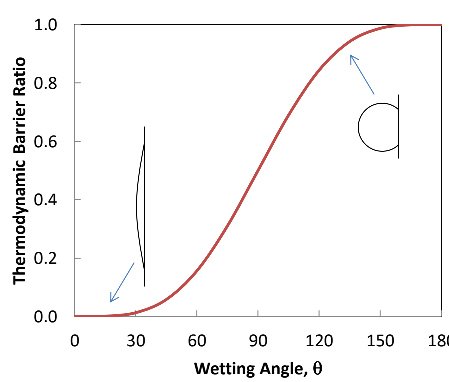
$$\Delta G^*_{het} = f(\theta)\,.\,\Delta G^*_{hom}$$

ΔG^*_{het} → heterogeneous nucleating barrier

ΔG^*_{hom} → homogeneous nucleating barrier

$$f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$

This varies from **-1** to **1**



- For θ = **180°** (i.e., surface of substrate is **non-wetted** by the liquid):

$$\Delta G^*_{het} = \Delta G^*_{hom}$$

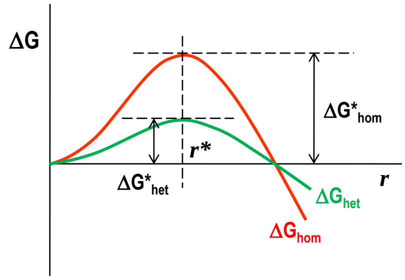
- Oxides are, therefore, **not good nuclei** for heterogeneous nucleation of solids because of their non-wetting surface.

- For all other cases, where θ <180°

$$\Delta G^*_{het} < \Delta G^*_{hom}$$

and the substrate aids nucleating the solid

- For θ = **0°** (i.e., surface of substrate is **completely wetted** by the liquid), the energy barrier to nucleation is the minimum.



$$r^*_{het} = -\left(\frac{2\gamma_{sl}T_e}{L}\right)\frac{1}{\Delta T}$$

$$\Delta G^*_{het} = f(\theta).\left(\frac{16\,\pi\,\gamma_{sl}^3\,T_e^2}{3\,L^2}\right)\frac{1}{\Delta T^2}$$

- The critical radius r^* is the same for both homogeneous AND heterogeneous nucleation.
- Also, since **$R^* = r^* \sin\theta$**, as θ is decreased, R^* also decreases, which indicates that the volume of the heterogeneous nucleus (and thus ΔG^*) can become significantly smaller and hence requires fewer atoms for its formation.

To summarise:

- Heterogeneous nucleation involves nucleation of solid on a pre-existing interfaces inside liquid metal in an attempt to reduce the surface energy barrier.
- For a second phase to act as a nucleating site, it must be capable of being wetted by the liquid, form a low contact angle, and must possess some structural affinity with the crystalline solid.
- Materials with good metallic properties (e.g. borides, nitrides, carbides, intermetallic compounds) always wetted by the liquid and are served as better nucleus.
- Also, foreign particles must remain in the solid form in the liquid metal in order to help the nucleation process.

4. Growth of nucleated crystal

- The growth of an embryo will only occur if heat is extracted through the solid, cooling the freezing front below the equilibrium value.

- As the rate of heat extraction increases, the temperature of the solidification front falls, and the rate of advance, **R**, of the front correspondingly increases.

- The mode of growth of individual crystal as well as of the general solid mass depends mainly on three factors:
  1. thermal conditions in the freezing zone,
  2. constitution of the alloy, and
  3. shapes of the melt, solid, and mould

4.1 The solid - liquid Interface

- The solid-liquid interface can be **'smooth'** (when the boundary is discrete) or **'rough'** (when the transition extends over a number of atomic layers)

- The structure and form of the growing interface influences
  (1) the microstructural morphology of the resultant solid, and
  (2) the number and distribution of imperfections within the solid

- The interface also affects thermal and constitutional changes in the adjacent liquid, which in turn leads to growth modifications

- For a spherical embryo of radius $\boldsymbol{r}$:

$$r^* = -\left(\frac{2\gamma_{sl}T_e}{L}\right)\frac{1}{\Delta T} \quad ; \quad \Delta G^* = \left(\frac{16\,\pi\,\gamma_{sl}^3\,T_e^2}{3\,L^2}\right)\frac{1}{\Delta T^2}$$

  - ✓ r^* varies inversely with ΔT
  - ✓ ΔG^* varies inversely with $(\Delta T)^2$

- Liquid metal is always in contact with the mould material
  - ➔ the area of the largest ΔT (and the minimum ΔG^*) must always exist at the metal-mould interface, not at the centre of liquid or any other place

- **Nucleation occurs most readily at the mould interface**

- A nucleus makes contact with a foreign solid in different ways (such as with the plane, edge, or point)

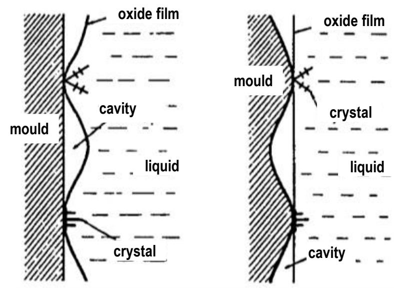
- The growth directions are different for those crystals having different types of contact with the foreign solids, because crystal grows opposite to the direction of heat flow.

- In all those growth directions, there exists a **preferential growth direction** of the nucleated crystal at the mould wall.

- Besides, the interface is not microscopically uniform due to the presence of oxide film and rough sand grains.

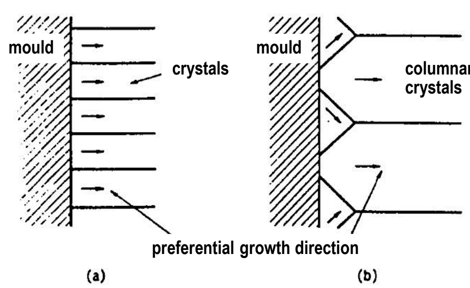
- As a result, melt does not come in contact uniformly with the mould wall and wetting is different in different positions.

- Thus, only those nuclei having good contact to the mould wall will have higher ΔT and will grow preferentially.



irregular contact of molten metal with mould wall and nucleation of crystal on the mould wall

- A **chill zone** of randomly nucleated crystals is, therefore, always found in the outer region of cast metals because of high undercooling.



preferential growth direction of crystal on the mould wall

- Among all those chill crystals only a few have the most preferential growth directions, and, therefore, grow further as **columnar crystals**.

- Those not, is suppressed for further growth.

To summarise:

- ❑ Since undercooling is the maximum at the mould wall solid crystal is always nucleated at the mould wall and form **equiaxed chill zone**.
- ❑ Some of these randomly nucleated chill crystals will have good thermal contact with the mould wall due to its rough surface and grow preferentially to form **columnar zone**.

Next Class
MME **345**, Lecture **B:04**

Solidification and Crystallisation

3. Solidification of metals and alloys