

# D. Microstructure

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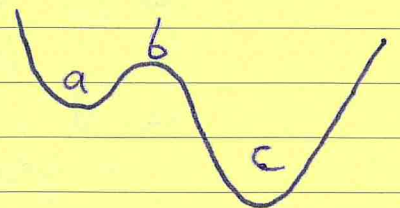
## Microscopy

- 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

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

↳ i.e. change in internal energy = heat added + work done on system.

↳ we have  $\delta q = CdT$  and  $\delta w = -PdV$

$$\therefore dU = CdT - PdV$$

↳ for systems at constant volume

$$dU = C_v dT \Rightarrow U = U_0 + \int_0^{T_1} C_v dT + \sum_i L_i$$

internal energy at 0K      heat required.

Latent heat of transitions up to  $T_1$

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

$$\therefore H = H_0 + \int_0^{T_1} C_p dT + \sum_i L_i$$

- 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.  $dS_{univ} \geq 0$

↳ for a reversible process,  $dS = 0$

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

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

$$\therefore dG = \delta q + VdP - Tds - SdT$$

or  $dG = \delta q - Tds$  for constant  $P, T$ .

↳  $dG = 0$  for reversible changes at equilibrium

↳  $dG < 0$  otherwise.

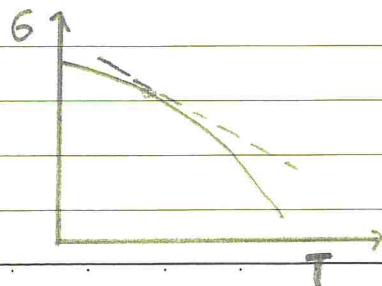
↳  $G$  tends to a minimum at equilibrium

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

↳  $G$  is decreasing in  $T$ :

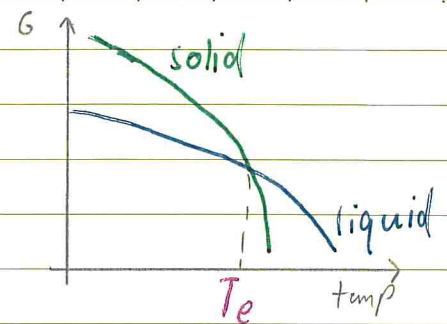
- gradient =  $-S$

- as temp  $T$ ,  $S \uparrow \therefore$  gradient + more negative.

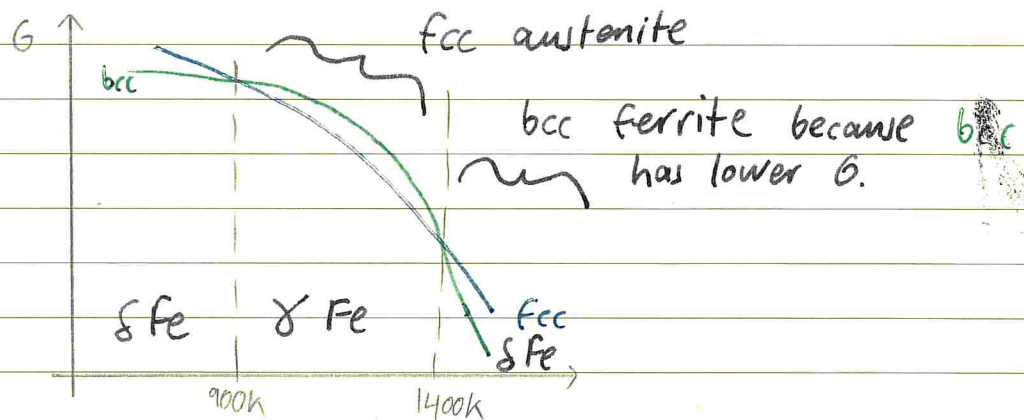




- For a pure substance, we can plot  $G$  against  $T$  for each phase.
- At  $T_e$ , both coexist at equilibrium
- Above and below  $T_e$ , one phase is preferred, though the other can exist metastably.
- Phase transitions are first order because latent heat means that there are discontinuous changes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

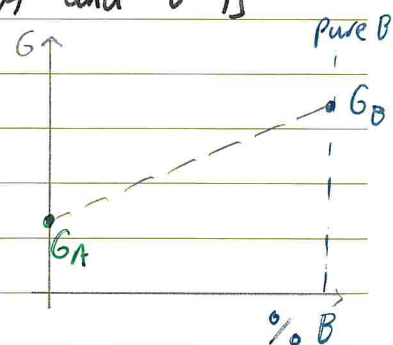


- Iron is unusual, because it transforms  $bcc \rightarrow fcc \rightarrow bcc$  as temp  $\uparrow$



### 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:  $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$   
i.e.  $(G_s - G_{mm}) = (H_s - H_{mm}) - T(S_s - S_{mm})$
- If  $\Delta G$  is negative, a solution is preferred to a mechanical mixture.

- The **regular solution model** can be used to estimate  $\Delta G_{mix}$ .
- Estimating  $\Delta H_{mix}$  requires consideration of bond interactions.
  - ↳ Let the system have  $N$  atoms,  $X_A \equiv$  fraction A,  $X_B \equiv$  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

$$\therefore H_{mm} = \frac{N_A Z}{2} (X_A E_{AA} + X_B E_{BB})$$

↳ In solution,  $P(A-A \text{ bond}) = X_A^2$ ,  $P(A-B \text{ bond}) = 2X_A X_B$

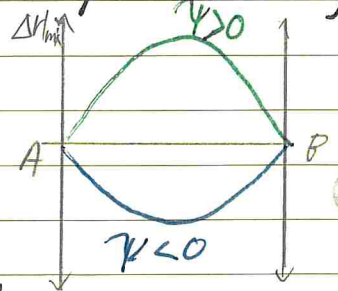
$$\therefore H_s = \frac{N_A Z}{2} (X_A^2 E_{AA} + X_B^2 E_{BB} + 2X_A X_B E_{AB})$$

↳ Then the **enthalpy of mixing** is given by:

$$\Delta H_{mix} = X_A X_B \psi, \quad \text{where } \psi \equiv \frac{1}{2} N_A Z (2E_{AB} - E_{AA} - E_{BB})$$

- $-\psi$  is the **interaction parameter**, constant for a given system
- $-\psi = 0$  is an **ideal solution** with random arrangement
- $-\psi < 0$  gives **negative deviations from ideality**, tending towards mixing
- $-\psi > 0$  encourages segregation.

↳  $\Delta H_{mix}$  is symmetrical about  $X_A = X_B = \frac{1}{2}$



- To model  $\Delta S_{mix}$ , we only consider the changes in configuration

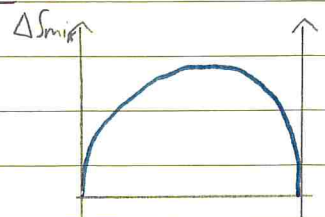
↳  $S = k \ln \Omega$ , where  $\Omega \equiv$  n ways of arranging.

↳  $\Omega_{mm} = 1$  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.

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

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





Then we have  $\Delta G_{mix} = X_A X_B \Psi + RT (X_A \ln X_A + X_B \ln X_B)$

- if  $\Psi \leq 0$ ,  $\Delta H_{mix} \leq 0 \Rightarrow \Delta G_{mix} < 0$  (because  $\Delta S_{mix} > 0$ ).

i.e the system will form a solution

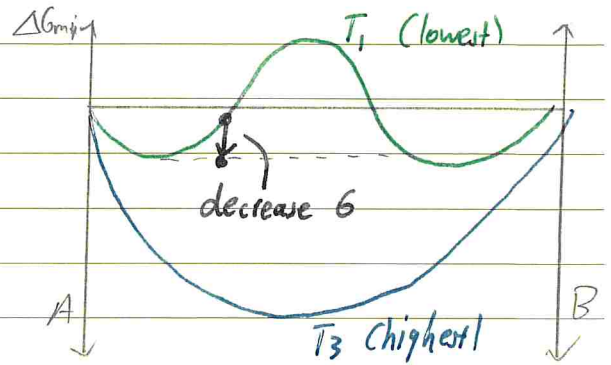
- if  $\Psi > 0$ ,  $\Delta G_{mix}$  depends on the temperature.

↳ for lower & high T there is complete solution

\* ↳ for low T,  $\Delta G_{mix}$  has two minima: for  $X_B$  between minima, G can be lowered by forming a weighted average of two phases.

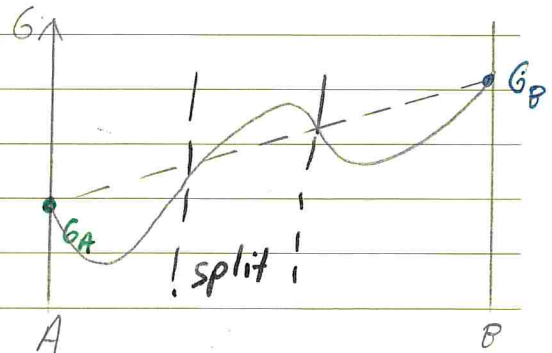
↳ i.e mixture of two distinct phases

↳ as temp cools further, the phases become more pure.



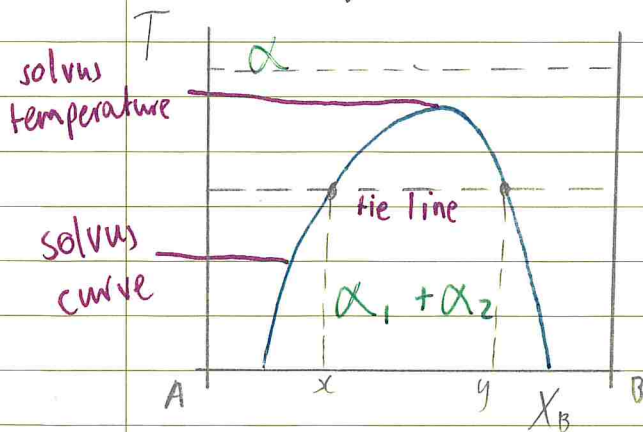
We can find  $G_s$  using  $G_s = \Delta G_{mix} + G_{mm}$

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

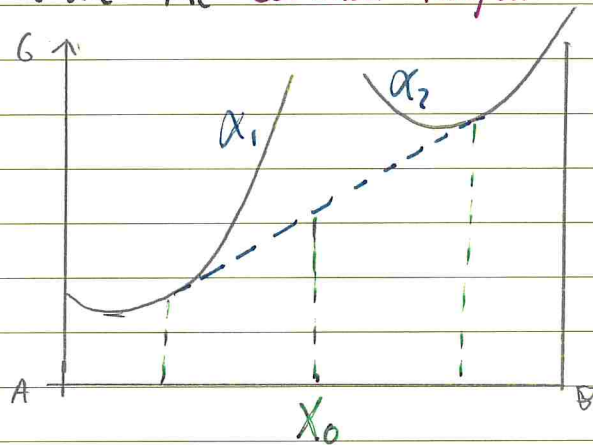
$$\frac{\partial^2 \Delta G}{\partial X^2} \Big|_{x=0.5} = 0$$

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

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

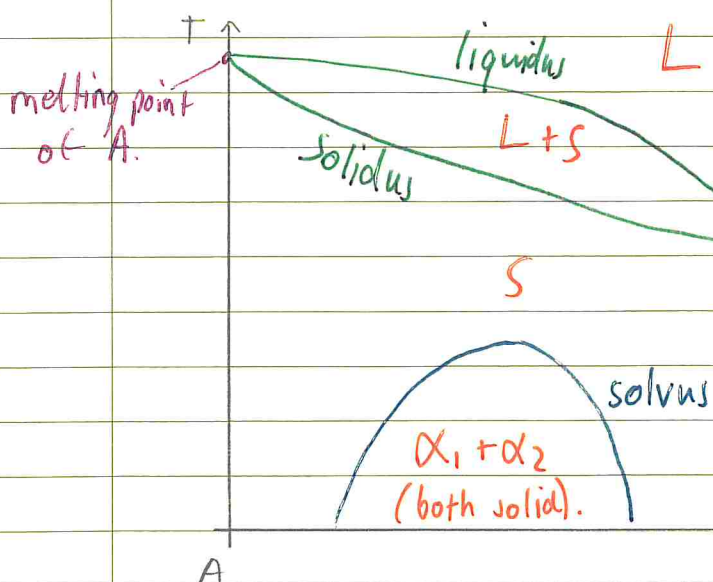
i.e.  $X_1 f_1 + X_2 f_2 = X_0 (f_1 + f_2)$ .

- 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**



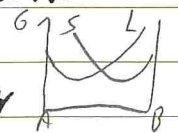
## Solidification

- 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.



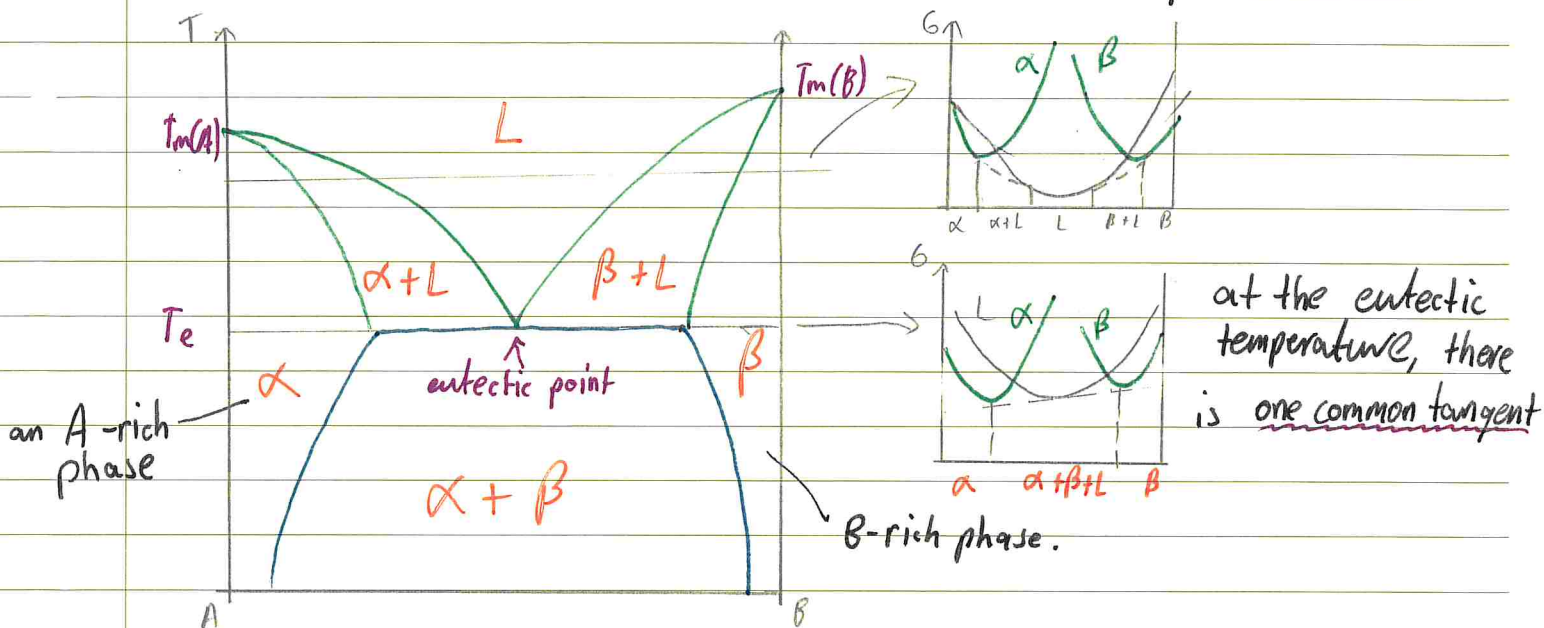
For some temperature range, there will be complete solid solubility for any composition.



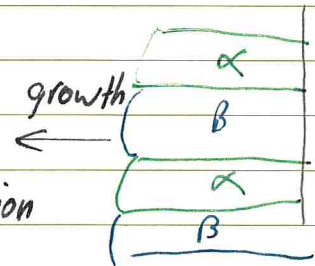
## Incomplete solid solubility

- It may be the case (if  $\psi > 0$ ) 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



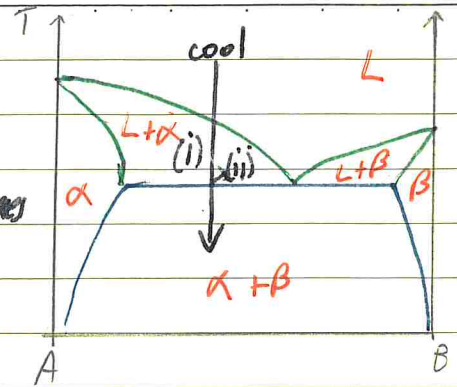
- The phases show **cooperative growth**:
  - when some  $\alpha$  forms, B atoms are rejected
  - this encourages  $\beta$  to form adjacent to  $\alpha$
  - results in **lamellae** as the solute redistributes
  - gives a **stripy cross-section**
  - when cooled rapidly, less solute redistribution occurs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

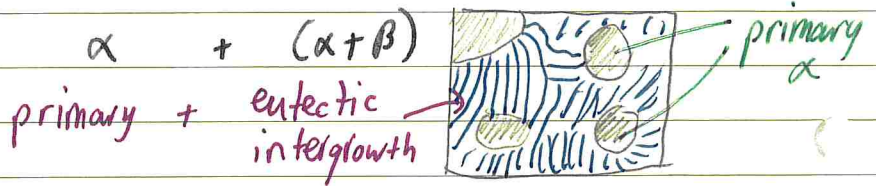
• Even non-eutectic initial compositions result in eutectic microstructure.

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



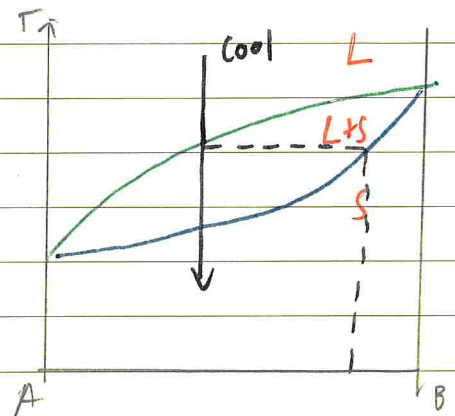
↳ final microstructure:  $\alpha$  +  $(\alpha + \beta)$

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



## Coring

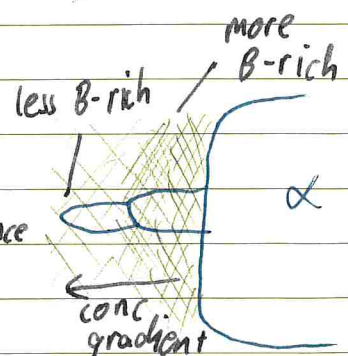
- During slow cooling through a 2-phase region, the first solid that forms will be B-rich.
- As cooling continues (in equilibrium), the composition of the solid changes but remains uniform due to diffusion.



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

## Dendrites

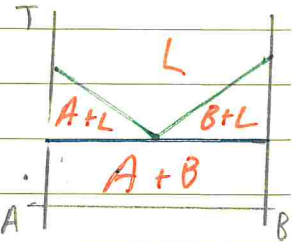
- When an A-rich  $\alpha$  phase forms, it is surrounded by a B-rich region, whose conc decreases with distance
- A random proturbance will be in a less B-rich env., so will grow rapidly to form dendrites.
- Dendrites favour crystallographic directions, leading to tree-like dendritic structures.



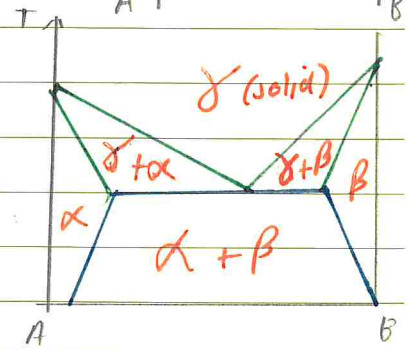


### Other phase diagrams

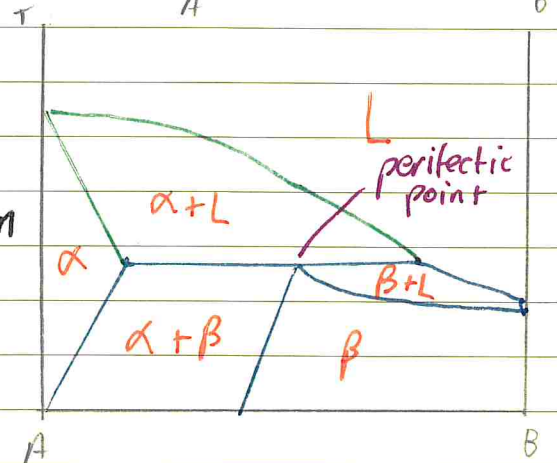
- A eutectic need not involve solid solution ( $\alpha$  or  $\beta$ ), in which case two pure phases will exist



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

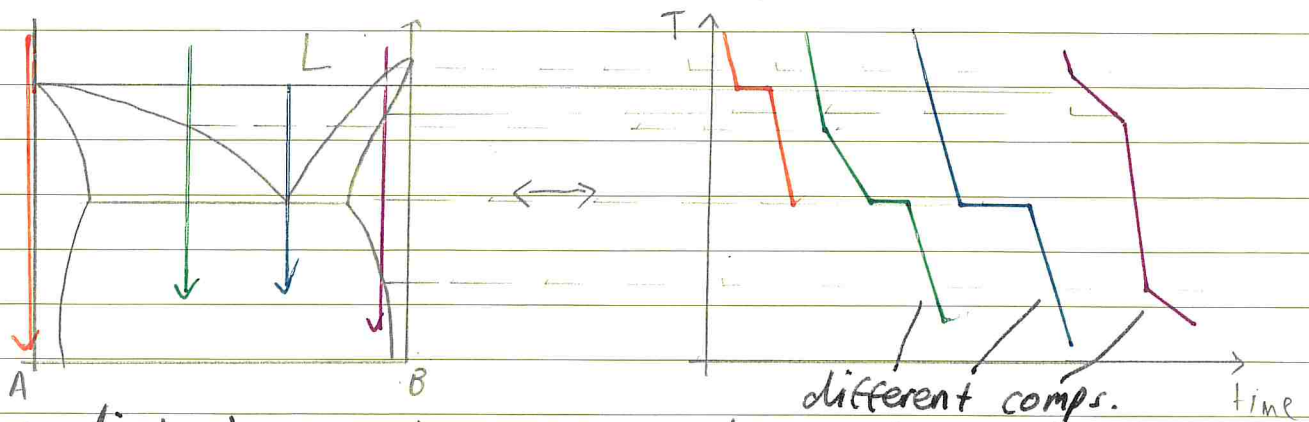


- A **peritectic reaction** involves a ~~solid~~ solid + liquid phase becoming a different solid phase:  $\alpha + L \rightarrow \beta$
- Near the peritectic temp, the reaction slows down because  $\beta$  forms around  $\alpha$ , so  $\alpha$  is separated from L.



### 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**  $r^*$  maximises  $W_n$ :

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

↳ 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.

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

↳  $U > 0$  so driving force reduced

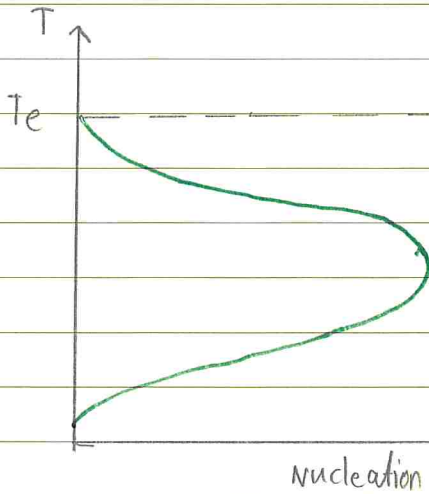
↳ i.e. strain increases  $r^*$  and  $W_n^*$ , hindering nucleation

- 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

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

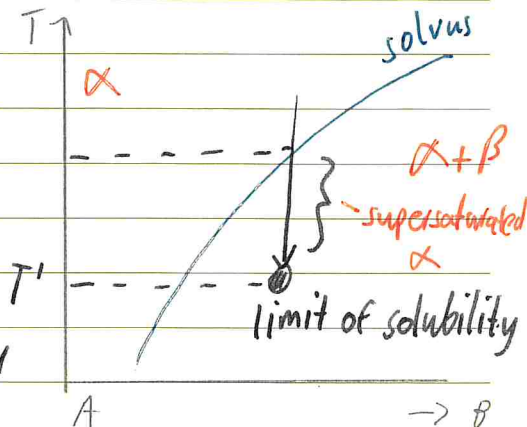


- At  $T_e$  there is no nucleation because  $\Delta G_v = 0$ .

- Below  $T_e$ ,  $\Delta G_v \uparrow$  so  $W_n^*$ . At some  $T$ ,  $I$  will be maximised.

- Reducing  $T$  further, atomic mobility becomes slow (low  $kT$ ) so the nucleation rate decreases.

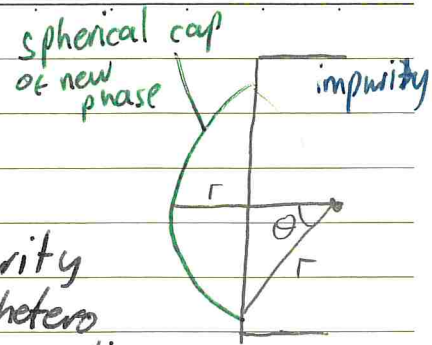
- Because of the strain, it may be difficult to precipitate one solid phase in another.
- Consider cooling an A-rich  $\alpha$  phase below the solvus. B should precipitate according to the diagram, but may not.
- Thus  $\alpha$  exists with an excess of B dissolved  
↳ supersaturated solid solution



- Eventually at some  $T'$ , the limit of solubility of B in  $\alpha$  will be reached and  $\beta$  must precipitate.

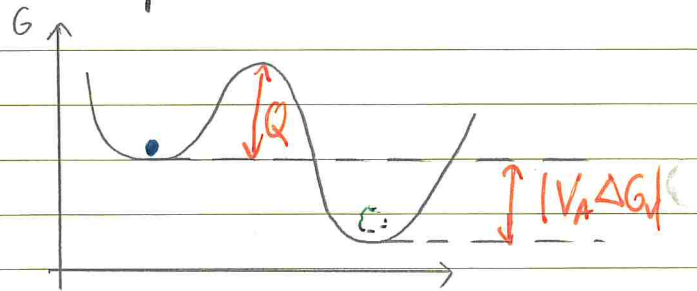
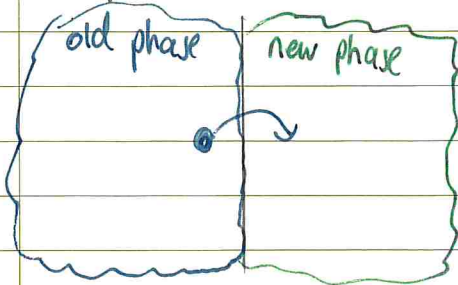
## Heterogeneous nucleation

- Nucleation can be catalysed by impurities or container walls.
- Modeled 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  $V_A \Delta G_V$  ( $V_A \equiv$  volume of atom), but an energy barrier of  $Q$ . The growth rate  $v$  is proportional to (old  $\rightarrow$  new) jumps minus (new  $\rightarrow$  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





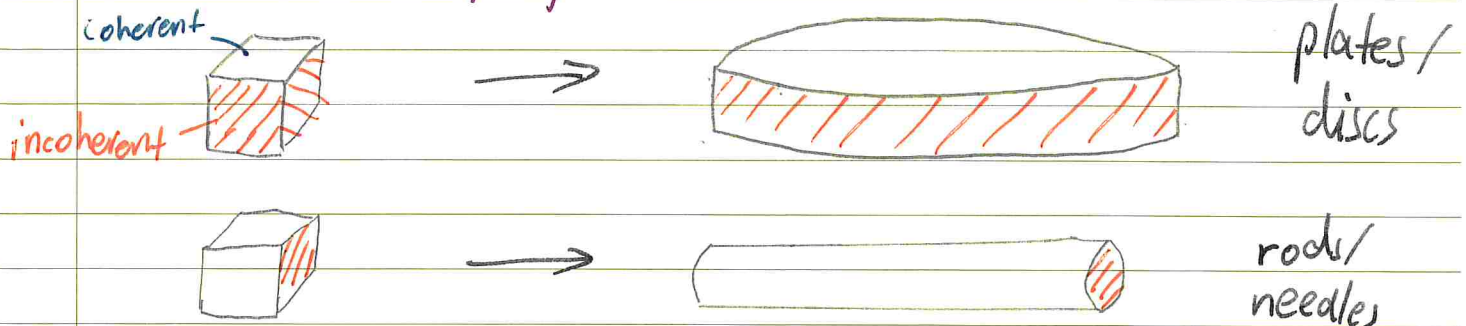
## Solid-Solid Interfaces

- 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

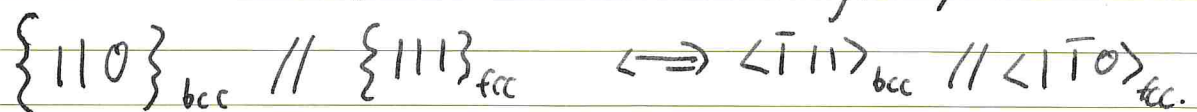
↳ precipitate grows to maximise the coherent surface area

↳ i.e. **anisotropic growth**



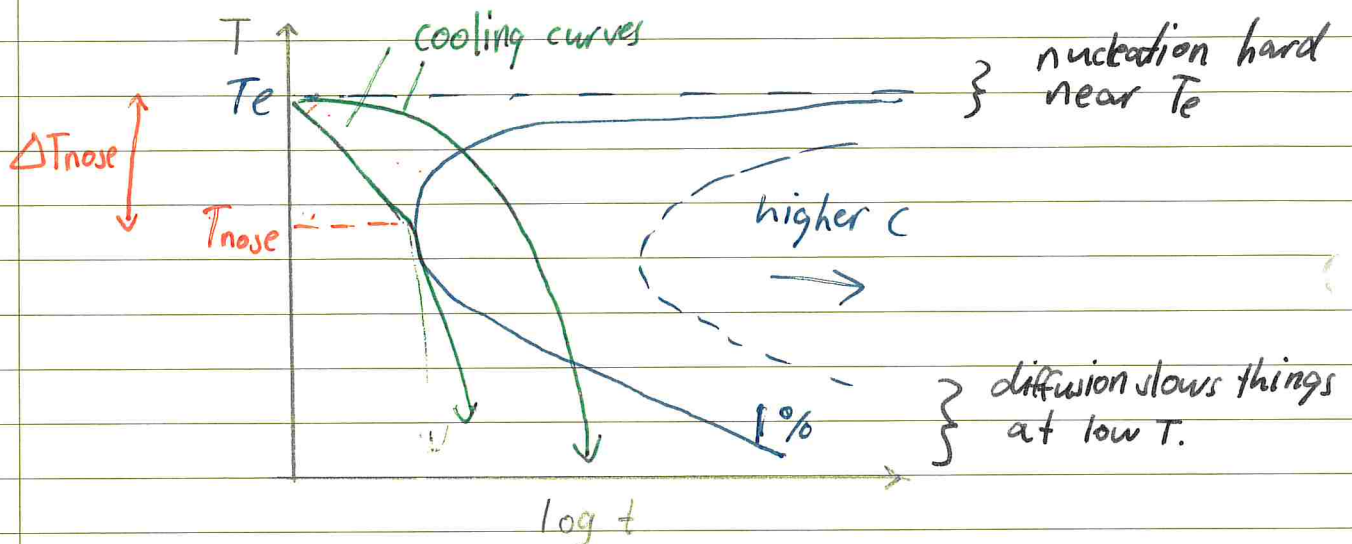
• If a solid solution is left to cool for millions of years (e.g. in meteors) then it may show the **Widmanstätten microstructure**

- 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.



## TTT diagrams

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

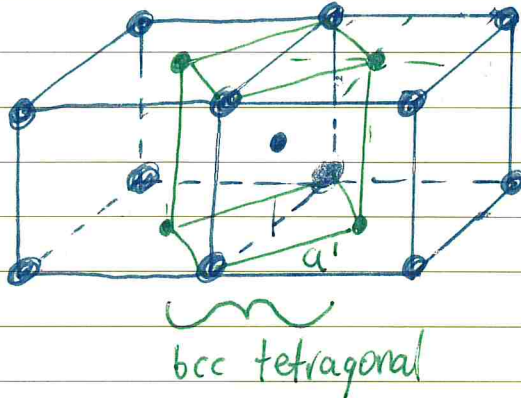


- This TTT diagram is strictly for **isothermal transformation**, but we can use it to estimate the critical quench rate.
- Continuous cooling follows  $e^{-kt}$ , which becomes like  $\square \searrow$  on the log scale.
- The critical quench rate is the cooling curve that just touches the nose of the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

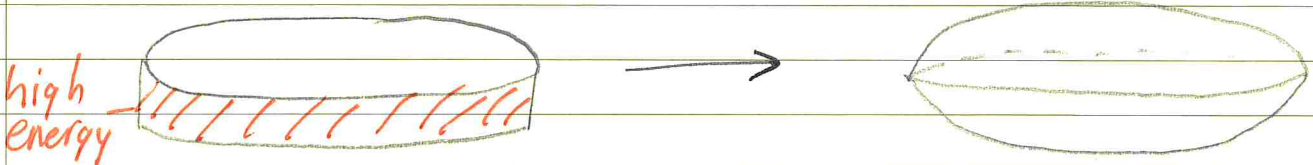


## Displacive phase transitions

- 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.



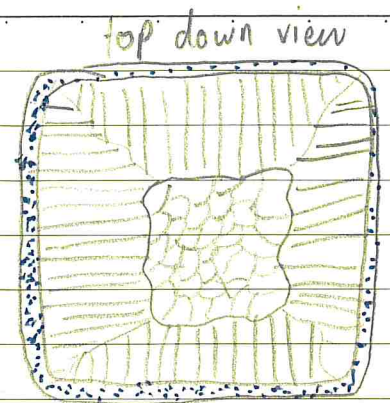
## Materials processing

- 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

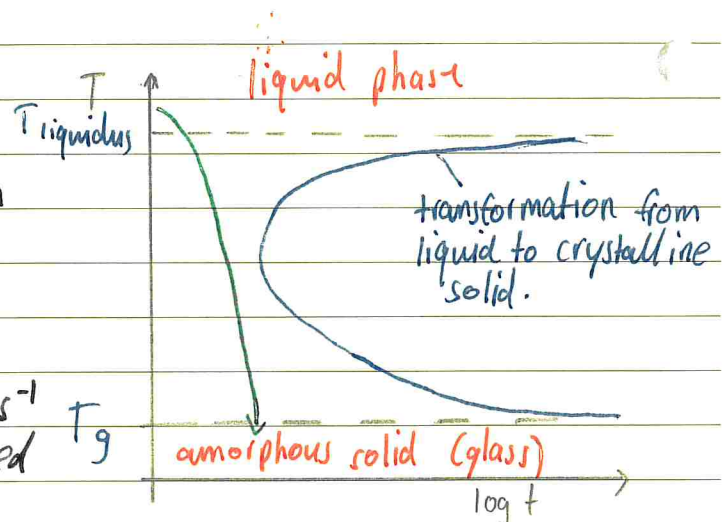
- During casting, liquid metal is poured into a mould and left to solidify.
- The mould walls are sites of hetero. nucleation and have a lower faster cooling rate, leading to smaller grains at the edge.

- 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.

$$\rightarrow \Delta G_{\text{total}} = \Delta G_v + \frac{2}{\lambda} \gamma_{\alpha\beta}$$

$\Delta G_v$  ← driving force given by  $\Delta G_v = \frac{\Delta H \Delta T}{T_e}$  — undercooling  
 $\frac{2}{\lambda} \gamma_{\alpha\beta}$  ← energy per area of interface

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

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

- ↳ 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  $\rightarrow \delta + \text{Fe}_3\text{C}$  (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.

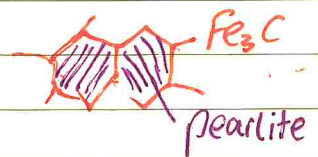
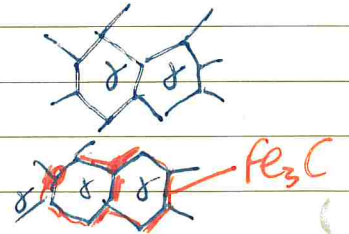
• Eutectoid: Fe - 0.8 wt% C



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

• **Hypereutectoid steel**: Fe - 1.0 wt% C

- on cooling from 1000°C, we start with grains of  $\delta$
- at the phase boundary,  $\text{Fe}_3\text{C}$  precipitates on heterogeneous nucleation sites
- below the eutectoid temp,



• **Hypoeutectoid steel**: Fe - 0.1 wt% C

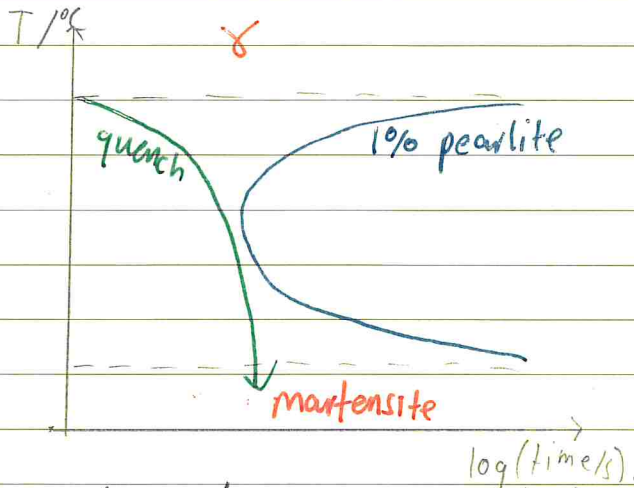
- ferrite ( $\alpha$ ) initially precipitates on grain boundaries, but eventually forms large grains near  $T_E$
- at  $T_E$ , remaining  $\delta$  undergoes the eutectoid transition to form pearlite
- with lower zooms, this pearlite may appear uniform

• Steels (especially hypoeutectoid) are widely used because they are cheap, versatile, and generally have good mechanical properties



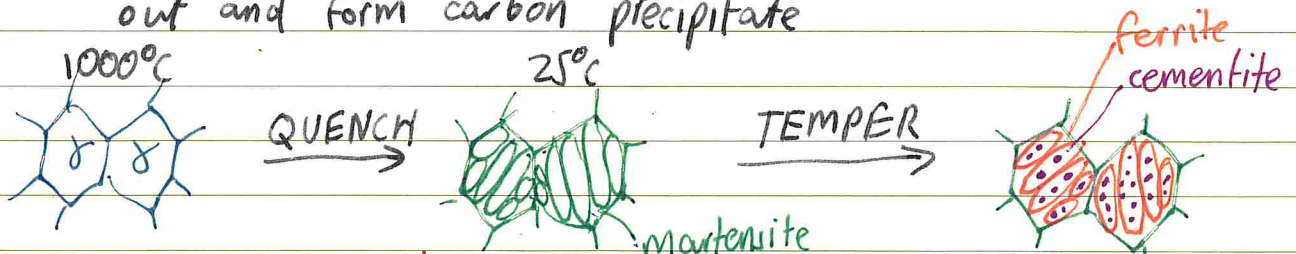
## Rapid cooling of steel

- 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  $350^\circ\text{C}$  to allow trapped carbon to diffuse out and form carbon precipitate

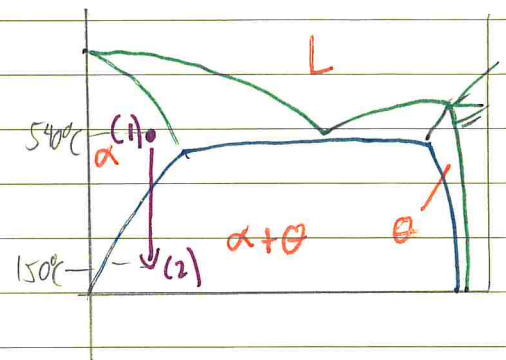


- ↳ result is **laths** of ferrite containing small precipitates of cementite
- ↳ i.e. same position on equilibrium phase diagram, but NOT pearlite.
- ↳ result is harder than pearlite but less brittle than un-tempered martensite.

# Al-Cu alloys

- Aerospace requires high-strength low density materials. Aluminium-Copper alloys are often used.
- Below  $\sim 55\%$  Cu, the phase diagram is eutectic
  - ccp  $\alpha$  (Al-rich) to the left of the solvus
  - compound  $\theta \approx \text{Al}_2\text{Cu}$  to the right.
- Similar to steels, eutectic microstructures can form, e.g.  $\alpha$  dendrites in  $\alpha + \theta$  eutectic, intergrowth (quite fine).
- But these alloys are not very strong - we need finer precipitates!

- Anneal ( $\sim 540^\circ\text{C}$ )  $\alpha$  4 wt% Cu alloy
  - $\rightarrow$  all Cu will be in solution
- Quench to obtain a supersaturated solid solution of single phase  $\alpha$ 
  - $\rightarrow$  more Cu than phase diagram predicts, so strong driving force.
- Anneal ( $\sim 150^\circ\text{C}$ ) to develop precipitates.



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

look like  
lines on  
 $\alpha$  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.

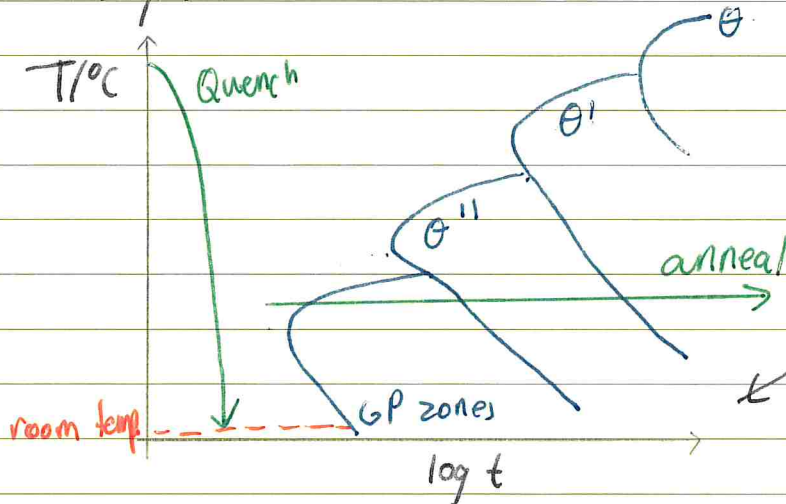


- During each of these transitions, Gibbs free energy is reduced.
- As  $\theta''$ ,  $\theta'$  and  $\theta$  precipitate out, the Cu content of remaining  $\alpha$  decreases:

more Cu rich  $\alpha_0 \rightarrow \alpha_1 + GP \rightarrow \alpha_2 + \theta'' \rightarrow \alpha_3 + \theta' \rightarrow \alpha_4 + \theta$   
 equilibrium

- 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.



GP zones readily form at room temp., but takes a long time for  $\theta''$  and  $\theta$  because of slow diffusion.

