FS 2024/25

MSE-422 – Advanced Metallurgy

2.1 - Reminder: Thermodynamics, Phase Diagrams, Kinetics

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Outline

- Thermodynamics of alloys
- Phase diagrams
- Phase transformations – nucleation and growth

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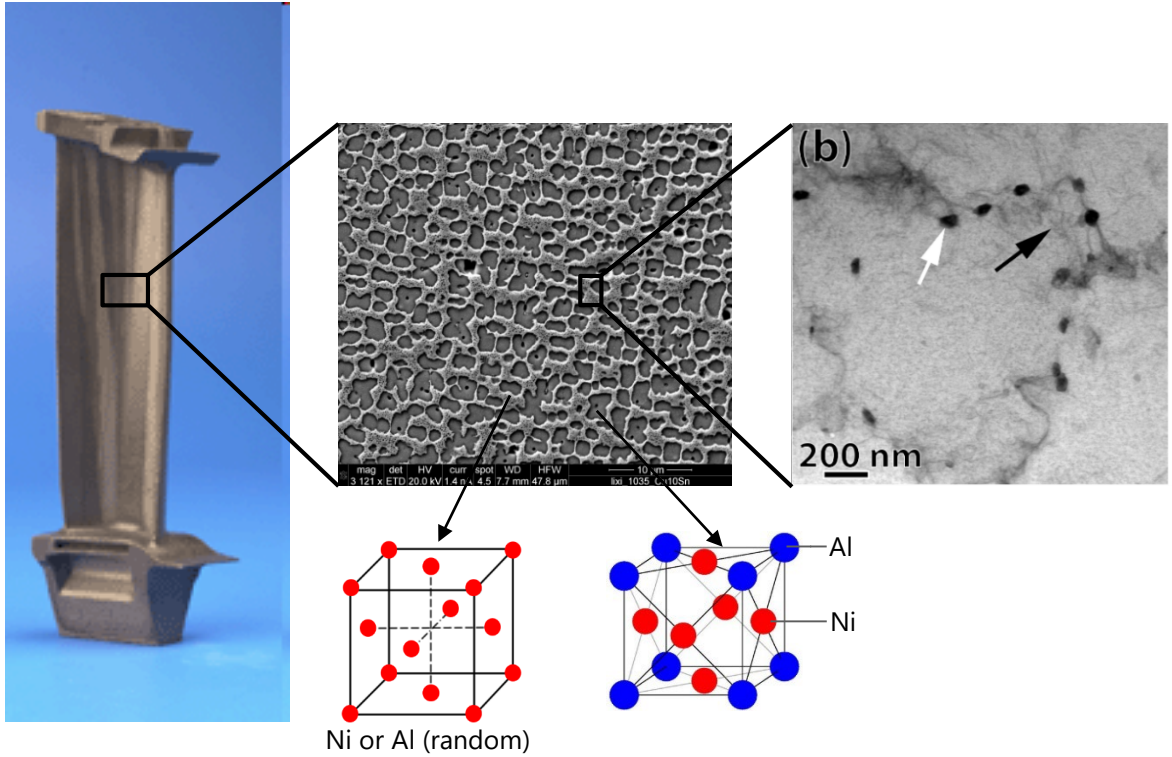
- Phase transformations – nucleation and growth

Why thermodynamics?

Let's have a look into a turbine blade made from a Ni superalloy



- The blade has seen several thermal cycles (soldification, heat treatment) during manufacturing.
- What phases do we see in the microstrurcture and why?
- Is this microstructure stable at elevated temperatures in service?

Thermodynamics

Basic definitions

- Thermodynamics = study of behavior of matter under action of external fields (e.g. temperature, pressure)
- Description of equilibrium states and transitions from one state to another
- The system of matter may contain one or several *components* or *elements*
- There may also be several *phases* = portion of a system that are physically distinct wrt their state (solid, liquid, vapor), crystal structure or composition
- A system of matter is defined by the *thermodynamic variables*
  - Intensive variables (i.e. not dependent on amount of material): Temperature T; pressure p
  - Extensive variables (i.e. dependent on amount of material): Volume V
  - Two variables are independent; the third is obtained through an equation of state, e.g. V = V(p,T)

Thermodynamics

Basic definitions

- *State variables* can be written as a function of the thermodynamic variables
  - Internal energy U (total energy contained in system of matter of volume V)
  - Entropy S (physical property that is most commonly associated with a state of disorder or randomness of the system)
  - Enthalpy: H = U + pV
  - Gibbs free energy: G = U + pV - TS = H - TS
  - Helmholtz free energy: F = U - TS

- In thermodynamics, one compares different states and the corresponding relative changes in the thermodynamic quantities, e.g. the difference dU

$$dU(T,V) = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{dT} + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{dV}$$

Thermodynamics

- *First Law of Thermodynamics*
  - In a system of constant mass, energy can neither be created nor destroyed.
  - The change in internal energy (dU) in the system is the sum of any heat added (dQ) plus work done by external forces (dW)

$$dU = dQ + dW$$

  - For gas/liquid, work only arises from compression, so dW = -pdV

$$dU = dQ - pdV$$

- *Second Law of Thermodynamics*
  - The entropy of a closed system can only increase (in an irreversible reaction) or stay constant (in equilibrium)

$$dS = \frac{dQ}{T} \geq 0$$

Thermodynamics

- Including the entropy in the first law of thermodynamics it follows:

$$dU = TdS - pdV$$

- The enthalpy change dH can be written as

$$dH = dU + pdV + Vdp = TdS + Vdp$$

- The Gibbs free energy change dG, which decides whether a process will occur, is

$$dG = dH - SdT + Vdp = Vdp - SdT$$

- At constant volume (dV = 0), we can use dF instead of dH:

$$dF = -SdT$$

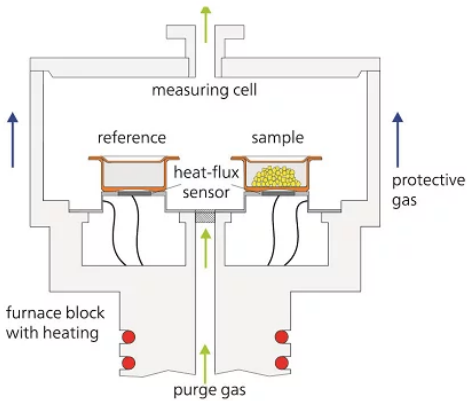
- A reaction can only take place if $dG < 0$
- At equilibrium, no further reaction takes place → the Gibbs free energy has reached its minimum (or the entropy its maximum)
- The Entropy S can be re-written as: $S = -\left(\frac{\partial G}{\partial T}\right)_p$
- The specific heat c_p is defined as: $c_p = \left(\frac{\partial H}{\partial T}\right)_p = T\frac{\partial S}{\partial T}$

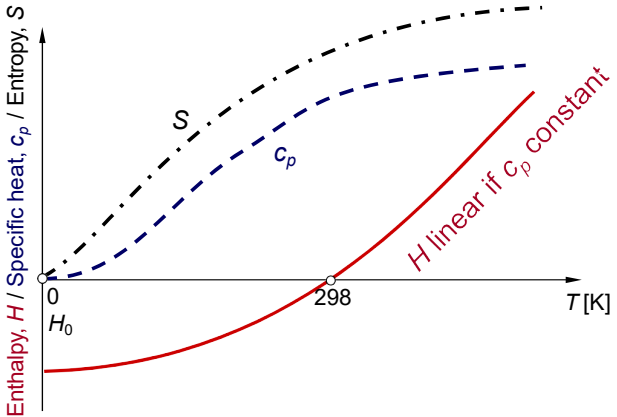
Thermodynamics of unary systems

Determination of thermodynamic quantities

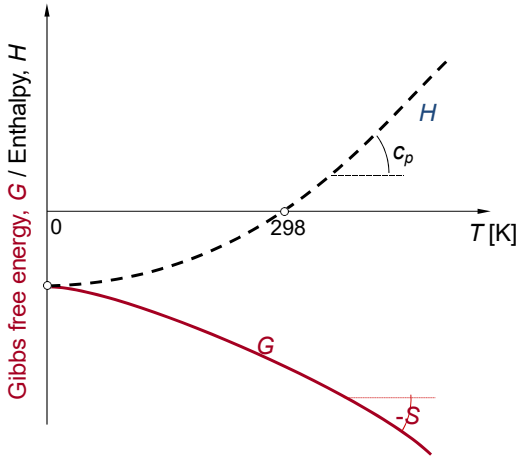
- c_p can be measured by Differential Scanning Calorimetry (DSC): $c_p = \frac{\Delta Q}{m \Delta T}$
- With $c_p = \left(\frac{\partial H}{\partial T}\right)_p = T \frac{\partial S}{\partial T} \rightarrow H = \int_0^T c_p(\theta) d\theta - H_0 \,;\; S(T) = \int_0^T \frac{c_p(\theta)}{\theta} d\theta ;\; G = H - TS$
- H, S, G and c_p can be given for every possible phase as f(T,p)

DSC - setup





/courtesy C. Cayron, MSE302/



Thermodynamics of unary systems

Phase equilibria

- Consider a closed system consisting of two phases α and β with mole fractions x_α and x_β in thermal and mechanical equilibrium (i.e. T and p are fixed)
- The (molar) Gibbs free energy of the system is $G^m = x_\alpha G_\alpha^m + x_\beta G_\beta^m$
- Since the system is closed → $x_\alpha + x_\beta = 1$
- To reach equilibrium, matter must be repartitioned between α and β until

$$\frac{\partial G^m}{\partial x_\alpha} = 0 = G_\alpha^m - G_\beta^m$$

→ At equilibrium, a unary system consisting of two phases satisfies the following conditions:

- $T_\alpha = T_\beta = T$
- $p_\alpha = p_\beta = p$
- $G_\alpha^m = G_\beta^m = G^m$

The number of degrees of freedom, F, or number of independent variables which can be changed and still maintain the same number of phases in equilibrium is 0

Thermodynamics of unary systems

Phase equilibria

- Consider melting of a pure substance upon heating. The Gibbs free energies of the solid and the liquid phase are

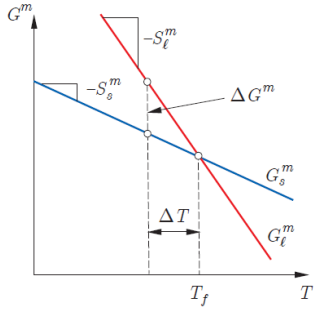
$$G_l^m(T) = H_l^m(T) - TS_l^m \text{ and } G_s^m(T) = H_s^m(T) - TS_s^m$$

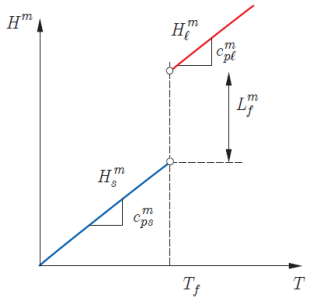
- The point where the Gibbs free energies of the solid and liquid phase are equal is the equilibrium melting point T_f
- For the slopes of G_l^m and G_s^m we find (the liquid is more disordered)

$$\frac{dG_l^m}{dT} = -S_l^m > \frac{dG_l^m}{dT} = -S_s^m \rightarrow \Delta S_f^m = S_l^m - S_s^m \text{ (entropy of fusion)}$$

- At T = T_f: $G_l^m(T_f) = G_s^m(T_f) \rightarrow \Delta G_{s\rightarrow l}^m(T_f) = 0$
  and thus $\Delta H_{s\rightarrow l}^m(T_f) = L_m = T_f \Delta S_f^m(T_f)$ (latent heat of fusion)
- Upon cooling, solidification is induced when a certain undercooling ΔT is reached. The Gibbs free energy change is

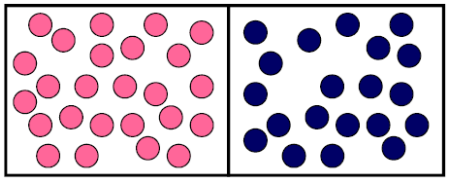
$$\Delta G_{l\rightarrow s}^m = -\Delta S_f^m \Delta T$$





/J.A. Dantzig and M. Rappaz, Solidification, 2016/

Thermodynamics of binary systems



- Consider a system consisting of N_A moles of element A and N_B moles of element B without mixing A and B.
- When an increment dN_A is added to the whole system, the Gibbs free energy will be increased by

$$\left(\frac{\partial G}{\partial N_A}\right)_{N_B,p,T} := \mu_A \text{ (chemical potential)}$$

→ $dG = Vdp - SdT + \sum_i \mu_i dN_i$

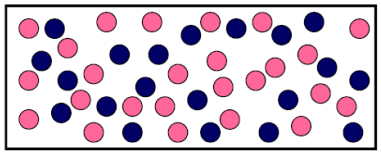
- For constant T and p the Gibbs free energy is thus

$G = N_A G_A + N_B G_B$ or for one mole $G^m = X_A G_A^m + X_B\, G_B^m$

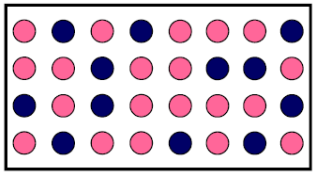
Thermodynamics of binary systems

- After mixing and considering that all bonds between the atoms are equal (ideal solution), only the entropy is increased

$$G^m = X_A G_A^m + X_B\, G_B^m + RT(X_A lnX_A + X_B lnX_B)$$



- In regular solutions the bonds are not equal and a mixing enthalpy $\Delta H_{mix} = \Omega X_A X_B$ needs to be added
- Ω is a parameter that describes the interaction between A and B atoms



$$\Omega = N_a z\left(\varepsilon_{AB} - \left(\frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}\right)\right)$$

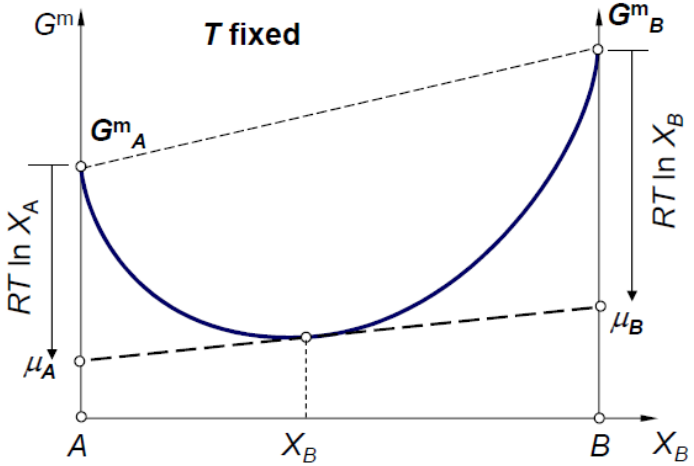
N_a: Avogrado constant
z: coordination number

→ $G^m = X_A G_A^m + X_B\, G_B^m + RT(X_A lnX_A + X_B lnX_B) + \Omega X_A X_B$

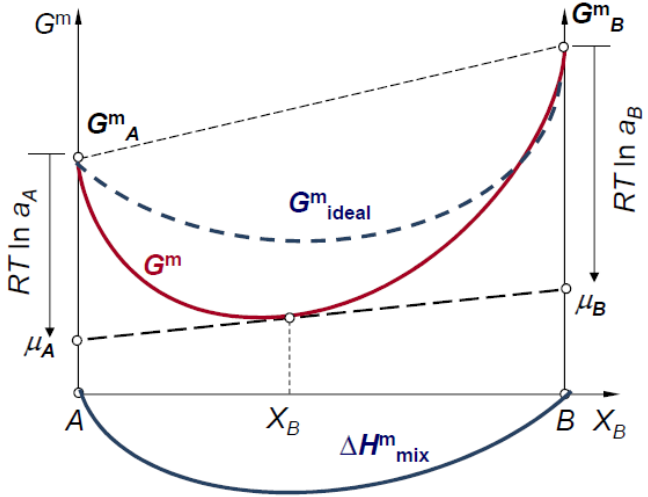
- Depending on the type of bonds, $\Omega<0$ (A and B "like" each other) or $\Omega>0$ (A and B "dislike" each other)

Thermodynamics of binary systems

Ideal solution



Regular solution with Ω<0



/courtesy C. Cayron, MSE302/

- Thermodynamics of alloys
- Phase diagrams
- Phase transformations – nucleation and growth

Phase diagrams

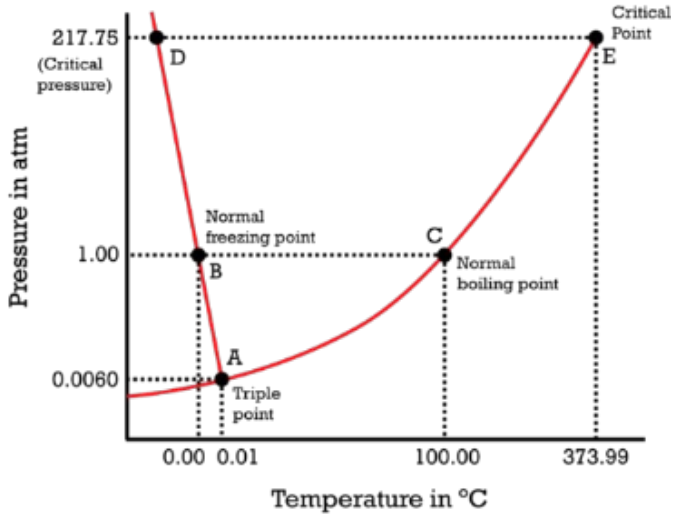
Road maps for alloy design and processing

- A Phase diagram describes the state of a materials system in thermodynamic equilibrium as a function of temperature, pressure and composition.
- Phase diagrams are maps of the equilibrium phases associated with various combinations of temperature, pressure, and composition.
- Phase diagrams are an essential tool when it comes to the design of novel alloys

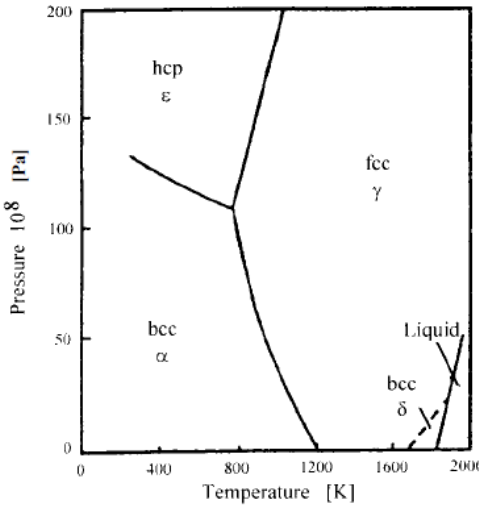
Unary phase diagrams

- Unary phase diagrams show the stable phases of a single element as a function of temperature and pressure

Phase diagram for water



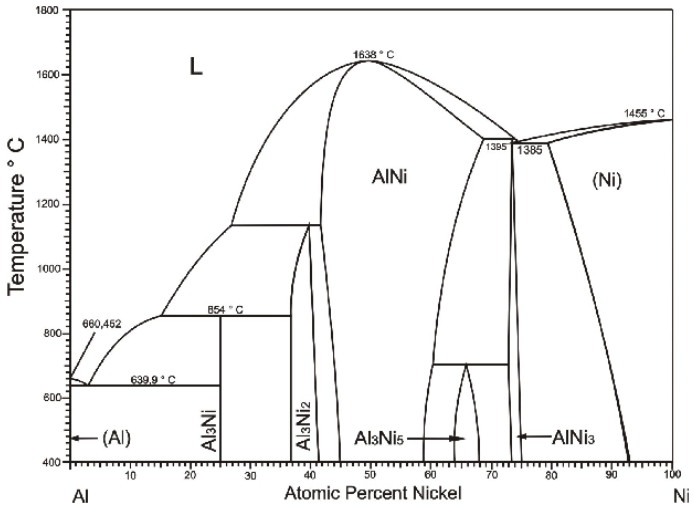
Phase diagram for iron



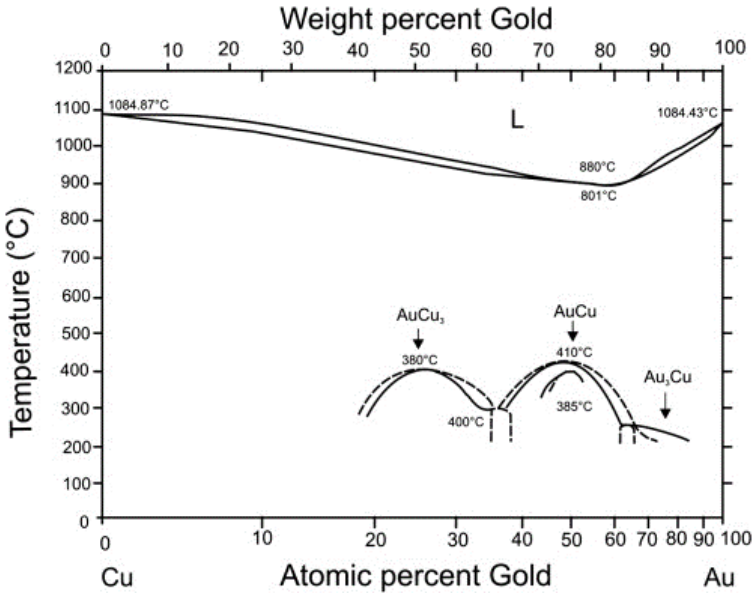
Binary phase diagrams

- Binary phase diagrams show the stable phases of a two-component system as a function of temperature and composition

Al-Ni



Au-Cu



The Gibbs phase rule

- The number of degrees of freedom F for a given thermodynamic condition, that is: how many variables (pressure, temperature, composition, etc.) can be altered while maintaining this condition

$$F = C + 2 - P$$

Where:

F – number of independent variables = degrees of freedom

P – number of phases in equilibrium coexistence

C – number of components in the system

2 – thermodynamic control parameters (*temperature* and *pressure*)

Condensed Phase rule (p = const.): $F = C + 1 - P$

Variance (F)	*Number of phases (P)*	*Equilibrium*	*Geometry*
0	c + 1	Invariant	**Point**
1	c	Monovariant	**Line**
2	c – 1	Bivariant	**Area**
3	c – 2	Trivariant	**Volume**

The lever rule

- The lever rule allows calculating the amount of each phase in a two-phase field

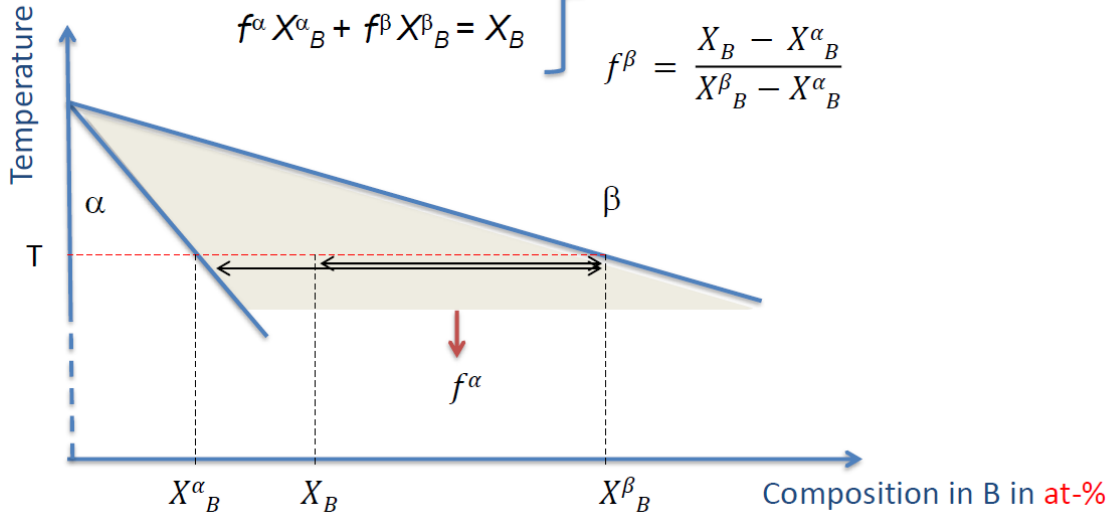
Lever rule :

$$f^{\alpha} + f^{\beta} = 1$$

$$f^{\alpha} X^{\alpha}_B + f^{\beta} X^{\beta}_B = X_B$$

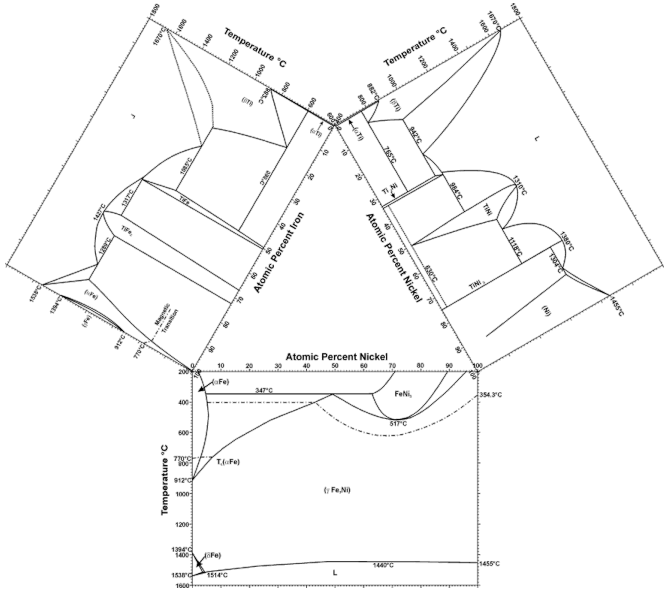
$$f^{\alpha} = \frac{X^{\beta}_B - X_B}{X^{\beta}_B - X^{\alpha}_B}$$

$$f^{\beta} = \frac{X_B - X^{\alpha}_B}{X^{\beta}_B - X^{\alpha}_B}$$



Ternary phase diagrams

- Ternary phase diagrams show the phase equilibria in a three-component system
- Since they include three binary boundary systems, they are actually 3D diagrams
- As they are presented in 2D, one often finds projections or 2D sections



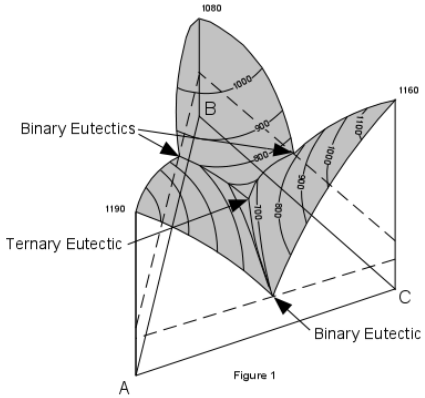


Figure 1

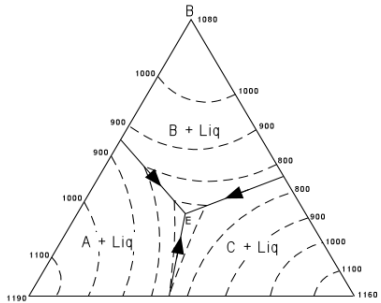
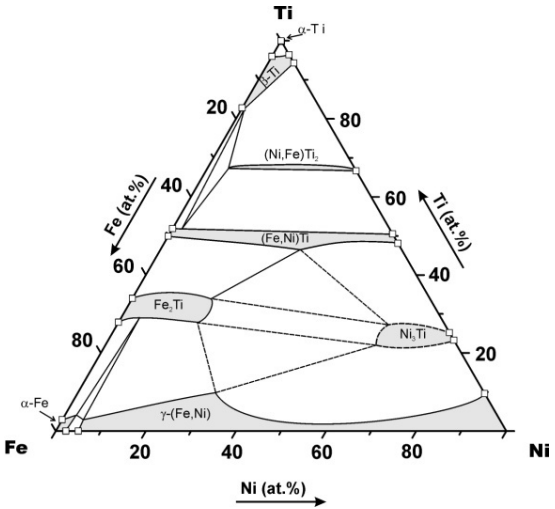


Figure 2

Ternary phase diagrams

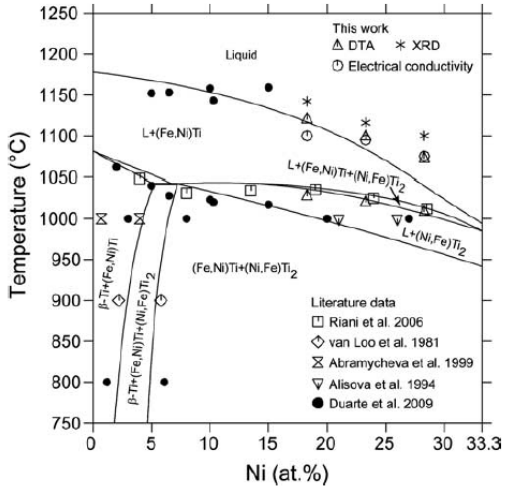
- Isothermal sections show the phase equilibria at a fixed Temperature (horizontal cut)
- Isoplethal sections show the phase equilibria at a fixed composition (vertical cut)

Fe-Ni-Ti
isothermal section at 1000°C

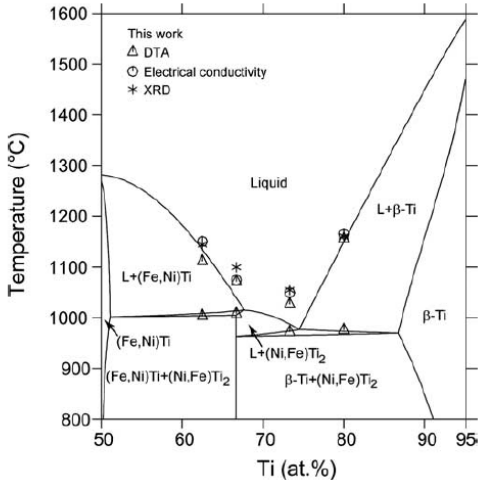


/L. Duarte et al, Intermetallics 18(3) (2010) 374-384/

Fe-Ni-Ti
vertical section at 66.7 at.% Ti



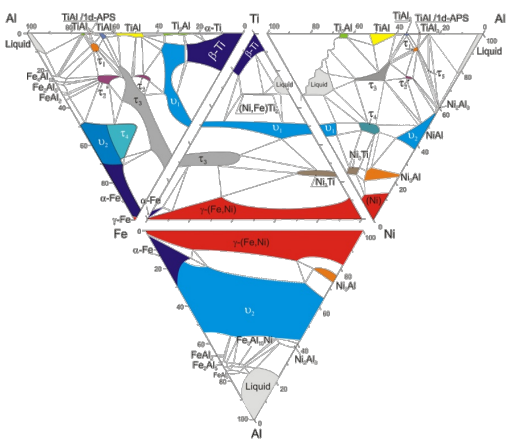
Fe-Ni-Ti
vertical section at 5 at.% Ti

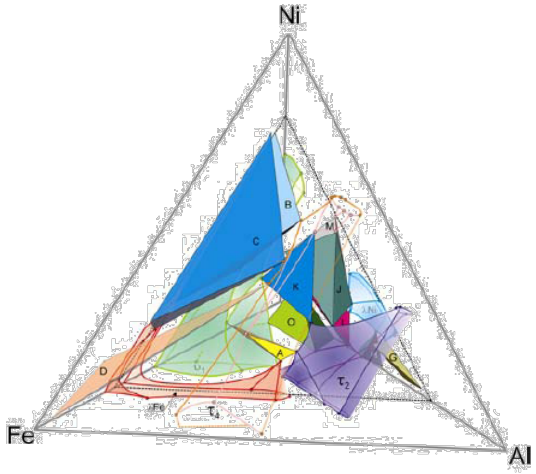


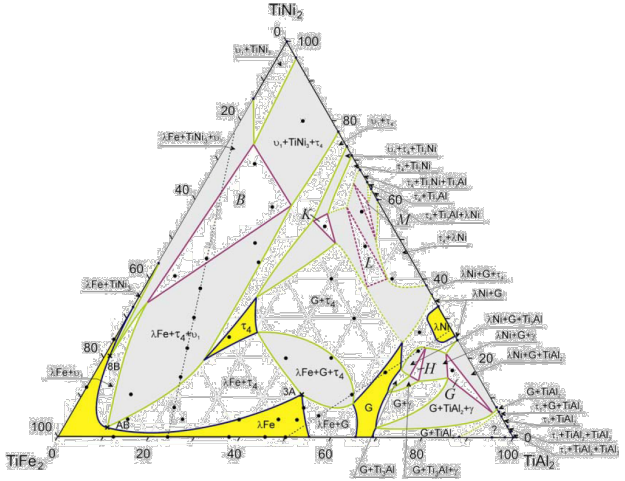
/L. Duarte et al, Int. J. Mater. Res 102(3) (2011) 248-256/

Quaternary phase diagramns

- Quaternary phase diagrams are composed of four ternary boundary phase diagrams
- Their graphical representation becomes more complicated; e.g. an isothermal section is a tetraeder







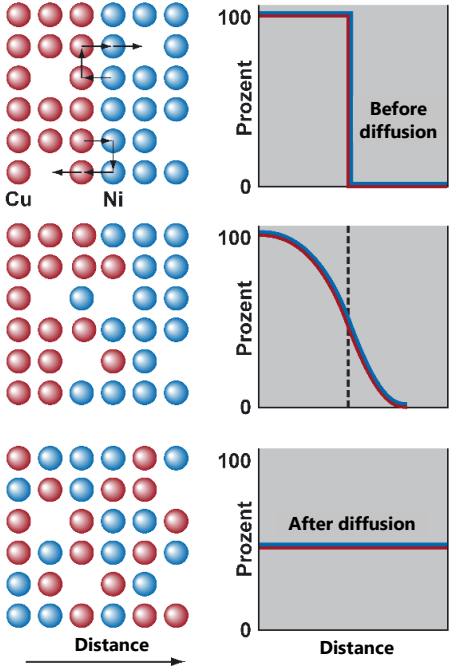
- Thermodynamics of alloys
- Phase diagrams
- Phase transformations – nucleation and growth

Phase transformations in alloys

- When the conditions in an alloy system change (e.g. change in temperature or composition), a certain phase might no longer be stable and a phase transformaton occurs
- The driving force for a phase transformation is the difference in the Gibbs free energy of two phases
- Phase transformations do not occur instantaneously, but they require time
- Phase transformations can be of diffusive or displacive nature
  - Diffusive transformations are based on the diffusion of alloying elements; they can be separated into a nucleation stage and growth state
  - Displacive transformations are based on the collective displacement of atoms with very high speed

Diffusion

- Diffusion is the transport in materials via random individual migration steps (‘jumps’) of atoms
- Self-diffusion: place-changing processes in the crystal lattice, which is constructed purely from one type of atom. Equilibration of the kinetic energy
- Substitutional diffusion: place change processes of one atomic species in the lattice of another. Equilibration of concentration differences, but also by electric and magnetic fields, temperature gradients (thermo-diffusion effect)
- Interstitial diffusion: diffusion occurs by solute atoms jumping from one interstitial site into a neighboring one



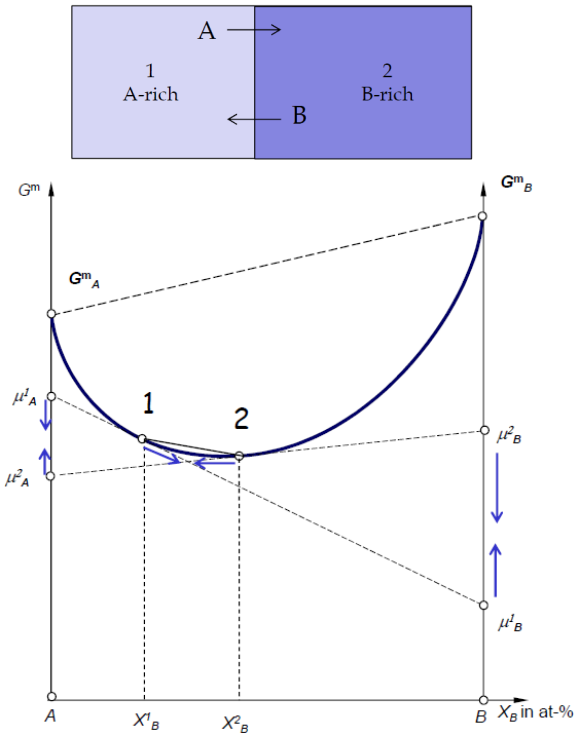
Diffusion

- The driving force for diffusion is the difference in the chemical potentials
- Consider a diffusion couple between an A-rich and a B-rich alloy. The A-rich region has the composition x_B^1
  - $\mu_A^1 > \mu_A^2$ → A goes from 1 to 2
  - $\mu_B^2 > \mu_B^1$ → B goes from 2 to 1
- For ideal solutions, the flux of solute atoms B, J_B [mol m^{-2} s^{-1}] in a gradient of concentration c_B [mol m^{-3}] is:

$$\boldsymbol{J}_B = -D_B grad(c_B) \text{ (Fick's 1st law)}$$

- The diffusion coefficient D_B is a function of T

$$D_B = D_B^0 exp\left(-\frac{Q}{RT}\right)$$



Diffusion

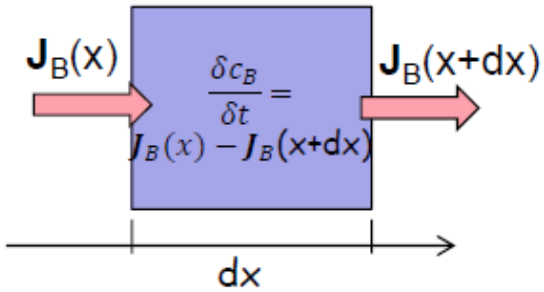
- The solute balance is also a function of time
- Assuming no global transport and no chemical reaction, the solute balance for a small volume element ΔV (with ρ_B constant) is given as :

$$\frac{\partial c_B}{\partial t} = -div(\boldsymbol{J}_B) = div\left(D_B grad(c_B)\right)$$ (Fick's 2nd law)

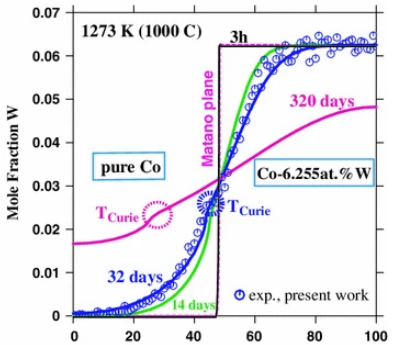
- In 1D and with D_B = const.

$$\frac{\partial c_B}{\partial t} = D_B \frac{\partial^2 c_B}{\partial x^2}$$

- Diffusion couples can be used to determine the diffusion coefficient by measuring thje compositional change in the vicinity of the interface over time (T = const.)



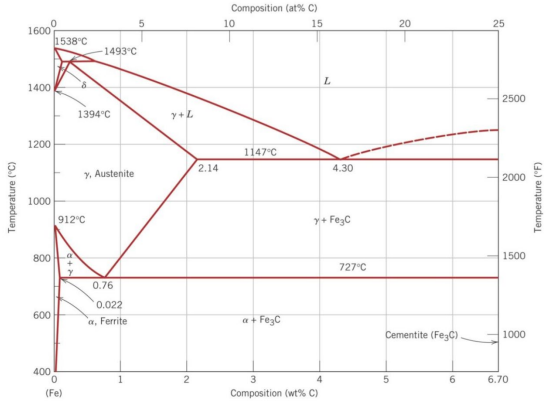
Diffusion couple Co-W at 1000°C



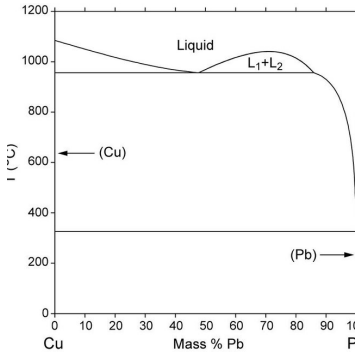
/Y.W. Cui et al., Met. Mater. Trans. A 44 (2013) 1621-1625/

Invariant reactions in binary alloy systems

- Invariant reaction for a binary alloy is one occurring when three phases are in equilibrium
- Invariant reactions including the liquid phase
  - Eutectic: $L \rightarrow \alpha + \beta$
  - Peritectic $L + \alpha \rightarrow \beta$
  - Monotectic: $L_1 \rightarrow L_2 + \alpha$
- Invariant reactions in the solid state
  - Eutectoid: $\alpha \rightarrow \beta + \gamma$
  - Peritectoid: $\alpha + \beta \rightarrow \gamma$
  - Monotectoid: $\alpha_1 \rightarrow \alpha_2 + \beta$

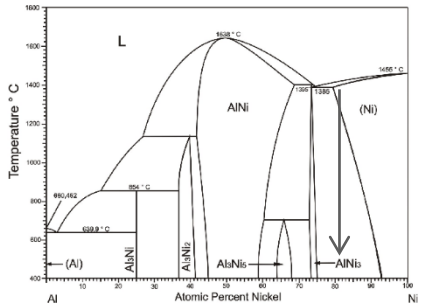


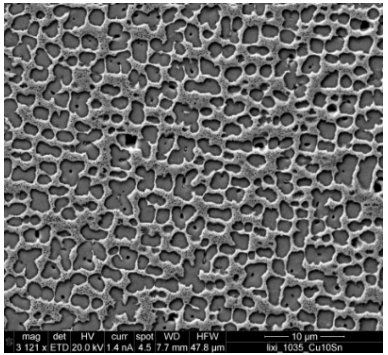
/www.chegg.com/



Diffusive phase transformations

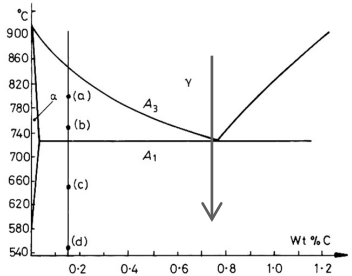
- Precipitation

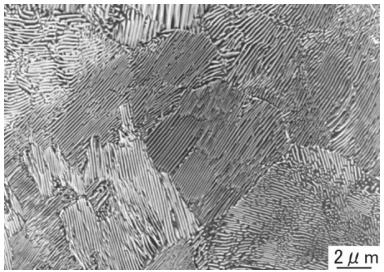




Ni_3Al precipitates in Ni

- Eutectoid

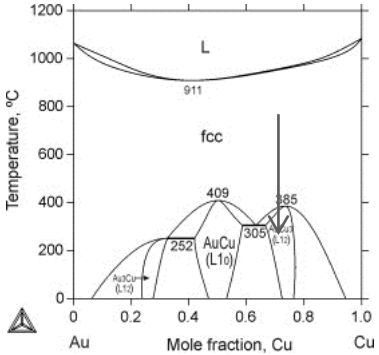


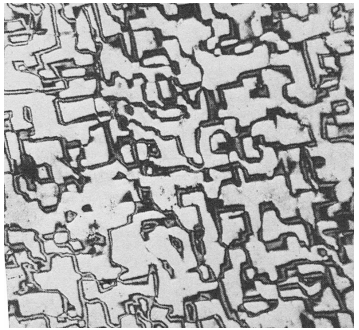


Formation of pearlite in steel

Diffusive phase transformations

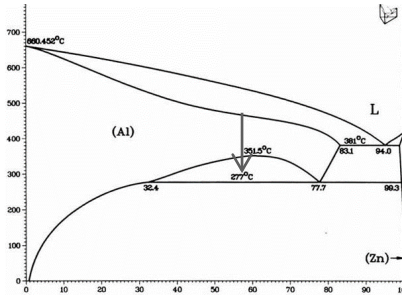
- Ordering

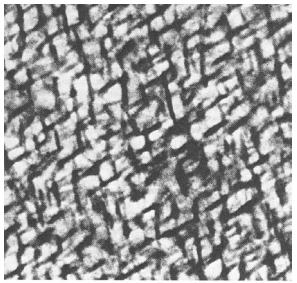




Cu_3Au
(with antiphase boundaries)

- Spinodal

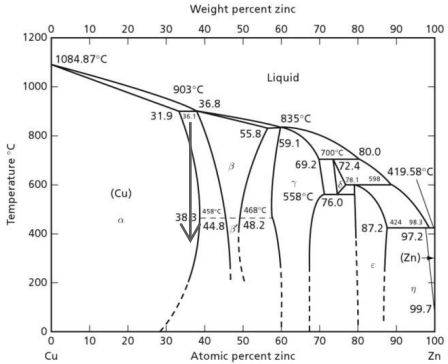


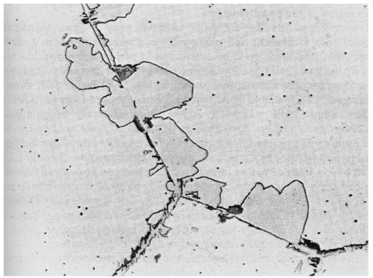


Spontaneous decomposition of Al into Al1 and Al2

Diffusive phase transformations

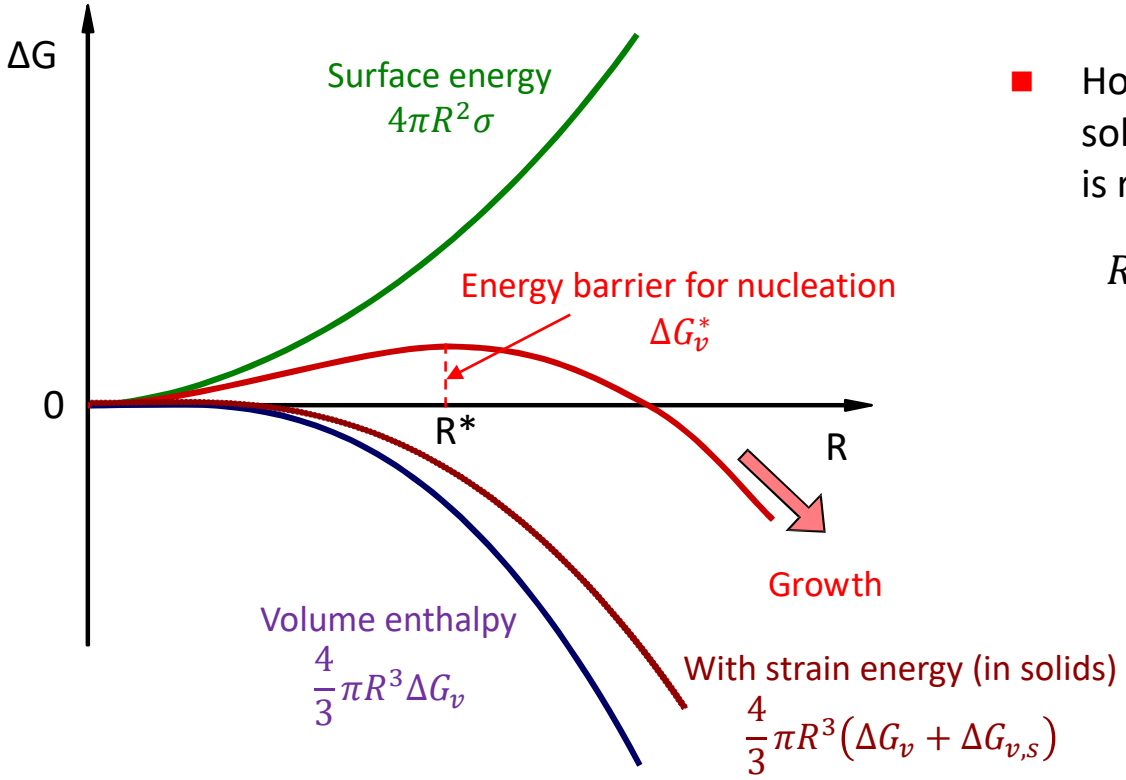
- Massive





Massive α grains in Cu-38.7wt%Zn

Nucleation and growth



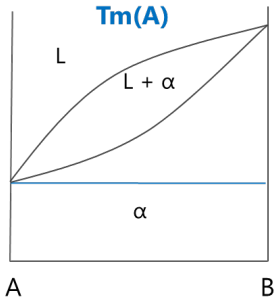
- Homogeneous nucleation in a liquid or solid occurs when a critically radius R* is reached

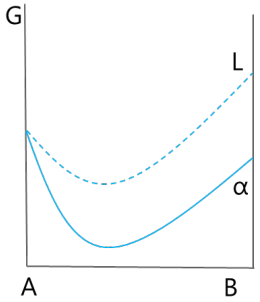
$$R^* = -\frac{2\sigma}{(\Delta G_v + \Delta G_{v,s})}$$

σ: interfacial energy
ΔG_v: Gibbs free energy per unit volume (typically negative)
$\Delta G_{v,s}$: deformation energy per unit volume (always positive)
ΔG_v^*: energy barrier for nucleation

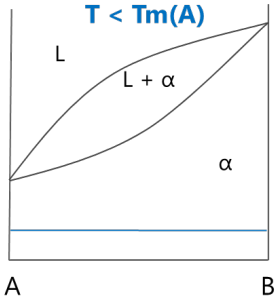
Nucleation and growth

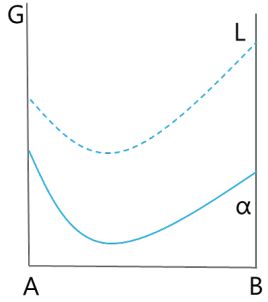
- Nucleation is governed by variation in G





$$G_A^L = G_A^\alpha$$





$$G_A^L > G_A^\alpha$$

$$\Delta G_V = G_A^\alpha - G_A^L < 0$$

→ solidification

$$\Delta G_V = G_A^\alpha - G_A^L$$

$$\Delta G_V = \frac{\Delta H_v (T_m - T)}{T_m}$$

Driving force for solification

$$\Delta G^* = \frac{16\pi}{3} \frac{\gamma^2}{{\Delta G_V}^2}$$

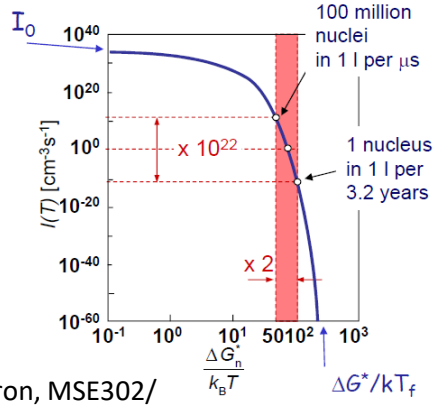
Activation energy

$$\mathrm{I} = Ae^{-\frac{\Delta G^*}{RT}}$$

Nucleation rate

Nucleation kinetics

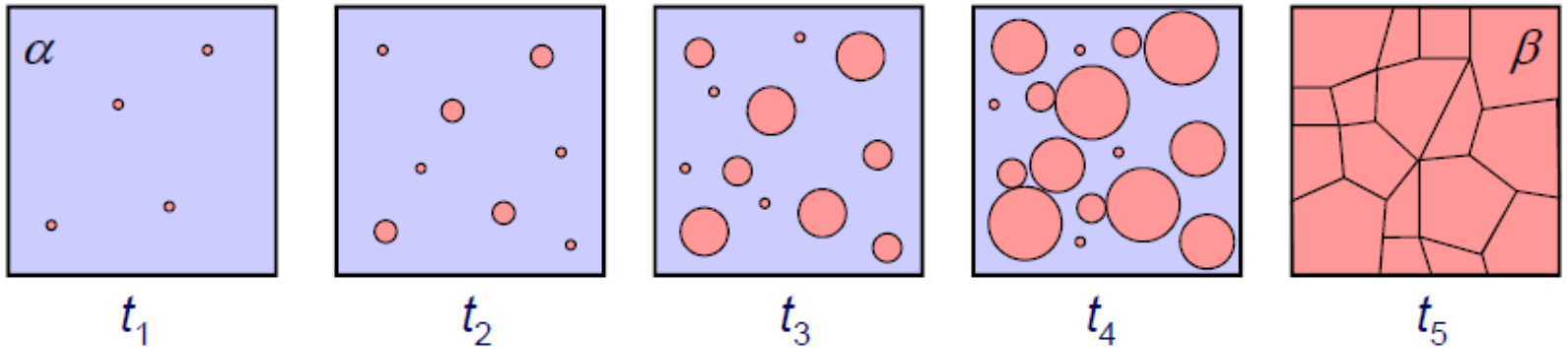
- Nucleation is determined by
  - The evolution of the critical radius R^* with undercooling ΔT: $R^* = \frac{2\sigma}{\Delta S_f^m \Delta T}$
  - The evolution of the number of atoms N_c in the critical clusters with ΔT: $N_c = \frac{4\pi N_A}{3V^m} R^{*3}$
  - The evolution of the activation barrier ΔG_v^* with ΔT: $\Delta G_v^* = \frac{16\pi}{3} \frac{\sigma^3}{\Delta S_f^{m^2} \Delta T^2}$
- The rate of formation of stable nuclei per volume $I(t)$ is affected by both the thermal activation kT and the undercooling ΔT
  - $I(t) = I_0 exp\left(\frac{-\Delta G_v^*}{kT}\right)$
  - $I(t) = I_0 exp\left(\frac{16\pi}{3kT} \frac{\sigma^3}{\Delta S_f^{m^2} \Delta T^2}\right)$



/courtesy C. Cayron, MSE302/

Nucleation kinetics

- Consider a small volume element, V, of uniform (and constant) temperature, T, in which nucleation and growth occurs.
- At t_1, first β-nuclei appear in the α phase. They grow between t_1 and t_2 while new nuclei appear.
- The process is repeated during the following time steps. At t_4, grain impingement occurs



/courtesy C. Cayron, MSE302/

Nucleation kinetics

- Consider that the precipitates are spherical, the nucleation rate is constant I = I_0 and the growth velocity is constant: v = const.

$$f_g^e(t) = I_0 \int_0^t \frac{4}{3}\pi v^3 (t-\tau)^3 d\tau = I_0 \frac{\pi}{3} v^3 t^4$$

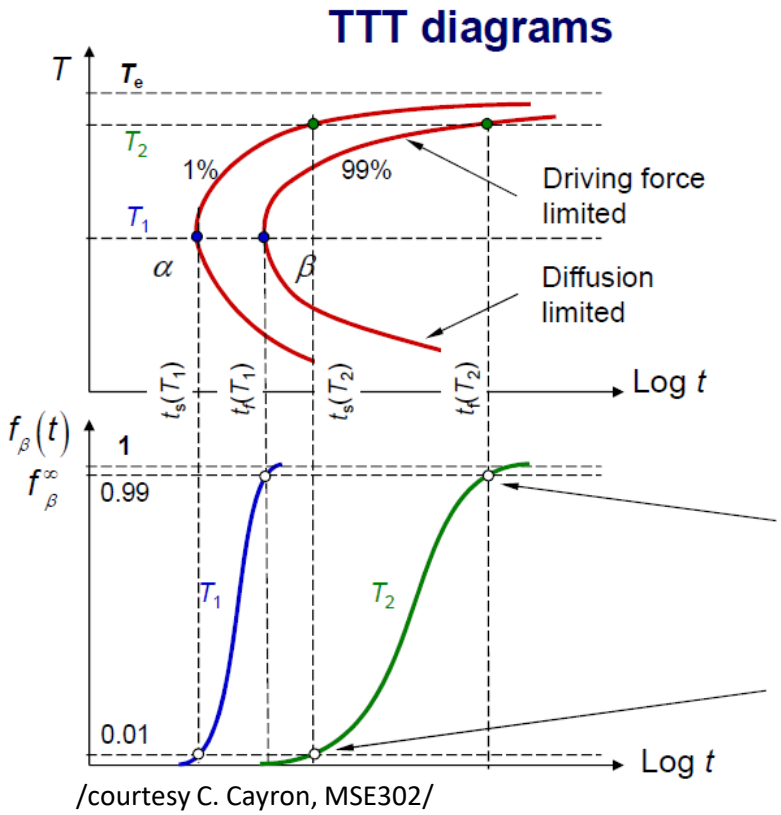
- Actual increment of volume fraction of β is given by the increment of the extended volume fraction and the probability of having a point of the interfaces of the grains not already in contact with another grain.

$$df_\beta(t) = \left(1 - f_\beta\right) df_\beta^e \longrightarrow f_\beta(t) = 1 - \exp\left[-f_g^e(t)\right]$$

- The expressions derived before for the extended volume fraction of b can be used. But as nucleation and growth processes are very complex, in particular if growth is not the same in all directions, one tends to rather fit the fraction of β by:

$$f_\beta(t) = f_\beta^\infty \left(1 - exp\left[-k(T) t^{n(T)}\right]\right)$$

Nucleation kinetics



/courtesy C. Cayron, MSE302/

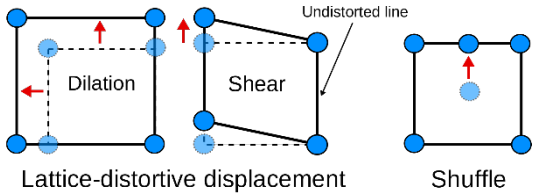
- Final evolution of $f_\beta(t)$ typically follows a sigmoid curve.
- Construction of Temperature-Time-Transformation (TTT) diagrams
- TTT diagrams give the times of start (1% transformed) and finish (99% transformed) of transformation (with respect to the equilibrium value)

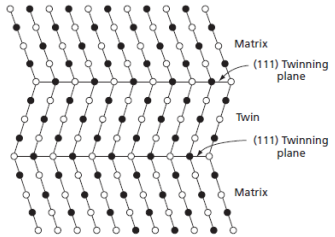
end of the sigmoid curve is governed by impingement, but also by equilibration of the matrix

Beginning of sigmoid curve is associated with an increase of $S_{\alpha\beta}$ interface (by nucleation and growth)

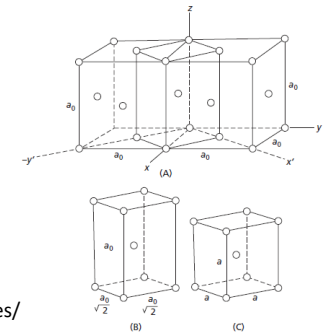
Displacive phase transformations

- Displacive phase transformations are diffusionless transformations based on a coordinated displacement of atoms with and without a lattice distortion
- The atomic movements are small (less than the interatomic distance)
- Examples: martensitic transformation and twinning
- These transformations are complex in their nature; they can occur upon cooling, isothermally or deformation induced
- Besides hardening of steels, these transformations are important for TRIP/TWIP steels (→ we will get back to this)





Twins

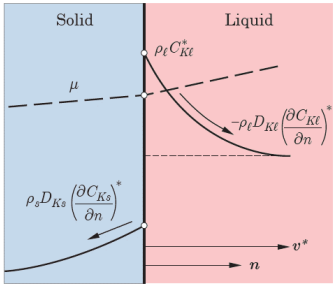


Martensite
Bain distortion

/R. Abbaschian et al., Physical Metallurgy Principles/

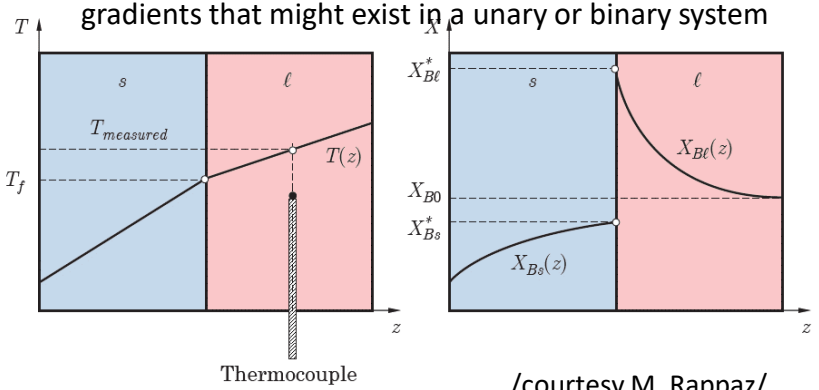
Solidification

- Solidification is an important step during the fabrication and processing of technical alloys (e.g. casting, welding, additive manufacturing…)
- The processes at the liquid/solid interface are of particular importance for the microstructure
  - Heat transport and local undercooling
  - Dissipation of solidification heat into the liquid and into the solid
  - Chemical diffusion and mass fluxes of species (in alloys)



Schematic of the composition and solute mass fluxes near the solid/liquid interface.

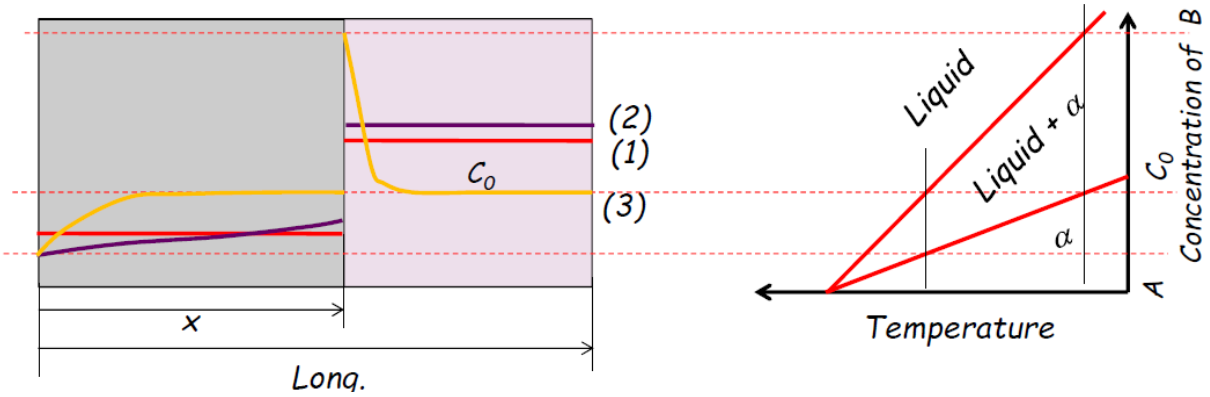
Schematic of the temperature gradients and solute gradients that might exist in a unary or binary system



/courtesy M. Rappaz/

Solidification

- In alloys, the chemical diffusion in the vicinity of the solid/liquid interface is the governing parameter
- Three cases possible

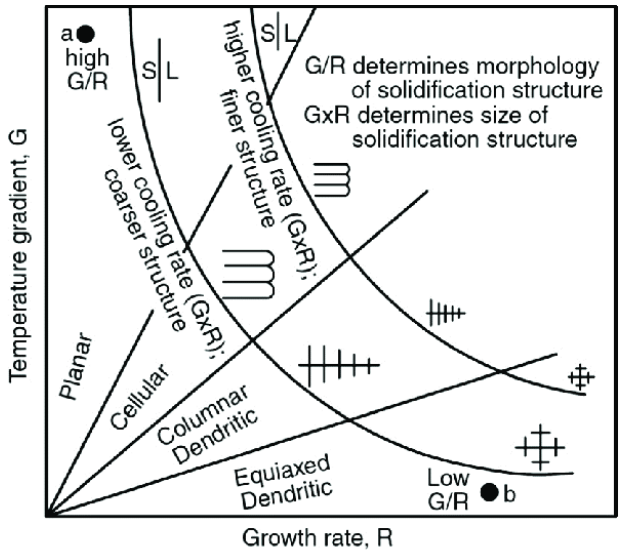


- *Global equilibrium, complete diffusion (Lever Rule) (1)*
- *Local equilibrium, no diffusion in the solid, complete diffusion in the liquid (Scheil-Gulliver) (2)*
- *Limited diffusion in liquid (solute diffusion layer) (3)*

/courtesy C. Cayron, MSE302/

Solidification

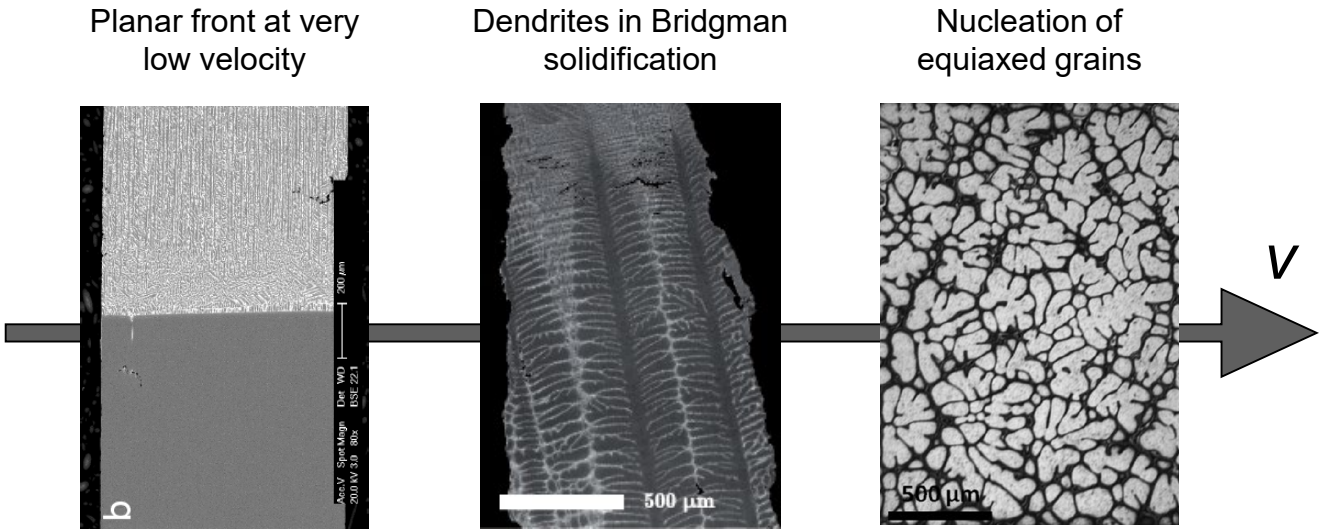
- Solidification microstructures are governed by
  - The thermal gradient G
  - The solidification front velocity or growth rate R
- Depending on the ratio G/R, a variety of solidification morphologies can be observed
  - Equiaxed dendritic
  - Columnar dendritic
  - Cellular
  - Planar
- The size of the solidification structure is determined by the product GxR



/S. Kou: Welding Metallurgy, 2nd ed., Wiley, New York, NY, 2003/

Solidification microstructures

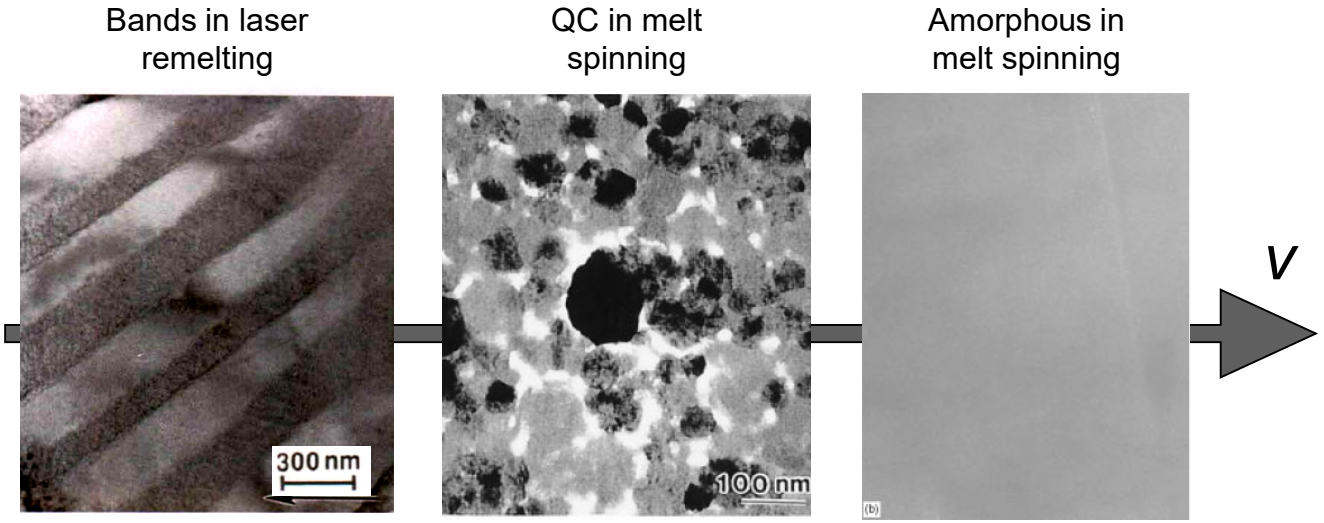
- As the speed of the isotherms during solidification is increased, one sees a transition from planar front growth (~mm/s), to cells, columnar dendrites and equiaxed grains. But the interface can still be considered at equilibrium



/courtesy M. Rappaz/

Solidification microstructures

- As the speed is increased, several phenomena can occur: formation of metastable phases, formation of new microstructures (bands), glass formation



/courtesy M. Rappaz/

Literature

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- R. Abbaschian, L. Abbaschian, R.E. Reed-Hill, Physical Metallurgy Principles
- G. Gottstein, Physical Foundations of Materials Science
- M. Rappaz, J.A. Dantzig, Solidification