METRO
MEtallurgical TRaining On-line

Basic phenomena accompanying alloy solidification

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Education and Culture

Surface Energy

Definition of surface energy

$$\boxed{\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,p}}$$

Where:

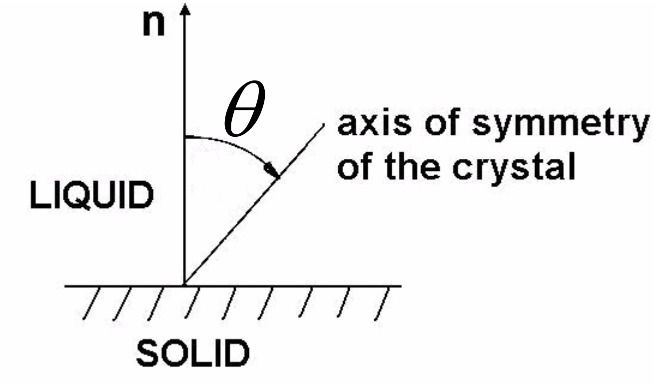
G - Gibbs free energy

A - Surface area

Surface Energy

Dependence of surface energy on different factors

$$\boxed{\gamma = \gamma(T, C, \theta)}$$



where:

T - temperature

C - concentration of species

θ - angle between normal to the surface and crystallographic axis

Surface Energy

Dependence of surface energy on angle from normal to the interface

$$\gamma(\theta,T,C)=\gamma_0(T,C)\left[1+A_s[\frac{8}{3}\sin^4(\frac{1}{2}m_s(\theta-\phi_s))-1]\right]$$

Where:

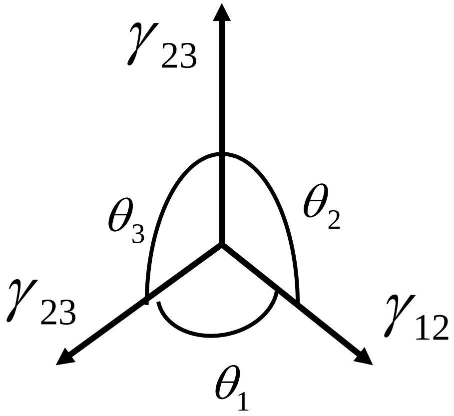
A_s - magnitude of anisotropy

ϕ_s - angle of symmetry axis with respect to the interface normal

m_s - mode of symmetry of the crystal

Surface Energy

Relative surface energies between three phases

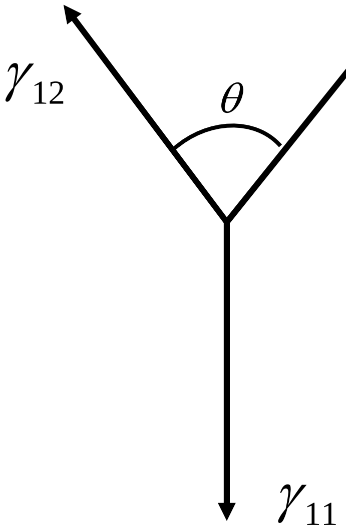


$$\boxed{\frac{\sin\gamma_{23}}{\theta_1} = \frac{\sin\gamma_{13}}{\theta_2} = \frac{\sin\gamma_{12}}{\theta_3}}$$

Surface Energy

Measurement of surface energy in solids

Thermal etching or grooving

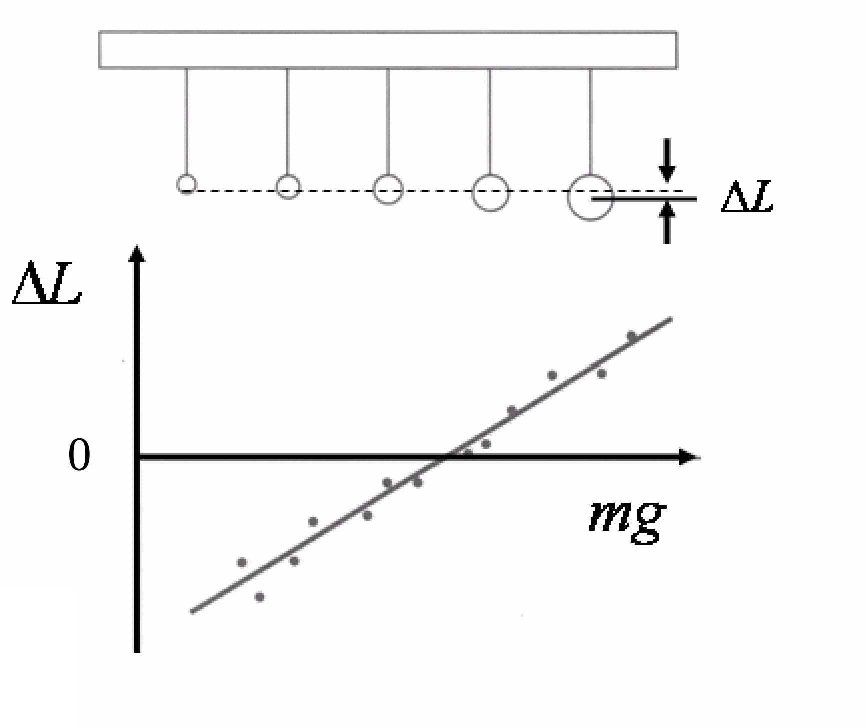


$$\boxed{\gamma_{11} = 2\gamma_{12}\cos(\theta/2)}$$

Surface Energy

Measurement of surface energy in solids

Elongation method



$$\boxed{\gamma_{sg} = \frac{mg}{\pi r}}$$

where:

mg - weight applied

r - wire radius

Surface Energy

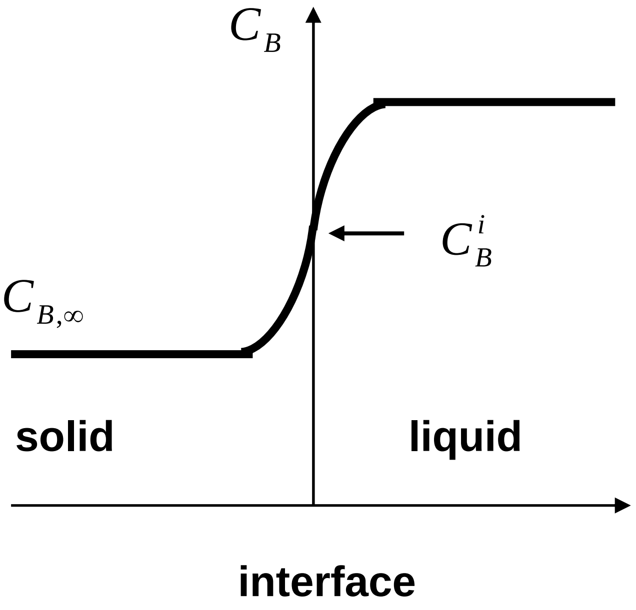
Effect of temperature on the surface energy

$$\boxed{\left(\frac{\partial \gamma}{\partial T}\right)_{A,p} = S_A}$$

where: S_A - surface entropy

Surface Energy

Segregation of components at the interface



$$\boxed{\Gamma_B^i = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial x_B}\right)_T}$$

where:

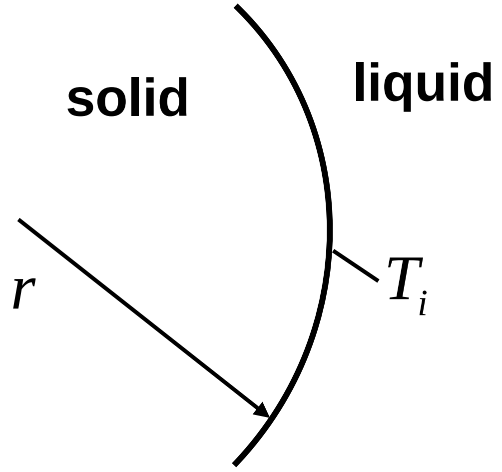
Γ_B^i - surface concentration, $\Gamma_B^i = C_B^i - C_{B,\infty}$

x_B - mole fraction of the solute

R - universal gas constant

Surface Energy

Solidification temperature of the curved interface



$$\boxed{T_i = T_m - \frac{2V_{ms}\gamma_{ls}}{\Delta S_m}\kappa}$$

where:

T_i - interface temperature

T_m - equilibrium solidification temperature

V_{ms} - molar volume of the solid phase

ΔS_m - entropy change during solidification per mole

κ - interface curvature, $\kappa = r^{-1}$

Surface Energy

Solidification temperature of the curved interface

$$\boxed{\Delta S_m = \frac{\Delta H_m}{T_m} = \frac{L_m}{T_m}}$$

where:

ΔH_m - enthalpy change during solidification per mole

L_m - latent heat of solidification per mole

Surface Energy

Solidification temperature of the curved interface

$$\boxed{T_i = T_m + m_l C_l - \frac{2V_{ms}\gamma_{ls}}{\Delta S_m}\kappa}$$

where:

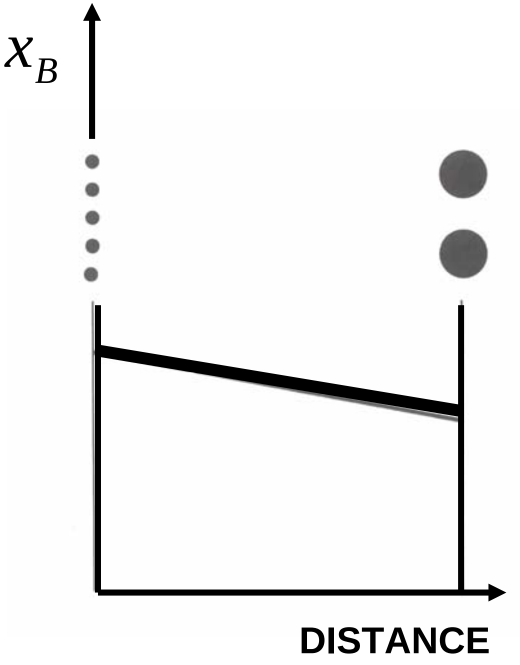
m_l - liquidus slope

C_l - solute concentaration in the liquid phase

κ - interface curvature, $\kappa = \frac{1}{2}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$

Surface Energy

Coarsening of solid grains



$$x_B(r) = x_B(r \to \infty)\exp\left[\frac{2V_{ms}\gamma_{\alpha\beta}}{RT}\kappa\right]$$

where:

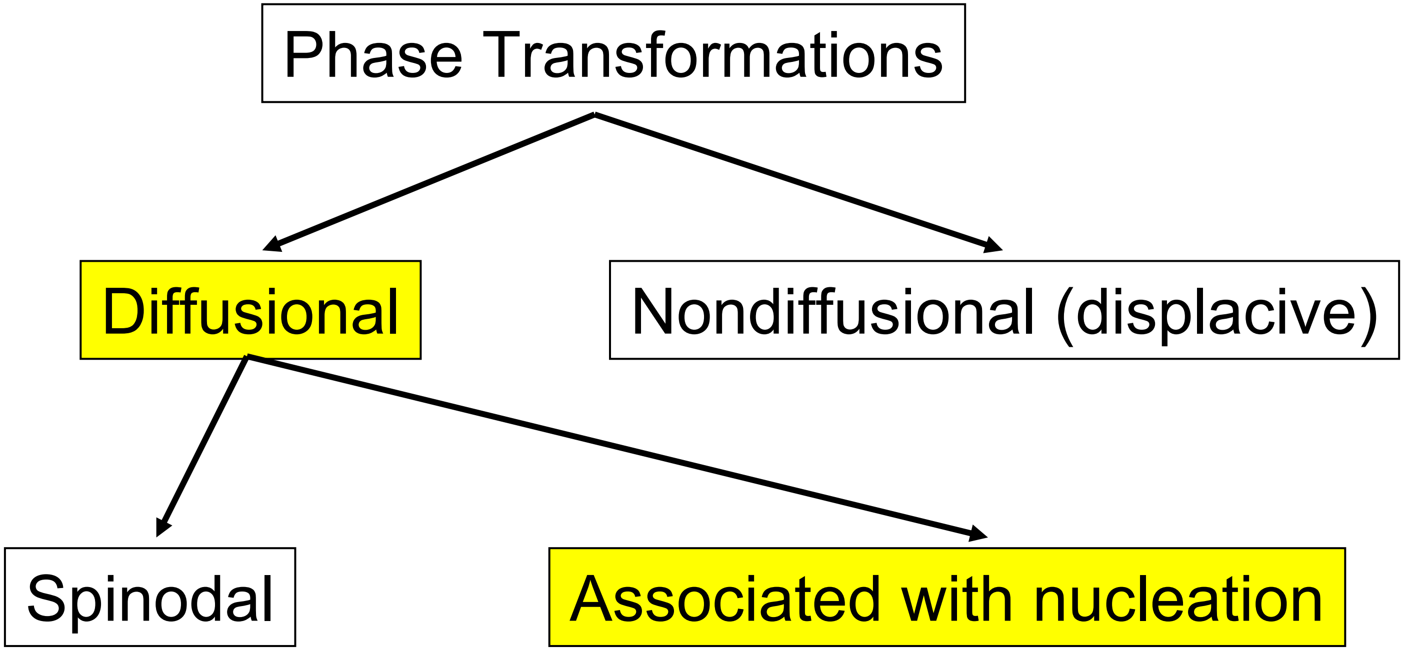
$x_B(r)$ - mole fraction of component B in the solid phase for curvatured interface

$x_B(r \to \infty)$ - mole fraction of component B in the solid phase for plane interface

$\gamma_{\alpha\beta}$ - surface energy between phases α and β

Nucleation of solid phase

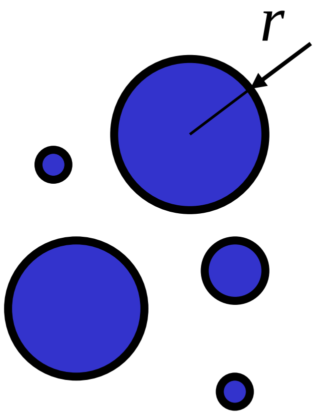
Types of phase change transformations



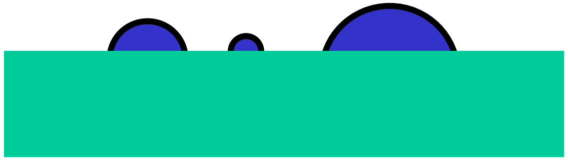
- Phase Transformations
  - Diffusional
    - Spinodal
    - Associated with nucleation
  - Nondiffusional (displacive)

Nucleation of solid phase

Types of nucleation



- homogeneous



- heterogeneous

Nucleation of solid phase

Size distribution of nuclei

$$\boxed{n(r) = n_o \exp\left(-\frac{\Delta G_f}{kT}\right)}$$

where:

$n(r)$ - number of particles clusters of radius *r per unit volume*

n_o - number of liquid particles *per unit volume*

ΔG_f - Gibbs free energy of formation of the new phase

k - Boltzmann constant, $k=1.38 \cdot 10^{-23}$ J/K

Nucleation of solid phase

Size distrubution of nuclei for solidification temperature

$$\boxed{\Delta G_f = 4\pi r^2 \gamma_{sl}}$$

hence

$$\boxed{n(r) = n_o \exp\left(-\frac{4\pi r^2 \gamma_{sl}}{kT_m} \right)}$$

Nucleation of solid phase

Gibbs free energy change associated with phase transformation

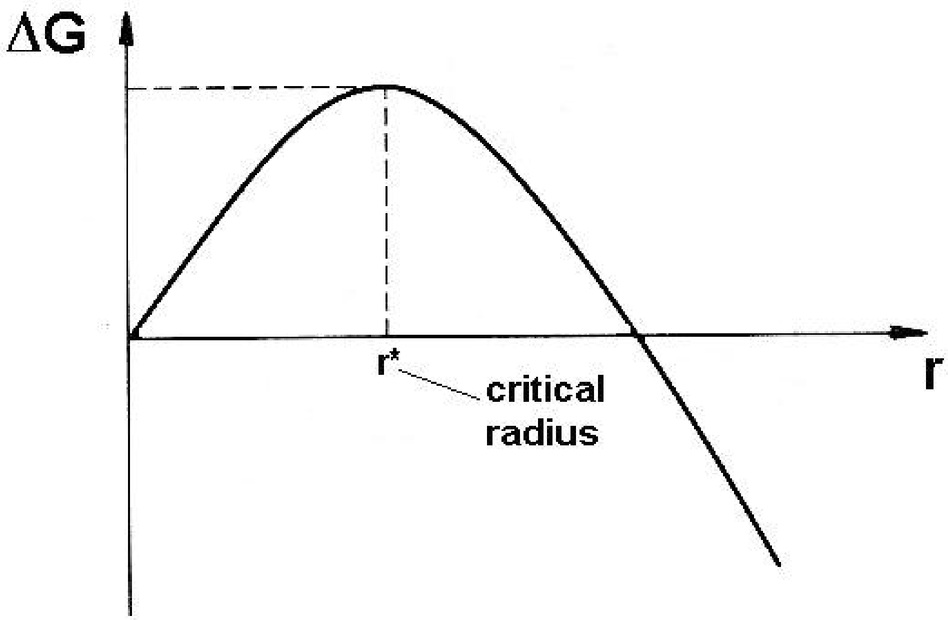
$$\boxed{\Delta G_r = \frac{4\pi}{3} r^3 \Delta G_v + 4\pi r^2 \gamma_{sl}}$$

where:

ΔG_v - number of particles clusters of radius *r per unit volume*

Nucleation of solid phase

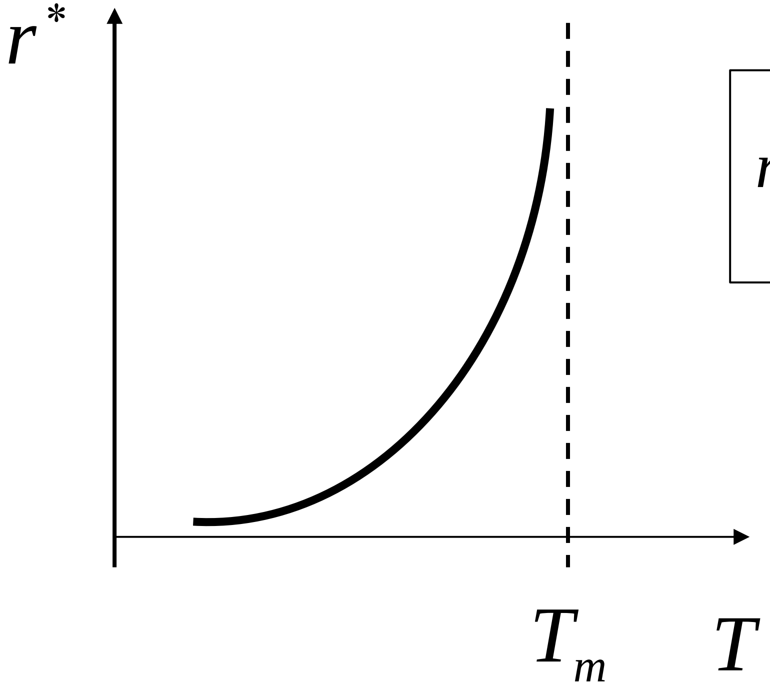
Minimum radius of nuclei



$$\boxed{r^* = -\frac{2\gamma_{sl}}{\Delta G_v}}$$

Nucleation of solid phase

Influence of undercooling on critical radius



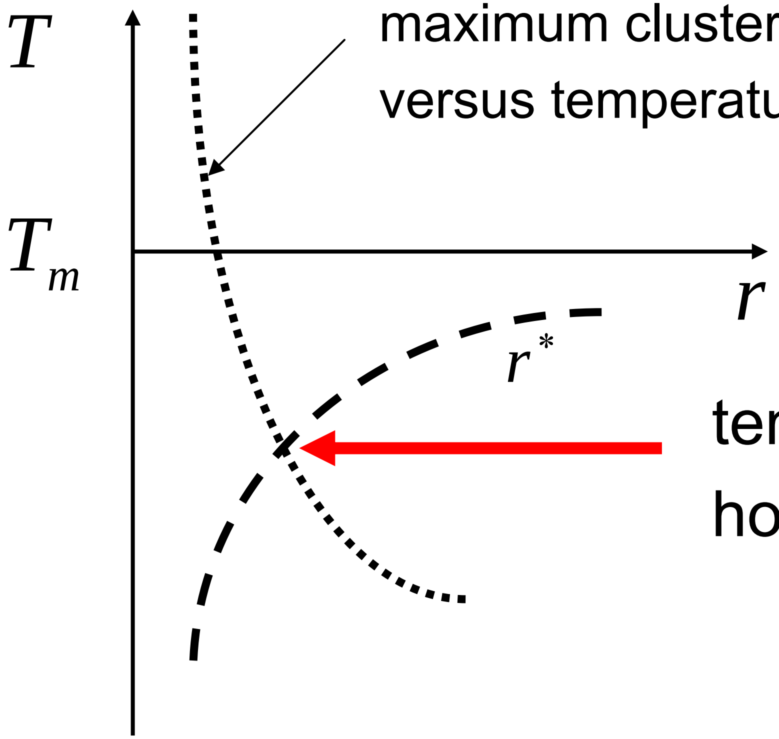
$$\boxed{r^* = -\frac{2\gamma_{sl} T_m V_m}{L_m (T - T_m)}}$$

where:

V_m - molar volume

Nucleation of solid phase

Influence of undercooling on critical radius

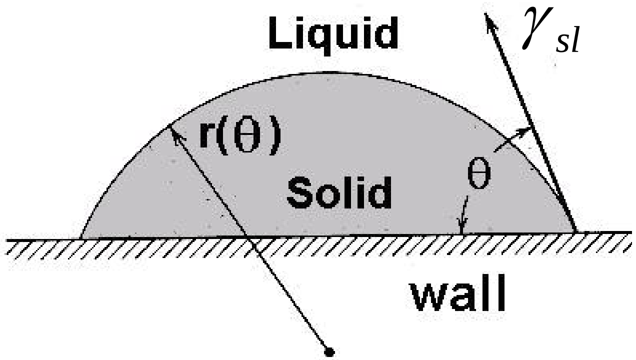


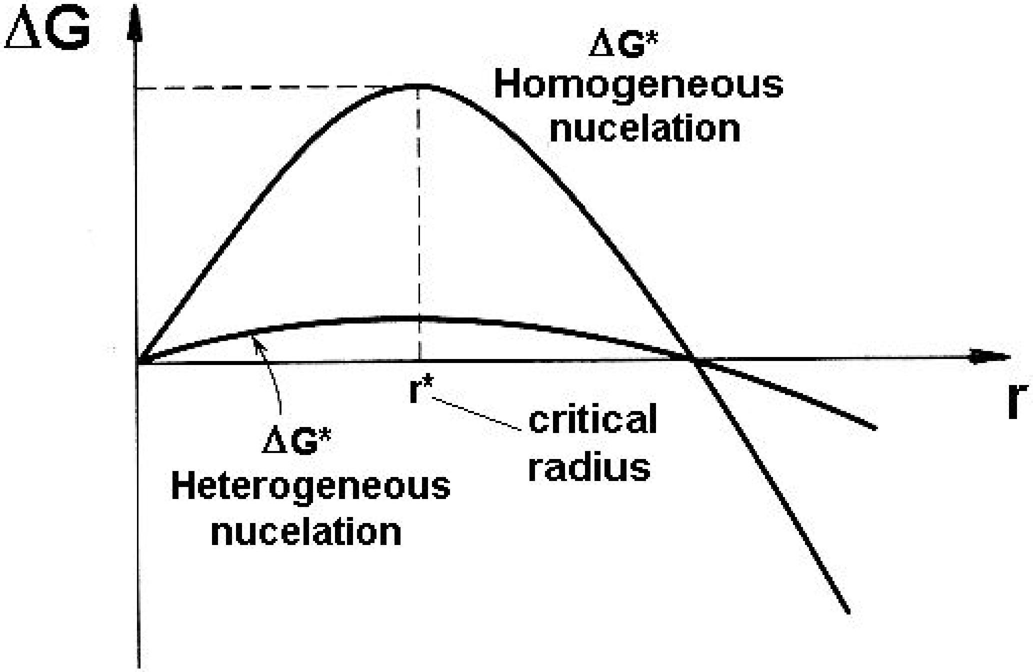
maximum cluster radius
versus temperature

temperature of
homogeneous nucleation

Nucleation of solid phase

Influence of mould surface on nucleation





Nonequilibrium solidification

Velocity of the liquid/solid interface

$$\boxed{w_i(T_i, C_s, C_l) = w_c(T_i)\left[1 - \exp(\Delta G_m(T_i, C_s, C_l)/RT)\right]}$$

where:

ΔG_m - Gibbs free energy change per mole of alloy solidified

w_c - characteristic speed of crystallization

C_s - composition of the growing solid

C_l - composition of the liquid at the interface

T_i - interface temperature

Nonequilibrium solidification

Partition coefficient for nonequilibrium solidification

$$\boxed{\kappa_p(w_i) = \frac{\kappa_{pe} + w_i / w_D}{1 + w_i / w_D}}$$

where: κ_p - partition coefficient for non-equilibrium solidification

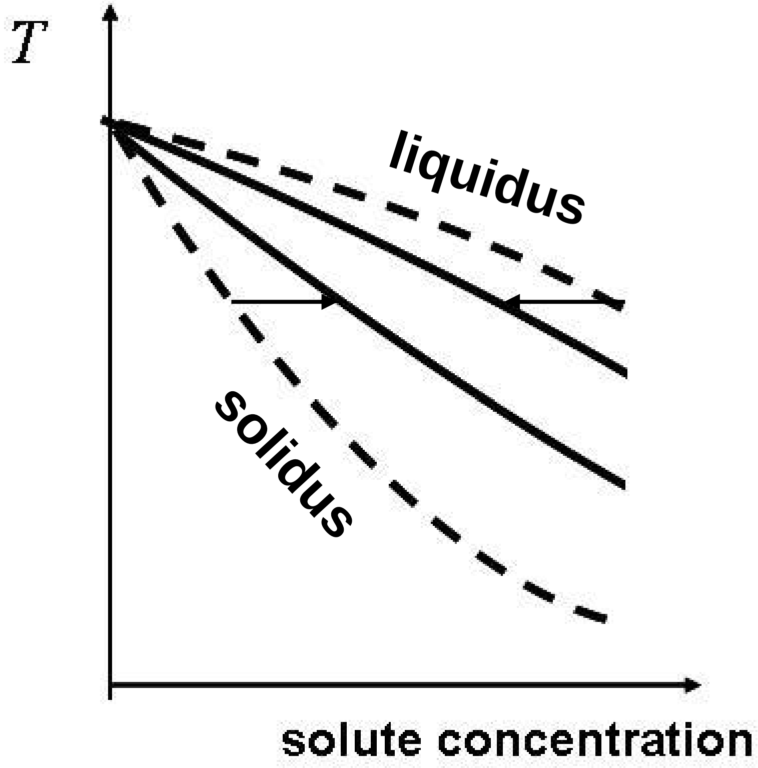
κ_{pe} - partition coefficient for equilibrium solidification

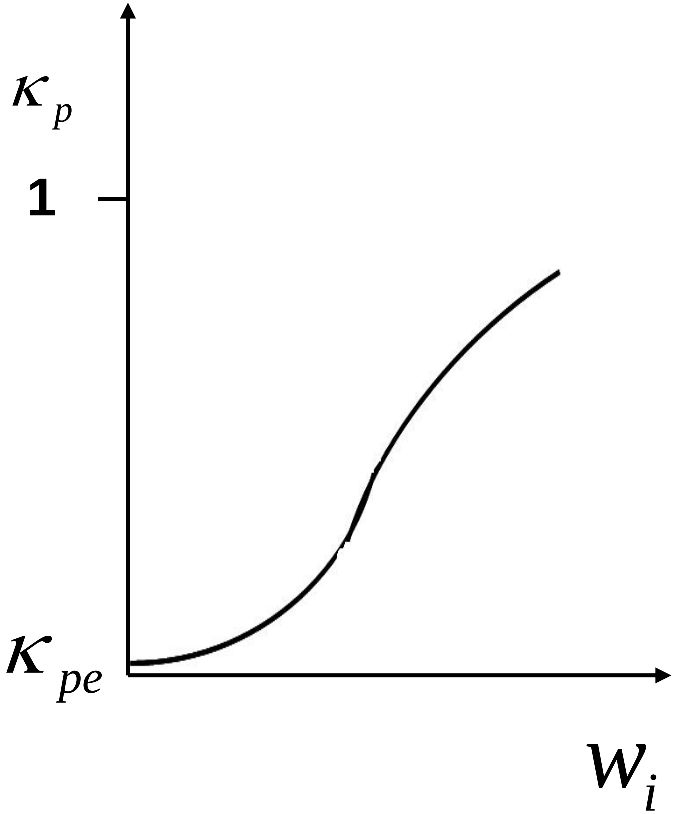
w_i - velocity of liquid/solid interface

w_D - diffusive speed

Nonequilibrium solidification

Partition coefficient for nonequilibrium solidification





Nonequilibrium solidification

Interface temperature during rapid solidification

$$T_i = T_m + m_l(w_i)C_l - \frac{RT^2}{L_m}\frac{w_i}{w_s}$$

where: R - universal gas constant

L_m - latent heat of solidification

w_i - velocity of liquid/solid interface

w_s - sound velocity

C_l - solute concentration

m_l - slope of the liquidus line

Nonequilibrium solidification

Slope of the liquidus line during rapid solidification

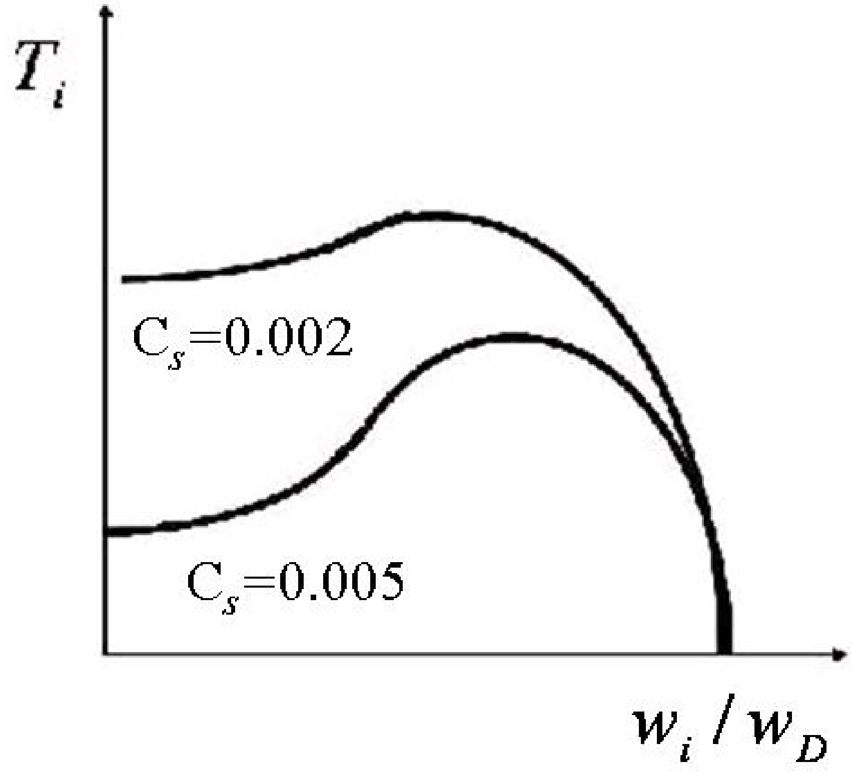
$$\boxed{m_l(w_i) = m_l^e \, \frac{1-\kappa_p(w_i)\left[1-\ln\left(\kappa_p(w_i)/k_e\right)\right]}{1-\kappa_{pe}}}$$

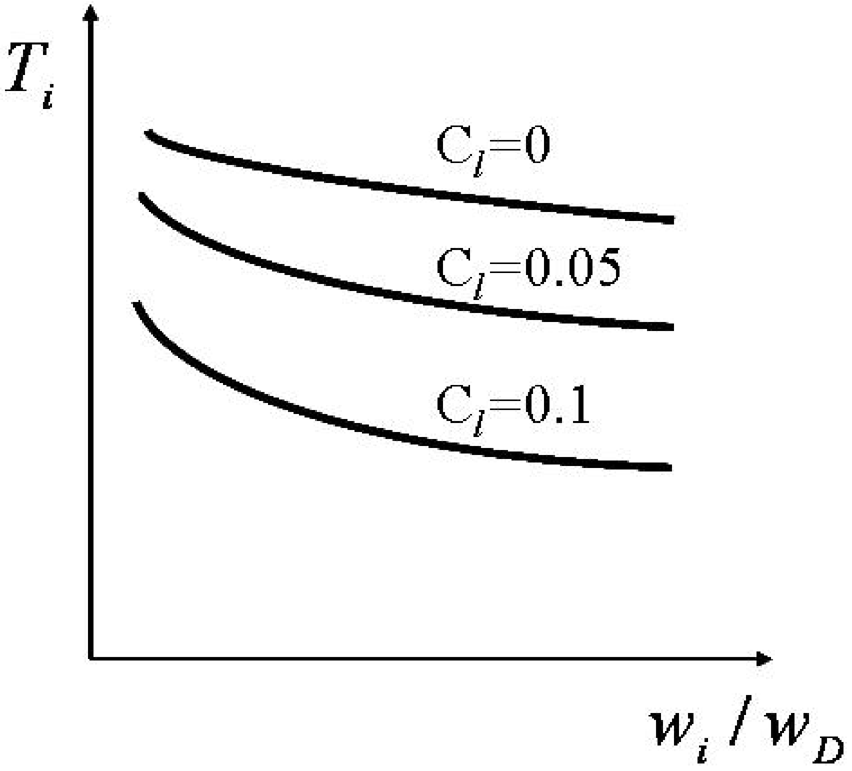
where: m_l^e - slope of the liquidus line in the case of equilibrium

κ_{pe} - equilibrium partition factor

$\kappa_p(w_i)$ - nonequilibrium (kinetic) partition factor

Nonequilibrium solidification





Nonequilibrium solidification

Interface temperature during rapid solidification for curved interface

$$T_i = T_m + m_l(w_i)C_l - \frac{RT^2}{L_m}\frac{w_i}{w_s} - \frac{2\gamma_{ls}V_a T_m}{L_m}\kappa$$

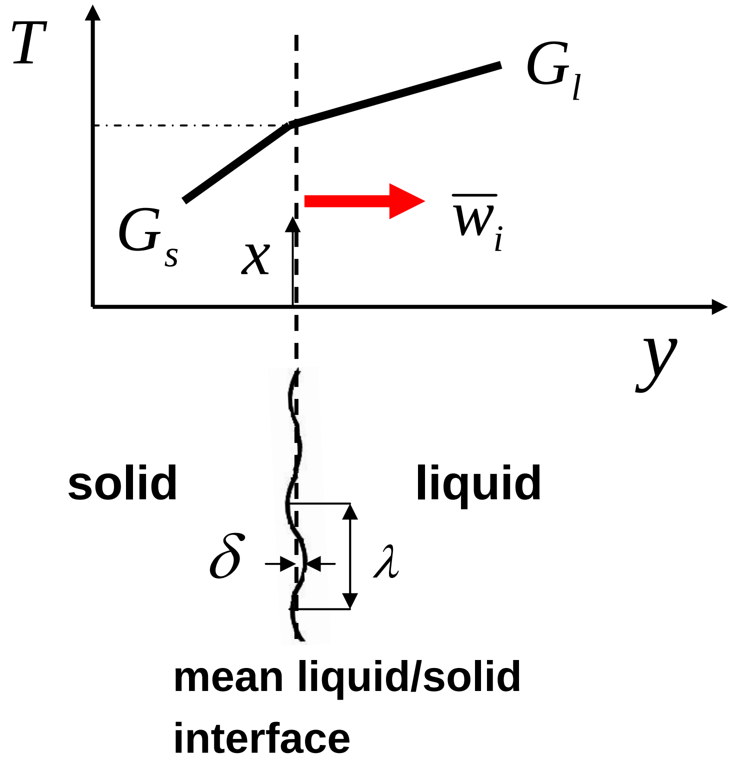
where:

V_a - atomic volume

κ - interface curvature

Instability of alloy solidification

Instability of the planar liquid/solid interface



where:

G_s - temperature gradient in the solid

G_l - temperature gradient in the liquid

w_i - interface velocity

<u>Sinusoidal perturbation of the solid/liquid interface</u>

$$\boxed{y = \delta \sin \omega x}$$

where: $\omega = \dfrac{2\pi}{\lambda}$

Instability of alloy solidification

Stability criterion

$$\boxed{\frac{\left(\dfrac{\partial\delta}{\partial t}\right)}{\delta} < 0}$$

stable interface

$$\boxed{\frac{\left(\dfrac{\partial\delta}{\partial t}\right)}{\delta} > 0}$$

unstable interface

Instability of alloy solidification

Influence of different factors on stability

For negligible G_l

$$\boxed{\frac{\left(\dfrac{\partial\delta}{\partial t}\right)}{\delta} = f(V, Q, \tilde{\omega})}$$

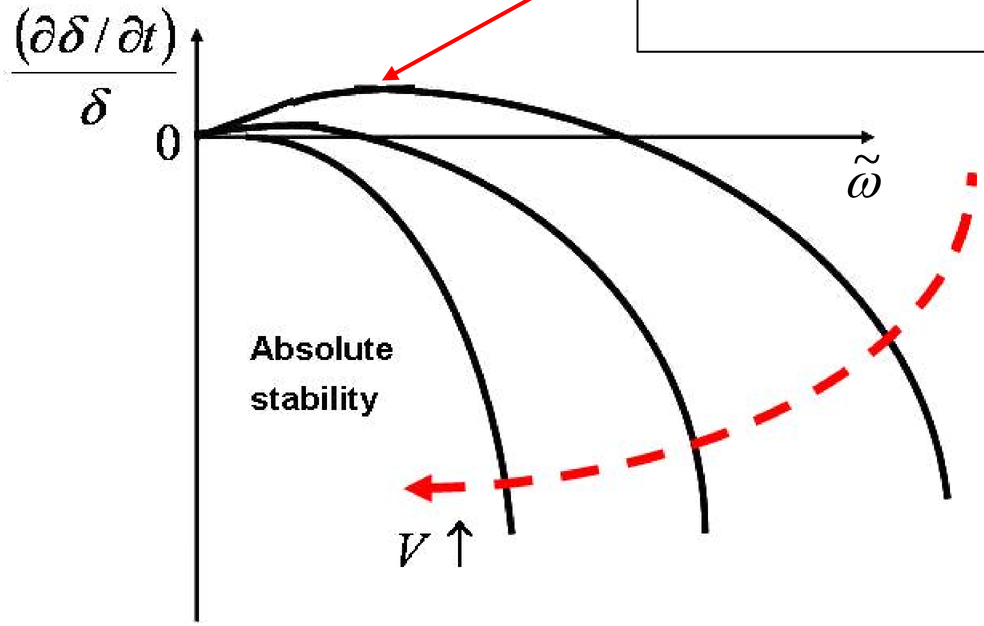
where:

$$V = \frac{\gamma_{sl} T_m k_s \overline{w}_i}{D_l {L_m}^2}, \quad Q = \frac{\kappa_p D_l L_m}{m_l C_l k_s}, \qquad \tilde{\omega} = \omega \frac{D_l}{\overline{w}_i}$$

Instability of alloy solidification

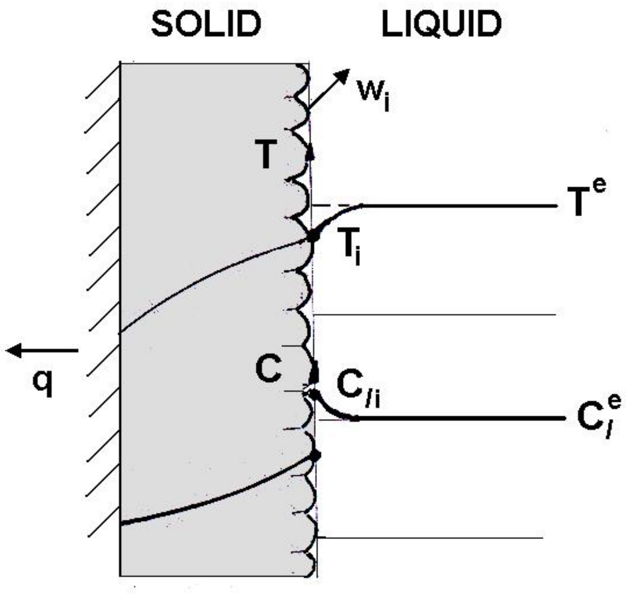
Influence of different factors on stability

$$\lambda_{\min}^2 \overline{w}_i = 12\pi^2 \frac{\gamma_{ls} T_m D_l}{(1-\kappa_p)|m_l| L_m C_l}$$

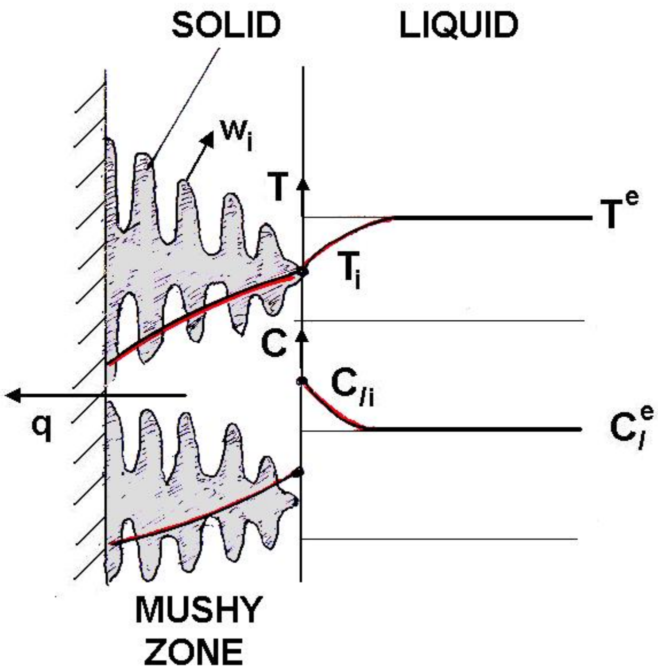


Formation of mushy zone

Growth of dendritic structure



columnar growth



columnar dendritic growth

Formation of mushy zone

Critical thermal gradient in the liquid at which the cellular microstructure pattern can be developed

$$\boxed{\left(\frac{\partial T}{\partial n}\right)_l \geq \frac{m_l C_0 (1-\kappa_p)}{\kappa_p D_l} w_i}$$

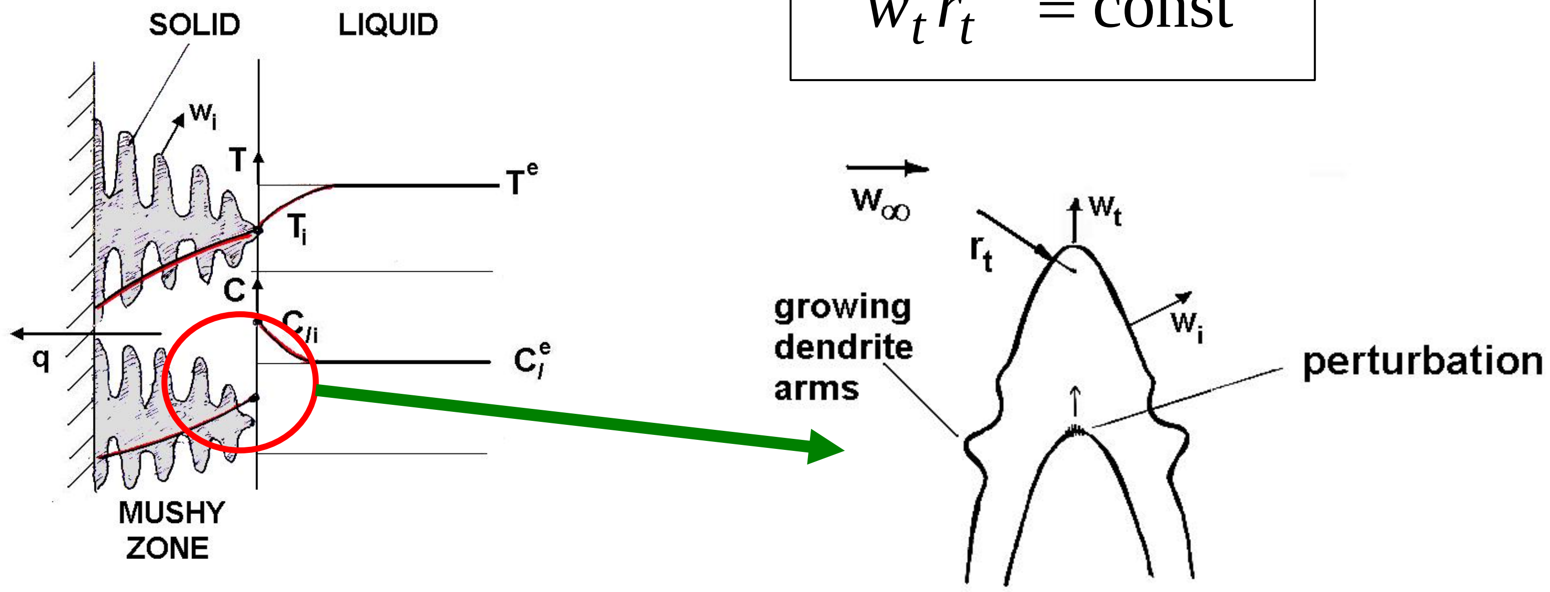
where:

C_0 - initial solute concentration

Formation of mushy zone

Growth a separate columnar dendrite

$$\boxed{w_t r_t^{\,2} = \text{const}}$$



Formation of mushy zone

Undercooling of a dendrite with a parabolic tip

$$\Delta T_t = \frac{L_m I\nu(\mathrm{Pe})}{c_{pl}} + m_l \left[1 - \frac{1}{1-(1-\kappa_p)\, I\nu(\mathrm{Pe})} \right] C_0 + 2\frac{\Gamma}{r_t}$$

where $Pe_t = \frac{w_t r_t}{a_l}$ - Peclet number, Γ - Gibbs-Thomson coefficient,

c_{pl} - liquid specific heat, a_l - liquid thermal diffusivity

$I\nu(Pe)$ - Ivanstov function, $I\nu(Pe) = Pe\exp(Pe)E(Pe)$

Formation of mushy zone

Tip radius of a dendrite with a parabolic tip

$$\boxed{r_t = \frac{\dfrac{\Gamma}{\sigma^*}}{\dfrac{\mathrm{Pe}\,L_m}{c_{pl}} + \dfrac{\mathrm{Sc}\,m_l C_0 (1-\kappa_p)}{\left[1-(1-\kappa_p)\,I\nu(\mathrm{Sc})\right]}}}$$

where Sc - Schmit number

$$\mathrm{Sc} = \frac{w_t r_t}{D_l}$$

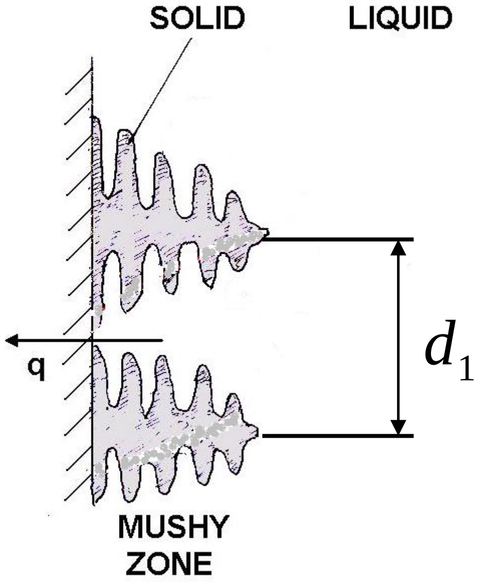
D_l - solute diffusion coefficient in the liquid,

σ^* - constant following from the marginal theory

Formation of mushy zone

The primary arms spacing

$$d_1 = \frac{A(D_l\Gamma)^{1/4}}{\sqrt{\left(\frac{\partial T}{\partial n}\right)_l w_t\, r_t}}$$

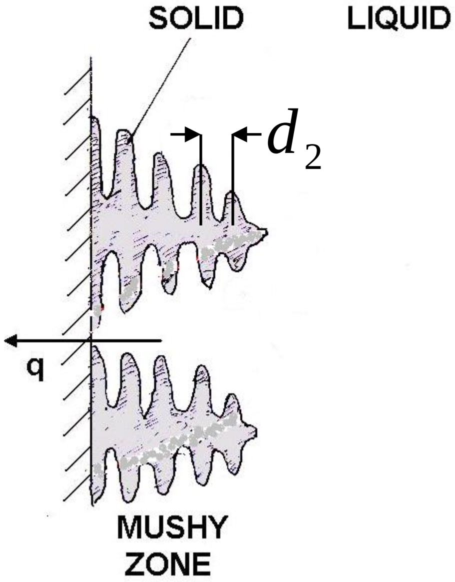


where

A - a numerical constant.

Formation of mushy zone

The secondary arms spacing



$$\boxed{d_2 = \sqrt[3]{l_T l_C d_o}}$$

where

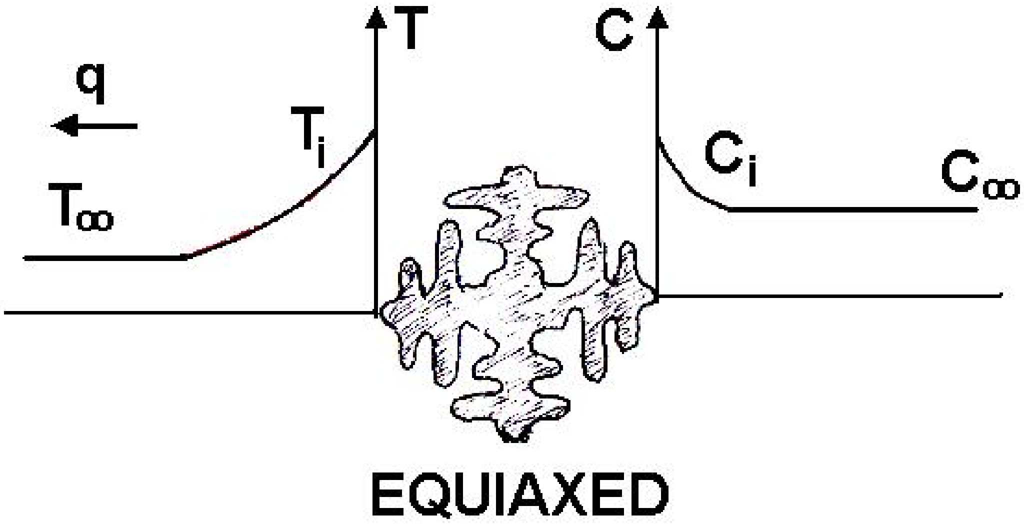
l_T - thermal field lengthscale

l_C - solutal field lengthscale

d_o - capillary lengthscale

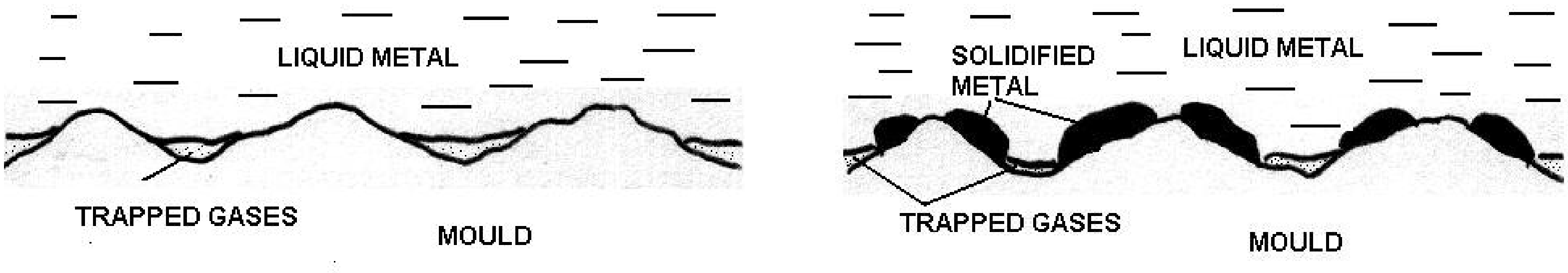
Nonequilibrium solidification

Growth of separate equiaxed grains



Mould-melt interaction

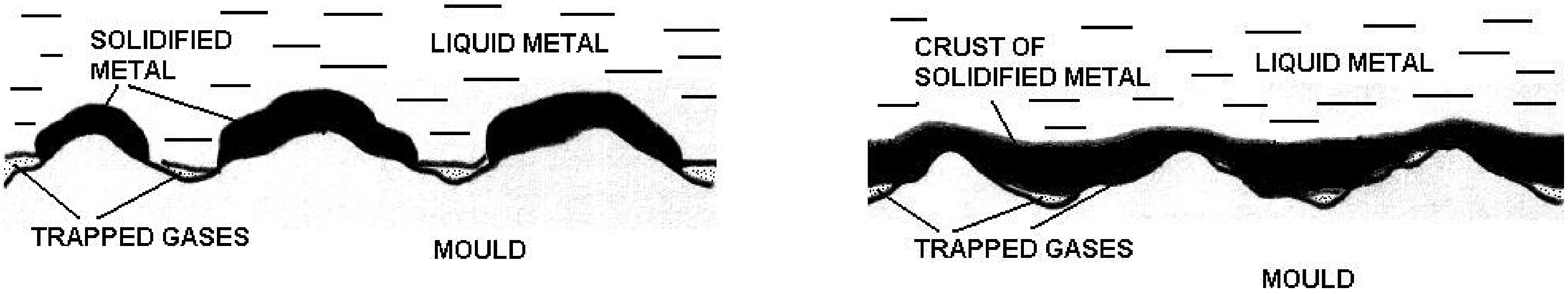
Growth of solid on the mould surface



Evolution of the solidification process
at the alloy-mould interface

Mould-melt interaction

Growth of solid on the mould surface



Evolution of the solidification process at the alloy-mould interface

Summary

Basic phenomena associated with solidification of pure metals and alloys

- surface energy
- nucleation of solid phase
- non-equilibrium effects during solidification
- instability of the solid/liquid interface
- formation of the mushy zone
- mould/melt interactions