Lecture 3: Solidification

Driving Force

Solidification is undoubtedly the most important processing route for metals and alloys. Consider a pure metal (Fig. 1). At the fusion temperature T_f, $\Delta G = 0$ so that

$$\Delta G = \Delta H_f - T_f \Delta S_f = 0 \qquad \text{or} \qquad \Delta H_f = T_f \Delta S_f$$

where ΔH_f is the latent heat of fusion and ΔS_f is positive for melting. For any temperature other than T_f,

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ &\simeq \Delta H_f - T\Delta S_f \\ &= \Delta S_f (T_f - T) = \Delta S_f \quad \underbrace{\Delta T}_{undercooling} \end{aligned}$$

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

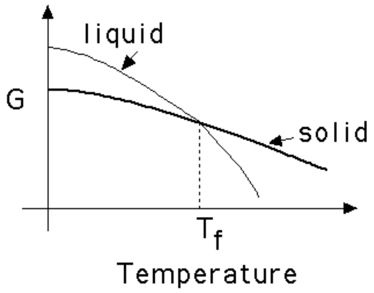

Fig. 1: Driving force for solidification

Nucleation and Growth

Homogeneous nucleation occurs only at very large ΔT, for example, in containerless experiments where a pure liquid is isolated from its environment. In general, solidification is by heterogeneous nucleation, either on impurity particles or wherever the liquid comes into contact with the container surface.

The velocity v of the transformation front is related to the difference in the rate of liquid→solid atom jumps and the solid→liquid atom jumps:

$$v \propto \exp\left\{-\frac{Q}{kT}\right\}\left[1-\exp\left\{-\frac{\Delta G}{kT}\right\}\right]$$

$$\text{i.e. for small } \Delta G \quad v \propto \Delta G$$

$$v \propto \Delta T$$

The last two proportionalities assume that the undercooling is small, in which case $\exp\{x\} \simeq 1 + x$.

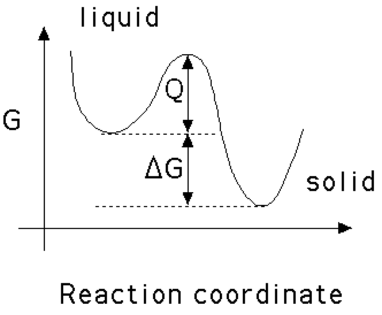

Fig. 1: Barrier to interface motion

Geometry of Solidification

Fig. 2 shows the grain structures possible. The chill zone contains fine crystals nucleated at the mould surface. There is then selective growth into the liquid as heat is extracted from the mould. If the liquid in the centre of the mould is undercooled sufficiently there may also be equiaxed grains forming.

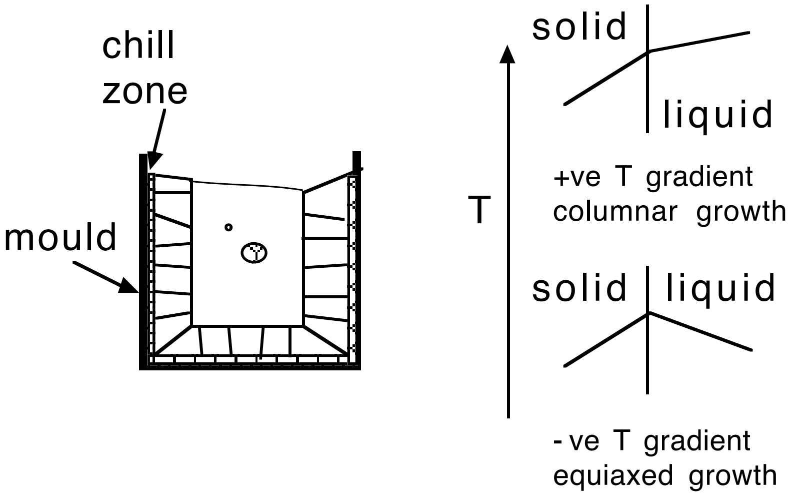

Fig. 2: Geometry of solidification

Equiaxed growth in a pure metal shows morphological instabilities, *i.e.* thermal dendrites (Fig. 3). This is because a small perturbation at the interface ends up in even more supercooled liquid so the interface becomes unstable. Dendrites have preferred growth directions, almost always $< 1\ 0\ 0 >$ in cubic metals.

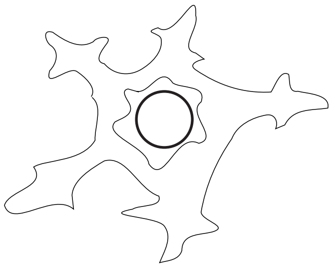

Fig. 3: Thermal dendrite formation when the temperature gradient in the liquid is negative.

Alloys: Solute Partitioning

Dendrite formation is extremely common in alloys, where solute partitions between the solid and liquid phases (Fig. 4). By convention, we shall label the composition of the solid phase which is in equilibrium with the liquid as C^{SL} and a similar interpretation applies to C^{LS}. C_0 represents the average composition of the alloy. The partition coefficient k is written

$$k = \frac{C^{SL}}{C^{LS}} \qquad \text{frequently} < 1$$

Under equilibrium conditions the compositions of the solid and liquid at all stages of solidification are given by a tie–line of the phase diagram, and the proportions of the phases at any temperature by the lever rule.

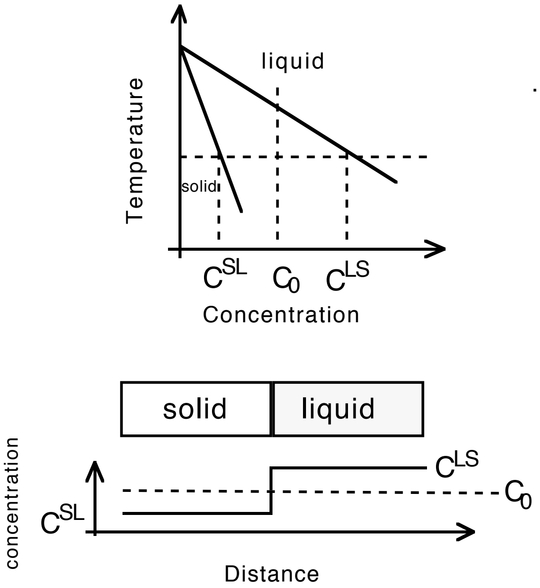

Fig. 4: Solidification under equilibrium conditions

In practice, equilibrium will only be maintained at the interface (Fig. 5), where the compositions agree with the phase diagram. The composition of the solid follows the solidus. Steady state solidification occurs when the temperature is T^*, when $C^{SL} = C_0$ and there is no further solute partitioned into the remaining liquid.

From AH8,

$$\begin{aligned} C &= C^{SL} + (C^{LS} - C^{SL}) \exp\left\{-\frac{x}{D/v}\right\} \\ &\equiv C_0 + \frac{C_0(1-k)}{k} \exp\left\{-\frac{x}{D/v}\right\} \end{aligned}$$

Note that D/v has dimensions of length, approximately the diffusion distance into the liquid. It is typically about 0.5 mm but can be just a few micrometres in rapid solidification processing.

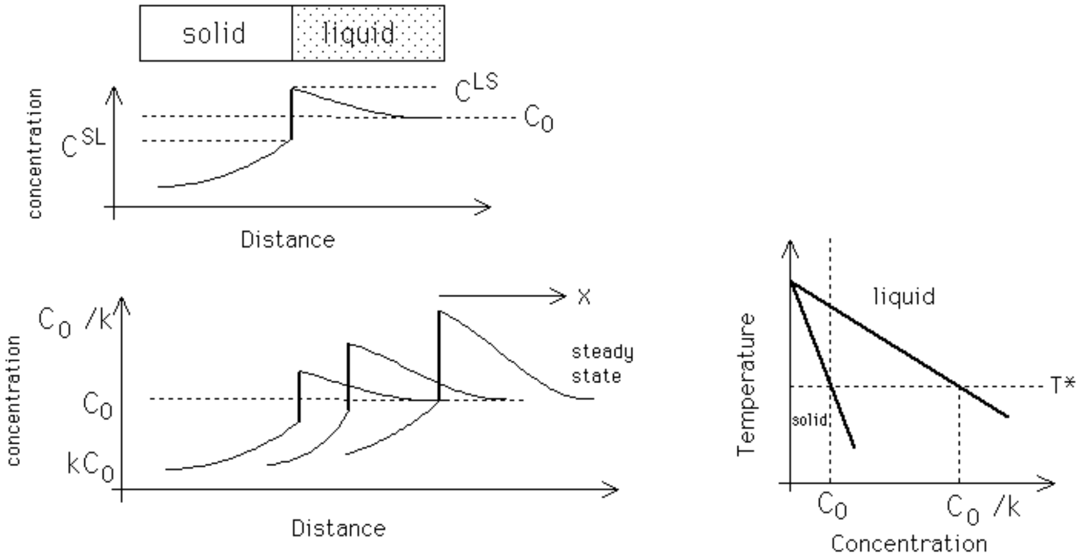

Fig. 5: Solidification under nonequilibrium conditions

1602, 1603	Levitation
T607	dendrite, cast aluminium
	Video of succinonitrile

Lecture 4: Solidification

Mixing in the Liquid

Convection can cause mixing, reducing solute gradients in the liquid. A limiting case is where the liquid is uniform in composition throughout solidification (Fig. 6).

For liquid of composition C^L (note change in terminology since it is no longer in equilibrium with solid), the composition of the solid phase at the interface is given by $C^S = kC^L$. If f_s is the fraction solidified, then from AH9,

$$(C^L - kC^L)df = (1-f)dC^L$$

$$\int_0^{f_s} \frac{df}{1-f} = \int_{C_0}^{C^L} \frac{dC^L}{C^L(1-k)}$$

so that $\quad C^L = C_0(1-f_s)^{k-1} \quad$ and $\quad C^S = kC_0(1-f_s)^{k-1}$

This last relation is known as the *Scheil Equation.*

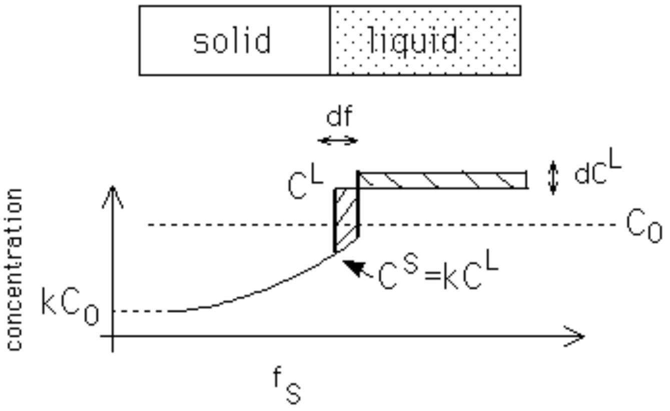

Fig. 6: Mixing in the liquid

The redistribution of solute is larger when there is mixing in the liquid (Fig. 7). This can be used in *zone refining*, *e.g.* of silicon, with a repeated sweeping in one direction, leading to purification (elements for which $k > 1$ would be swept in the other direction). By moving the furnace to and fro, one can obtain *zone levelling*.

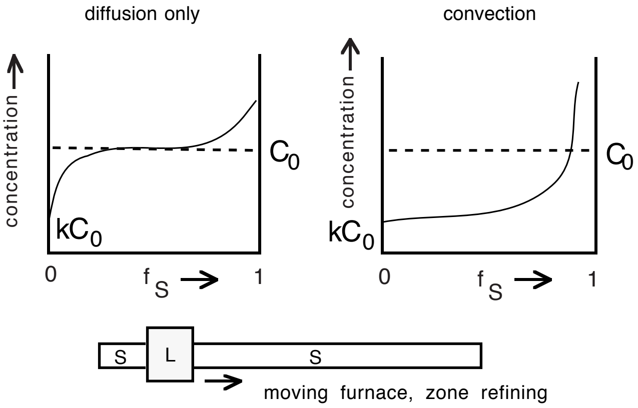

Fig. 7: Distribution of solute

Constitutional Supercooling (AH10)

Solute is partitioned into the liquid ahead of the solidification front. This causes a corresponding variation in the liquidus temperature (the temperature below which freezing begins). There is, however, a positive temperature gradient in the liquid, giving rise to a supercooled zone of liquid ahead of the interface (Fig. 8). This is called constitutional supercooling because it is caused by composition changes.

A small perturbation on the interface will therefore expand into a supercooled liquid. This gives rise to dendrites.

It follows that a supercooled zone only occurs when the liquidus–temperature (T_L) gradient at the interface is larger than the temperature

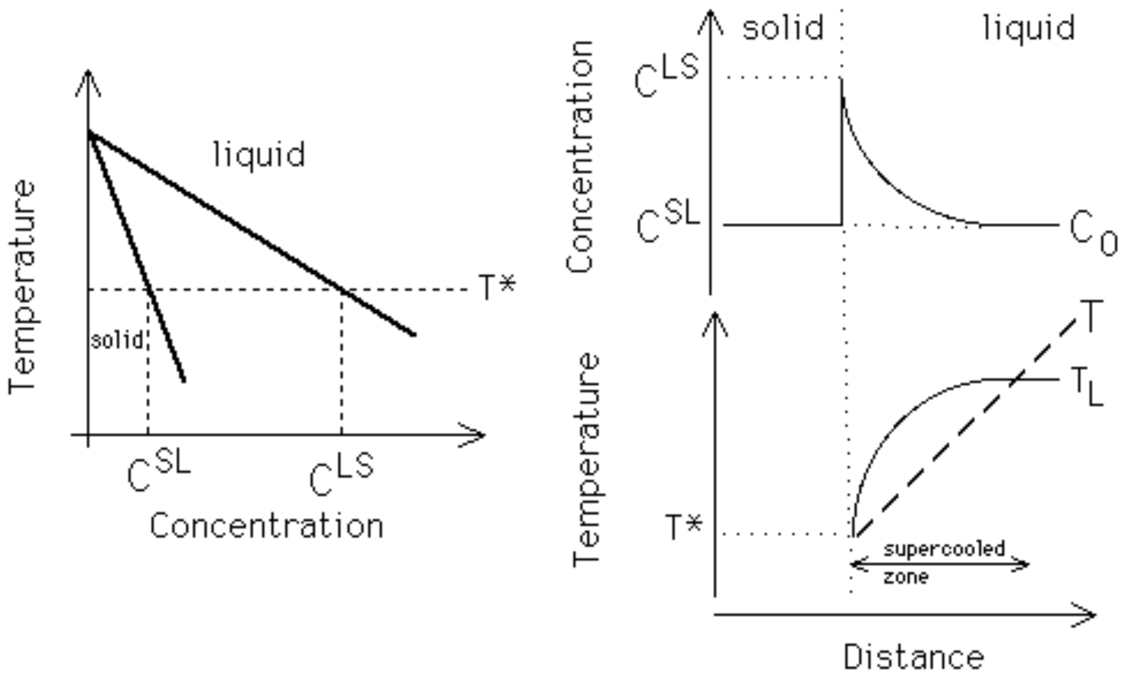

Fig. 8: Diagram illustrating constitutional supercooling.

gradient:

$$\left.\frac{\partial T_L}{\partial x}\right|_{x=0} > \frac{\partial T}{\partial x} \qquad \text{i.e.,} \qquad m\left.\frac{\partial C_L}{\partial x}\right|_{x=0} > \frac{\partial T}{\partial x}$$

where m is the magnitude of the slope of the liquidus phase boundary on the phase diagram. From AH8 we note that

$$\left.\frac{\partial C_L}{\partial x}\right|_{x=0} = -\frac{C^{LS} - C^{SL}}{D/v}$$

so that the minimum thermal gradient required for a stable solidification front is

$$\frac{\partial T}{\partial x} < \frac{mC_0(1-k)v}{kD}$$

It is very difficult to avoid constitutional supercooling in practice because the velocity required is very small indeed. Directional solidification with a planar front is possible only at low growth rates, for example in the production of silicon single crystals. In most cases the interface is unstable (Fig. 9):

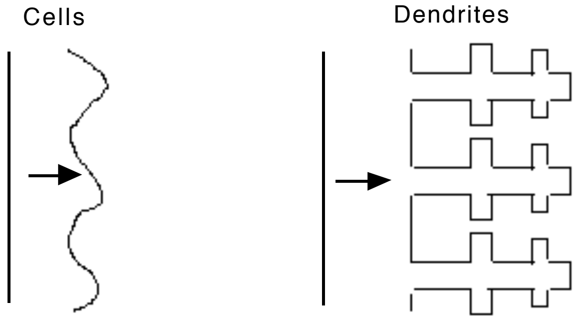

Fig. 9: Cells and dendrites

Microsegregation

There is little or no segregation ahead of dendrite tip because the main partitioning is of solute trapped between the dendrite side arms (metallography specimen M2). The scale of this segregation can be reduced by increasing the solidification rate because the dendrite arm spacing then decreases. A rough explanation of this phenomenon is that a large undercooling permits the creation of a greater surface, *i.e.* smaller dendrite spacing. Segregation can also be reduced by inducing a greater number density of nuclei, for example, by adding inoculants such as titanium boride in aluminium (the TiB_2 particles coat with Al_3Ti which in turn nucleates aluminium. Anything which refines the scale of the microstructure will lead to less segregation.

This chemical segregation can lead to the formation of phases (such as eutectic) which are not expected under equilibrium conditions.

806	Cell formation
807	Plan view of cells
786	Dendrites
1281	Solute segregation
1287	Dendrite arm spacing
828,829	Al-Si, Al-Si-Na

Lecture 5: Solidification

Solidification Processing

A key phenomenon in solidification processing is the transfer of heat by radiation, direct contact with the mould, conduction through air and convection in the air gap between the mould and ingot. Casting situations may be divided according to whether or not significant thermal gradients are set up in the solidifying metal.

The transfer of heat across a gap (an interface) is given by

$$q = h\Delta T$$

where q is the heat flux, h is the thermal conductance of the interface and ΔT the temperature difference between the source and the sink. Values of the heat transfer coefficient vary widely: $10 \rightarrow 10^2$ for large air gap; $10^3 \rightarrow 10^4$ for normal castings with gravity contact; $10^5 \rightarrow 10^6$ for excellent contact as in pressure casting. The temperature profile obtained depends on the a comparison of the heat conductance of the interface with that of the whole casting. The thermal conductance of a casting is written K/L where where K is the thermal conductivity of a casting of length L in the direction of heat flow. The ratio of the thermal conductance of the interface (h) to that of the casting, termed the Biot number:

$$Bi = \frac{h}{K/L} = \frac{hL}{K}$$

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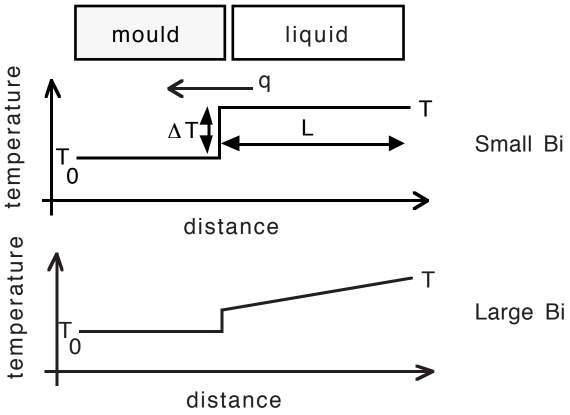


Fig. 10: The two different heat transfer situations that arise in casting.

For small Bi the thermal resistance of the interface dominates that of the casting, which therefore remains at approximately a constant temperature. This is called *Newtonian cooling*.

Newtonian cooling is favoured by high conductivity metals such as Al and Cu or for small castings.

Chill Mould Castings

Chill casting uses a massive metal mould with a large thermal capacity or a water cooled metal mould so that $Bi \ll 1$. When the metal is poured in at a temperature well above its melting temperature T_m, it first cools and begins solidification when $T = T_m$. For the first stage, illustrated in Fig. 11, it follows that

$$q = h\Delta T = \dot{T} C_V L \qquad \text{so that} \qquad \dot{T} = \frac{h\Delta T}{L C_V}$$

where C_V is the heat capacity of the liquid ($\mathrm{J\,m^{-3}\,K^{-1}}$) and $\dot{T}$ is the cooling rate of the liquid. Note that $h\Delta T$ is the heat flow into the mould and $\dot{T} C_V L$ is the heat liberated by the liquid.

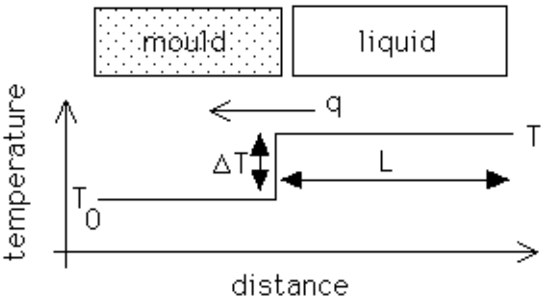


Fig. 11: Chill mould. The liquid is at a temperature higher than T_m, the melting temperature.

This cooling of the liquid will be followed by the second stage which is isothermal solidification (Fig. 12). For this case, the speed v of the solidification front can be obtained by balancing heat evolution against heat extraction:

$$q = h\Delta T = v\Delta H_F \qquad \text{i.e.,} \qquad v = \frac{h\Delta T}{\Delta H_F}$$

where q is the heat flux and ΔH_F is latent heat released on solidification.

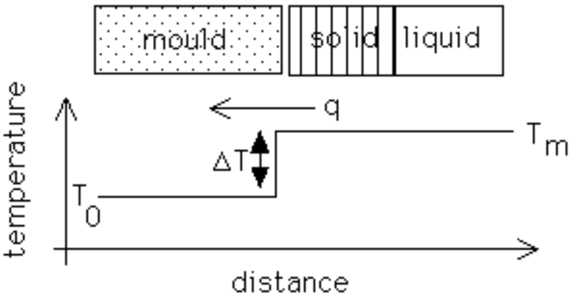
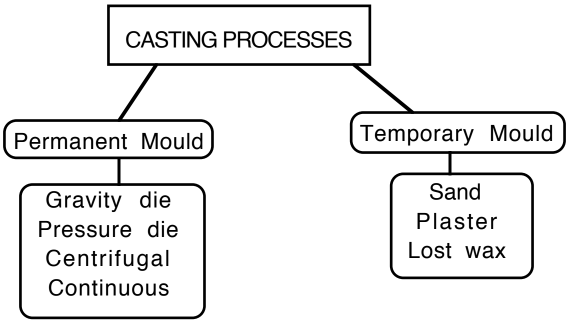


Fig. 12: Chill mould. The casting is now at the melting temperature T_m

Casting Processes



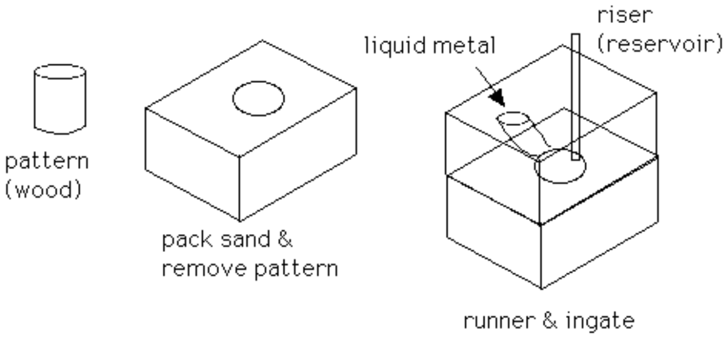


Fig. 12: Procedure for sand casting. This process is usually automated.

Sand Casting

In sand casting a mould is made by packing sand around a pattern (Fig. 13), removing the pattern and hardening the sand with polymer or silicate. The metal is then poured into the resulting mould in a controlled manner so that solidification proceeds in an orderly manner without leaving any holes or porosity. To avoid the blockage of channels, chill blocks may be used to permit certain parst to solidify first. Risers are used to feed metal into the mould as it freezes and contracts.

Examples of sand cast components include automobile engine blocks, ship propellers, huge steel components for power plant boilers, nodes for North Sea oil platforms.

Die Casting

Die casting involves the injection of a low–melting temperature alloy into a steel mould. Zn-4Al wt%, which is a eutectic composition, is a classic die–casting alloy melting at 419 °C. The process is usually for non–structural components since the casting inevitably contains internal pores and because Zn does not have particularly good mechanical properties. However, productivity can be high and the surface finish is good. Toys, boxes *etc.*

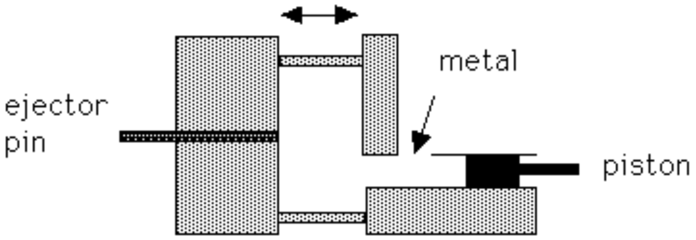


Fig. 13: The metal may be injected in at pressure

Centrifugal Casting

Centrifugal casting has a rotating cylindrical mould; molten matter poured into the mould solidifies to give a pipe. The quality is excellent and the process is used for making long pipelines for the chemical industry.

Continuous Casting

Continuous casting is illustrated in AH12 and is the primary casting process in the manufacture of steel and aluminium.

Others

Lost wax process, rapid solidification.

1444	Continuous casting
	Continuous casting video (Scunthorpe Steel)
865	Melt spinning