MME 345

Lecture **B:02**

Solidification and Crystallisation

1. Heat transfer

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. Introduction
2. The ingot structure
3. Transfer of heat from liquid

1. Introduction

- Most metal products (except P/M and electroplated products) undergo solidification at some stages of their manufacturing.

- The mode of solidification exercise a two-fold influence upon the final properties of a casting:

  [1] The **structure** (grain size, shape, orientation; distribution of alloying elements; the crystal structure and its imperfections) formed immediately after solidification determines the properties of the final products.

  [2] The properties and service performance of casting also depend on its **soundness** – the degree of true metallic continuity. Defects formed at this stage cannot be eliminated during subsequent operations (forging, heat treatment etc.).

- Structure and soundness – both depend upon the mechanism of solidification, and influenced by factors such as

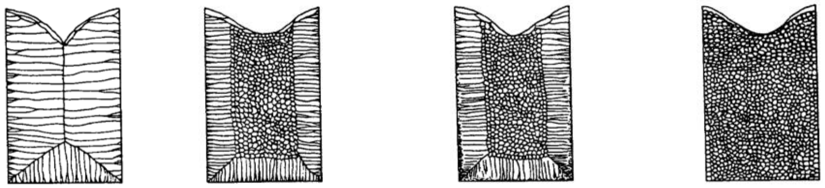
  [1] constitution and physical properties of the alloy,

  [2] Properties, size and shape of the mould, and

  [3] Pouring temperature and technique

- In this chapter we shall discuss how the structure is formed and the techniques used in controlling the structure.

2. The ingot structure



(a) columnar grains only

(b) columnar grains & equiaxed grains at the centre

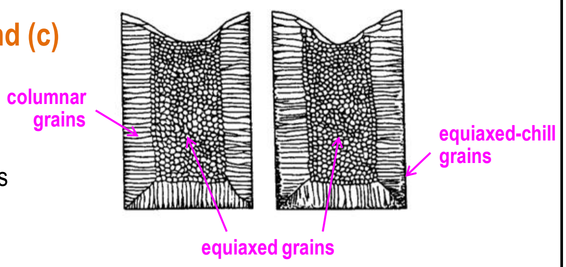
(c) fine equiaxed chill grains, columnar grains & equiaxed grains at the centre

(d) equiaxed grains only

Possible ingot structures in pure metals and in alloys

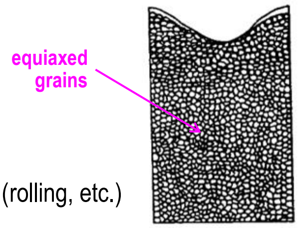
Structures shown in (b) and (c)

- Most common
- Seldom homogeneous; contains **segregation** defects



Structures shown in (d)

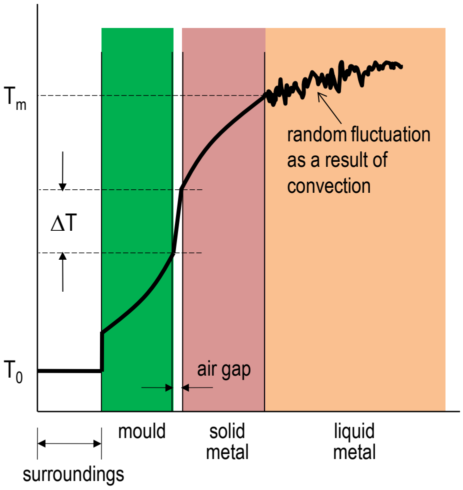
- Most desirable
- Random orientation
- Homogeneous and isotropic properties
- Most suitable for subsequent fabrication work (rolling, etc.)



Thus, knowledge on how the structure is formed and on the techniques of controlling structure is important

3. Transfer of heat from liquid

- The liquid metal must loose heat first before it solidifies.
- The hot molten liquid takes time to loose its heat and solidify.
- Resistances to heat flow :
  1. The liquid
  2. The solidified metal
  3. The metal-mould interface
  4. The mould
  5. The surroundings of mould



temperature profile across a casting freezing in a mould

- In nearly all cases, resistance (**1**) offered by liquid is negligible

  due to **bulk flow of liquid metal** by forced convection during filling and thermal convection during cooling

  the turbulent flow and mixing quickly transport heat and so smooth out the temperature gradient

  this happens quickly as the bulk flow of liquid is fast compared to diffusion process in solids which controls the other resistances

- In many cases, resistance (**5**) offered by the surroundings is also negligible in practice

  for normal sand mould, the atmosphere does not affect solidification as the outer surface of the mould hardly warm by the time casting solidified inside

  exceptions:
  - thin-walled moulds (e.g., investment/shell moulding),
  - metal dies (cool faster when the back of the dies are cooled by water)

- Major fundamental resistance to heat flow from the liquid are items (**2**), (**3**) and (**4**).

  all of these resistances can be simulated with varying degree of success by different software

  but the problem is both physically and mathematically complex, especially for castings of complex geometry

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Resistance (4): the mould (which is insulating)

☐ Applicable in cases when mould is relatively insulating compared to the casting

- Al, Mg, Cu casting in sand mould
- Cu casting in steel mould
- Steel casting in sand mould ???

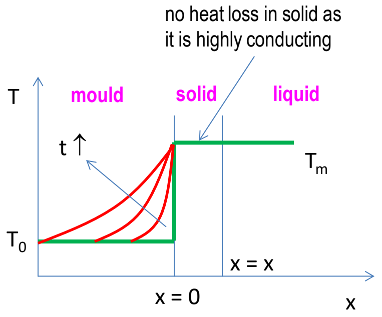
☐ Assumption to made:

(1) **Insulating mould**

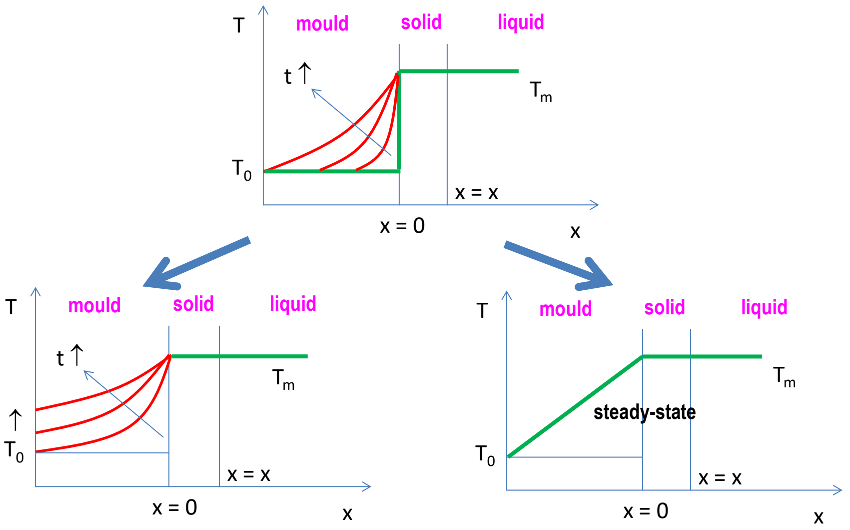
(2) **Conducting solid**

(3) **Liquid is poured at T_m with no superheat ($\Delta T = T - T_m = 0$)**

(4) **Semi-infinite mould**



no heat loss in solid as it is highly conducting



- finite mould ➔ outside temperature can rise above T_0 after certain time
- semi-infinite mould ➔ solidification rate is fast enough so that outside temperature does to rise above T_0

- outside temperature is artificially fixed at a certain value
- e.g., by cooling of outside mould surface by water spraying

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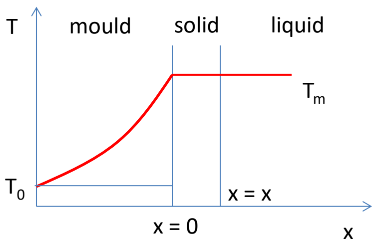
❑ For unidirectional transient heat flow from the liquid metal poured exactly at its melting point T_m against a thick, flat mould wall initially at temperature T_0

$$\frac{\partial T}{\partial t} = \alpha_m \frac{\partial^2 T}{\partial x^2} \qquad (1)$$

α_m = thermal diffusivity of mould, cm^2/s



❑ Solution of this equation using the boundary condition

$$\frac{T_m - T}{T_m - T_0} = erf\left(\frac{x}{2\sqrt{\alpha_m t}}\right) \qquad (2)$$

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy$$

erf (0) = 0
erf (∞) = 1

Initial conditions:

At t = 0,

$T = T_m$ @ x = 0
$T = T_0$ @ x < 0

Boundary conditions:

At t > 0,

$T = T_m$ @ x = 0
$T = T_0$ @ x = - ∞

- The rate of heat flow into the solid at the liquid-solid interface

$$\left(\frac{q}{A}\right)_{x=0} = -K_m \left(\frac{\partial T}{\partial x}\right)_{x=0} \qquad (3)$$

K_s = thermal conductivity of mould, cal/cm °C s

- Partial differencing eq(2) with respect to x and letting x = 0

$$\frac{T_m - T}{T_m - T_0} = erf\left(\frac{x}{2\sqrt{\alpha_m t}}\right) \qquad (2)$$

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-y^2} dy$$

$$T_m - T = erf\left(\frac{x}{2\sqrt{\alpha_m t}}\right)(T_m - T_0)$$

$$\frac{d}{dx}[\operatorname{erf}(x)] = \frac{2\exp(-x^2)}{\sqrt{\pi}}$$

$$-\frac{\partial T}{\partial x} = \frac{1}{2\sqrt{\alpha_m t}}\left[\frac{2}{\sqrt{\pi}}\exp\left(\frac{-x^2}{4\alpha_m t}\right)\right](T_m - T_0)$$

- For x = 0

$$\left(\frac{\partial T}{\partial x}\right)_{x=0} = \frac{-1}{\sqrt{\pi t}}\frac{1}{\sqrt{\alpha_m}}(T_m - T_0) = \frac{-1}{\sqrt{\pi t}}\frac{\sqrt{\rho_m C_m}}{\sqrt{K_m}}(T_m - T_0) \qquad \mathbf{(4)}$$

$$\alpha = K/\rho C$$

ρ_m = density of mould, g/cm^3
C_m = specific heat of mould, cal/g

- Then using eq(3) and eq(4):

$$\left(\frac{q}{A}\right)_{x=0} = K_m \frac{-1}{\sqrt{\pi t}}\frac{\sqrt{\rho_m C_m}}{\sqrt{K_m}}(T_m - T_0) = \frac{-1}{\sqrt{\pi t}}\sqrt{K_m \rho_m C_m}\,(T_m - T_0) \qquad \mathbf{(5)}$$

- Now heat entering the mould comes only from the latent heat of fusion L of the solidifying liquid (as there is no superheat available in the liquid). Thus

$$\left(\frac{q}{A}\right)_{x=0} = -\rho_s\, L\left(\frac{\partial S}{\partial t}\right) \qquad \mathbf{(6)}$$

- Then using eq(5) and eq(6):

$$\left(\frac{\partial S}{\partial t}\right) = \frac{\sqrt{K_m \rho_m C_m}}{\sqrt{\pi t}}\left(\frac{T_m - T_0}{\rho_s L}\right) \qquad \mathbf{(7)}$$

$$\left(\frac{\partial S}{\partial t}\right) = \frac{\sqrt{K_m \rho_m C_m}}{\sqrt{\pi t}} \left(\frac{T_m - T_0}{\rho_s L}\right) \qquad (7)$$

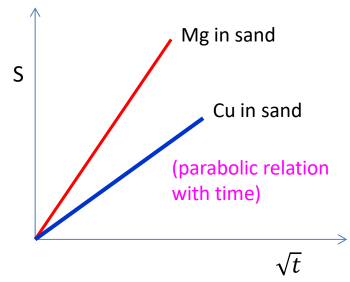
- ❑ Integrating Eq(7) with respect to t to obtain distance solidified S:

$$S = \frac{2}{\sqrt{\pi}} \left(\frac{T_m - T_0}{\rho_s L}\right) \sqrt{K_m \rho_m C_m}\ \sqrt{t} \qquad (8)$$

metal **mould**

$(K_m \rho_m c_m)^{1/2}$ = heat diffusivity, a measure of the rate of heat absorbed by the mould

Eq(7) predicts the manner in which thermal properties of metal and mould combine to determine the freezing rate of metal cast in a relatively insulating mould.



- ❑ For simple shaped casting, S can be replaced with V/A and t = t_f. Then

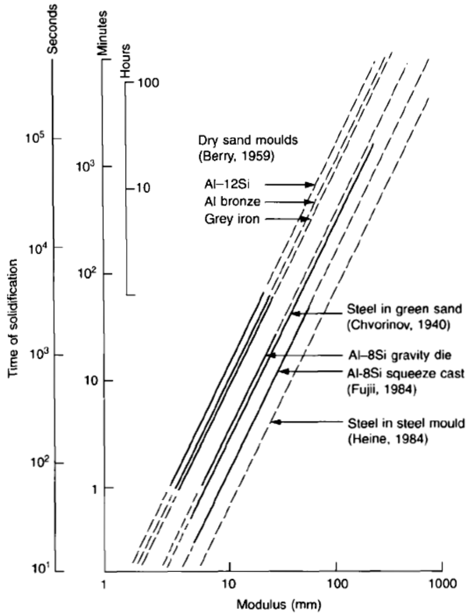
$$S = \frac{V}{A} = \frac{2}{\sqrt{\pi}} \left(\frac{T_m - T_0}{\rho_s L}\right) \sqrt{K_m \rho_m C_m}\ \sqrt{t}$$

$$t_f = C \left(\frac{V}{A}\right)^2 \qquad (9)$$

V = volume of casting solidified at time t
A = surface area of casting
V/A = M = Modulus of casting
t_f = freezing time or solidification time
C = constant for a given metal-mould system
(its value varies from 1.5 to 2.0)

Eq(9) is the well-known Chvorinov's Rule for determining the solidification time

- most accurate for the highly conducting non-ferrous metals
- less good for iron and steel



Freezing times for plate-shaped castings in different alloys and moulds

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- **Chvorinov's rule** is one of the most useful guides to the casting designer.
  - **It provides a powerful general method of tackling the feeding of castings to ensure their soundness.**
  - **Since a feeder and a casting are both within the same mould and fill with the same metal under the same conditions, Chvorinov's rule can be used to ensure that the casting will solidify before the feeder by designing a feeder with a higher modulus than the casting.**

- Chvorinov's rule has some **limitations**:
  - **It is an application of one-dimensional analytical model into a three-dimensional actual casting.**
  - **Shape has a definite effect on the heat flow and the actual solidification time.**

- Considering a shape factor, ***n***,
  Chvorinov's rule can be corrected as follows:

$$\frac{\partial T}{\partial t} = \alpha_m \left(\frac{\partial^2 T}{\partial x^2} + \frac{n \partial T}{r \partial r} \right)$$

r = casting radius
n = shape factor (n=0 for plate,
1 for cylinder, 2 for sphere)

the solution to this equation is:

$$\frac{V}{A} = \left(\frac{T_m - T_0}{\rho_s L} \right) \left\{ \frac{2}{\sqrt{\pi}} \sqrt{K_m \rho_m C_m}\ \sqrt{t_f} + \frac{n K_m t_f}{2r} \right\} \qquad \mathbf{(10)}$$

- For a given V/A ratio, a sphere freezes more rapidly than a cylinder and a cylinder more rapidly than a plate

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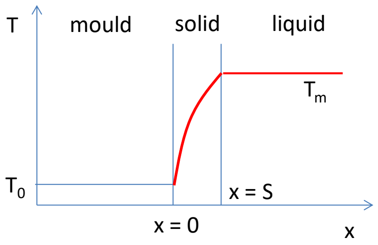
Resistance (2): the casting

- Applicable in cases when less conductive metals are cast in more conductive moulds
  - Pb-Sb alloy into steel dies (battery grids & terminals)
  - steel into a copper mould
  - wax patterns for investment casting into metal dies
  - plastics in metal die for plastics industry



- For unidirectional transient heat flow

$$\frac{\partial T}{\partial t} = \alpha_s \frac{\partial^2 T}{\partial x^2} \qquad (1)$$

α_s = thermal diffusivity of solid

- At the solidification front, rate of heat evolution must be equal to the rate of heat conduction:

$$L\ \rho_s \left(\frac{\partial S}{\partial T} \right) = K_s \left(\frac{\partial T}{\partial x} \right)_{x=S}$$

K_s = thermal conductivity of solid

Boundary conditions:
x = 0, T = T_0
x = S, T = T_m

- The solution is:

$$S = 2\gamma\sqrt{\alpha_s t}$$

where γ is determined from

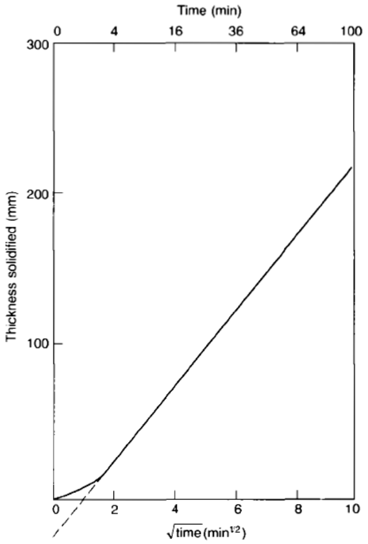
$$\gamma\exp(\gamma^2)\operatorname{erf}(\gamma) = (T_m - T_0)\frac{C_s}{L\sqrt{\pi}}$$

- This equation agrees well with experimental observations.
- For example, thickness of steel solidifying against a cast iron mould is found to be

$$S = a\sqrt{t} - b$$ (constants **a** ≈25 mm $s^{-1/2}$, **b** ≈3 mm)

- The delay (b) at the beginning of solidification occurs due to

(1) loss of superheat due to turbulence, and
(2) interface resistance.



Unidirectional solidification of pure iron against a cast iron mould coated with a protective wash

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Resistance (3): the metal-mould interface

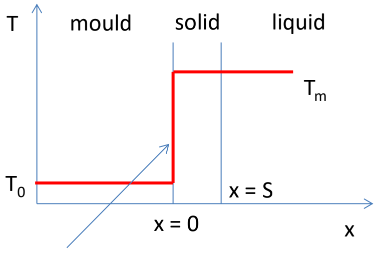
- Applicable to cases when both casting and mould are conductive, and the heat flow is controlled to a significant extent by the mould-metal interface
  - **use of insulating mould coat in die casting of light alloys**
  - **formation an air gap as the casting cools and shrinks away from the mould**

- **For unidirectional heat flow, rate of heat released during solidification of a casting of density ρ_s and latent heat *L***

$$q = -\rho_s L\, A\left(\frac{\partial S}{\partial t}\right)$$

- **The heat transfer coefficient *h* for a sufficiently large mould**

$$h = -\frac{q}{A(T_m - T_0)}$$



all temperature drop is across the interface

- Equating and integrating from $S = 0$ at $t = 0$ gives

$$S = \frac{h\,(T_m - T_0)}{\rho_s L}\;t$$

- For simple-shaped castings, S may be generalised to modulus (or, V/A ratio) to calculate the solidification time

$$t_f = \frac{\rho_s L}{h\,(T_m - T_0)}\left(\frac{V}{A}\right)$$

Air Gap Formation

- With time, the casting contracts inwards as it cools and the mould expands outward as it heats up.
- So an air gap between the solidified casting and the mould is form.
- If all these expansions are homogeneous, the air-gap size d as a function of casting diameter D can be estimated to be

$$\frac{d}{D} = \alpha_s\left(T_f - T\right) + \alpha_m\left(T_{mi} - T_0\right)$$

T_f = freezing temperature
T_{mi} = mould interface temperature
T_0 = original mould temperature

It is worth mentioning that the name 'air gap' is perhaps a misnomer. The gap usually contains about 50% mould gases (high in hydrogen) and 50% air.

E.g., for Al casting at room temperature

D = 1 m	D = 2 mm
d = 10 mm	d = 10 μm

Mould and metal constants

Material	*Melting point* (°C)	*Liquid–solid contraction* (%)	*Specific heat* (J.Kg K)			*Density* (kg/m^3)			*Thermal conductivity* (J/m K s)		
			Solid		*Liquid*	*Solid*		*Liquid*	*Solid*		*Liquid*
			20°C	*m.p.*	*m.p*	*20°C*	*m.p.*	*m.p.*	*20°C*	*m.p.*	*m.p.*
Pb	327	3.22	130	(138)	152	11680	11020	10678	39.4	(29.4)	15.4
Zn	420	4.08	394	(443)	481	7140	(6843)	6575	119	95	9.5
Mg	650	4.2	1038	(1300)	1360	1740	(1657)	1590	155	(90)?	78
Al	660	7.14	917	(1200)	1080	2700	(2550)	2385	238	–	94
Cu	1084	5.30	386	(480)	495	8960	8382	8000	397	(235)	166
Fe	1536	3.16	456	(1130)	795	7870	7265	7015	73	14)?	–
Graphite	–	–	1515	–	–	2200	–	–	147		
Silica sand	–	–	1130	–	–	1500	–	–	0.0061	–	
Investment (Mullite)			750	–	–	1600	–	–	0.0038	–	–
Plaster	–	–	840	–	–	1100	–	–	0.0035	–	–

Thermal properties of mould and chill materials at 20 C

Material	*Heat Diffusivity* $(K\rho C)^{1/2}$ (Jm^{-2} K^{-1}s$^{-1/2}$)	*Thermal Diffusivity* $K/\rho C$ (m^{2}s^{-1})	*Heat Capacity per unit volume* ρC (JK^{-1}m^{-3})
Silica sand	3.21×10^3	3.60×10^{-9}	1.70×10^6
Investment	2.12×10^3	3.17×10^{-9}	1.20×10^6
Plaster	1.8×10^3	3.79×10^{-9}	0.92×10^6
Iron (pure Fe)	16.2×10^3	20.3×10^{-6}	3.94×10^6
Graphite	22.1×10^3	44.1×10^{-6}	3.33×10^6
Aluminium	24.3×10^3	96.1×10^{-6}	2.48×10^6
Copper	37.0×10^3	114.8×10^{-6}	3.60×10^6

3.1 Increased Heat Transfer

- Fine grained castings produced by faster cooling have excellent mechanical properties
- In practice, the casting engineer can manipulate the rate of heat extraction from a casting using a number of tricks to obtain fine-grained structure.
- Common ways to increase the rate of heat transfer:
  1. Use of **metal** moulds
  2. In sand moulds
     - (a) use of **chill** (external / internal) blocks in the mould, adjacent to the casting
     - (b) use of **fins** (solid / cast-on) attached to the casting

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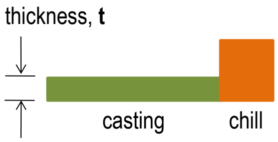
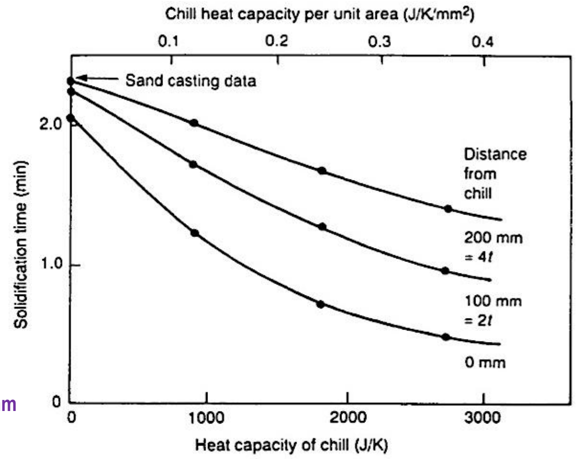
Use of Chill

- Various refractory mould materials - sand, investment and plaster - are all poor absorbers of heat.
- The various chill materials are all in a league of their own, having chilling powers orders of magnitude higher than the refractory mould materials.
- Metal pieces, placed adjacent to the pattern and subsequently packing the sand around it to make the rest of the mould in the normal way, are strictly known as **external chills.**
- **Internal chills** are metal pieces that are deliberately put inside the mould cavity to cause localised cooling and become integral part with the casting.
  - To have an **effective bonding** with the liquid metal and to **eliminate causing porosity problem**, the metal piece must be cleaned thoroughly (devoid of any oxide film and moisture).





Freezing time of a plate 225 x 150 x 50 mm in Al-5Si-3Cu alloy at various distances from the chilled end

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- The ability of a metal to be a **chill** depends on its capacity of absorbing heat, known as **heat diffusivity, $(K\rho C)^{1/2}$**

K = thermal conductivity
ρ= density
C = heat capacity

Thermal diffusivity = K/ρC

Material	Heat diffusivity ($J\ m^{-2}\ K^{-1}\ s^{-1/2}$)
Copper	37000
Graphite	22136
Pure iron	16186
Sand	1015
Investment	671
Plaster	566

Which material has the highest chilling power?

Copper

- A full chilling power of a material can only be developed if the material is **infinitely thick**

  otherwise, the piece of metal becomes saturated with the heat and, after a time, it can absorb no more heat

- The amount of heat a chill can actually absorb can be defined by the term **volumetric heat capacity, ρCV**.

ρ = density of chill material
C = sp. heat of chill material
V = volume of chill

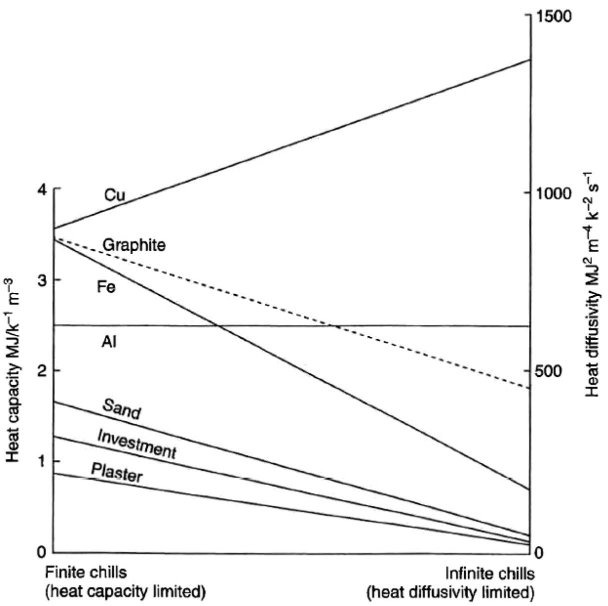


Figure 6.16 *Relative diffusivities (ability to diffuse heat away if a large chill) and heat capacities (ability to absorb heat if relatively small) of chill materials.*

Use of Fins

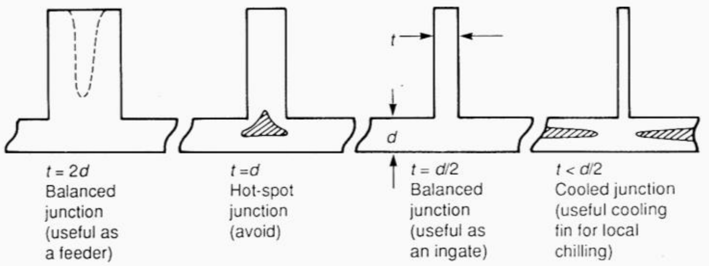
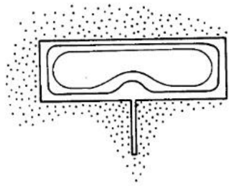


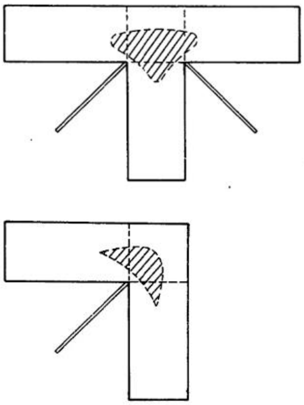
Figure 4.9 *A spectrum of T-junctions, showing how some are hot, some are cold, and some are neither.*

- When the wall forming the upright of the T-junction is thin, it acts as a cooling fin, chilling the junction and the adjacent wall (the top cross of the T) of the casting.
- When the upright of the T-section has increased to a thickness of half the casting section thickness then the junction is close to thermal balance, the cooling effect of the fin balancing the hot-spot effect of the concentration of metal in the junction.

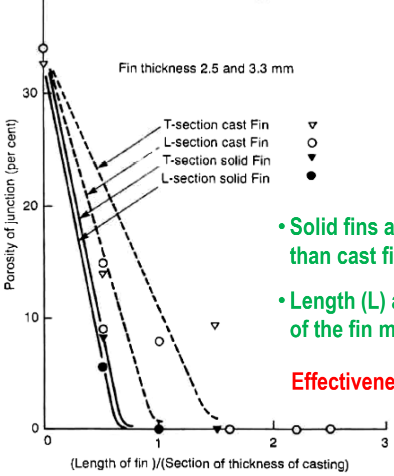
- ☐ Fins are thin projections of solids used for localised cooling.



T-junction showing successive position of the freezing front



The position fins added to T- and L-junctions to eliminate cavity is shown



- **Solid fins are more effective than cast fins**
- **Length (L) and thickness (t) of the fin must be optimum**

Effectiveness of fin $= \frac{2L}{t}$

The practical benefits to the use of a fin as opposed to a chill

1. The fin is always provided on the casting, because it is an integral part of the tooling. Thus, unlike a chill, the placing of it cannot be **forgotten**.

2. It is always exactly in the **correct place**. It cannot be wrongly sited before the making of the mould. (The incorrect positioning of a chill is easily appreciated, because although the location of the chill is normally carefully painted on the pattern, the application of the first coat of mould release agent usually does an effective job in eliminating all traces of this.)

3. It **cannot be displaced** or lifted during the making of the mould. If the chill lift slightly during the filling of the tooling with sand the resulting sand penetration under the edges of the chill, and the casting of additional metal into the roughly shaped gap, make an unsightly local mess of the casting surface.

   Displacement or complete falling out from the mould is a common danger, sometimes requiring studs to support the chill if awkwardly angled or on a vertical face. Displacement commonly results in sand inclusion defects around the chill or can add to defects elsewhere. All this is expensive to dress off.

4. An **increase in productivity** has been reported as a result of not having to find, place and carefully tuck in a block chill into a sand mould.

5. It is **easily cut off**. In contrast, the witness from a chill also usually requires substantial dressing, especially if the chill was equipped with v-grooves, or if it became misplaced during moulding, as mentioned above.

6. The fin **does not cause scrap castings** because of condensation of moisture and other volatiles, with consequential blow defect as is a real danger from chills.

7. The fin **does not require to be retrieved** from the sand system, cleaned by shot blasting, stored in special bins, re-located, counted losses made up by re-ordering new chills, casting new chill (particularly if the chill is shaped) and finally ensuring that the correct number in good condition, re-coated and dried, is delivered to the moulder on the required date.

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8. The fin **does not wear out**. Old chills become rounded to the point that they are effectively worn out. In addition, in iron and steel foundries, grey iron chills are said to ‘lose their nature’ after some use. This seems to be the result of the oxidation of the graphite flakes in the iron, thus impairing the thermal conductivity of the chill.

9. Sometimes it is possible to **solve a localized feeding problem** (the typical example is the isolated boss in the centre of the plate) by chilling with a fin instead of providing a local supply of feed metal. In this case the fin is enormously cheaper than the feeder.

Next Class

MME **345**, Lecture **B:03**

Solidification and Crystallisation

2. Nucleation and growth of solid