

D. Microstructure

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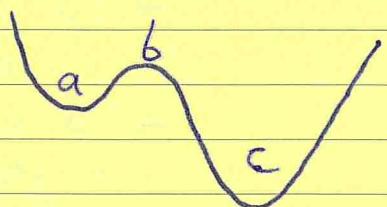
Microscopy

- 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 λ 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 $\delta q = C_v dT$ and $\delta w = -P dV$

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

↳ 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 $dS_{univ} > 0$

↳ for a reversible process, $dS = 0$

↳ for a given system: $dS \geq \frac{\delta q}{T}$ $\leftarrow dS_{sys}$ 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 $\delta G = \delta q - T dS$ for constant P, T.

↳ $dG = 0$ for reversible changes at equilibrium

↳ $dG < 0$ otherwise.

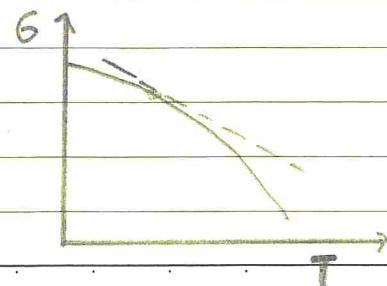
↳ $\{G\}$ tends to a minimum at equilibrium

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

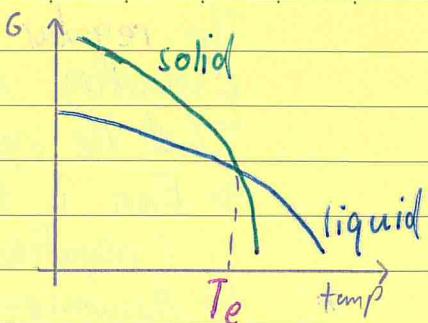
↳ G is decreasing in T:

- gradient = $-S$

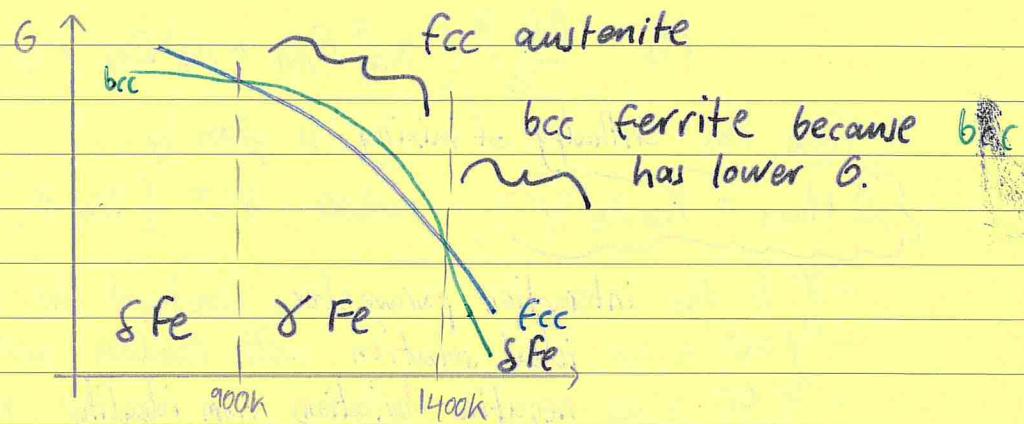
- as temp T , $S \uparrow \therefore$ gradient more negative.



- 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.

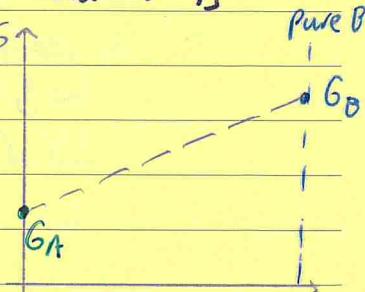


- Iron is unusual, because it transforms $bcc \rightarrow fcc \rightarrow bcc$ as temp T



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:
 - ΔH because A-B interactions are different to A-A / B-B
 - ΔS 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 ΔG is negative, a solution is preferred to a mechanical mixture.



- The regular solution model can be used to estimate ΔG_{mix} .
 - Estimating ΔH_{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
 - * $\therefore H_{\text{mix}} = \frac{N_A Z}{2} (X_A E_{AA} + X_B E_{BB})$
 - \hookrightarrow In solution, $P(A-A \text{ bond}) = X_A^2$, $P(A-B \text{ bond}) = 2X_A X_B$
 - $\therefore H_s = \frac{N_A Z}{2} (X_A^2 E_{AA} + X_B^2 E_{BB} + 2X_A X_B E_{AB})$
 - \hookrightarrow Then the enthalpy of mixing is given by:
- $\Delta H_{\text{mix}} = X_A X_B \gamma$, where $\gamma \equiv \frac{1}{2} N_A Z (2E_{AB} - E_{AA} - E_{BB})$
- γ 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.
- $\hookrightarrow \Delta H_{\text{mix}}$ is symmetrical about $X_A = X_B = 1/2$

- To model ΔS_{mix} , we only consider the changes in configuration

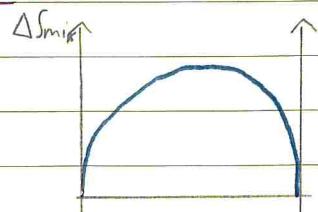
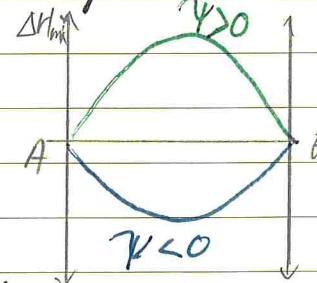
$$\hookrightarrow S = k \ln \Omega, \text{ where } \Omega \equiv n \text{ ways of arranging.}$$

$\hookrightarrow \Omega_{\text{mm}} = 1$ because phases are purely A or B

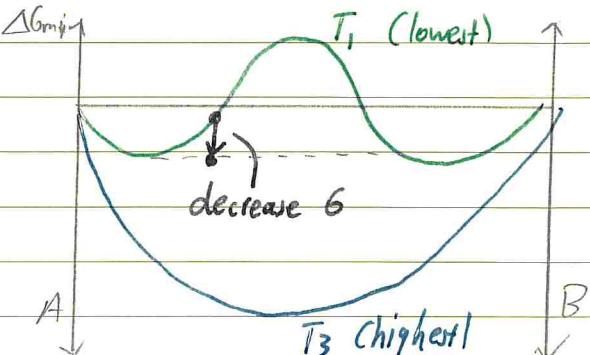
$$\hookrightarrow \Omega_s = \frac{N_A!}{(X_A N_A)! ((1-X_A) N_A)!} \quad \text{where } N_A \text{ is Avogadro's No.}$$

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

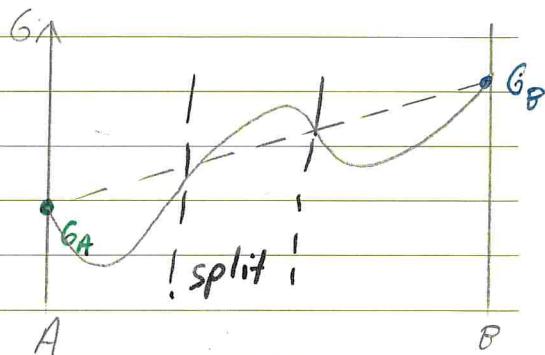
$\hookrightarrow \Delta S_{\text{mix}} > 0$ always, because making a solution increases disorder.



- 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 $\gamma > 0$, ΔG_{mix} depends on the temperature.
 - for low T there is complete solution
 - for low T , ΔG_{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.

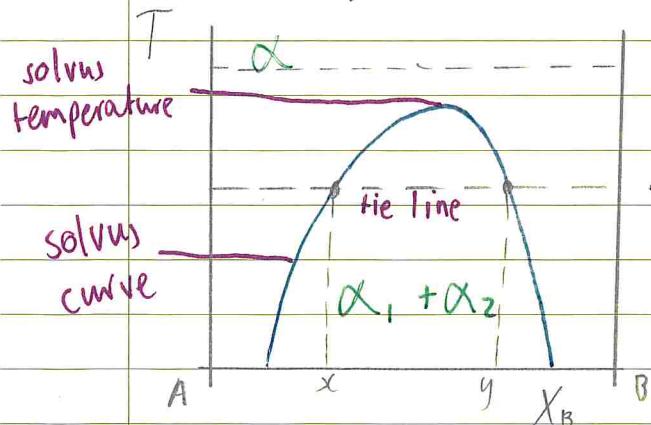


- We can find G_s using $G_s = \Delta G_{\text{mix}} + G_{\text{mm}}$
- In a certain range, G_s can be lowered by moving towards a mechanical mixture.



Equilibrium phase diagrams

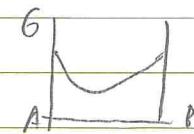
- This maps what phases will exist at each composition / temperature.



- 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

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



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

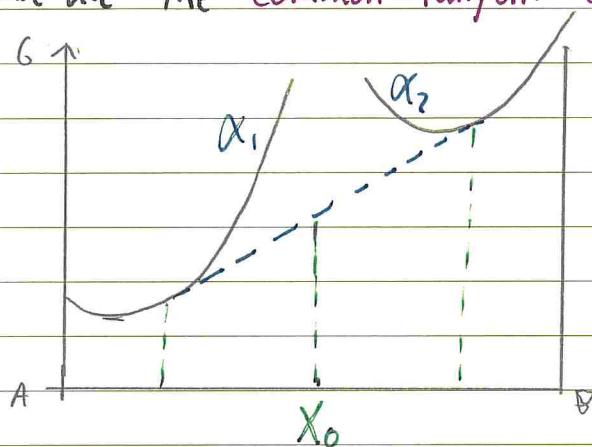
$$(\alpha_1 \text{ comp}) \times (\alpha_1 \text{ prop}) + (\alpha_2 \text{ comp}) \times (\alpha_2 \text{ prop}) = \text{total comp}$$

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.

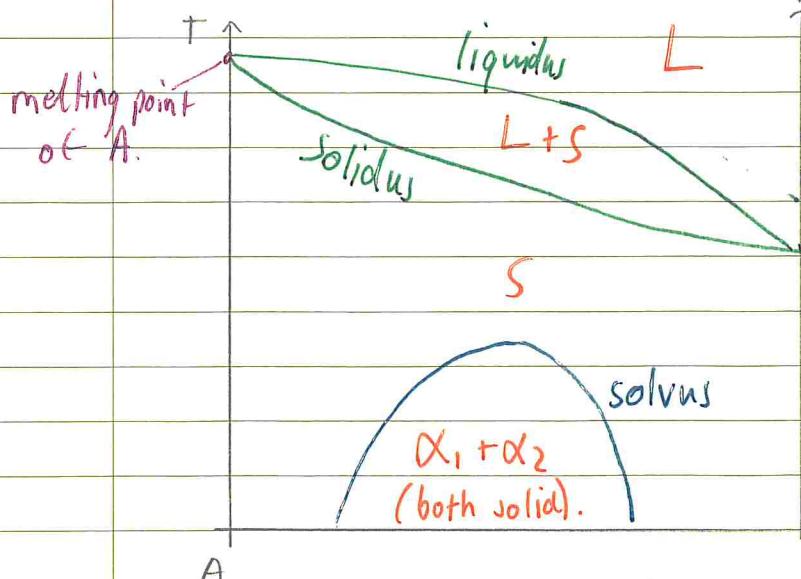
↳ equilibrium compositions are NOT weighted avg of minima

↳ 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:

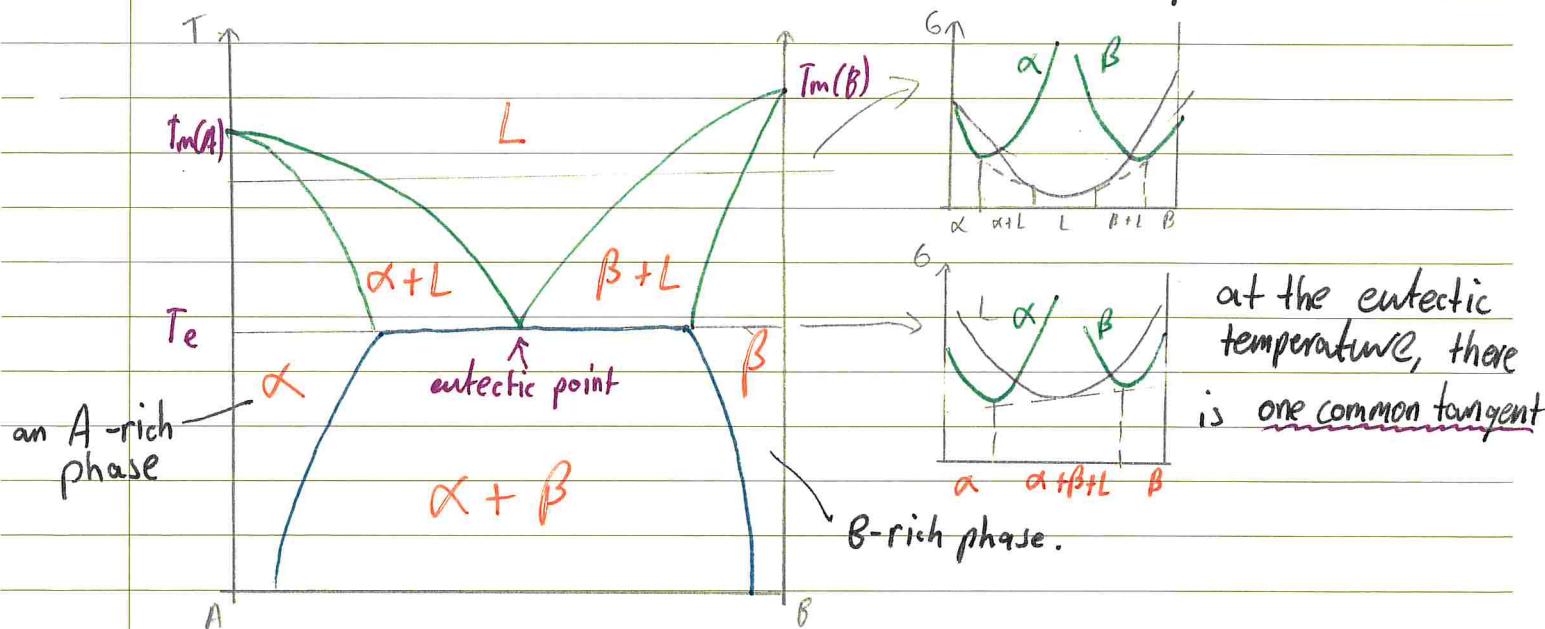
comp. found using lever rule.

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



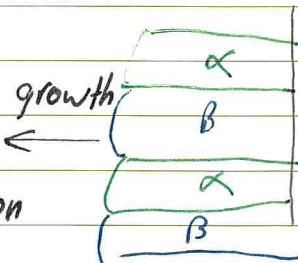
Incomplete solid solubility

- It may be the case (if $\gamma > 0$) 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**:

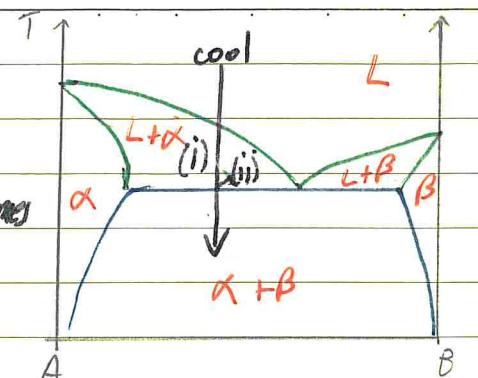
- when some α forms, β atoms are rejected
- this encourages β to form adjacent to α
- results in **lamellae** as the solute redistributes
- gives a **striped cross-section**
- when cooled rapidly, less solute redistribution occurs so the layers are finer.



- 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.

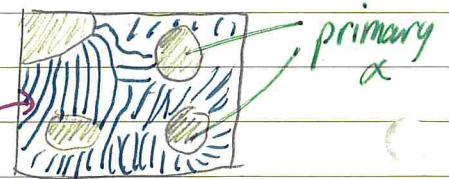
- Even non-eutectic initial compositions result in eutectic microstructure.

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



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

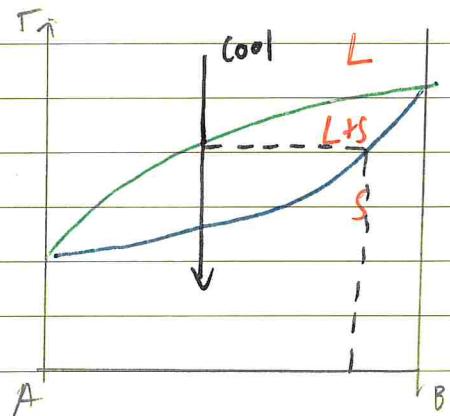
↳ we often assume that α remains at the eutectic comp.



Coring

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

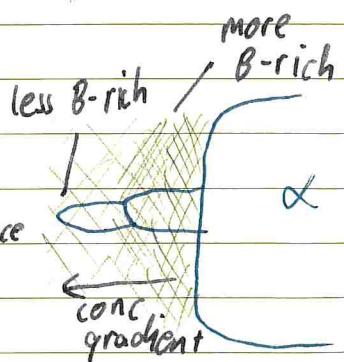
- As cooling continues (in equilibrium), the composition of the solid changes but remains uniform due to diffusion.



- 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

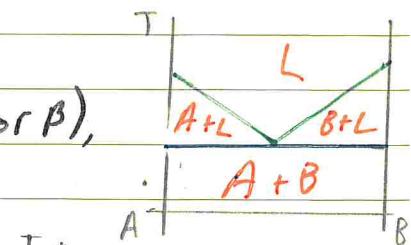
Dendrites

- When an A -rich α phase forms, it is surrounded by a B -rich region, whose conc decreases with distance
- A random protuberance 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.

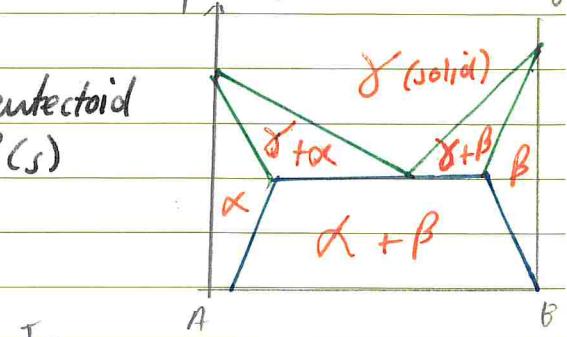


Other phase diagrams

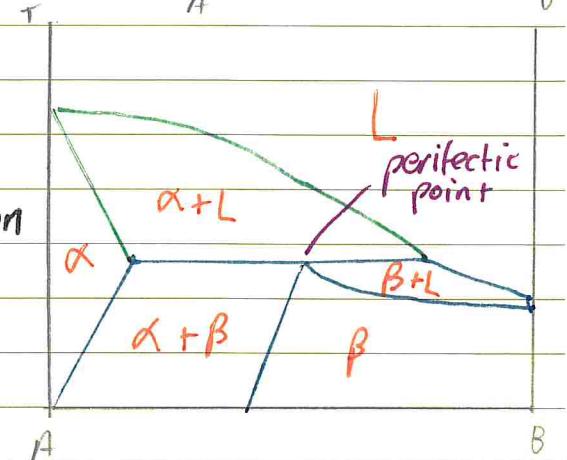
- A eutectic need not involve solid solution (α or β), in which case two pure phases will exist



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

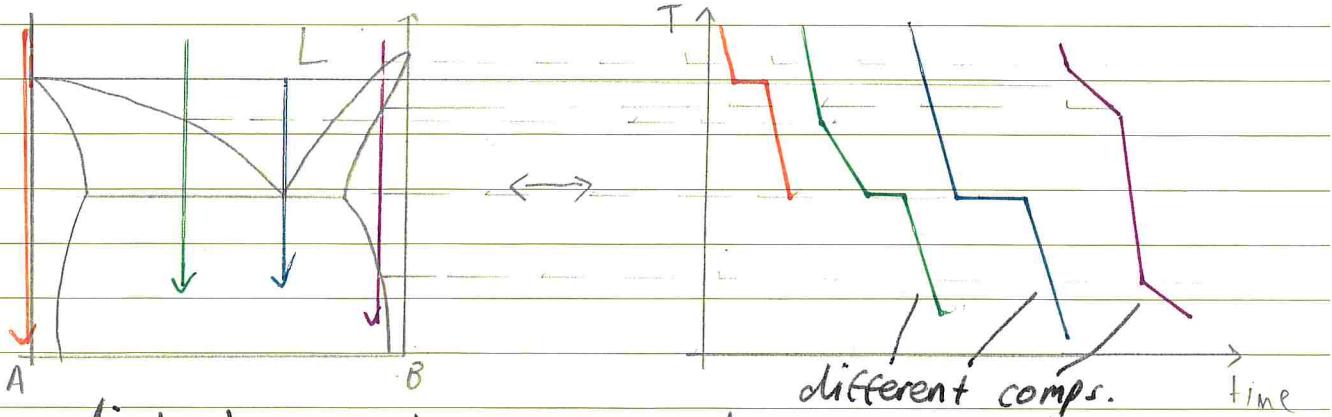


- A peritectic reaction involves a solid solid+liquid phase becoming a different solid phase: $\alpha + L \rightarrow \beta$
- Near the peritectic temp, the reaction slows down because β forms around α , so α is separated from L .



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 2nd 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 ΔG).
- 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: $W_n = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma$

↳ ΔG_v is the driving force per unit volume (negative)

↳ γ 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 V per unit volume.

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

$\hookrightarrow V > 0$ so driving force reduced

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

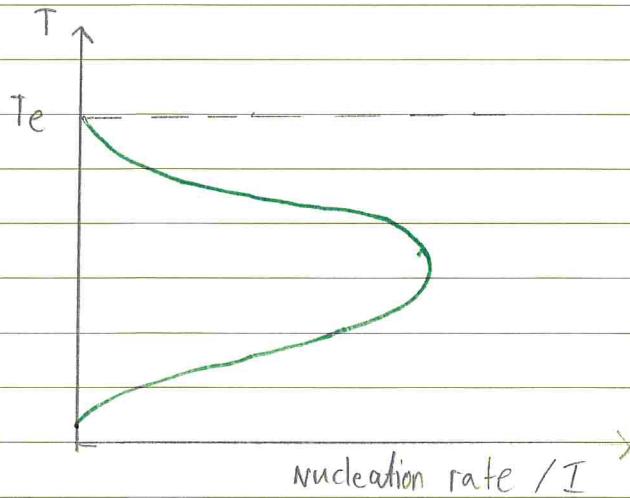
- The rate of nucleation is proportional to:

- population of critical nuclei $\propto \exp(-W_n^*/kT)$

- rate of atomic addition to a nucleus $\propto \exp(-Q/kT)$

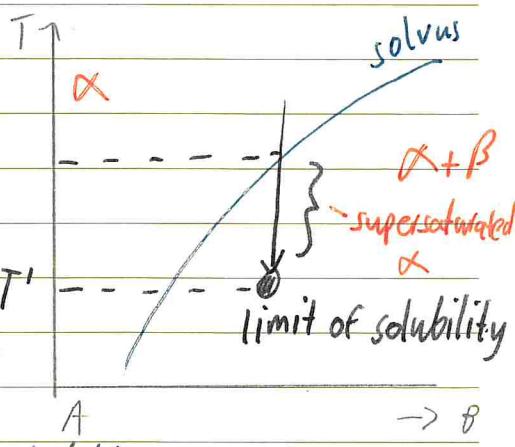
- Thus the nucleation frequency takes the form

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

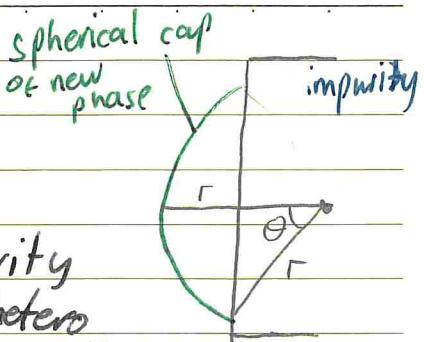


- At T_e there is no nucleation because $\Delta G_v = 0$.
- Below T_e , $\Delta G_v \uparrow$ so W_n^* . At some T , I will be maximised.
- Reducing T further, atomic mobility becomes slow (low kT) so the nucleation rate decreases.

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



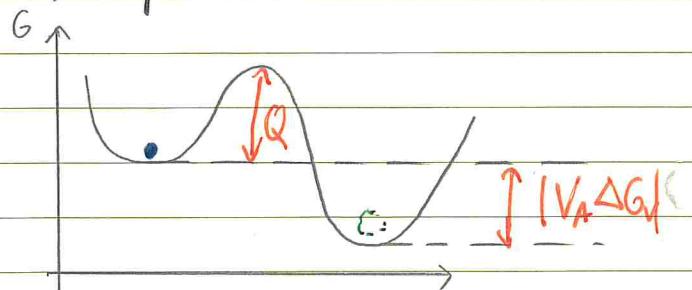
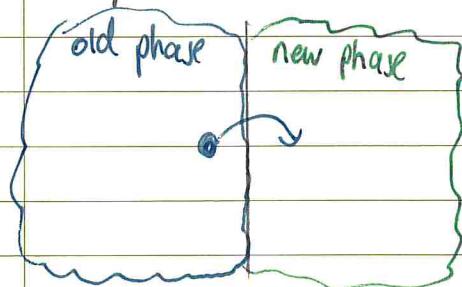
Heterogeneous nucleation



- 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 $Wn^*_{\text{hetero}} = Wn^*_{\text{homo}} \times \text{volume fraction}$
 - 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



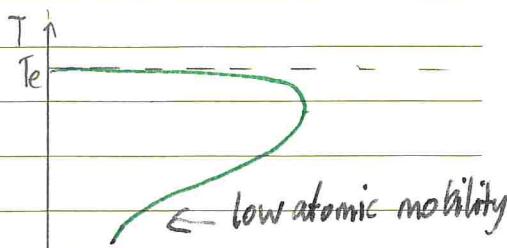
- There is a driving force of $V_A \Delta G_v$ (V_A ≡ volume of atom), but an energy barrier of Q . The growth rate v is proportional to $(\text{old} \rightarrow \text{new})$ jumps minus $(\text{new} \rightarrow \text{old})$ jumps

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

At first, $T=T_e \Rightarrow v=0$

But small deviations can result in large growth rates

→ if nuclei are present, only small driving forces needed



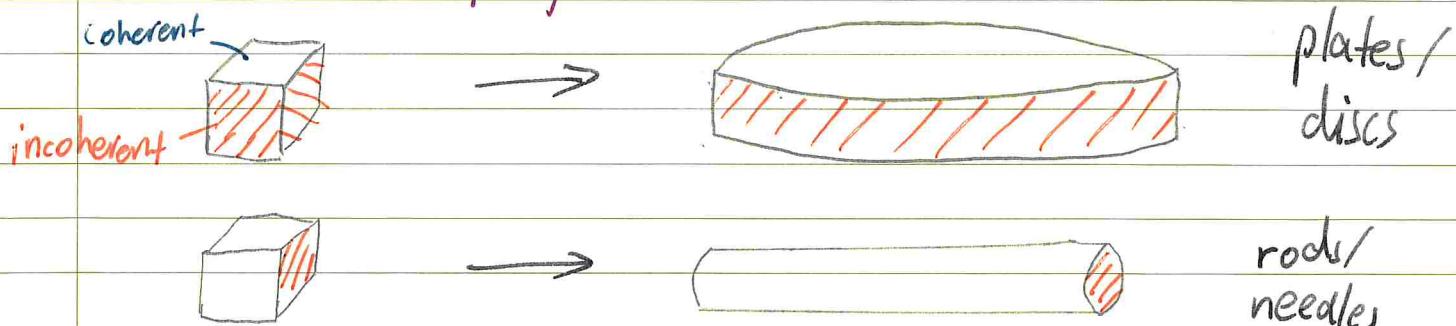
Solid-Solid Interfaces

- The interface between a solid phase α and a solid β nucleating in α can be of various types:
 - **coherent**: there is perfect alignment of α and β 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

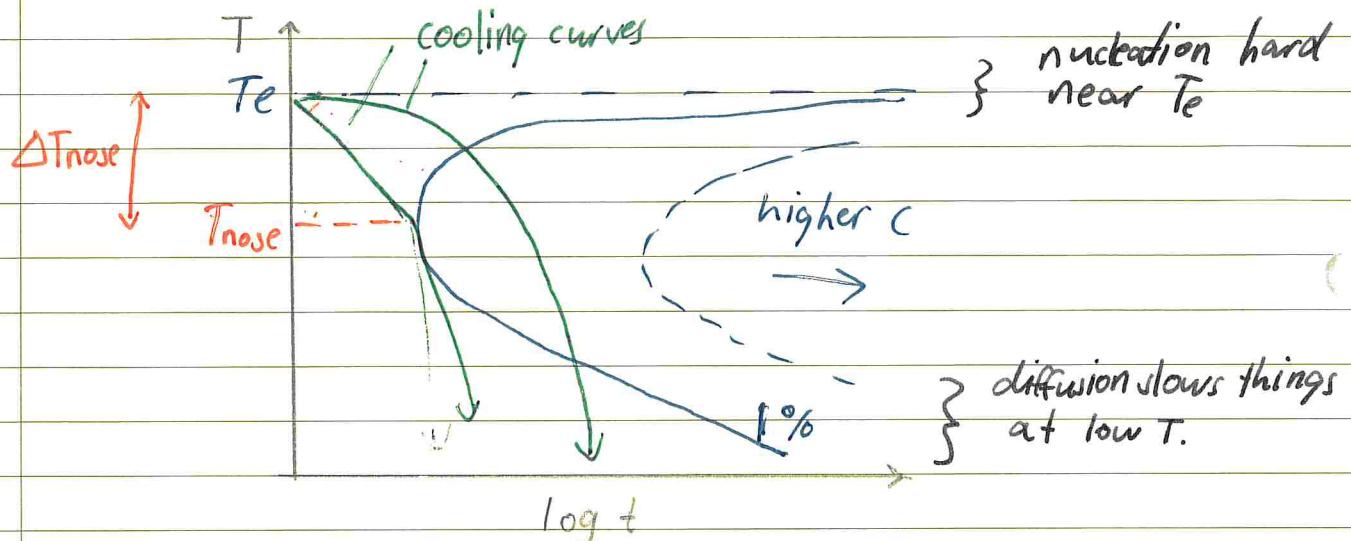


- If a solid solution is left to cool for millions of years (e.g. in meteors) then it may show the **Widmanstätten** microstructure
 - e.g. bcc precipitating out of an fcc matrix.
 - bcc and fcc will want to align along close-packed directions
 - leads to a microstructure with an angled grid.

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

TTT diagrams

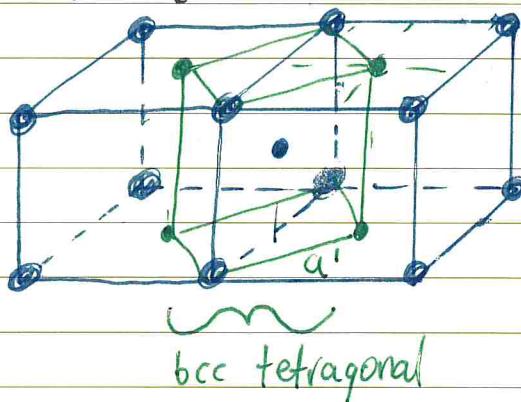
- A TTT diagram plots the time taken to form a certain composition $\alpha\beta$ as a function of temperature.
 ↳ contours of t known as C-curves.



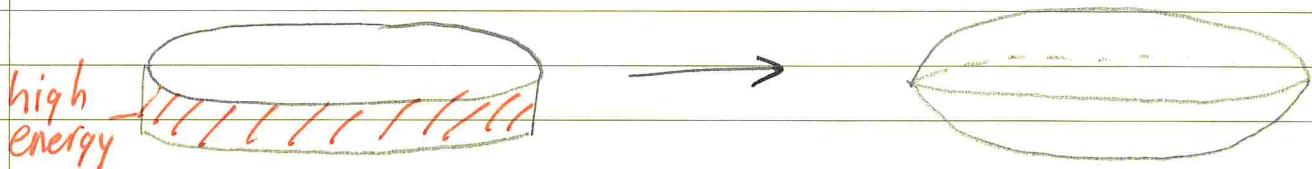
- This TTT diagram is strictly for *isothermal transformation*, but we can use it to estimate the critical quench rate.
 - Continuous cooling follows e^{-kt} , which becomes like \square on the log scale.
 - The critical quench rate is the cooling curve that just touches the nose of the C-curve.
 - For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



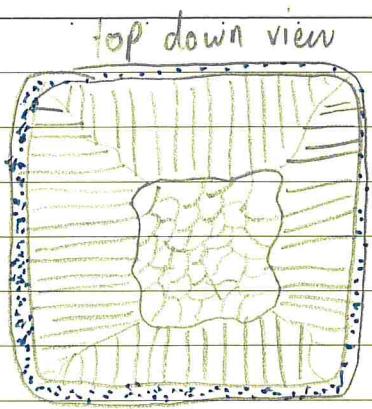
Materials processing

- 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 ΔG (driving force for nucleation) \Rightarrow many stable nuclei \Rightarrow small grains.

Casting

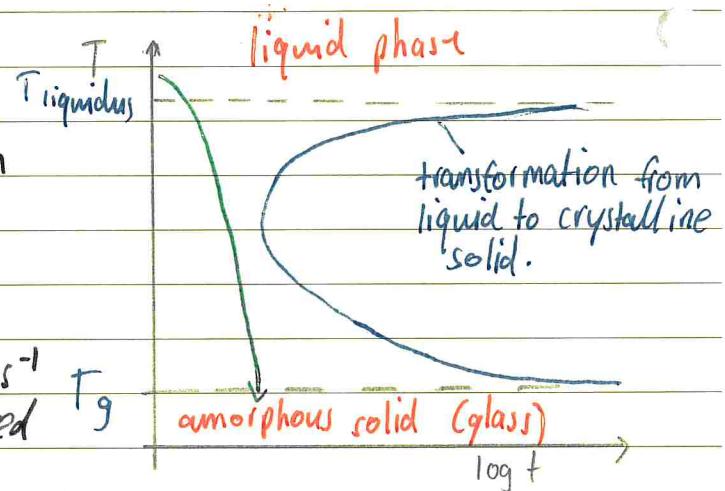
- During casting, liquid metal is poured into a mould and left to solidify.
- The mould walls are sites of hetero. nucleation and have a ~~lower~~ faster cooling rate, leading to smaller grains at the edge.

- 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 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 α/β 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 ΔT), λ^* decreases.

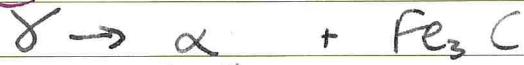
Deformation processing

- 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 (Fe_3C).
- 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.

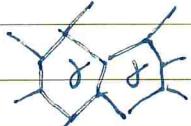
- Eutectoid: $\text{Fe} - 0.8\text{wt\% C}$



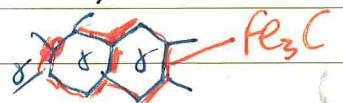
i.e. austenite \rightarrow ferrite + cementite (lamellae).
pearlite

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

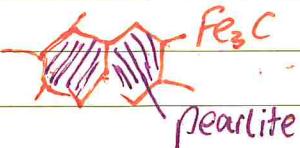
- on cooling from 1000°C , we start with grains of γ



- at the phase boundary, Fe_3C precipitates on heterogeneous nucleation sites



- below the eutectoid temp,



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

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

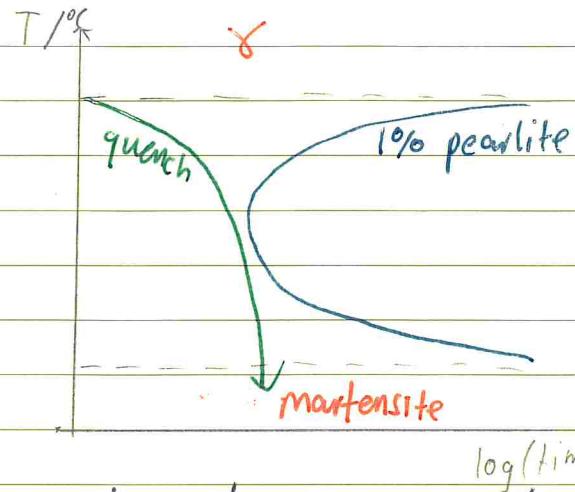
- at T_E , remaining γ undergoes the eutectoid transition to form pearlite

- with lower zoom, this pearlite may appear uniform

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

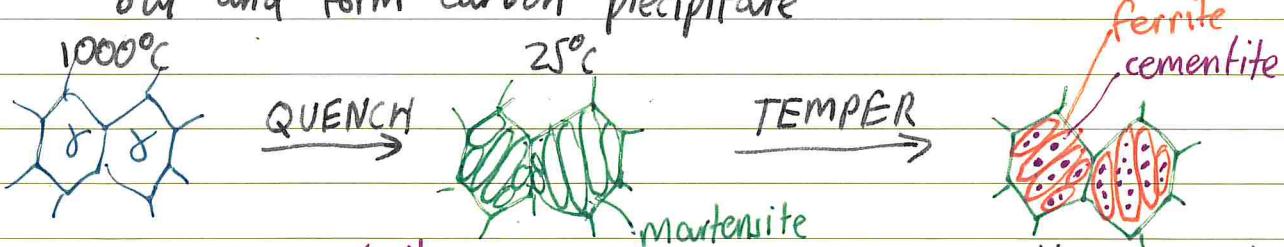
Rapid cooling of steel

- 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



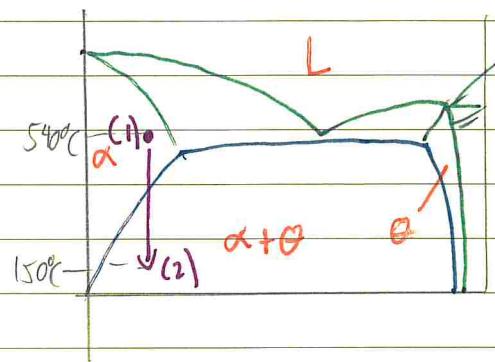
- result is laths of ferrite containing small precipitates of cementite
 - i.e same position on equilibrium phase diagram, but NOT pearlite.
 - result is harder than pearlite but less brittle than un-tempered martensite.

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 α (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. α dendrites in $\alpha + \Theta$ eutectic intergrowths (quite fine).
- But these alloys are not very strong - we need finer precipitates!

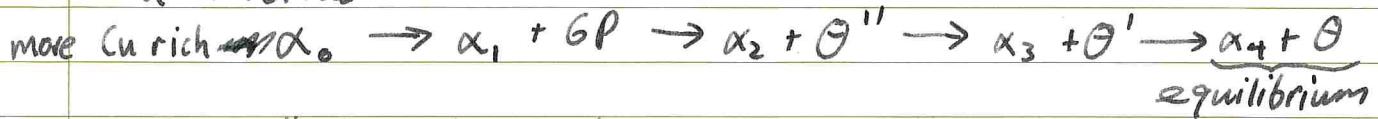
- Anneal ($\sim 540^\circ C$) at 4 wt% Cu al by
 - ↳ all Cu will be in solution
- Quench to obtain a supersaturated solid solution of single phase α
 - ↳ more Cu than phase diagram predicts, so strong driving force.
- Anneal ($\sim 150^\circ C$) to develop precipitates.

- Because Θ has a complex tetragonal structure, any new precipitates will have high energy incoherent interfaces.
 - ↳ 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. Θ'' precipitates heterogeneously onto the GP zones. It forms a coherent tetragonal crystal, but with sides that are more strained so it forms discs.
 3. Θ' is a tetragonal structure with 2 incoherent sides, so can only nucleate heterogeneously on defects.
 4. Θ 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 Θ'' , Θ' and Θ precipitate out, the Cu content of remaining α decreases:



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

