

## D. Microstructure

No. |

Date 22. 1 . 19

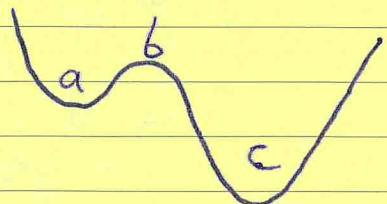
### Microscopy

- Reflected light microscopy requires the sample to be grinded and polished to achieve a flat, level surface.
- The surface must then be chemically etched
  - ↳ occurs faster at grain boundaries  $\Rightarrow$  appear darker
  - ↳ different phases etch at different rates
  - ↳ angle of reflected light depends on crystallographic orientation.
- Transmitted light microscopy requires an optically transparent sample
- Contrast arises from differences in absorption and birefringence.
- To improve resolution, lower  $\lambda$  needed  $\Rightarrow$  electron microscopy.
- SEMs require polished etched surfaces, but the sample must be a conductor otherwise charge will build up.
- Alternatively, atomic force microscopy does not depend on diffraction: a cantilever is scanned across a surface.

### Thermodynamics

- A phase diagram shows what the phase of a sample will be for some combination of variables (e.g. temp, pressure, composition).
- They show the equilibrium state, though the kinetics must also be considered.

- (a) Metastable equilibrium: stable to small perturbations but not the global minimum
- (b) Unstable equilibrium
- (c) Stable equilibrium: lowest energy state globally.



- The first law of thermodynamics is conservation of energy

$$\therefore dU = \delta q + \delta w$$

$\hookrightarrow$  i.e change in internal energy = heat added + work done on system.

$\hookrightarrow$  we have  $\delta q = C_v dT$  and  $\delta w = -P dV$

$$\therefore dU = C_v dT - P dV$$

$\hookrightarrow$  for systems at constant volume

$$dU = C_v dT \Rightarrow U = U_0 + \int_0^T C_v dT + \sum_i L_i$$

internal energy at 0K      heat required.

Latent heat  
of transitions  
up to T

- Most systems have constant pressure rather than volume, so we define the enthalpy as  $H = U + PV \Rightarrow dH = \delta q + V dP$

$$\therefore H = H_0 + \int_0^T C_p dT + \sum_i L_i$$

- Entropy is a measure of the disorder in a system:

- configurational disorder
- thermal vibrations.

- The second law of thermodynamics states that the entropy of the universe cannot decrease, i.e  $dS_{\text{univ}} > 0$

$\hookrightarrow$  for a reversible process,  $dS = 0$

$\hookrightarrow$  for a given system:  $dS \geq \frac{\delta q}{T}$   $\leftarrow dS_{\text{sys}}$  can be negative.

- The Gibbs free energy allows us to find equilibrium without considering the surroundings:  $G = H - TS$

$$\therefore dG = \delta q + V dP - T dS - S dT$$

or  $\cancel{dG = \delta q - T dS}$  for constant P, T.

$\hookrightarrow dG = 0$  for reversible changes at equilibrium

$\hookrightarrow dG < 0$  otherwise.

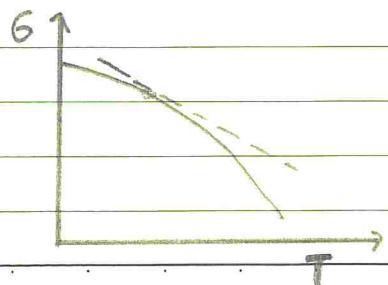
$\hookrightarrow G$  tends to a minimum at equilibrium

$\hookrightarrow \therefore$  if two phases are at equilibrium coexisting, G is the same

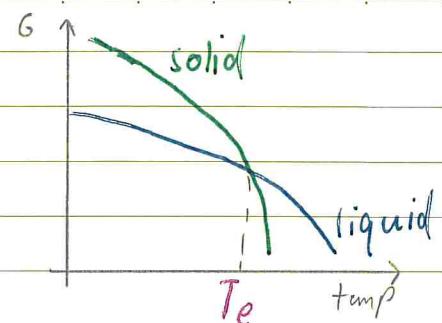
$\hookrightarrow G$  is decreasing in T:

- gradient =  $-S$

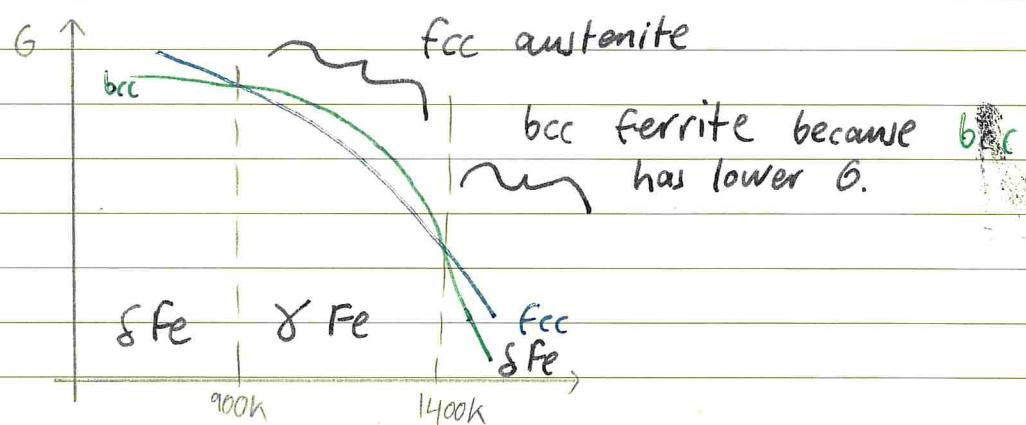
- as temp T, ST  $\therefore$  gradient more negative.



- For a pure substance, we can plot  $G$  against  $T$  for each phase.
- At  $T_e$ , both coexist at equilibrium
- Above and below  $T_e$ , one phase is preferred, though the other can exist metastably.
- Phase transitions are first order because latent heat means that there are discontinuous changes in entropy and enthalpy.

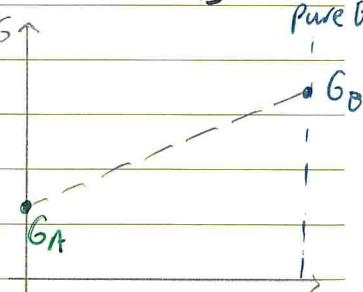


- Iron is unusual, because it transforms  $bcc \rightarrow fcc \rightarrow bcc$  as temp  $T$



### Variation of free energy with composition

- The free energy of a mechanical mixture of A and B is just the weighted average of  $G_A$  and  $G_B$
- Thus there is a linear dependence on the total  $G$  with composition.
- If some of this mixture were converted into a single solution phase, there would be:
  - $\Delta H$  because A-B interactions are different to A-A / B-B
  - $\Delta S$  from mixing.
- We can then write:  $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$   
i.e.  $(G_s - G_{\text{mm}}) = (H_s - H_{\text{mm}}) - T(S_s - S_{\text{mm}})$
- If  $\Delta G$  is negative, a solution is preferred to a mechanical mixture.

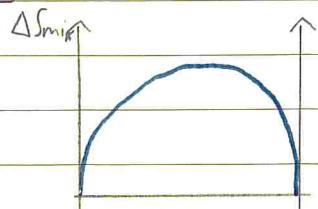
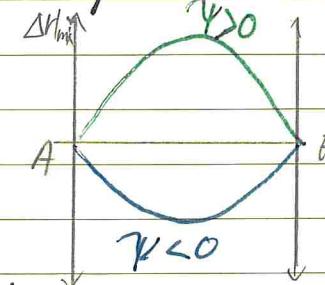


- The regular solution model can be used to estimate  $\Delta G_{\text{mix}}$ .
  - Estimating  $\Delta H_{\text{mix}}$  requires consideration of bond interactions.
    - Let the system have  $N$  atoms,  $X_A \equiv \text{Fraction A}$ ,  $X_B \equiv \text{Fraction B}$
    - $E_{AA}$  is the bond energy between A and its nearest neighbours (negative since work done to separate)
    - Assuming A and B have coordination  $Z$ , 1 mol of atoms has  $\frac{1}{2} N_A Z$  bonds
  - \*  $\therefore H_{\text{mix}} = \frac{N_A Z}{2} (X_A E_{AA} + X_B E_{BB})$
  - ↳ In solution,  $P(A-A \text{ bond}) = X_A^2$ ,  $P(A-B \text{ bond}) = 2X_A X_B$
  - $\therefore H_s = \frac{N_A Z}{2} (X_A^2 E_{AA} + X_B^2 E_{BB} + 2X_A X_B E_{AB})$
  - ↳ Then the enthalpy of mixing is given by:
- $\Delta H_{\text{mix}} = X_A X_B \gamma$ , where  $\gamma \equiv \frac{1}{2} N_A Z (2E_{AB} - E_{AA} - E_{BB})$
- $\gamma$  is the interaction parameter, constant for a given system
- $\gamma = 0$  is an ideal solution with random arrangement
  - $\gamma < 0$  gives negative deviations from ideality, tending towards mixing
  - $\gamma > 0$  encourages segregation.
- ↳  $\Delta H_{\text{mix}}$  is symmetrical about  $X_A = X_B = 1/2$

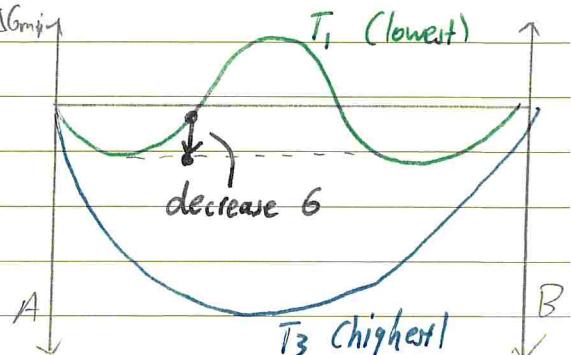
- To model  $\Delta S_{\text{mix}}$ , we only consider the changes in configuration
- $S = k \ln \Omega$ , where  $\Omega \equiv n$  ways of arranging.
- $\Omega_{\text{mm}} = 1$  because phases are purely A or B
- $\Omega_s = \frac{N_A!}{(X_A N_A)! ((1-X_A) N_A)!}$  where  $N_A$  is Avogadro's No.

$$\therefore \Delta S_{\text{mix}} \approx k \ln \Omega_s \approx -R(X_A \ln X_A + X_B \ln X_B)$$

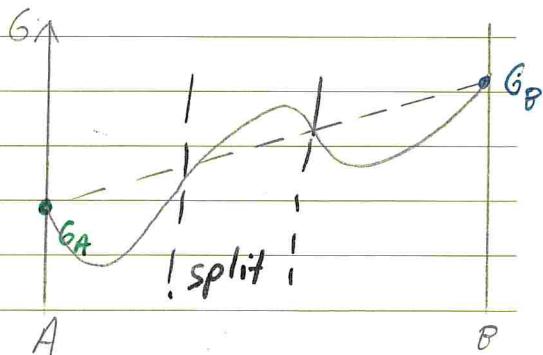
↳  $\Delta S_{\text{mix}} > 0$  always, because making a solution increases disorder.



- Then we have  $\Delta G_{\text{mix}} = X_A X_B \gamma + RT(X_A \ln X_A + X_B \ln X_B)$
- if  $\gamma \leq 0$ ,  $\Delta H_{\text{mix}} \leq 0 \Rightarrow \Delta G_{\text{mix}} < 0$  (because  $\Delta S_{\text{mix}} > 0$ ).  
i.e. the system will form a solution
- if  $\gamma > 0$ ,  $\Delta G_{\text{mix}}$  depends on the temperature.  
  - for low  $T$  high  $T$  there is complete solution
- \*  $\hookrightarrow$  for low  $T$ ,  $\Delta G_{\text{mix}}$  has two minima: for  $X_B$  between minima,  $G$  can be lowered by forming a weighted average of two phases.  
  - $\hookrightarrow$  i.e. mixture of two distinct phases
  - $\hookrightarrow$  as temp cools further, the phases become more pure.

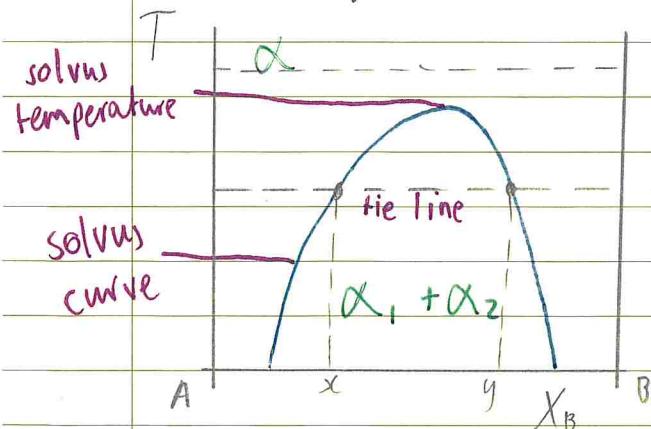


- We can find  $G_s$  using  $G_s = \Delta G_{\text{mix}} + G_{\text{mm}}$
- In a certain range,  $G_s$  can be lowered by moving towards a mechanical mixture.



### Equilibrium phase diagrams

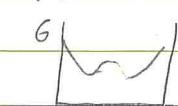
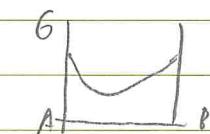
- This maps what phases will exist at each composition / temperature.



- At high temps, there is a single phase (complete mixing)
- Below the solvus temperature, the system exists in two phases, whose compositions are given by  $x$  and  $y$  (where the tie line intersects the solvus).

- The solvus temp can be found as

$$\frac{\partial^2 G}{\partial x^2} \Big|_{x=0.5} = 0$$

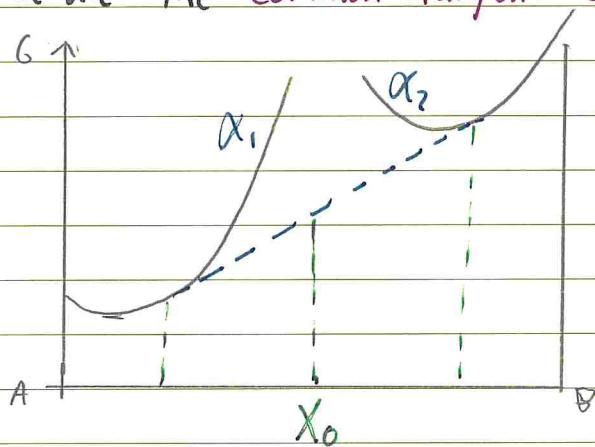


- The proportion of each phase, given their compositions, can be found with the lever rule, i.e a weighted sum calculation:

$$(\alpha_1 \text{ comp}) \times (\alpha_1 \text{ prop}) + (\alpha_2 \text{ comp}) \times (\alpha_2 \text{ prop}) = \text{total comp}$$

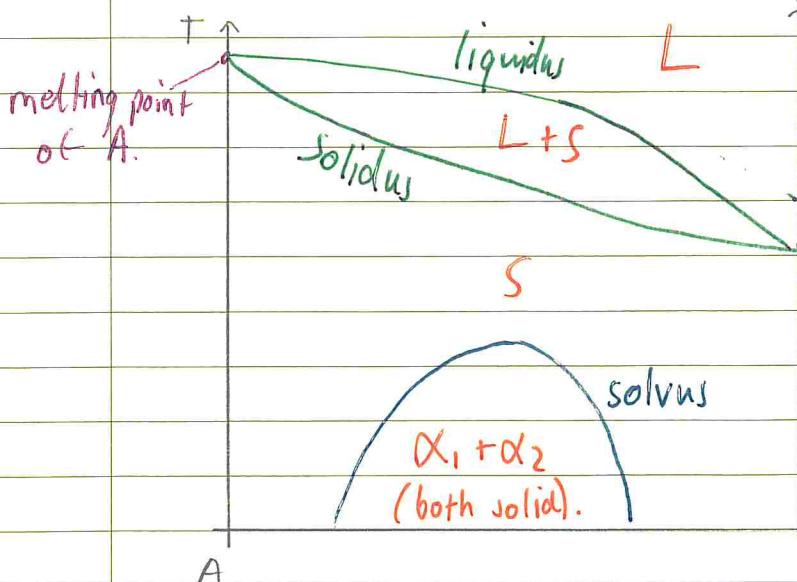
i.e  $x_1 f_1 + x_2 f_2 = x_0(f_1 + f_2)$ .

- If we have the free energies for each phase, we can construct the overall free energy as the weighted sum.
- ↳ equilibrium compositions are NOT weighted avg of minima  
 ↳ instead use the common-tangent construction



## Solidification

- Solidification of a liquid solution will occur over a range of temperatures - the phase diagram depends on solid solubility.



At high T, only liquid present

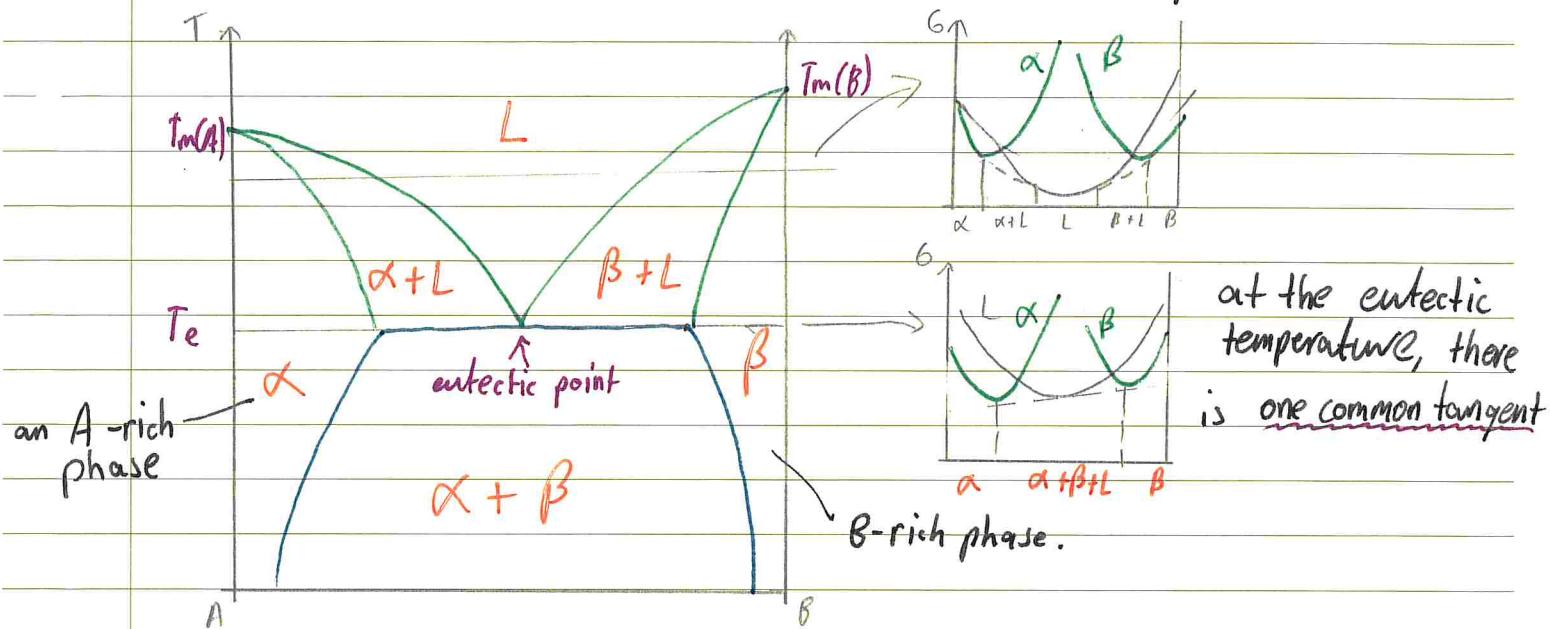
At a lower T, there will be some S and some L:  
 comp. found using lever rule.

For some temperature range, there will be complete solid solubility for any composition.



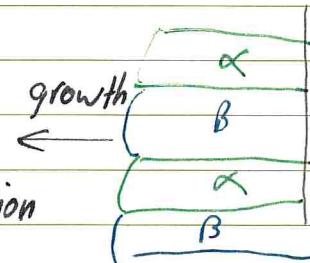
## Incomplete solid solubility

- It may be the case (if  $\gamma > 0$ ) that there is no temp. range with complete solid solubility across all compositions.
- This is a **Eutectic system**: there is a **eutectic point** such that  $L \rightarrow \alpha + \beta$ , i.e. a liquid solidifies directly into two solid phases.  
 ↳ i.e. the solvus meets the solidus and liquidus



- The phases show **cooperative growth**:

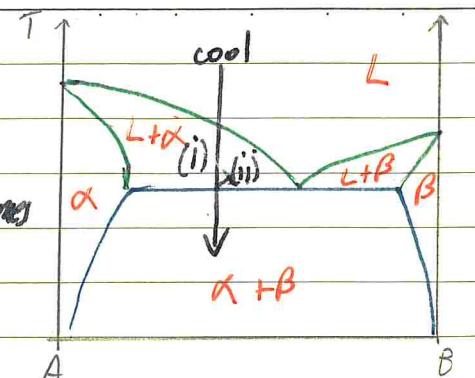
- when some  $\alpha$  forms,  $B$  atoms are rejected
- this encourages  $\beta$  to form adjacent to  $\alpha$
- results in **lamellae** as the solute redistributes
- gives a stripy cross-section
- when cooled rapidly, less solute redistribution occurs so the layers are finer.



- Producing an alloy with the eutectic composition lowers the melting point, e.g. Pb-Sn in solder
- Non-eutectic compositions will become mushy before freezing.

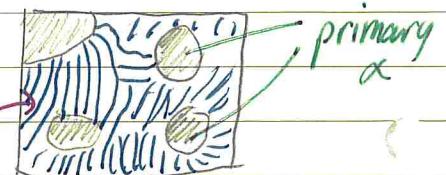
Even non-eutectic initial compositions result in eutectic microstructure.

- after passing the liquidus, primary  $\alpha$  starts to form. The remaining liquid becomes richer in  $B$
- at the solidus, the remaining liquid is at the eutectic comp.



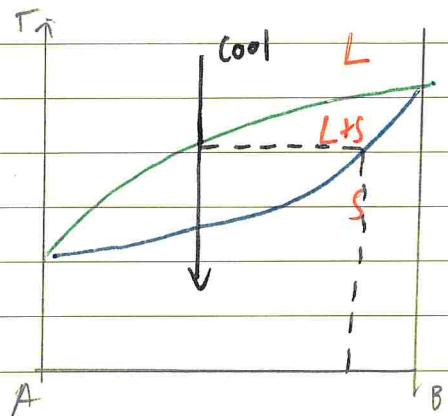
$\hookrightarrow$  final microstructure:  $\alpha + (\alpha + \beta)$

$\hookrightarrow$  we often assume that  $\alpha$  remains at the eutectic comp.



### Coring

- During slow cooling through a 2-phase region, the first solid that forms will be  $B$ -rich.

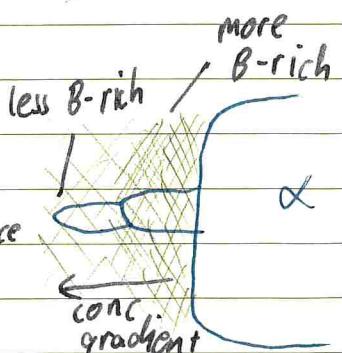


- As cooling continues (in equilibrium), the composition of the solid changes but remains uniform due to diffusion.

- However, if equilibrium is not maintained, the first solid that forms will be 'locked' as relatively  $B$ -rich cores
  - $\hookrightarrow$  the remaining liquid will be richer in  $A$  than diagram predicts
  - $\hookrightarrow$  the exact composition of the cores depends on diffusion

### Dendrites

- When an  $A$ -rich  $\alpha$  phase forms, it is surrounded by a  $B$ -rich region, whose conc decreases with distance

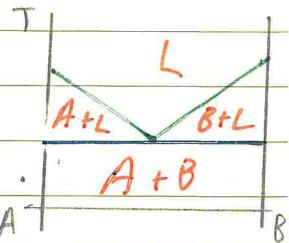


- A random proturbation will be in a less  $B$ -rich env., so will grow rapidly to form dendrites.

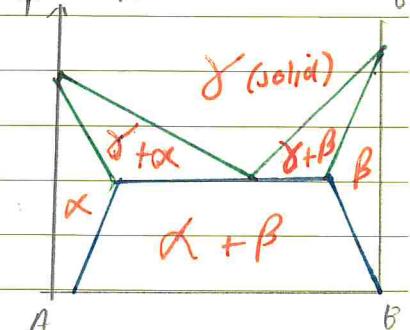
- Dendrites favour crystallographic directions, leading to tree-like dendritic structures.

## Other phase diagrams

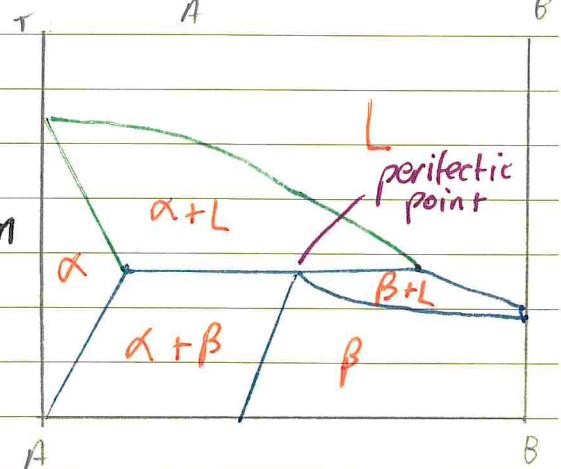
- A eutectic need not involve solid solution ( $\alpha$  or  $\beta$ ), in which case two pure phases will exist



- A eutectoid involves only solids
- At the eutectoid point, there is a eutectoid transformation:  $\gamma(s) \rightarrow \alpha(s) + \beta(s)$

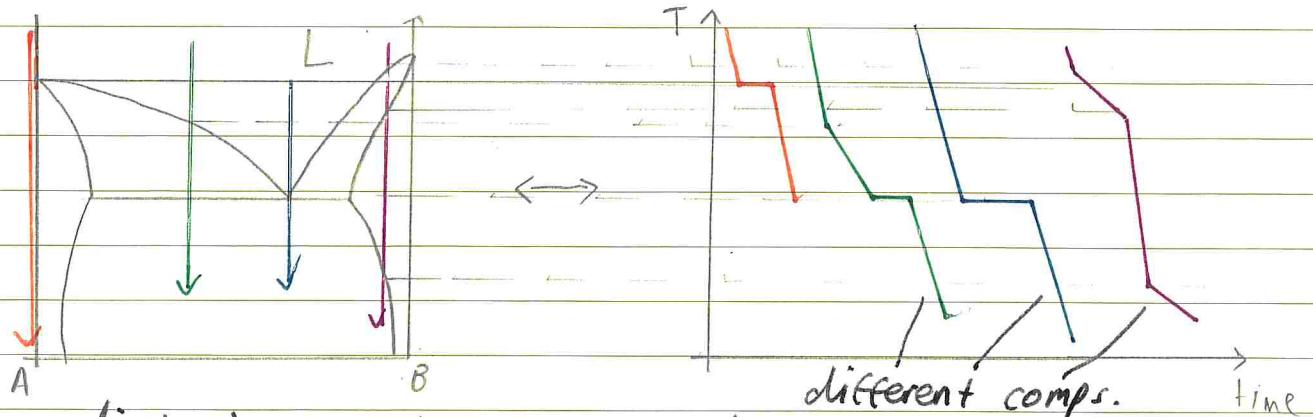


- A peritectic reaction involves a solid solid+liquid phase becoming a different solid phase:  $\alpha + L \rightarrow \beta$
- Near the peritectic temp, the reaction slows down because  $\beta$  forms around  $\alpha$ , so  $\alpha$  is separated from  $L$ .



## Determining phase diagrams

- Often determined by examining cooling curves for different comps.



- Gradient changes when crossing a phase; the gradient in an  $\alpha + L$  region will be shallower because some solidification occurs
- Flat lines will either be pure or eutectic.

# Diffusion and Phase Growth

- **Interstitial diffusion** is when small atoms move between interstices in a lattice - it is relatively fast.
- Large atoms can only move via **substitutional diffusion** from one vacancy to the next.
- Fick's 2<sup>nd</sup> law describes non-steady-state diffusion:

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} \Rightarrow x \sim \sqrt{Dt}$$

## Nucleation

- Nucleation requires a **driving force** (i.e negative  $\Delta G$ ).
- Using the fact that  $\Delta G=0$  at  $T_e$  (e.g. during melting), we have:  $\Delta H = T_e \Delta S \Rightarrow \Delta G = \Delta S(T_e - T)$   
 $= \frac{\Delta H \Delta T}{T_e}$

↳ driving force  $\propto$  deviation from equilibrium temp  
↳ assumes both phases have same heat capacity

- Consider the case of **homogeneous nucleation** when there are no impurities to form on. The work done to form a spherical nucleus of radius  $r$  is:  $W_n = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma$

↳  $\Delta G_v$  is the driving force per unit volume (negative)

↳  $\gamma$  is the surface energy term (positive).

↳ the **critical radius**  $r^*$  maximizes  $W_n$ :

$$r^* = -\frac{2\gamma}{\Delta G_v} \Rightarrow W_n^* = \frac{16\pi}{3} \frac{\gamma^3}{\Delta G_v^2}$$

↳ for  $r < r^*$ , nucleus shrinks. For  $r > r^*$ , nucleus grows.

↳ at  $T_e$ , i.e.  $\Delta G_v \rightarrow 0$ ,  $r^*$  and  $W_n^* \rightarrow \infty$  so nucleation is impossible.

- In reality, nucleation will involve strain with the surrounding solid, with a strain energy  $U$  per unit volume.

$$W_n = \frac{4}{3} \pi r^3 (\Delta G_v + U) + 4\pi r^2 Y$$

$\hookrightarrow U > 0$  so driving force reduced

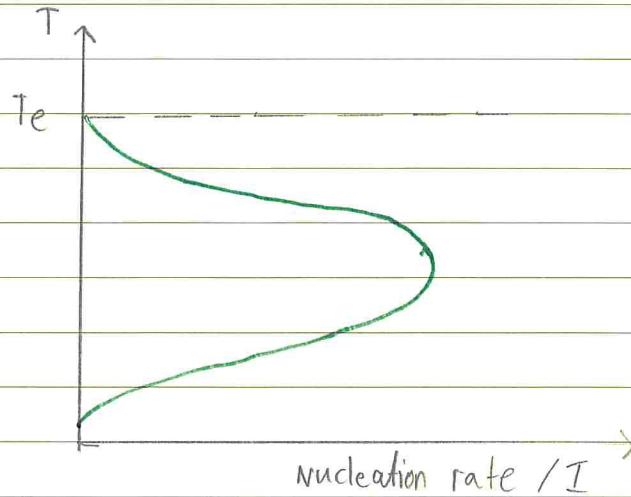
$\hookrightarrow$  i.e. strain increases  $r^*$  and  $W_n^*$ , hindering nucleation

- The rate of nucleation is proportional to:

- population of critical nuclei  $\propto \exp(-W_n^*/kT)$   
 - rate of atomic addition to a nucleus  $\propto \exp(-Q/kT)$

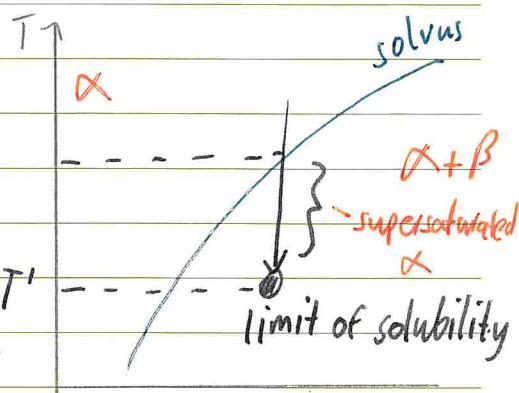
- Thus the **nucleation frequency** takes the form

$$I = C_n \exp\left(-\frac{(W_n^* + Q)}{kT}\right)$$



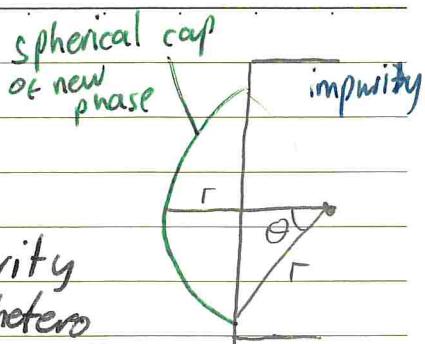
- At  $T_c$  there is no nucleation because  $\Delta G_v = 0$ .
- Below  $T_c$ ,  $\Delta G_v \uparrow$  so  $W_n^*$ . At some  $T$ ,  $I$  will be maximised.
- Reducing  $T$  further, atomic mobility becomes slow (low  $kT$ ) so the nucleation rate decreases.

- Because of the strain, it may be difficult to precipitate one solid phase in another.
- Consider cooling an A-rich  $\alpha$  phase below the solvus.  $\beta$  should precipitate according to the diagram, but may not.
- Thus  $\alpha$  exists with an excess of  $\beta$  dissolved  
 $\hookrightarrow$  supersaturated solid solution
- Eventually at some  $T'$ , the limit of solubility of  $\beta$  in  $\alpha$  will be reached and  $\beta$  must precipitate.



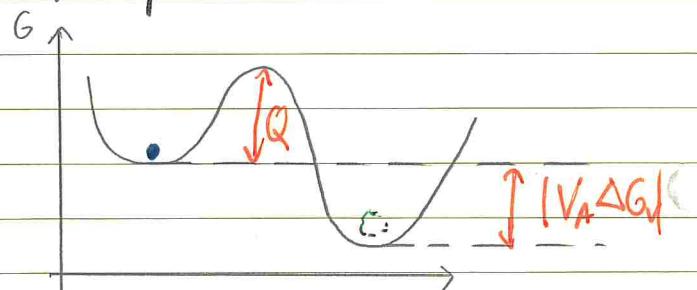
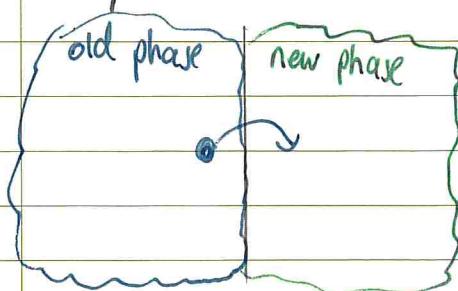
## Heterogeneous nucleation

- Nucleation can be catalysed by impurities or container walls.
- Modelled by spherical caps forming on the impurity
  - ↳  $r^*$  remains the same for homo vs hetero
  - ↳ but  $W_n^*_{\text{hetero}} = W_n^*_{\text{homo}} \times \text{volume fraction}$
  - ↳ i.e. less work needs to be done for heterogeneous nucleation
- Heterogeneous nucleation occurs at preferential sites:
  - grain boundaries
  - surfaces
  - defects
  - triple points



## Growth of a new phase

- Ignoring the limits of long term diffusion, the rate of growth depends on atomic jumps at the phase interface



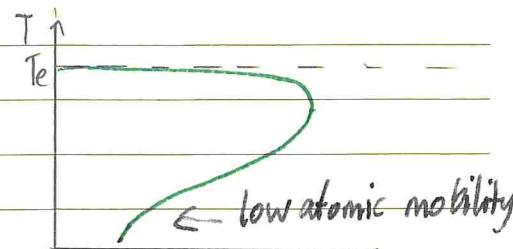
- There is a driving force of  $V_A \Delta G_v$  ( $V_A$  = volume of atom), but an energy barrier of  $Q$ . The growth rate  $v$  is proportional to  $(\text{old} \rightarrow \text{new})$  jumps minus  $(\text{new} \rightarrow \text{old})$

$$v = C_g \exp\left(-\frac{Q}{kT}\right) \left[ 1 - \exp\left(\frac{V_A \Delta G_v}{kT}\right) \right]$$

• As before,  $T = T_e \Rightarrow v=0$

• But small deviations can result in large growth rates

↳ if nuclei are present, only small driving forces needed

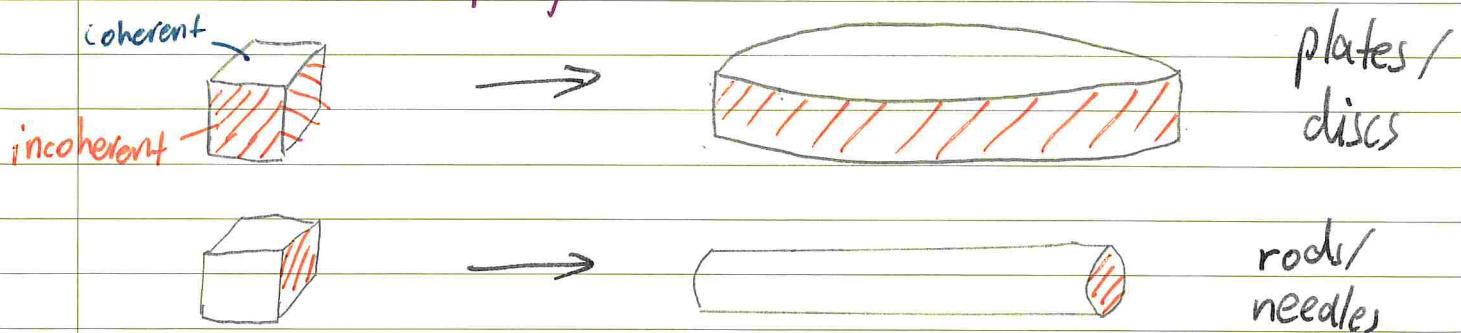


## Solid-Solid Interfaces

- The interface between a solid phase  $\alpha$  and a solid  $\beta$  nucleating in  $\alpha$  can be of various types:
  - **coherent**: there is perfect alignment of  $\alpha$  and  $\beta$  lattices, so low energy of nucleation.
  - **strained coherent**: lattices match in alignment but size may be different, resulting in elastic strain proportional to particle size.
  - **semi-coherent**: form from growing strained coherent interfaces. There will be **dislocations** (e.g. extra/missing atoms in the lattice) which add to the energy.
  - **incoherent**: no matching, high energy.

- Interfacial energy strongly affects microstructure

↳ precipitate grows to maximise the coherent surface area  
 ↳ i.e. anisotropic growth

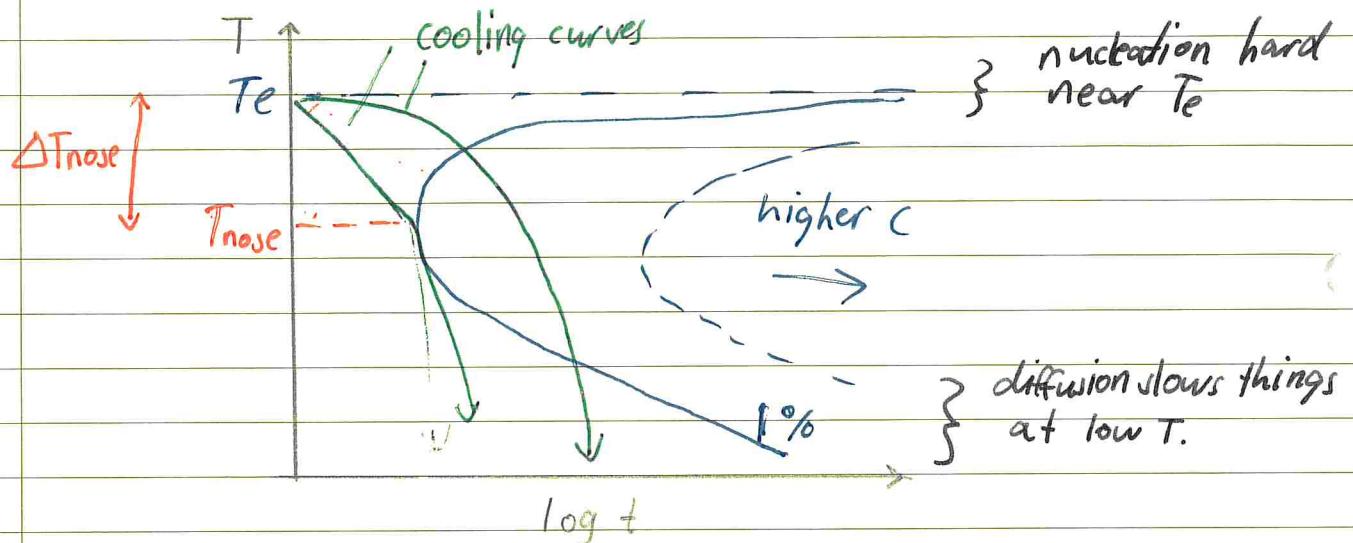


- If a solid solution is left to cool for millions of years (e.g. in meteors) then it may show the **Widmanstätten microstructure**
  - e.g. bcc precipitating out of an fcc matrix.
  - bcc and fcc will want to align along close-packed directions
  - leads to a microstructure with an angled grid.

$$\{110\}_{\text{bcc}} \parallel \{111\}_{\text{fcc}} \Leftrightarrow \langle\bar{1}11\rangle_{\text{bcc}} \parallel \langle1\bar{1}0\rangle_{\text{fcc}}$$

## TTT diagrams

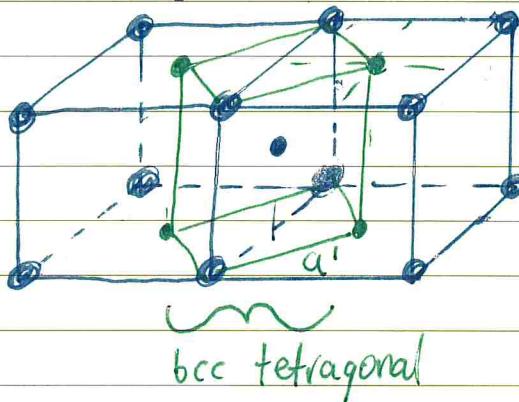
- A TTT diagram plots the time taken to form a certain composition  $\alpha$  as a function of temperature.  
 ↳ contours of  $t$  known as C-curves.



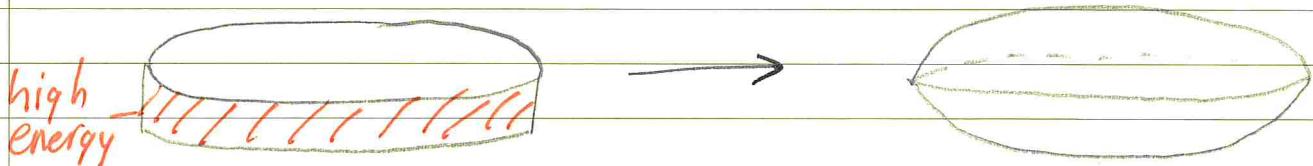
- This TTT diagram is strictly for isothermal transformation, but we can use it to estimate the critical quench rate.
  - Continuous cooling follows  $e^{-kt}$ , which becomes like  $\square$  on the log scale.
  - The critical quench rate is the cooling curve that just touches the nose of the C-curve.
  - For small  $C$ , we can approximate this as
- $$\text{critical cooling rate} = \dot{T}_{\text{crit}} \approx \frac{\Delta T_{\text{nose}}}{t_{\text{nose}}}$$
- This cooling will produce a metastable microstructure.

## Displacive phase transitions

- In these transformations, diffusion is not required.
- For example, martensite (bcc tetragonal) forms within fcc austenite.



- martensite forms when the fcc cell shrinks slightly vertically and  $a'$  lengthens slightly.
- leads to a lenticular morphology.



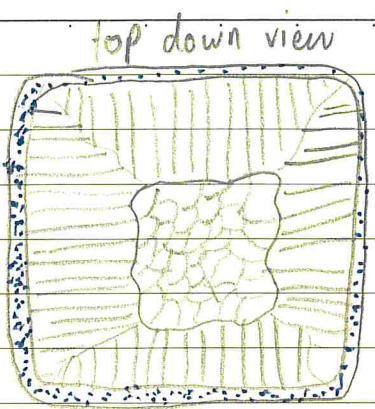
## Materials processing

- The cooling rate of a substance can be modified by changing the environment in which it is cooled:
  - air (low)
  - oil (~~high~~ moderate)
  - ice water (high).
- Faster cooling  $\Rightarrow$  larger undercooling  $\Delta T \Rightarrow$  large  $\Delta G$  (driving force for nucleation)  $\Rightarrow$  many stable nuclei  $\Rightarrow$  small grains.

## Casting

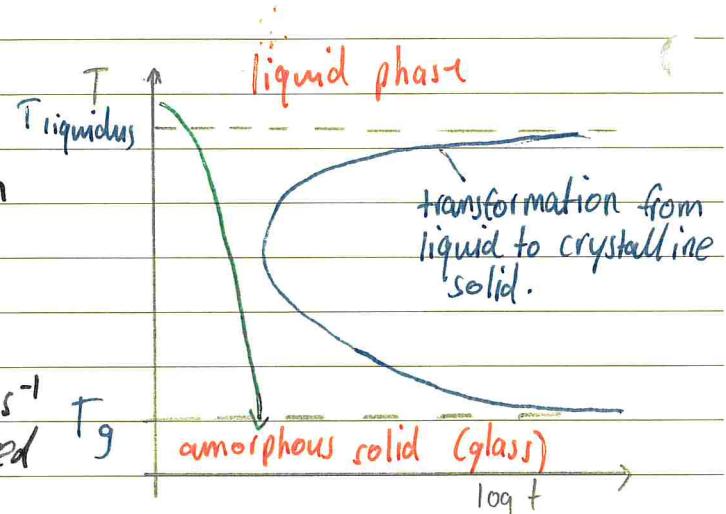
- During casting, liquid metal is poured into a mould and left to solidify.
- The mould walls are sites of hetero. nucleation and have a lower faster cooling rate, leading to smaller grains at the edge.

- Small **equiaxed** grains around the edge
- Away from the boundary, slower cooling rate means that there is more time for diffusion, forming **columnar** grains.
- In the centre, cooling is slowest  
↳ large equiaxed grains form.
- If there are preferred crystallographic orientations, grains may show some alignment.



### Glass formation

- If cooling is fast enough, we can avoid significant crystallisation, leading to an **amorphous solid** structure.
- Metallic glass requires  $10^6 \text{ K s}^{-1}$  cooling, which can be achieved by melt spinning.
- Alternatively, certain alloys need lower cooling rates because atomic mismatches can prevent crystallisation.
- Metallic glasses are strong and very closely-packed.  
↳ little elastic energy lost on contact because it doesn't deform much.  
↳ can thus be applied in golf clubs etc.



### Eutectics and eutectoids

- The **interlamellar spacing** in a eutectic depends on the surrounding temperature and thus the rate of cooling.
- For rapid cooling, lower T  $\Rightarrow$  slower diffusion. Also, with lower T there is more undercooling  $\Rightarrow$  higher driving force to form interfaces between lamellae.

- If  $\lambda \equiv$  interlamellar spacing, there will be  $1/\lambda$  layers per  $m^3$  of eutectic, and thus  $\frac{2}{\lambda} m^2$  of  $\alpha/\beta$  interface.

↳  $\Delta G_{\text{total}} = \Delta G_v + \frac{2}{\lambda} \gamma_{\alpha\beta}$  energy per area of interface

driving force given by  $\Delta G_v = \frac{\Delta H \Delta T}{T_e}$  - undercooling

- ↳ spacing is minimised when  $\Delta G_{\text{total}} = 0$

$$\Rightarrow \lambda^* = -\frac{2\gamma_{\alpha\beta}}{G_v} = -\frac{2\gamma_{\alpha\beta} T_e}{\Delta H \Delta T}$$

↳ i.e. for faster cooling (larger  $\Delta T$ ),  $\lambda^*$  decreases.

## Deformation processing

- Rolling** makes a slab of metal thinner by passing it through smooth rollers.
  - hot rolling leads to smaller grains and an oxide coating
  - cold rolling increases hardness because it introduces defects, but is more difficult and thus more expensive.
- Forging** is the mechanical deformation of a single piece of metal
  - good mechanical properties: strain hardening due to plastic deformation of the metal
- Extrusion** is when hot metal is forced through an aperture
- Drawing** involves pulling warm metal through an aperture
  - can produce very fine wires
  - metal can fracture if tension too high.
- Deep drawing** involves punching the metal in a die; care must be taken to avoid fracturing.

# The Fe-C system

- Rather than considering a true equilibrium phase diagram, which would involve graphite, we consider the quasi-equilibrium diagram that involves **cementite** ( $\text{Fe}_3\text{C}$ ).
- Cast irons are alloys with 2-4 wt% C.
  - microstructures influenced by the liquid  $\rightarrow \gamma + \text{Fe}_3\text{C}$  (austenite + cementite) eutectic transformation.
  - carbon will be either in cementite or graphite.
- Steels have < 1.5 wt% C: microstructure is determined by proximity to the eutectoid composition of 0.80 wt% C.

- Eutectoid:  $\text{Fe} - 0.8\text{wt\% C}$



i.e. austenite  $\rightarrow$  ferrite + cementite (lamellae).  
pearlite

- Hypereutectoid steel:  $\text{Fe} - 1.0\text{wt\% C}$

- on cooling from 1000°C, we start with grains of  $\gamma$



- at the phase boundary,  $\text{Fe}_3\text{C}$  precipitates on heterogeneous nucleation sites



- below the eutectoid temp,



- Hypo-eutectoid steel:  $\text{Fe} - 0.1\text{wt\% C}$

- ferrite ( $\alpha$ ) initially precipitates on grain boundaries, but eventually forms large grains near  $T_E$

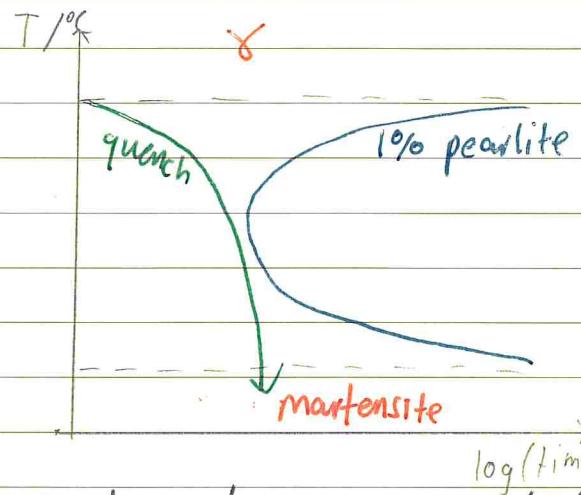
- at  $T_E$ , remaining  $\gamma$  undergoes the eutectoid transition to form pearlite

- with lower zooms, this pearlite may appear uniform

- Steels (especially hypo-eutectoid) are widely used because they are cheap, versatile, and generally have good mechanical properties

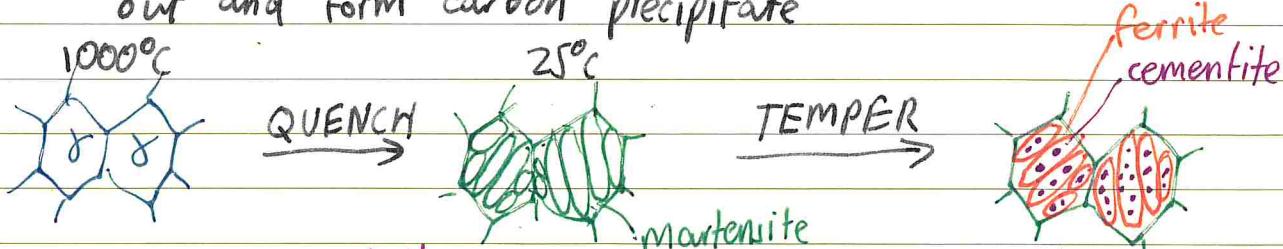
## Rapid cooling of steel

- The eutectoid transformation can be avoided by quenching.



- In this case, Martensite forms
  - metastable phase that is a supersaturated solid solution
  - more C-rich than phase diagram would predict.
  - formed by a diffusionless displacive phase transition.

- Carbon atoms are located in the octahedral interstices of the body-centred tetragonal Fe lattice
  - highly strained, hence martensite is very hard and brittle.
- Martensite is too brittle to be usable, so it must be tempered:
  - annealed at 350°C to allow trapped carbon to diffuse out and form carbon precipitate

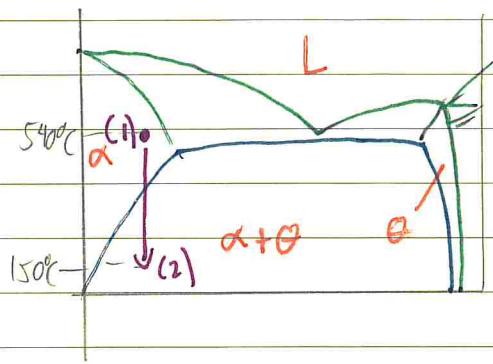


- result is laths of ferrite containing small precipitates of cementite
  - i.e same position on equilibrium phase diagram, but NOT pearlite.
  - result is harder than pearlite but less brittle than un-tempered martensite.

# Al-Cu alloys

- Aerospace requires high-strength low density materials.  
Aluminium-Copper alloys are often used.
- Below ~55% Cu, the phase diagram is eutectic
  - CCP  $\alpha$  (Al-rich) to the left of the solvus
  - compound  $\Theta \approx Al_2Cu$  to the right.
- Similar to steels, eutectic microstructures can form, e.g.  
 $\alpha$  dendrites in  $\alpha + \Theta$  eutectic intergrowths (quite fine).
- But these alloys are not very strong - we need finer precipitates.

- Anneal ( $\sim 540^\circ C$ ) at 4 wt% Cu al by  
 $\hookrightarrow$  all Cu will be in solution

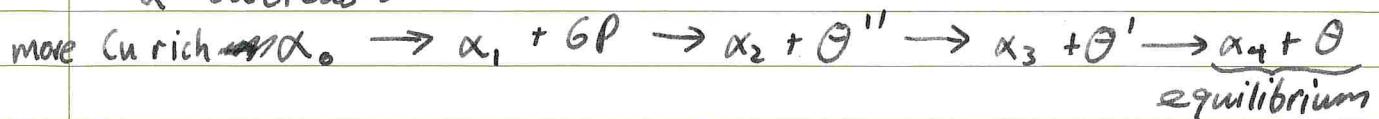


- Quench to obtain a supersaturated solid solution of single phase  $\alpha$   
 $\hookrightarrow$  more Cu than phase diagram predicts,  
so strong driving force.
- Anneal ( $\sim 150^\circ C$ ) to develop precipitates.

- Because  $\Theta$  has a complex tetragonal structure, any new precipitates will have high energy incoherent interfaces.  
 $\hookrightarrow$  metastable intermediate phases form first

- look like lines on a SEM scan.
1. Guinier-Preston (GP) zones form first by homogeneous nucleation.  
They are tiny (1-10nm) and form discs
  2.  $\Theta''$  precipitates heterogeneously onto the GP zones. It forms a coherent tetragonal crystal, but with sides that are more strained so it forms discs.
  3.  $\Theta'$  is a tetragonal structure with 2 incoherent sides, so can only nucleate heterogeneously on defects.
  4.  $\Theta$  is a tetragonal I crystal that is completely incoherent and can only precipitate on grain boundaries / interfaces. Tends to form spherically.

- During each of these transitions, Gibbs free energy is reduced.
- As  $\theta''$ ,  $\theta'$  and  $\theta$  precipitate out, the Cu content of remaining  $\alpha$  decreases:



- This path is followed because its transitions have much lower work of nucleation, compared to immediately nucleating highly incoherent  $\theta$  within the  $\alpha$  matrix.
- The best mechanical properties are associated with a fine dispersal of  $\theta''$  and  $\theta'$ .
- We can determine the necessary annealing conditions with a TTT diagram.

