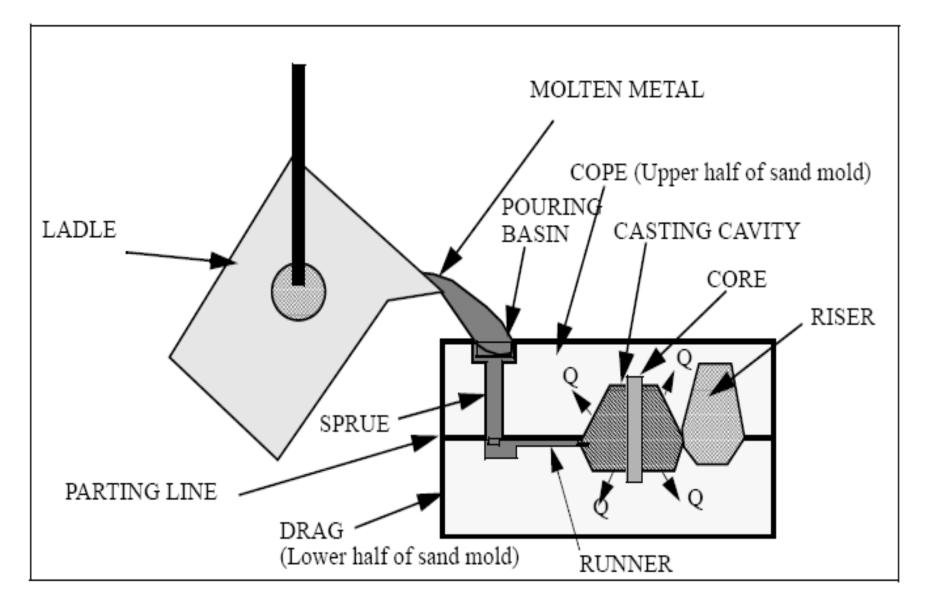
Solidification

- The solidification of metals and their alloys is an important industrial process.
- Not only do structural alloys start with the casting of ingots for processing into reinforcing bars or structural shapes, but when a metal is welded a small portion of metal near the weld melts and resolidifies.
- It also serves as a model to represent first order phase transformations in general.

METAL CASTING

QUICKEST LEAST EXPENSIVE ROUTE TO A NEAR NET SHAPE PRODUCT



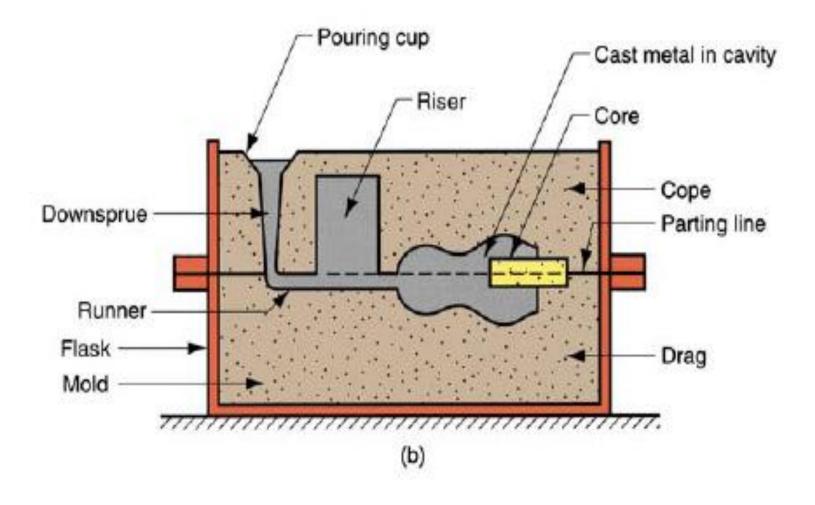
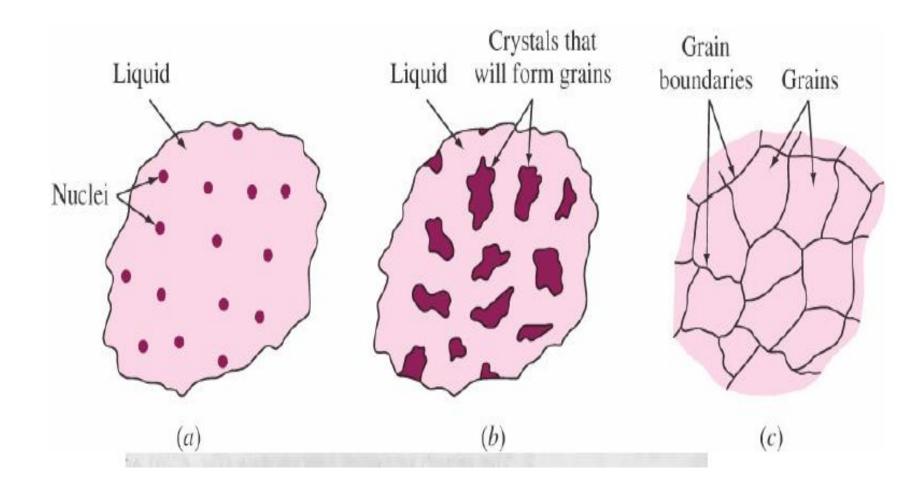


Figure 10.2 (b) Sand casting mold

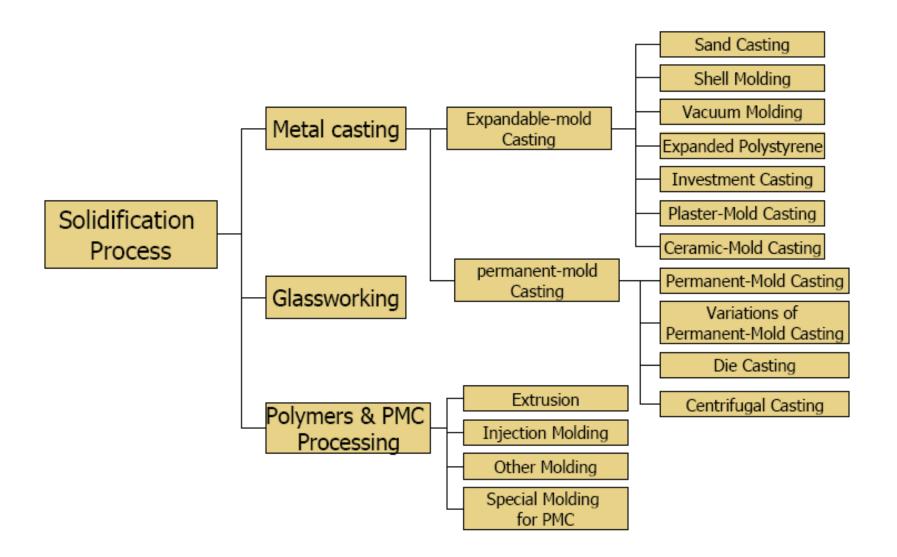
Solidification Processes

Starting work material is either a liquid or is in a highly plastic condition, and a part is created through solidification of the material

- Solidification processes can be classified according to engineering material processed:
 - Metals
 - Ceramics, specifically glasses
 - Polymers and polymer matrix composites (PMCs)



Classification



Simple Diffusion-dependent PT

· Example: solidification of a pure element

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

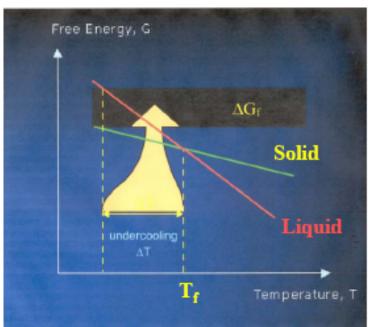
 $\Delta \mathbf{G}_{f} = \Delta \mathbf{H}_{f} - T_{f} \Delta \mathbf{S}_{f} = \mathbf{0} \text{ or } \Delta \mathbf{H}_{f} = \mathbf{T}_{f} \Delta \mathbf{S}_{f}$

where ΔH_f is the latent heat of fusion and $\Delta S_f > 0$ for melting.

For any temperature other than T_f,

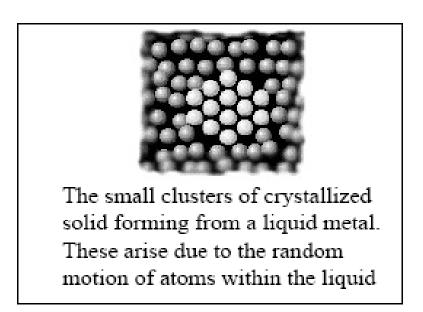
$$\Delta G = \Delta H - T\Delta S \cong \Delta H_f - T\Delta S_f = \Delta S_f (T_f - T) = \Delta S_f \Delta T$$

where ΔT is under cooling



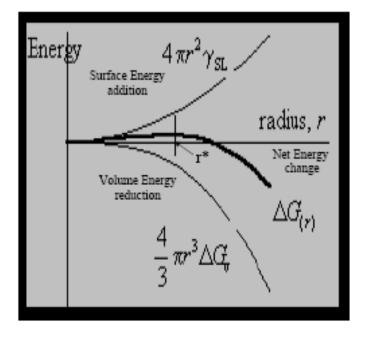
The *driving force* is therefore proportional to the *under cooling* because the latent heat and the entropy of fusion do not vary much with temperature

Nucleation



- Homogeneous Nucleation precipitation occurs within a completely homogeneous medium
- Heterogeneous Nucleation precipitation may occur also on the surfaces, which separate different media, e.g. walls of the reactor

Homogeneous Nucleation



•By assuming that solid phase nucleates are spherical 'clusters' of radius, r, one can define the excess of free energy change for a single nucleus, $\Delta G_{(r)}$:

$$\Delta G_{(r)} = \frac{4}{3} \pi r^3 \Delta G_{\pi} + 4 \pi r^2 \gamma_{\rm SL}$$

where γ_{SL} is the solid/liquid interfacial energy.

The critical radius r^* (defined as the radius at which $\Delta G_{(r)}$ is maximum) is given by:

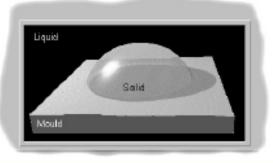
$$r^* = \frac{-2\gamma_{SL}}{\Delta G_{v}} = \frac{-2\gamma_{SL}T_{m}}{\Delta H_{v}\Delta T}$$

The associated energy barrier to homogeneous nucleation, ΔG^* is:

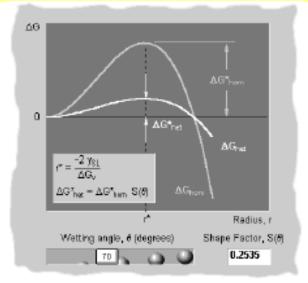
 $\Delta G^* = \frac{16 \pi \gamma_{SL}^3}{3 \Delta G_{\pi}^2} = \frac{16 \pi \gamma_{SL}^3 T_m^2}{\Delta H_{\pi}^2 \Delta T^2}$

Important : the temperature-dependence of these terms are: $r^* \propto 1/\Delta T$ and $\Delta G^* \propto 1/\Delta T^2$ **Higher under cooling – easy to form new phase !!**

Heterogeneous Nucleation



The nuclei can form at preferential sites (e.g. mould wall, impurities or catalysts). By this, the *energy barrier to nucleation*, ΔG^* can be *substantially reduced*.



•Let us consider that a solid cluster forms on a mould wall. In this case, one can define the excess of free energy change for a nucleus, $\Delta G_{(r)}$ as follows:

$$\Delta G_{(r)} = V \Delta G_{\pi} + A_{\rm SL} \gamma_{\rm SL} + A_{\rm SM} \gamma_{\rm SM} - A_{\rm SM} \gamma_{\rm ML}$$

Note that as compared to homogeneous case two new interface should be taken into account i.e. solid-mould and liquid mould

• It can be shown that the critical radius r^*_{het} for heterogeneous nucleation *is equal* to r^*_{hom} :

$$\begin{split} r_{\rm het}^{\bullet} &= \frac{-2\gamma_{\rm SL}}{\bigtriangleup G_{\rm v}} = r_{\rm hom}^{\bullet} \\ \bullet \, {\rm And:} & \\ \bigtriangleup G_{\rm het}^{\bullet} &= \frac{16\pi\gamma_{\rm SL}^3}{3\bigtriangleup G_{\rm v}^2}S(\theta) = \bigtriangleup G_{\rm hom}^{\bullet}S(\theta) \end{split}$$

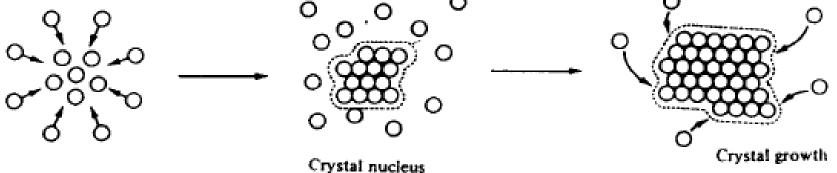
where $S(\theta)$ is a geometrical factor and θ is a wetting angle: $S(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4}$

Heterogeneous Nucleation is Faster than Homogeneous Process !!



Homogeneous Nucleation

- Homogeneous nucleation occurs when there are no special objects inside a phase which can cause nucleation.
- For instance when a pure liquid metal is slowly cooled below its equilibrium freezing temperature to a sufficient degree numerous homogeneous nuclei are created by slow-moving atoms bonding together in a crystalline form.





Gibbs Free Energy

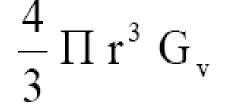
• G = U - TS

- where U = Internal Energy, T = Absolute Temperature, and S = Entropy
- Materials Scientists refer to the difference in G between the old and new phases as the <u>driving</u> <u>"force"</u> for the phase transformation.
- The release of heat when a metal solidifies indicates that the crystalline phase has a lower Gibbs Free Energy, G, than the liquid.
- At the equilibrium freezing temperature the Gibbs Free Energy of the liquid and the crystalline phase are equal.



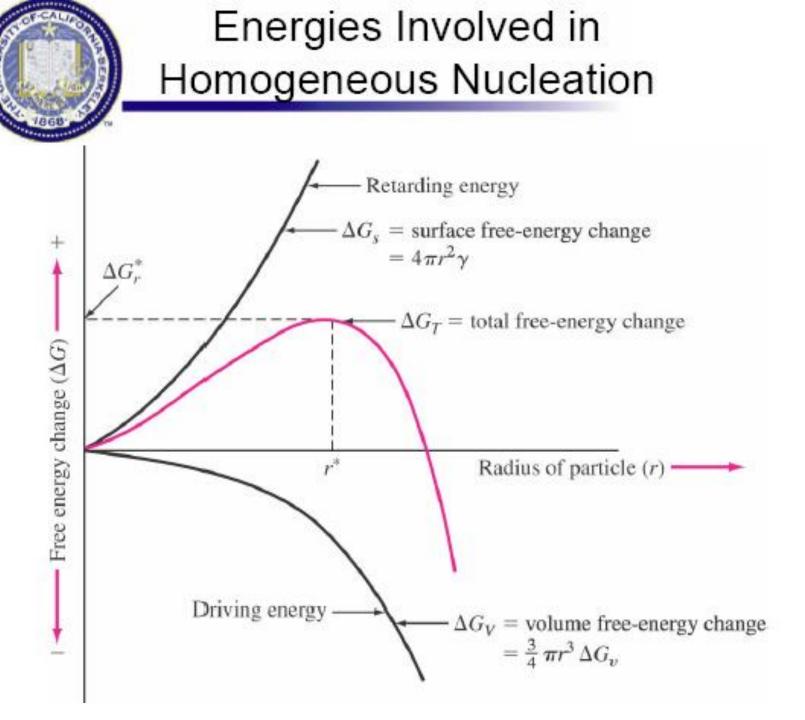
Energies Involved in Homogeneous Nucleation

(1)Volume free energy



(2) Surface energy

$$4 \Pi r^2 \gamma$$





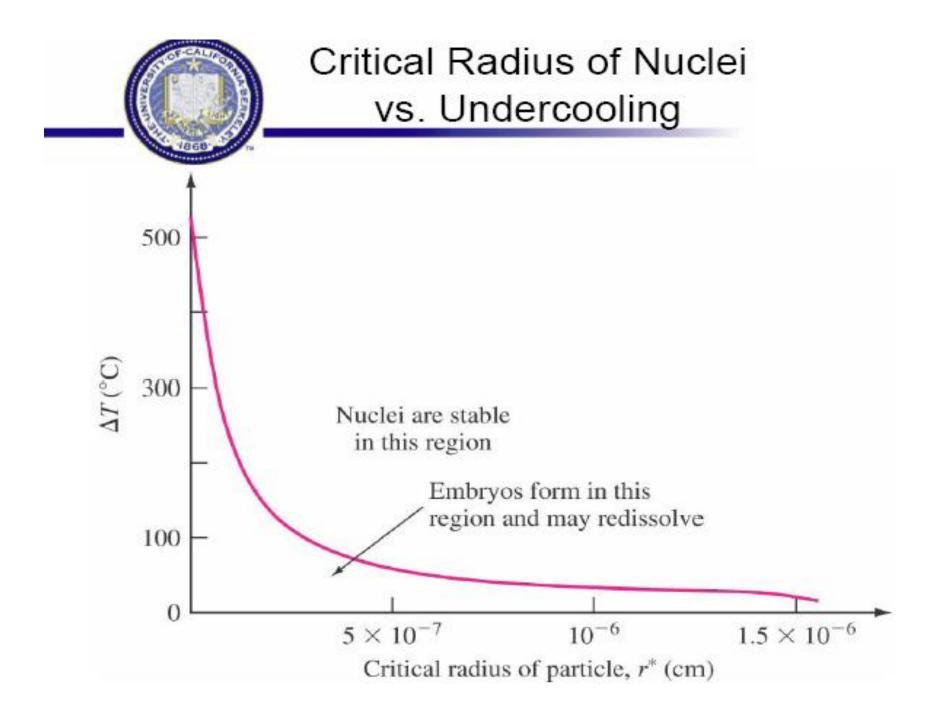
Critical radius

$$\Delta G = \frac{4}{3} \prod r^3 G_v - 4 \prod r^2 \gamma$$

To find the minimum

$$\frac{\mathrm{d}(\Delta \mathrm{G})}{\mathrm{d}r} = 0$$

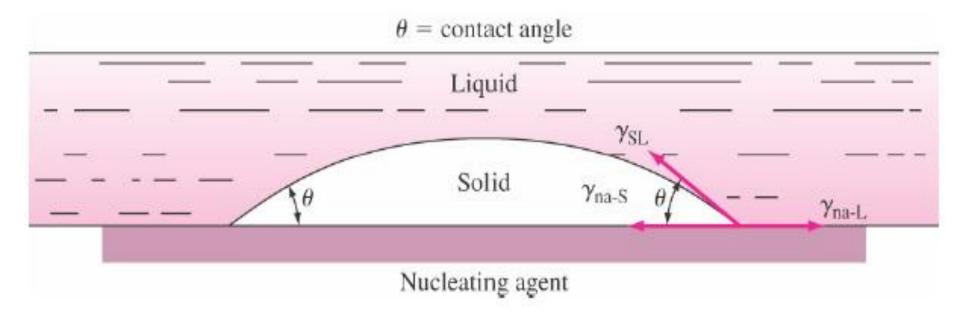
$$\mathbf{r} * = -\frac{2\gamma}{\Delta G}$$



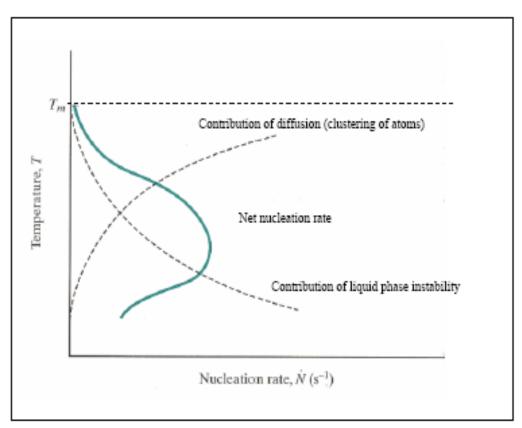


Heterogeneous Nucleation

 Heterogeneous nucleation occurs when there are special objects inside a phase which can cause nucleation.

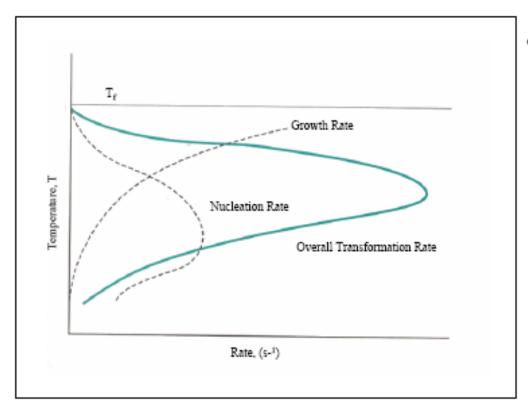


Nucleation Rate-Temperature Diagram



- The overall nucleation rate is a product of two opposite working factors:
 - the driving force for solidification increases with T decrease;
 - while the diffusion that is responsible for the clustering process *decrease* with T decrease.
- These explain the "knee-shaped" nature of the transformation curve with maximum at some value below T_f

Overall Transformation Rate-Temperature Diagram



- The overall transformation rate is a product of two factors:
 - nucleation;
 - *growth*, which is thermally activated process, typically described by Arrhennius function

PT rate achieves *maximum* at some T below T_f!!

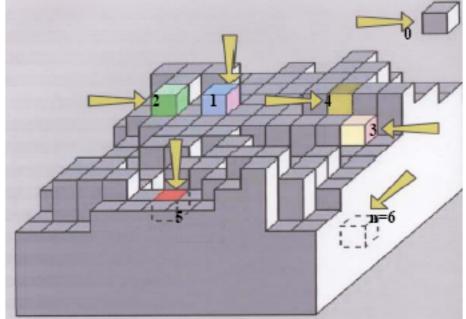
Solidification of a Pure Elements (1)

• Any molecule near the solid/liquid Interface have certain number of bonds (in the range 0 to 6) with solid phase.

• The molecules attached to the interface may become "*melted off*" into the liquid as a result of *thermal fluctuations* (*diffusion*).

• The molecule resists this to a degree which depends on the energy with which it is bound to the solid.

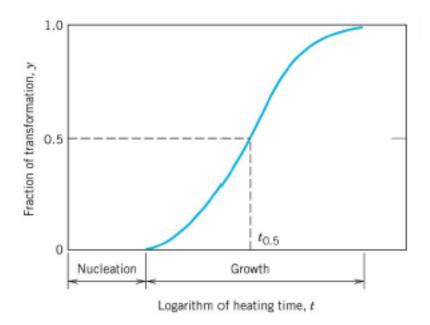
• Since the maximum binding energy is given by the enthalpy of fusion, $\Delta H_{\rm f}$, the value for a molecule exposed to the liquid will be $n\Delta H_{\rm f}/6$, where **n** is the number of bonds.



KINETICS of SOLID STATE TRANSFORMATION (1)

• Kinetics - a time dependence of transformation rate.

Example: typical kinetics for variety of solid-state transformation at constant temperature



Two stages of transformation process:

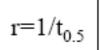
- *Nucleation* formation of extremely fine particles, i.e. *nuclei*, of *new phases*
- Growth increasing of nuclei size

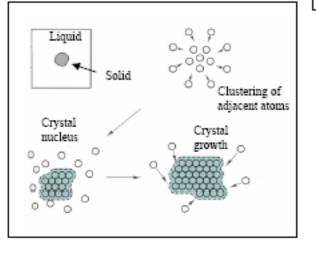
• Can be described by so-called Avrami Equation:

fraction
$$y = 1 - e^{-kt^{n}}$$

transformed time

• By convention, the rate of transformation r is taken as the reciprocal of time required to reach half completion:





Capabilities and Advantages of Casting

- Can create complex part geometries
- Can create both external and internal shapes
- Some casting processes are net shape; others are near net shape
- Can produce very large parts
- Some casting methods are suited to mass production

Casting

Process in which molten metal flows by gravity or other force into a mold where it solidifies in the shape of the mold cavity

- The term casting also applies to the part made in the process
- Steps in casting seem simple:
 - 1. Melt the metal
 - 2. Pour it into a mold
 - 3. Let it freeze

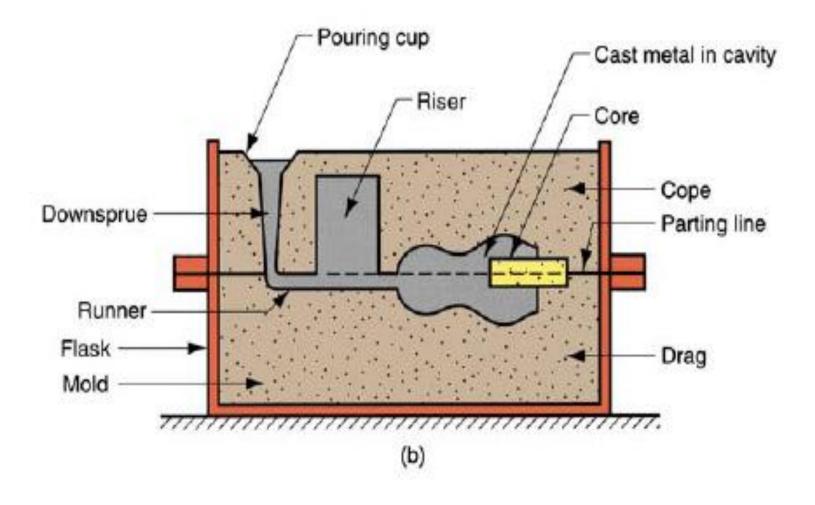


Figure 10.2 (b) Sand casting mold

Forming the Mold Cavity

- Mold cavity is formed by packing sand around a pattern, which has the shape of the part
- When the pattern is removed, the remaining cavity has desired shape of cast part
- The pattern is usually oversized to allow for shrinkage of metal as it solidifies and cools
- Sand for the mold is moist and contains a binder to maintain shape

A pure metal solidifies at a constant temperature equal to its freezing point (same as melting point)

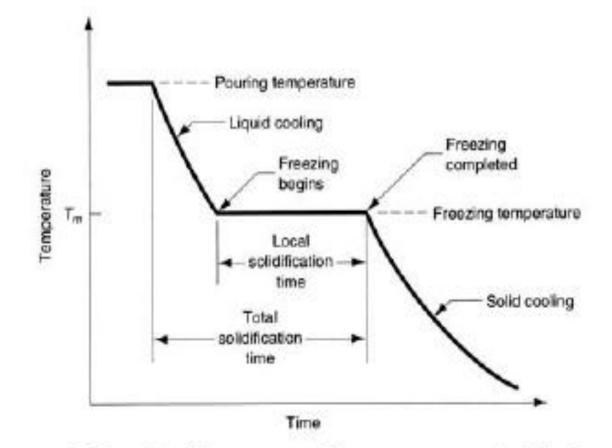


Figure 10.4 - Cooling curve for a pure metal during casting

Solidification of Pure Metals

- Due to chilling action of mold wall, a thin skin of solid metal is formed at the interface immediately after pouring
- Skin thickness increases to form a shell around the molten metal as solidification progresses
- Rate of freezing depends on heat transfer into mold, as well as thermal properties of the metal

Most alloys freeze over a temperature range rather than at a single temperature

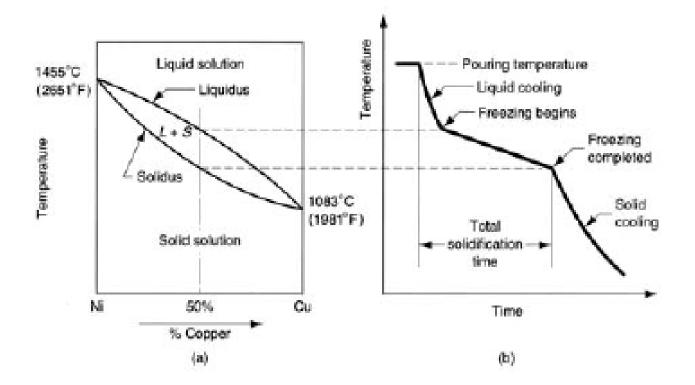


Figure 10.6 - (a) Phase diagram for a copper-nickel alloy system and (b) associated cooling curve for a 50%Ni-50%Cu composition during casting

Solidification Time

- · Solidification takes time
- Total solidification time TST = time required for casting to solidify after pouring
- TST depends on size and shape of casting by relationship known as Chvorinov's Rule

Chvorinov's Rule

$$TST = C_m \left(\frac{V}{A}\right)^n$$

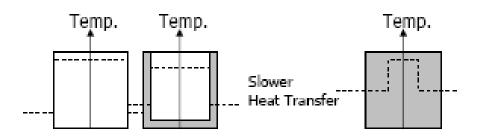
where TST = total solidification time; V =
volume of the casting; A = surface area of
casting; n = exponent usually taken to have a
value = 2; and C_m is mold constant

Mold Constant in Chvorinov's Rule

- C_m depends on mold material, thermal properties of casting metal, and pouring temperature relative to melting point
- Value of C_m for a given casting operation can be based on experimental data from previous operations carried out using same mold material, metal, and pouring temperature, even though the shape of the part may be quite different

Solidification of Pure Metals

- A thin skin of solid metal is formed at the cold mold wall immediately after pouring
- Skin thickness increases to form a shell around the molten metal as solidification progresses
- Rate of freezing depends on heat transfer into mold, as well as thermal properties of the metal





Randomly oriented grains of small size near the mold wall, and large columnar grains oriented toward the center of the casting (Dendritic growth)

Dendrite Growth

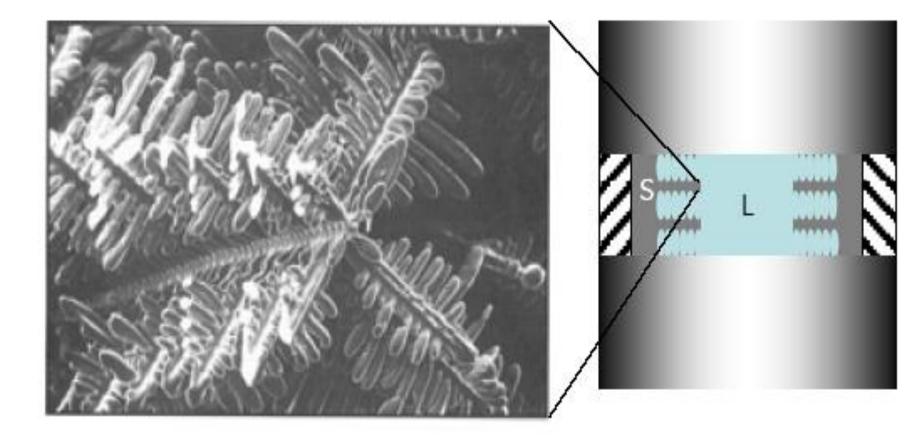




Figure 10.7 - Characteristic grain structure in an alloy casting, showing segregation of alloying components in center of casting

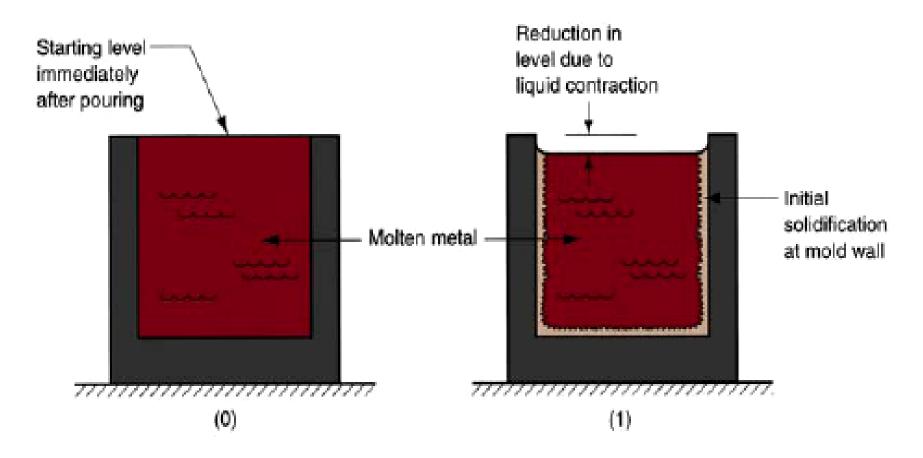


Figure 10.8 - Shrinkage of a cylindrical casting during solidification and cooling: (0) starting level of molten metal immediately after pouring; (1) reduction in level caused by liquid contraction during cooling (dimensional reductions are exaggerated for clarity in sketches)

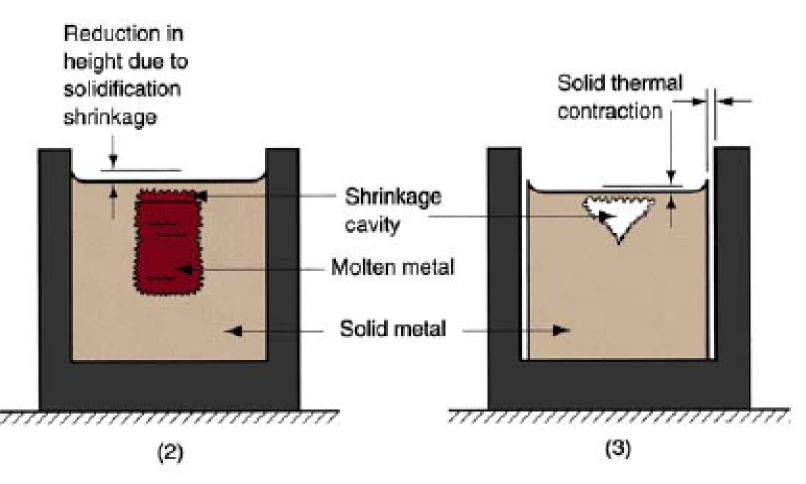


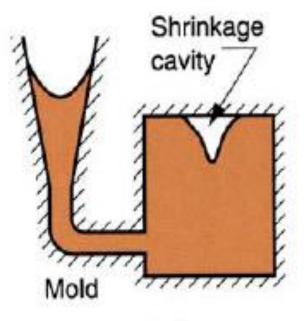
Figure 10.8 - (2) reduction in height and formation of shrinkage cavity caused by solidification shrinkage; (3) further reduction in height and diameter due to thermal contraction during cooling of the solid metal (dimensional reductions are exaggerated for clarity in our sketches)

Solidification Shrinkage

- Occurs in nearly all metals because the solid phase has a higher density than the liquid phase
- Thus, solidification causes a reduction in volume per unit weight of metal
- Exception: cast iron with high C content
 - Graphitization during final stages of freezing causes expansion that counteracts volumetric decrease associated with phase change

Shrinkage Cavity

Depression in surface or internal void caused by solidification shrinkage that restricts amount of molten metal available in last region to freeze



(d)

Figure 11.22 - Some common defects in castings: (d) shrinkage cavity

Pin Holes

Formation of many small gas cavities at or slightly below surface of casting

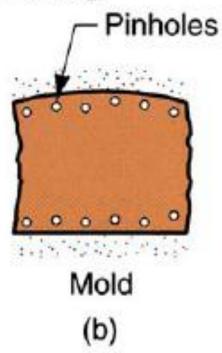


Figure 11.23 - Common defects in sand castings: (b) pin holes

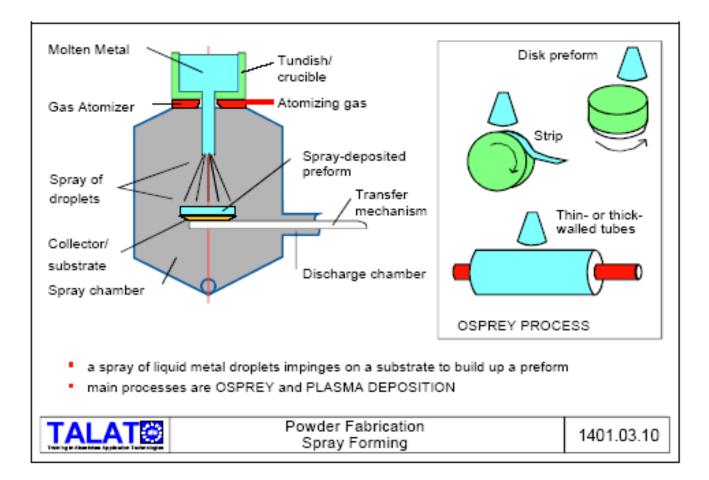
Directional Solidification

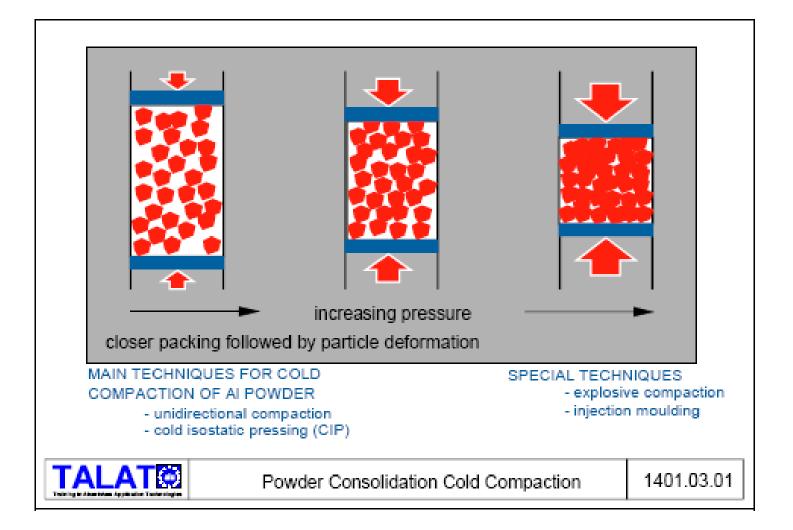
- To minimize damaging effects of shrinkage, it is desirable for regions of the casting most distant from the liquid metal supply to freeze first and for solidification to progress from these remote regions toward the riser(s)
 - Thus, molten metal is continually available from risers to prevent shrinkage voids
 - The term *directional solidification* describes this aspect of freezing and methods by which it is controlled

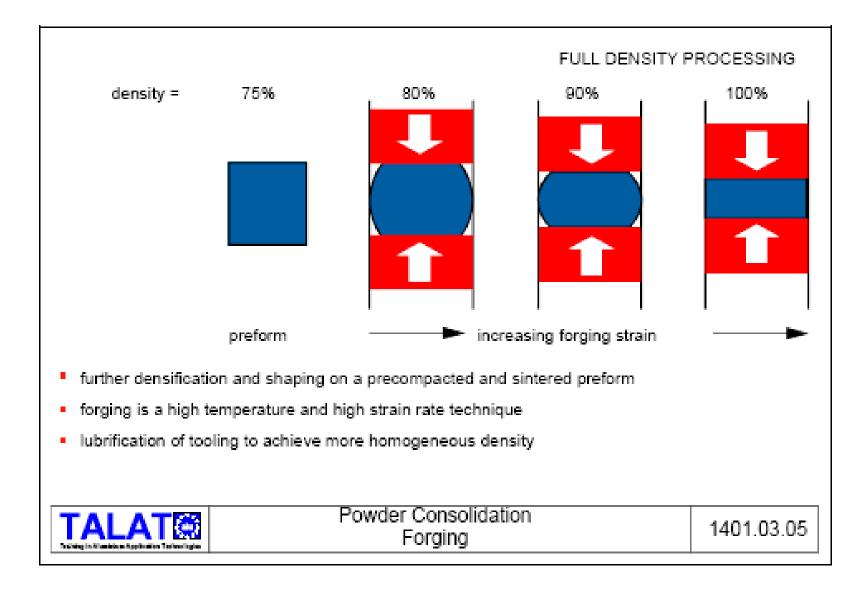
- Rapid Solidification (10⁵ K/s)
- Rapidly cool or quench to produce amorphous or glassy structure (metallic glass)

Rapid Solidification

- Cooling Rate > $10^4 10^7$ °K/s
- By processes such as: Atomization, melt spinning, rollerquenching or plasma spray or laser or electron beam surface treatment
- Non-eqm phase, no thermo. Restrictions, exceed solubility limits, melt solidifies without any chem changes.
- Crystalline or amorphous (improved mech. properties)
- Microsegregation-free structures
- Using powder metallurgy to process the materials.

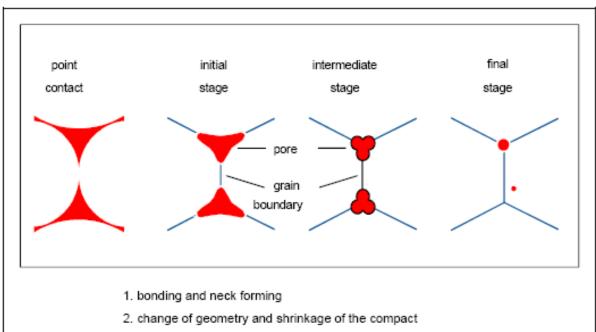




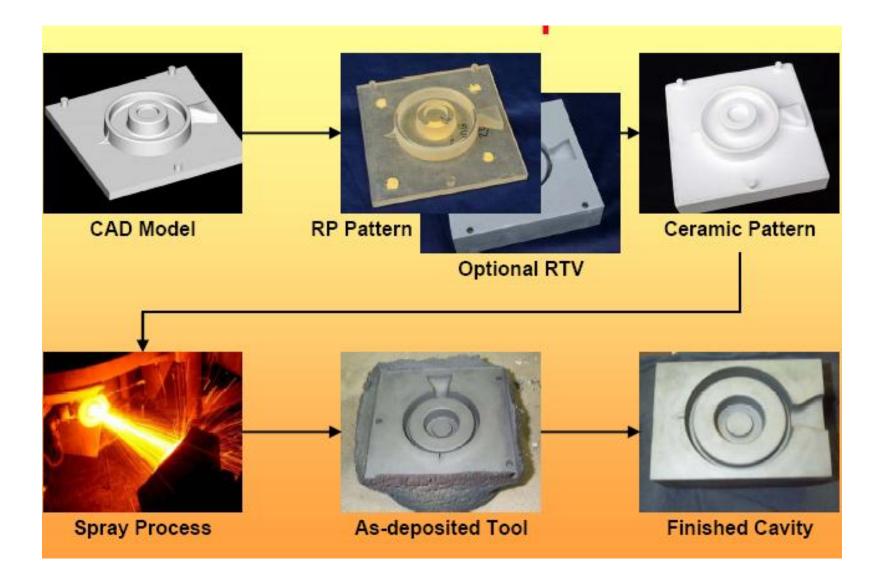


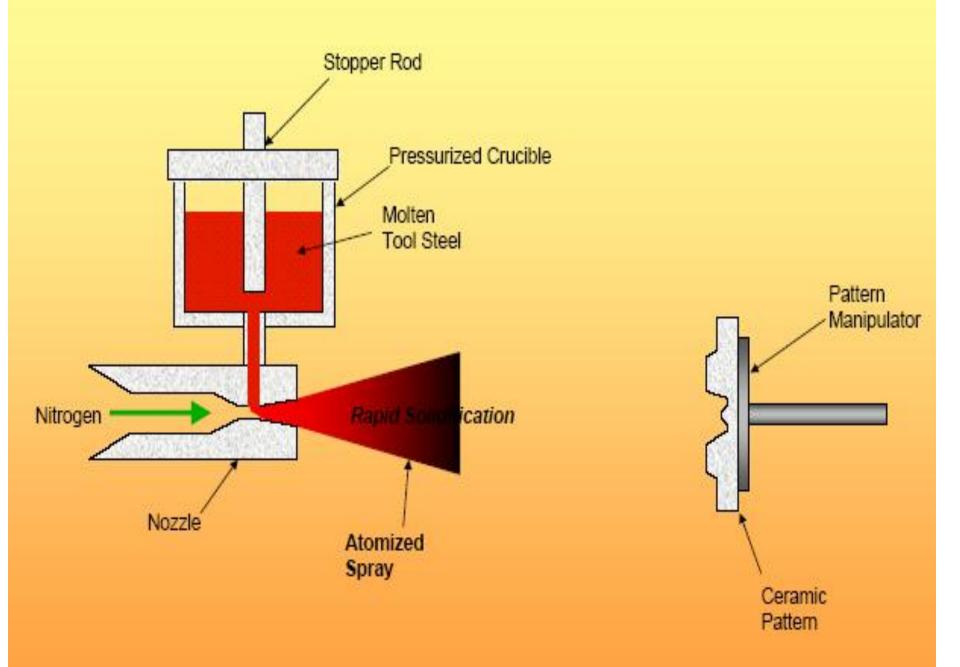
Solid State Sintering

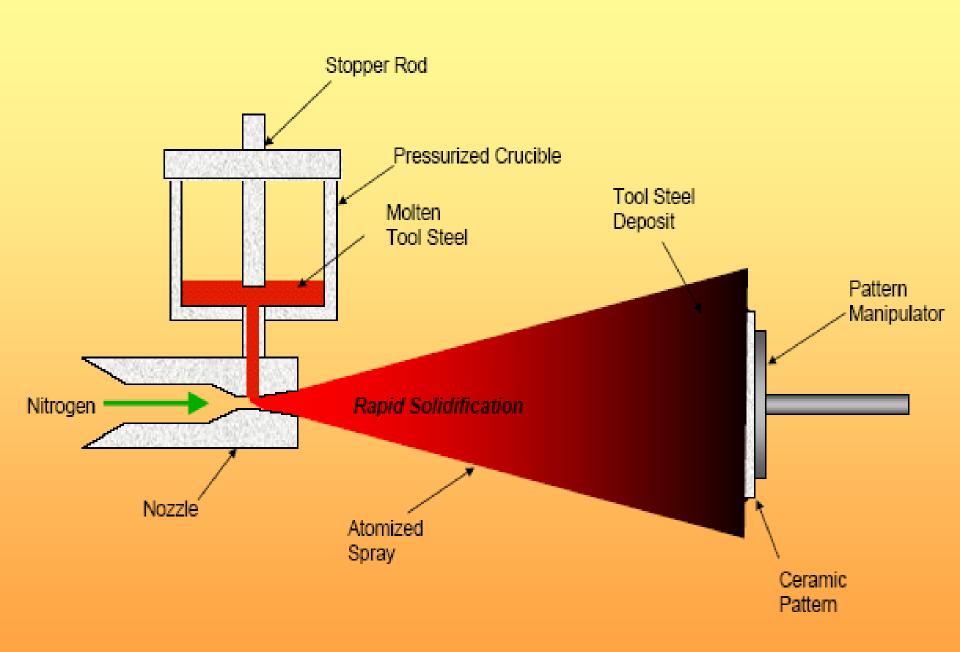
- 1. bonding of powder particles forming necks;
- 2. change of pore geometry and shrinkage of the compact;
- 3. isolation of pores by grain growth, elimination of residual porosity.

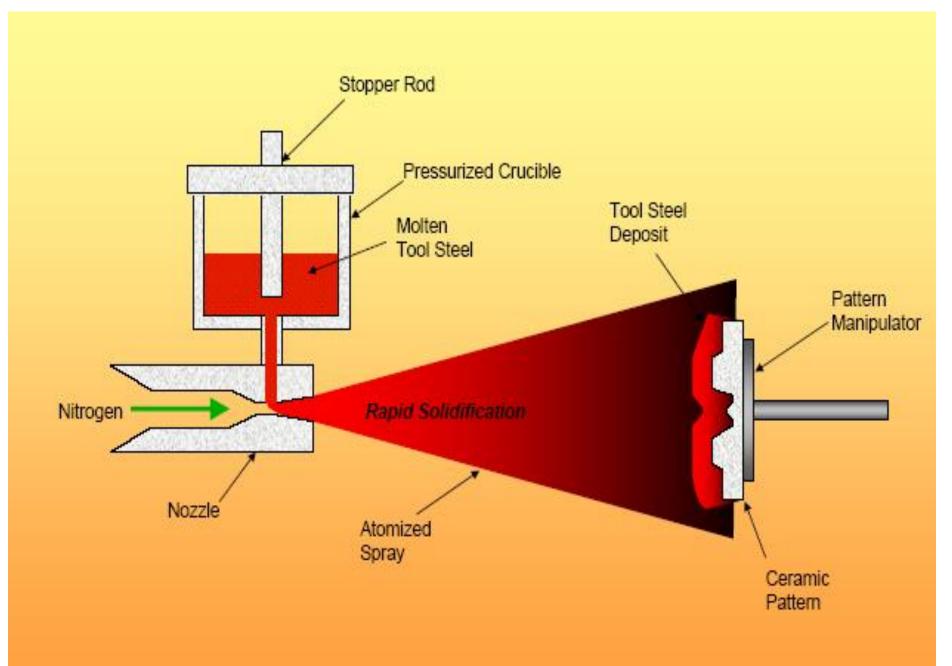


3. isolation of pores, elimination of porosity







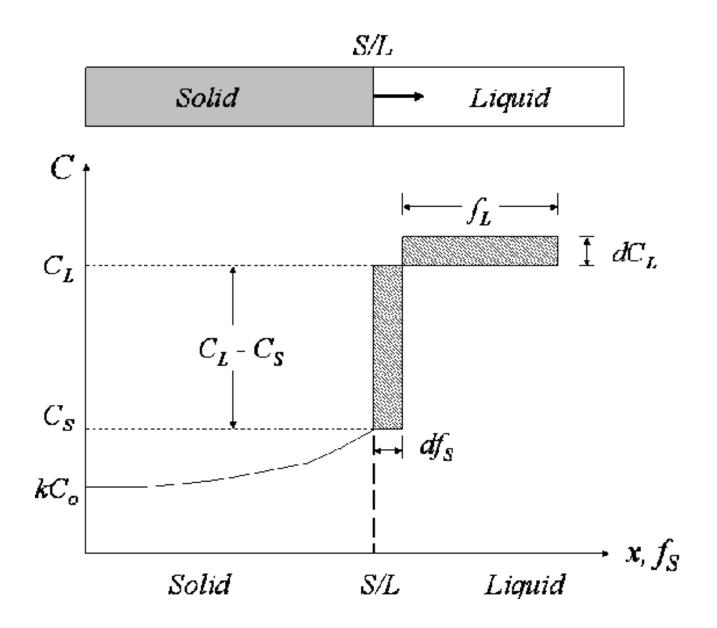


Scheil equation

- In metallurgy, the Scheil-Gulliver equation (or Scheil equation) describes solute redistribution during solidification of an alloy. This approach approximates non-equilibrium solidification by assuming a local equilibrium of the advancing solidification front at the solidliquid interface. This allows the use of equilibrium phase diagrams in solidification analysis.
- Unlike equilibrium solidification, solute does not diffuse back into the solid and is rejected completely into the liquid. Complete mixing of solute in the liquid is also assumed as a result of convection and/or stirring.

Derivation

- The following figure shows the solute redistribution for nonequilibrium solidification where there is no diffusion of solute in the solid and complete mixing of solute in the liquid.
- and $D_s = 0.0$ and $D_L = 00$
- Equilibrium is assumed at the interface which allows the use of an equilibrium phase diagram.



 The hatched areas in the figure represent the amount of solute in the solid and liquid. Considering that the total amount of solute in the system must be conserved, the areas are set equal as follows:

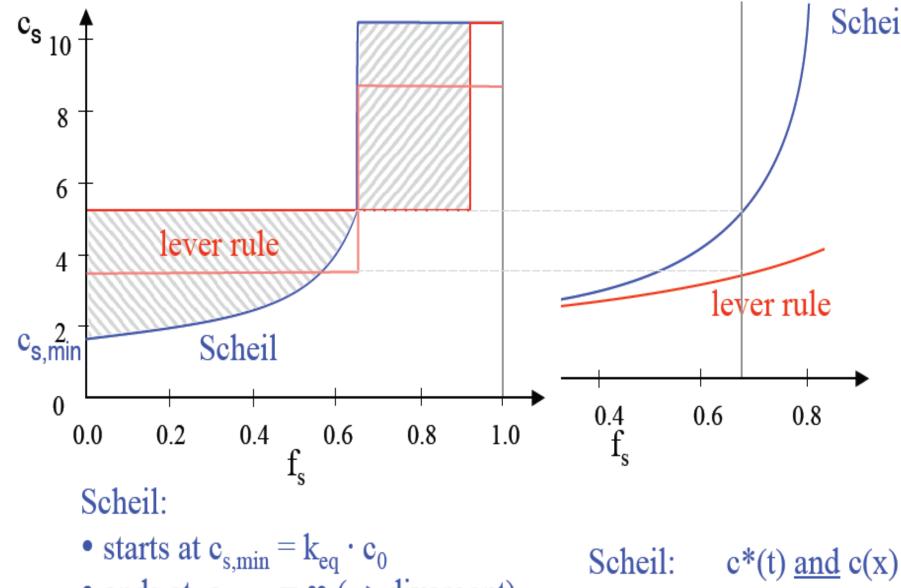
• .
$$(C_L - C_S) df_S = (f_L) dC_L$$

- Since the distribution coefficient is
- (determined from the phase diagram)
- and mass must be conserved $f_S + f_L = 1$

 $k = \frac{C_S}{C_s}$

the mass balance may be rewritten as





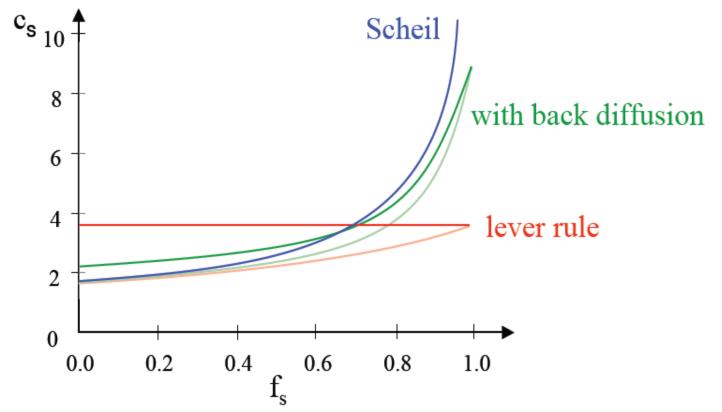
• ends at $c_{s,max} = \infty \implies divergent$

lever rule: $c^{*}(t)$

 $C_L(1-k) df_S = (1-f_S) dC_L$ $C_L = C_o$ at $f_S = 0$

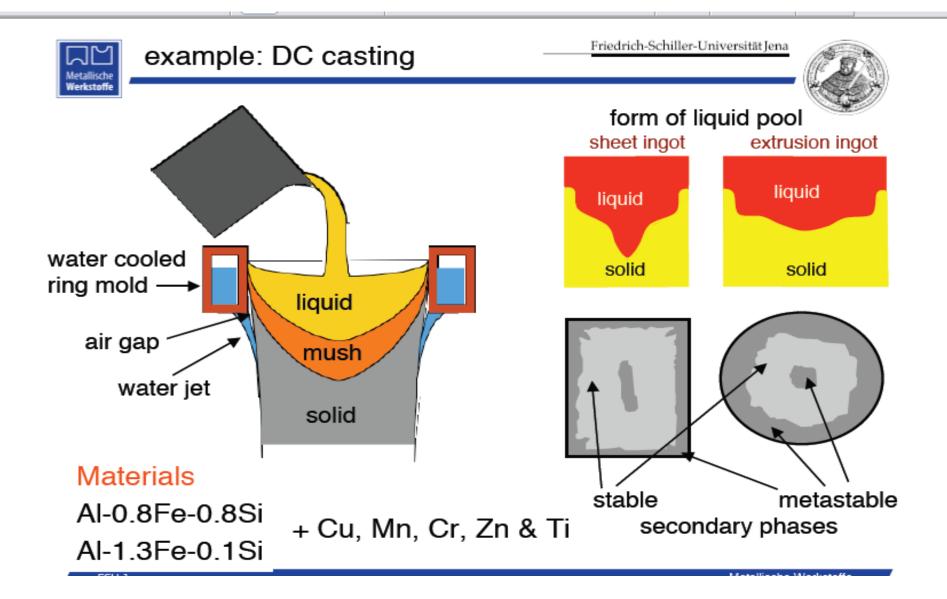
$$\int_{0}^{f_{S}} \frac{df_{S}}{1 - f_{S}} = \frac{1}{1 - k} \int_{C_{\circ}}^{C_{L}} \frac{dC_{L}}{C_{L}}$$

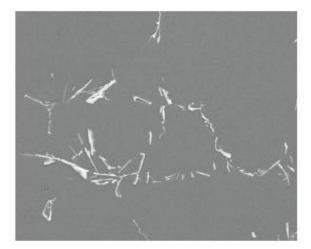
$$C_L = C_o (f_L)^{k-1}$$
$$C_S = k C_o (1 - f_S)^{k-1}$$



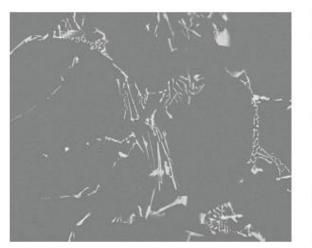
binary alloys:

- realistic interface concentrations between Scheil and lever rule
- realistic concentration profiles not necessarily between Scheil and lever rule

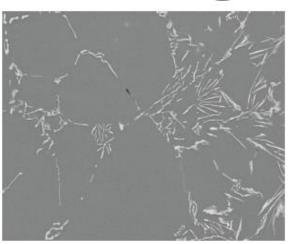




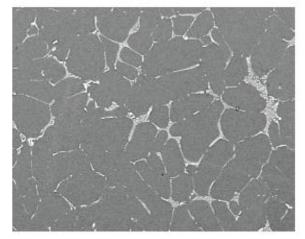
furnace

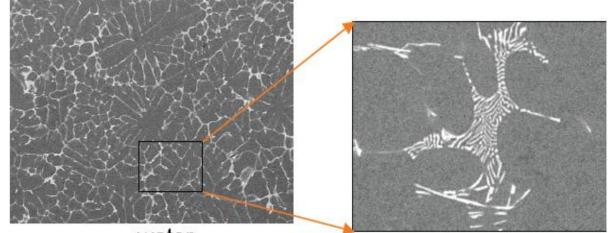


air



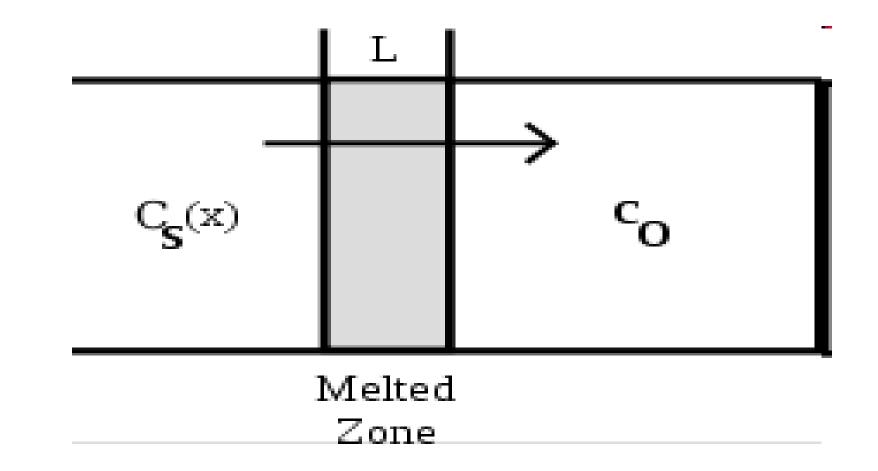
forced air





water

- Zone refining
- a process of purifying any of various metals and other materials, as germanium or silicon, by passing it in bar form through an induction coil.
- methods of purifying crystals, in which a narrow region of a crystal is molten, and this molten zone is moved along the crystal (in practice, the crystal is pulled through the heater). The molten region melts impure solid at its forward edge and leaves a wake of purer material solidified behind it as it moves through the ingot. The impurities concentrate in the melt, and are moved to one end of the ingot.



Liquid moves from left to right during melting in the float-zone crystal growth process

The number of impurities in the liquid changes in accordance with the expression below during the movement dx of the molten zon

$$dI = (C_O - k_O C_L) dx$$

$$C_L = I/L$$

$$I_O = C_O L$$

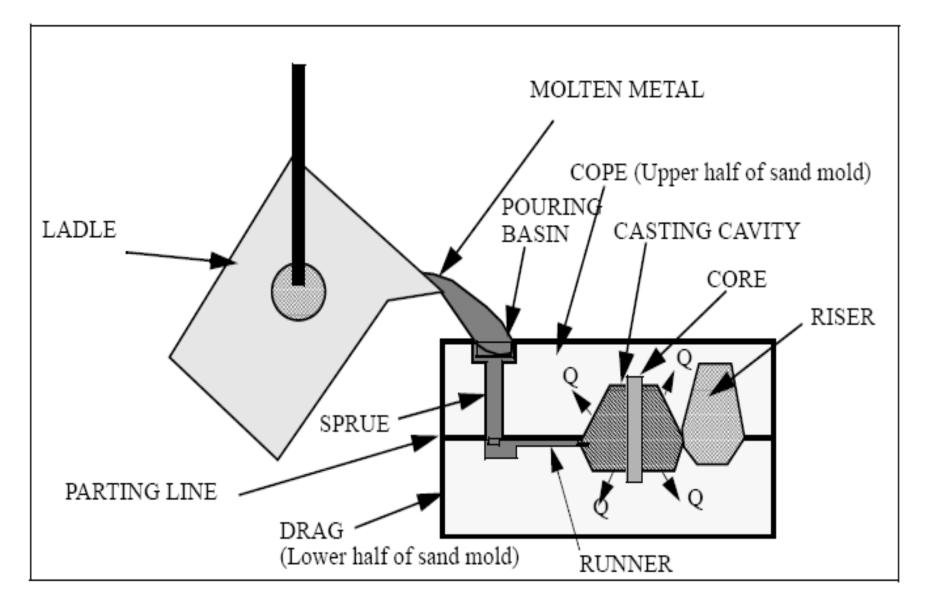
$$C_S = k_O I/L$$

$$\int_0^x dx = \int_{I_O}^I \frac{dI}{C_O - \frac{k_O I}{L}}$$

$$C_S(x) = C_O \left(1 - (1 - k_O)e^{-\frac{k_O x}{L}}\right)$$

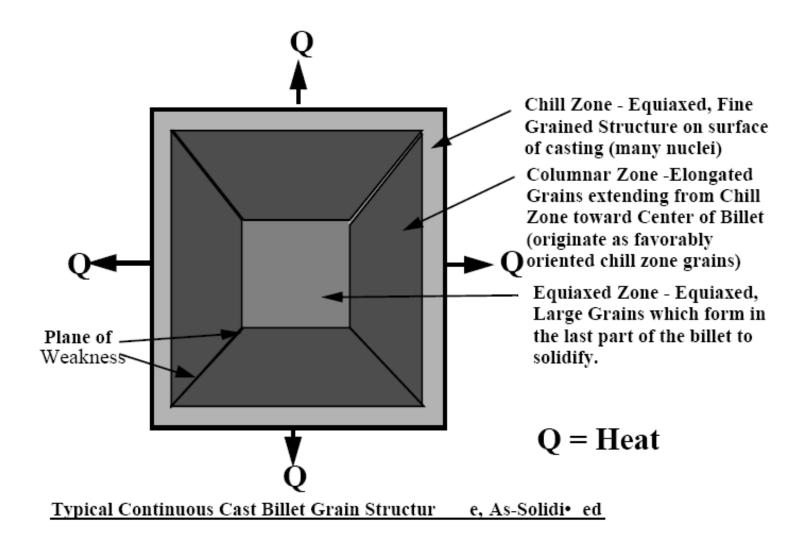
METAL CASTING

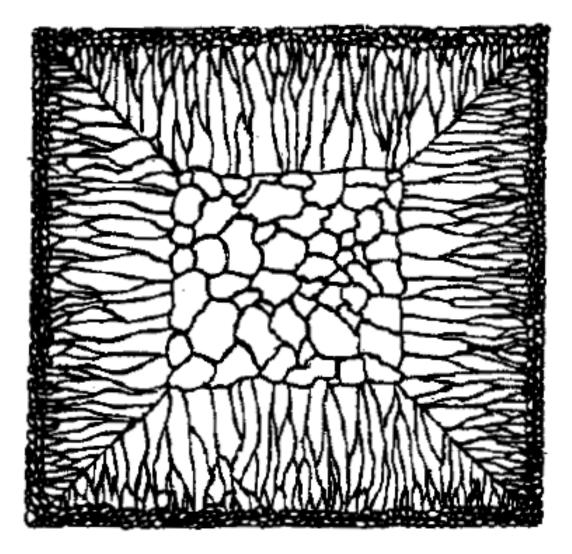
QUICKEST LEAST EXPENSIVE ROUTE TO A NEAR NET SHAPE PRODUCT



Microstructure of Continuous and Semi-continuous Castings

The microstructure of castings produced in this way is illustrated below:





Solidification of Ingots and Castings

Segregation

The non-uniform distribution of impurities or alloying elements. The degree of segregation depends not only on the chemical composition of the alloy, but also on the rate of cooling, both of the ingot as a whole, and of each individual point within the mass. For example, near the surface, where the rate of cooling is rapid, the segregated impurities are trapped in the rapidly growing crystals. Fur- their inside the ingot, where the cooling is slower, the segregates will collect together and produce the so-called ghosts, or they may tend to rise to the surface and collect in the scrapped ingot head. In normal segregation, the constituents with the lowest melting points concentrate in the last portions to solidify, but in inverse segregation this is reversed. The segregation tends to form in bands sloping inwards to the top of the ingot (A segregate) and at the same time, due to shrinkage, it takes a V shape (V segregate) along the upper part of the ingot axis.

Macrosegregation

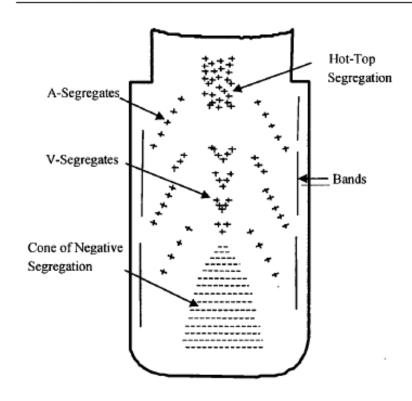


Figure 1 Schematic of the macrosegregation pattern in a steel ingot.

Microsegregation

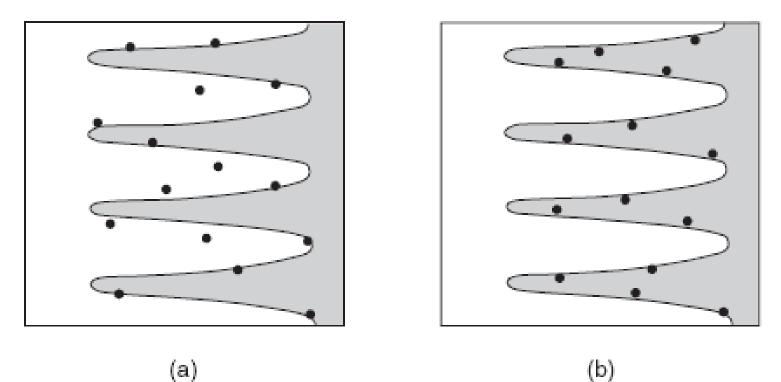


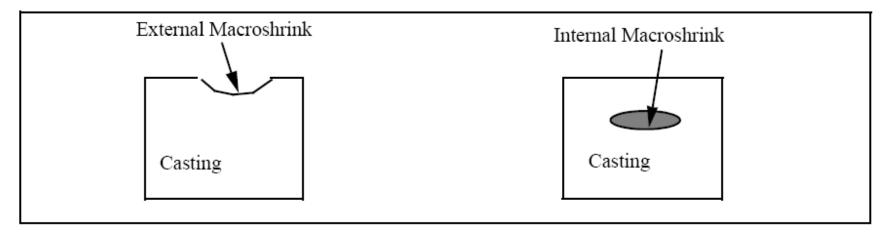
Fig. 6.5 Schematic diagram of inclusion formation during dendritic growth: (a) inclusions being pushed; (b) inclusions being entrapped.

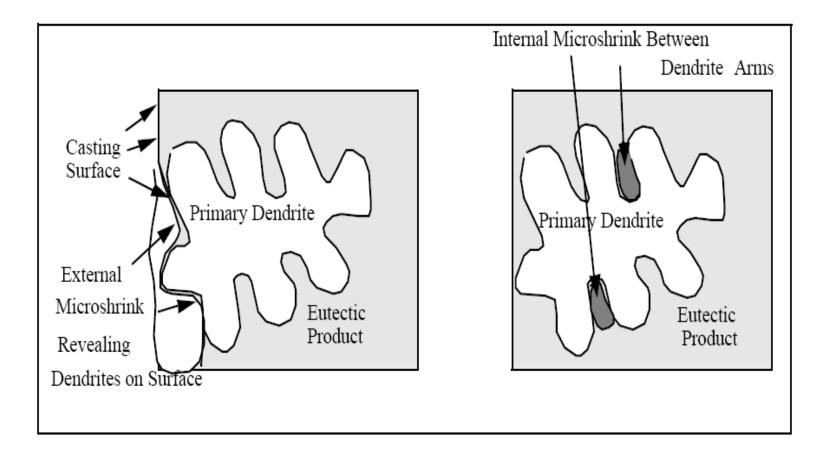
Macrosegregation

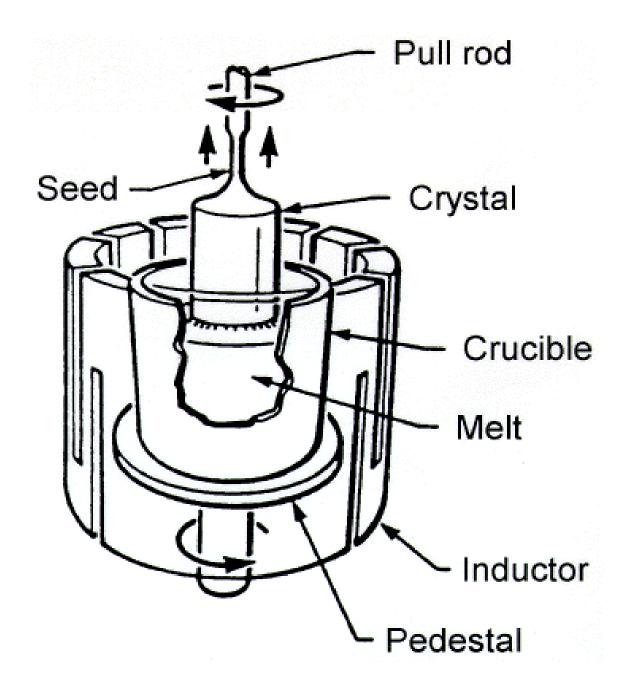
Macrosegregation refers to variations in composition that occur in alloy castings or ingots and range in scale from several millimeters to centimeters or even meters. These compositional variations have a detrimental impact on the subsequent processing behavior and properties of cast materials and can lead to rejection of cast components or processed products. Macrosegregation is present in virtually all casting processes, including continuous, ingot, and shape casting of steel and aluminum alloys, iron casting, casting of singlecrystal superalloys, semisolid casting, and even growth of semiconductor crystals. Because of the low diffusivity of the solutes in the solid state and the large distances involved, macrosegregation cannot be mitigated through processing of the casting after solidification is complete.

Solidification Shrinkage Types

Shrinkage porosity can appear within a casting in a number of ways depending upon the solidification temperature range $(T_L - T_S)$ and the effectiveness of risering. The type of shrinkage observed in castings can be broadly separated into two classes, macroshrinkage and microshrinkage. Macroshrinkage defects can be seen by the unaided eye and microshrinkage defects require a microscope to observe. There are two types of shrinkage within each class, shrinkage which can be observed externally on the casting surface and shrinkage which is observed internally after sectioning. Schematic examples of each of these defects is shown below:







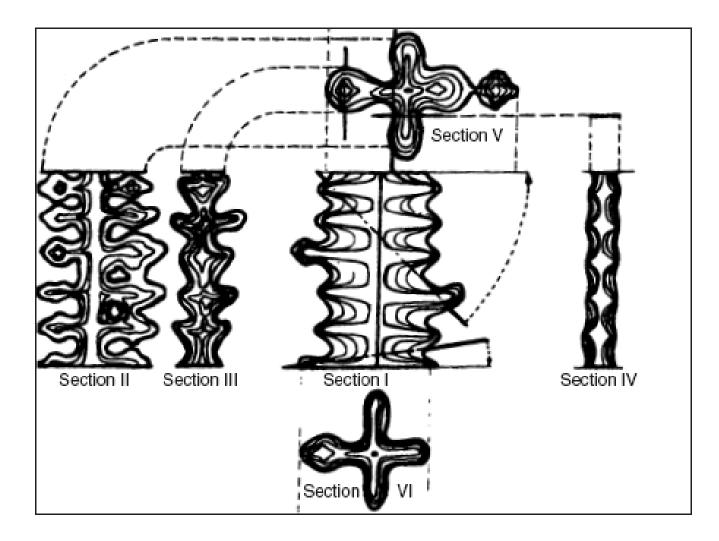
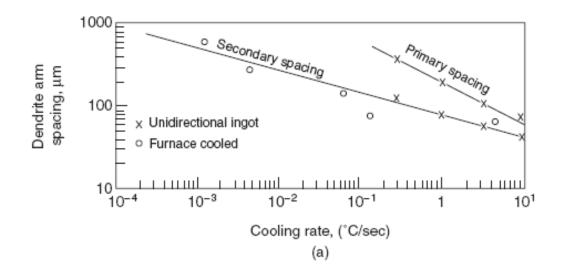


Fig. 6.2 Isoconcentration surfaces of a columnar dendrite, low-alloy steel. (From Ref. 1)



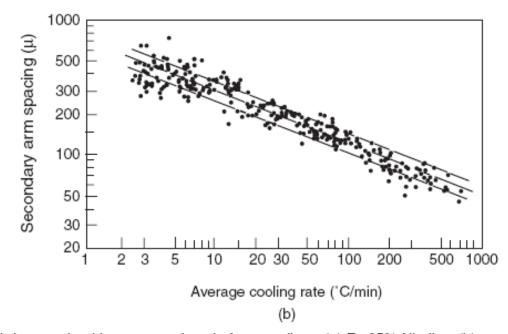


Fig. 6.4 Experimental data on dendrite arm spacings in ferrous alloys: (a) Fe-25% Ni alloy; (b) commercial steels containing from 0.1 to 0.9% C. From Ref. 1.

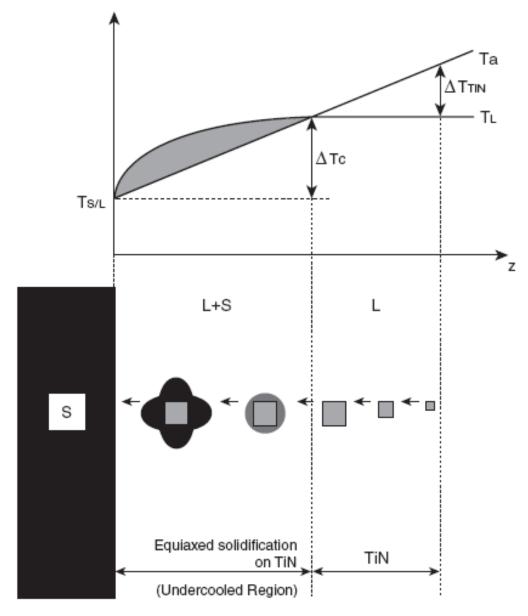
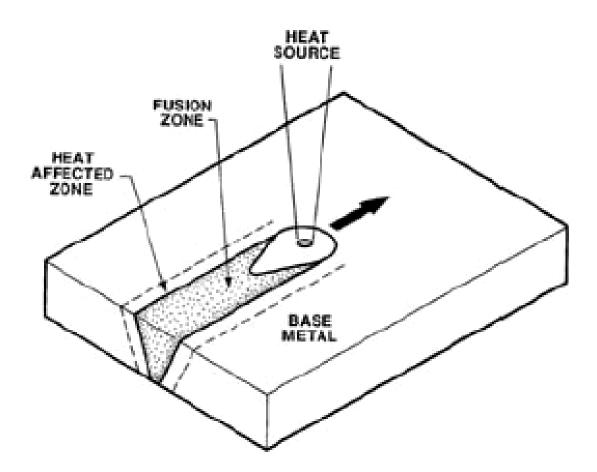
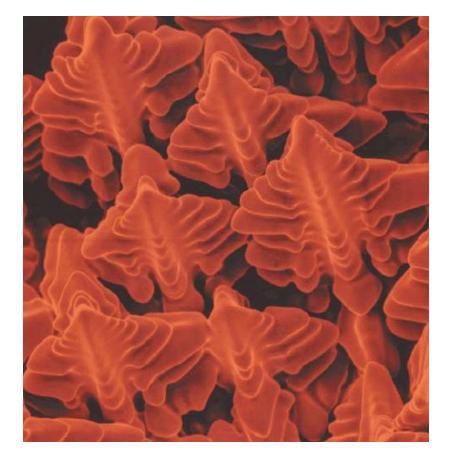


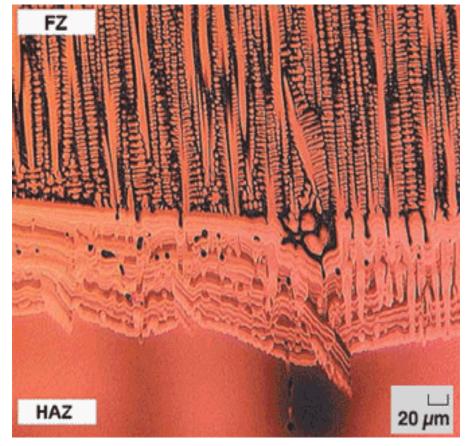
Fig. 6.6 A schematic diagram of equiaxed grain formation on titanium nitride in a constitutionally undercooled region.

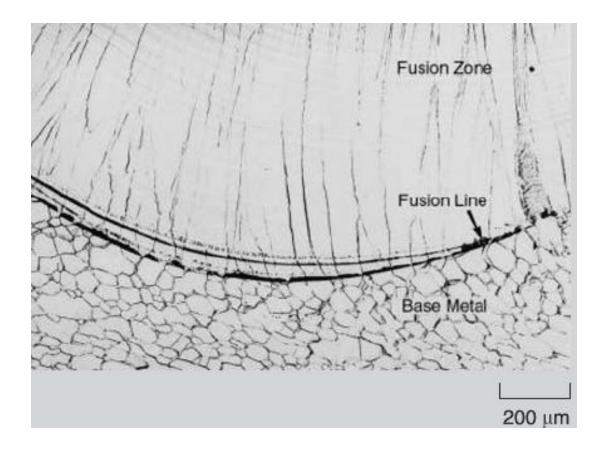


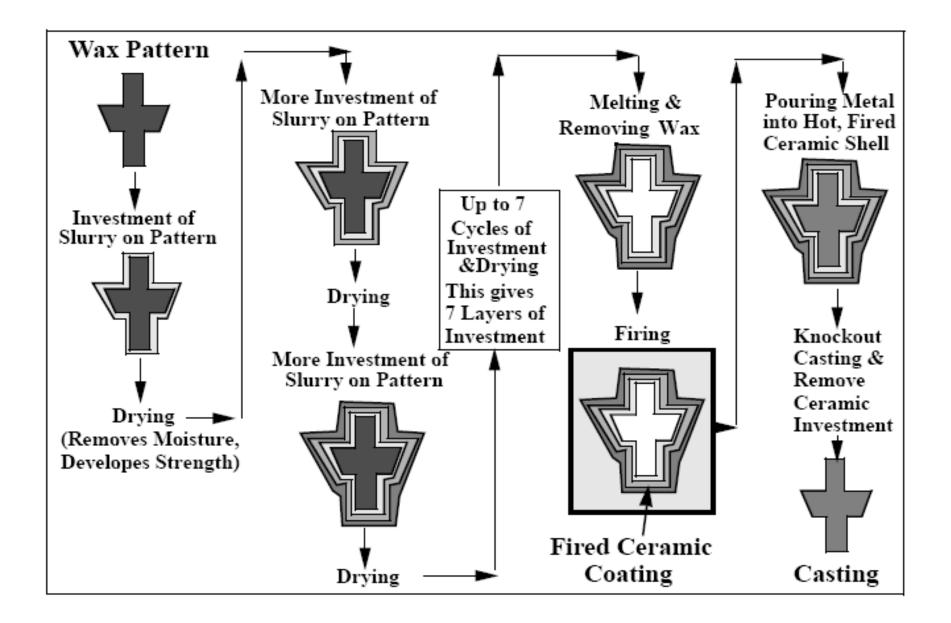
In welding, as the heat source interacts with the material, the severity of thermal excursions experienced by the material varies from region to region, resulting in three distinct regions in the weldment. These are the fusion zone (FZ), also known as the weld metal, the heat-affected zone (HAZ), and the unaffected base metal (BM). The FZ experiences melting and solidification, and its microstructural characteristics are the focus of this article.

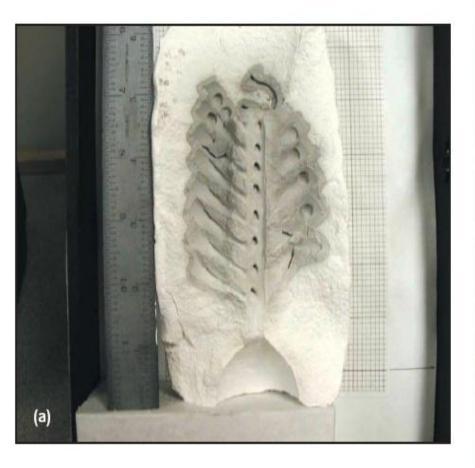
The microstructure development in the FZ depends on the solidification behavior of the weld pool. The principles of solidification control the size and shape of the grains, segregation, and the distribution of inclusions and porosity. Solidification is also critical to the hot-cracking behavior of alloys. Sometimes, it is convenient to consider the FZ as a minicasting. Therefore, parameters important in determining microstructures in casting, such as growth rate (R), temperature gradient (G), undercooling (DT), and alloy composition determine the development of microstructures in welds as well.











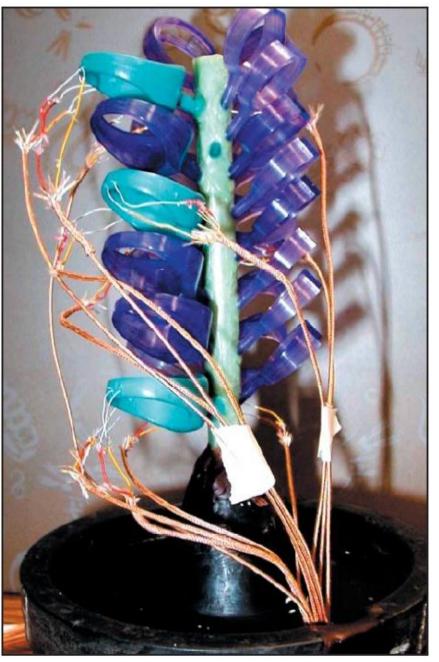


Figure 2 - Tree pattern with thermocouple attachments

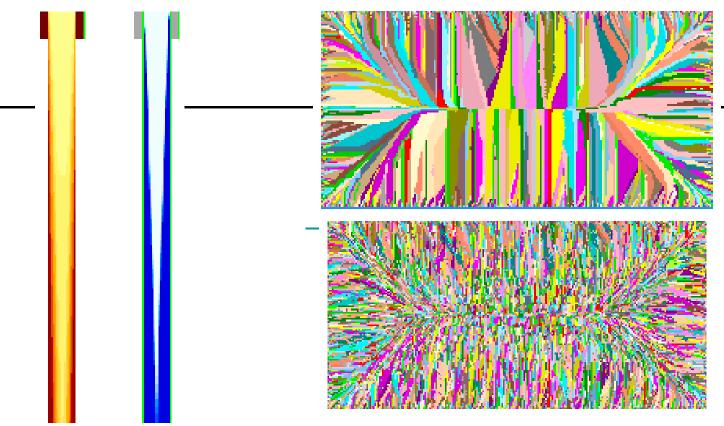
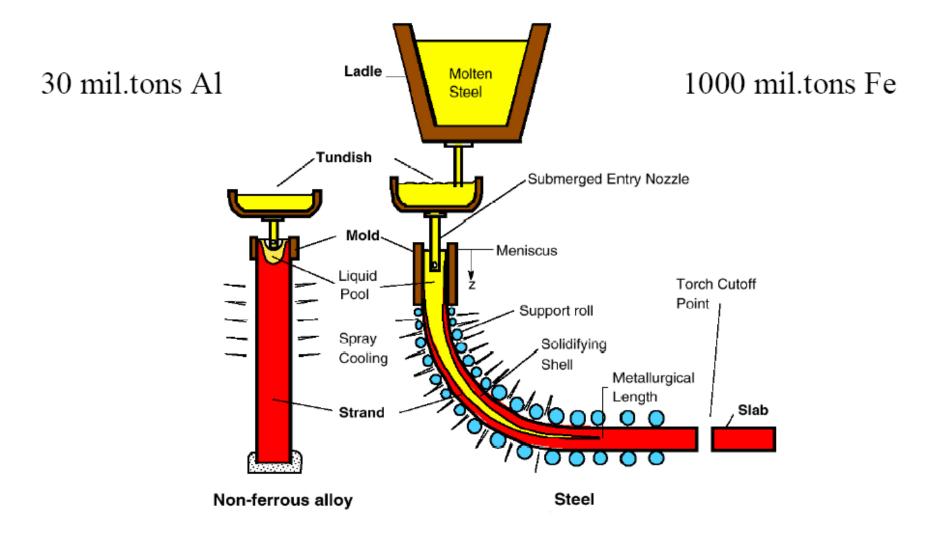
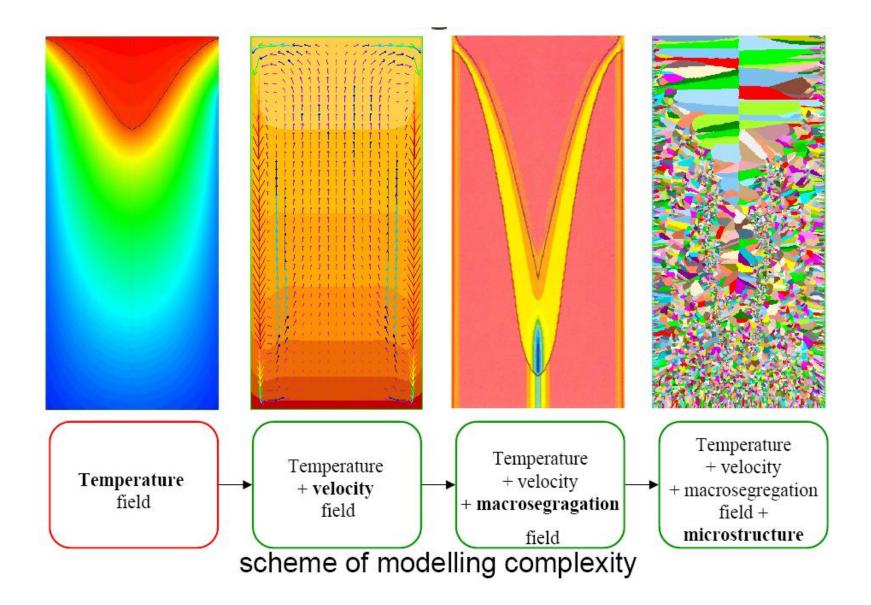


Figure 3 (a-left). The thermal and the fraction-of-solid fields in a continously cast steel slab. (b-top right) The grain structure in a steel slab transverse cross-section,2-4 with only columnar grains up to the center line. (c-bottom right). Equiaxed grains that result if inoculation is promoted (by electromagnetic stirring for example).



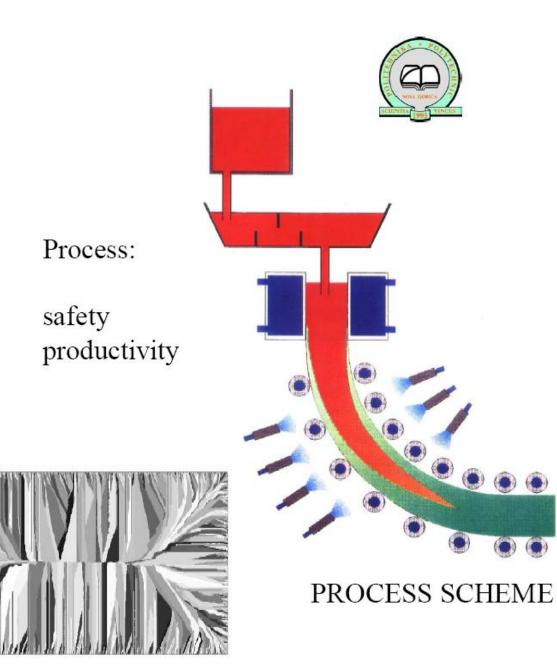


Continuous Casting/Welding Solidification

 $\Box \ \delta^2 T / \delta x^2 + \delta^2 T / \delta y^2 + \delta^2 T / \delta z^2 = 2 \kappa_s \sqrt{\delta T} / (\delta (x - vt))$

$$\Box \ \lambda_{(x,y,z)} \quad \alpha \ q/(K_s \ vt)$$

v welding speed/velocity of plate withdrawal K_s Thermal conductivity of metal t thickness of plate being welded or cast q the rate of heat input



Product:

correct shape no cracks no porosity desired composition desired structure http://www.tms.org/pubs/journals/JOM/0201/Thevoz/Thevoz-0201.html

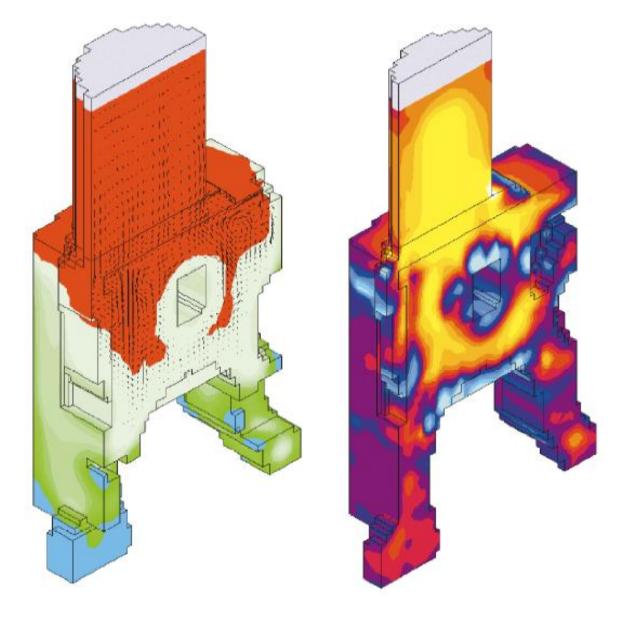
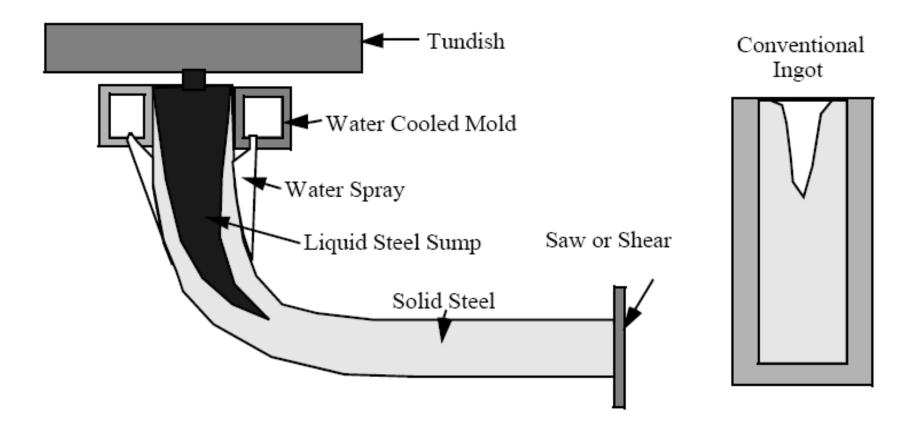
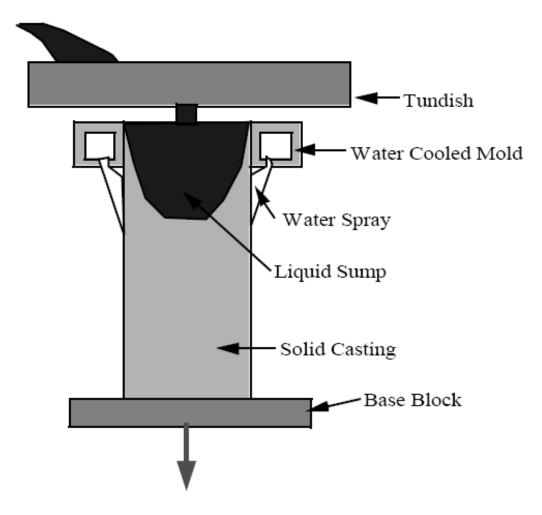


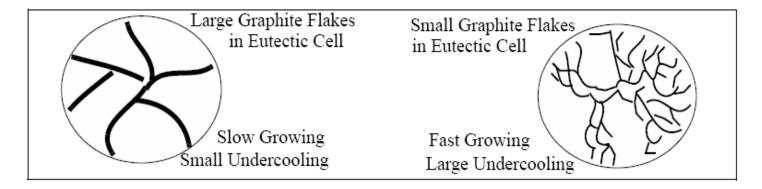
Figure 6

Simulation of macrosegregation formation in a large steel casting, showing liquid velocity vectors during solidification (left) and final carbon macrosegregation pattern (right).



Semi - Continuous casting of Aluminum Alloys, Free machining brass





Relative amounts and sizes of eutectic cells in equivalent volumes of inoculated and uninoculated

