

IB Paper 3: Materials

Materials Processing: Handout 1, Lectures 9-11 Heat Treatment of Metal Alloys

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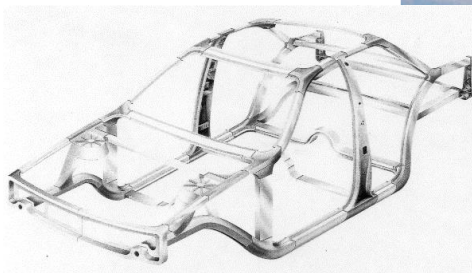


Image courtesy of Alcoa



Image courtesy of K-H Rendigs, Airbus

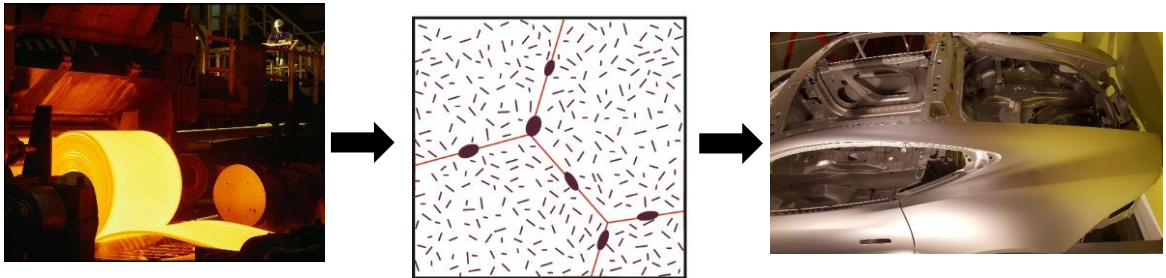
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1. Introduction

Materials processing refers to all the steps required to take a raw material to a finished product. In weeks 5-8 we will apply the fundamental principles of materials thermodynamics and diffusion learnt in weeks 1-4 to explain how **manufacturing processes** can be used to manipulate the microstructure and properties of materials.

The aim is to develop a more detailed understanding of how key process variables interact to deliver the required properties, for different classes of material:



Process variables (inputs):

- material type
- composition
- thermal history
- deformation history

Microstructure:

- phases present
- spatial distribution
- grain size / shape
- dislocation density

Material properties (outputs):

- stiffness (Young's modulus)
- yield strength (σ_y)
- fracture toughness (K_{IC})

The typical range of processing steps was introduced in Part IA. The following processes will be considered in Part IB:

Lectures 9-11: Heat Treatment

- Heat treatment of metal alloys:

Al alloys, steels
strength, toughness

- Diffusion in heat treatment

Lectures 12-14: Shaping Processes

- Casting of metals:

alloy choice
cast microstructures

- Deformation processes for metals:

rolling, forging loads
work hardening, annealing

Lectures 15-16:

- Polymer processing
- Creep: metals at high temperatures

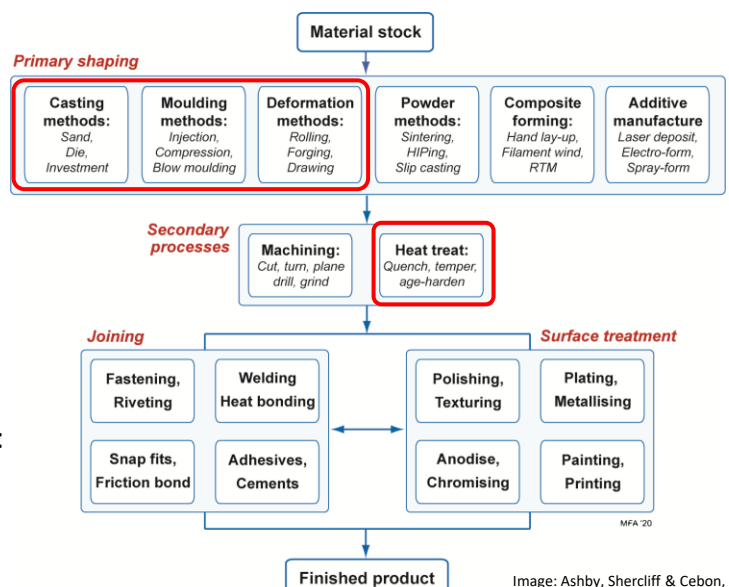


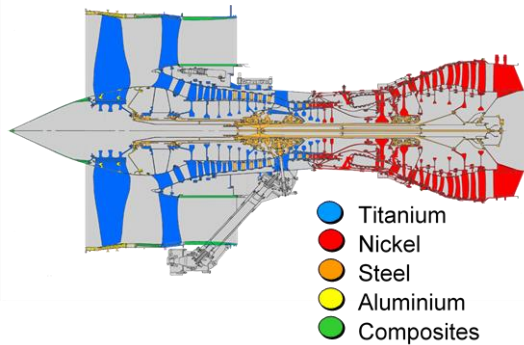
Image: Ashby, Shercliff & Cebon,
Materials Engineering, Science,
Processing & Design

Example application: improving fuel efficiency and reducing emissions in aerospace

- High strength lightweight alloys = less material, less weight (weeks 5-6 content)
- Alloys with higher operating temperatures = more efficient engines (week 8 content)



Airbus A380 wing box (Image: K-H Rendigs, Airbus)

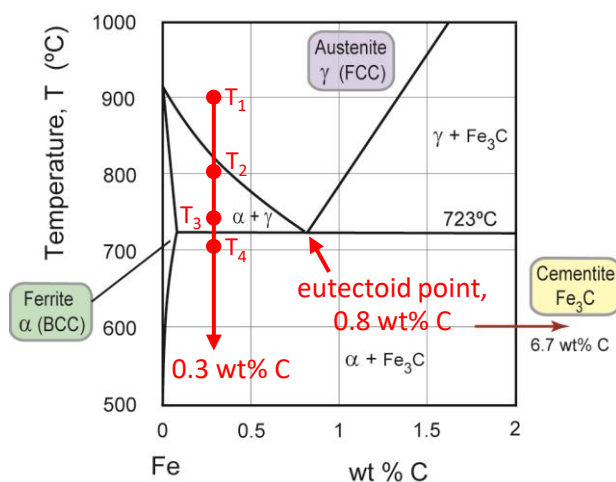


The lectures in weeks 5-8 will make use of the following previous content:

Part IB: materials thermodynamics and diffusion (weeks 1-4). Underpins microstructure development in materials (phases present, proportions, compositions, spatial distribution).

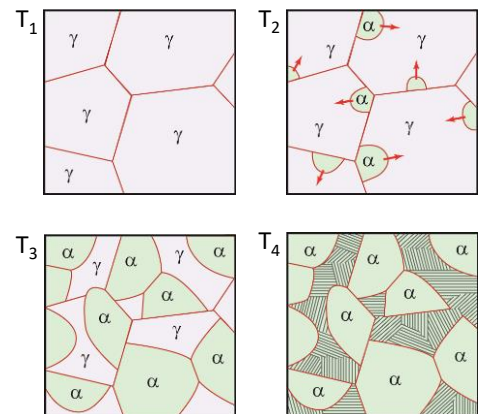
(a) The equilibrium phases:

- minimise Gibbs free energy (G)
- composition and temperature dependence



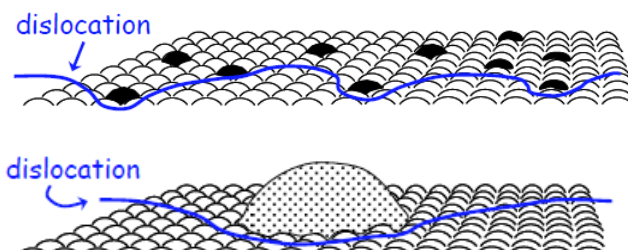
(b) Phase transformations:

- temperature and time dependence
- thermodynamic driving force ΔG
- atomic rearrangement by diffusion



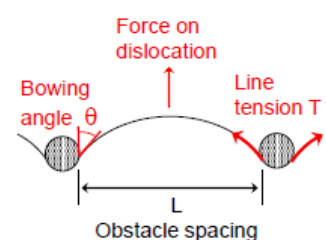
Part IA: microstructural origin and manipulation of properties.

- Property definitions: e.g. strength (yield stress, σ_y , or hardness) and toughness.
- Metals: microstructural basis of yielding, dislocations, hardening mechanisms.
- Polymers: role of molecular structure in stiffness and strength.



slip plane in
substitutional
solid solution

particle
intersecting
a slip plane



2. Heat treatment of aluminium alloys

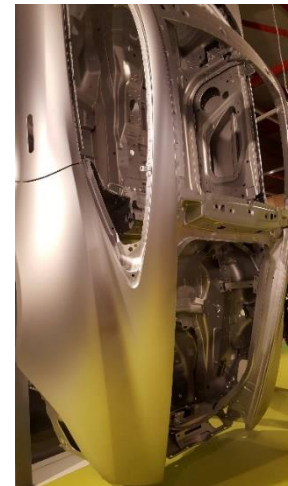
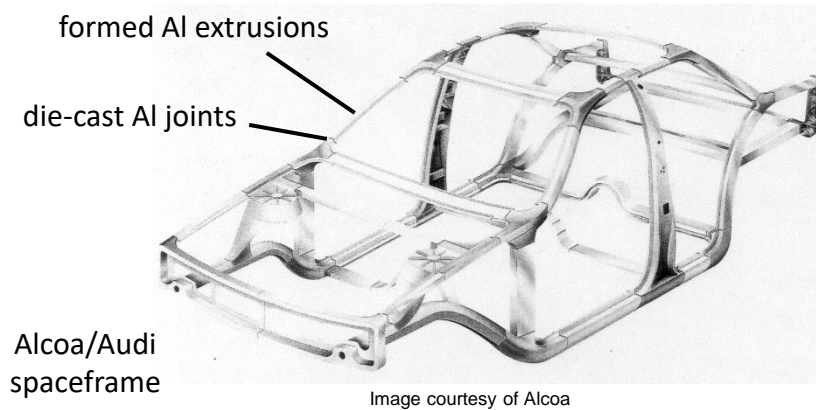
Aluminium (Al) alloys belong to the family of 'light alloys' (which includes titanium and magnesium). They play an important role in the design of lightweight components and structures. Aluminium has a density and stiffness about 1/3 that of steel:

$$\rho = 2700 \text{ kg/m}^3, \quad E = 70 \text{ GPa}$$

However, pure aluminium is soft (low strength): $\sigma_y = 40 \text{ MPa}$

For structural applications, the strength can be increased by a factor of 10 through alloying and heat treatment.

High strength aluminium alloys are particularly important for weight reduction in transport applications (automotive, aerospace, rail, marine).



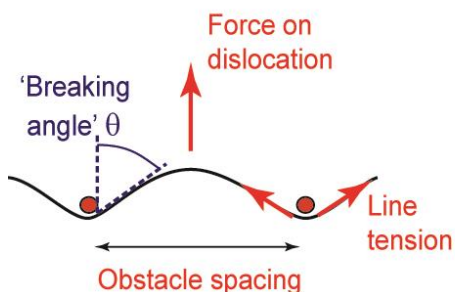
Jaguar F-Type

The most important hardening mechanism for high strength Al alloys is **precipitation hardening** – pinning of dislocations by strong, second phase particles. Heat treatment processes can be used to manipulate the **precipitation phase transformation** to produce strong, tough microstructures.

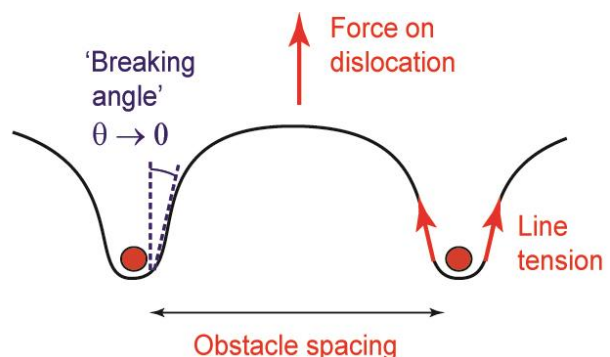
Recall from IA the key points for precipitation hardening:

- The yield stress is inversely proportional to the obstacle spacing.
- It also depends on the strength of the obstacle.

'Weak' dislocation pinning



'Strong' dislocation pinning

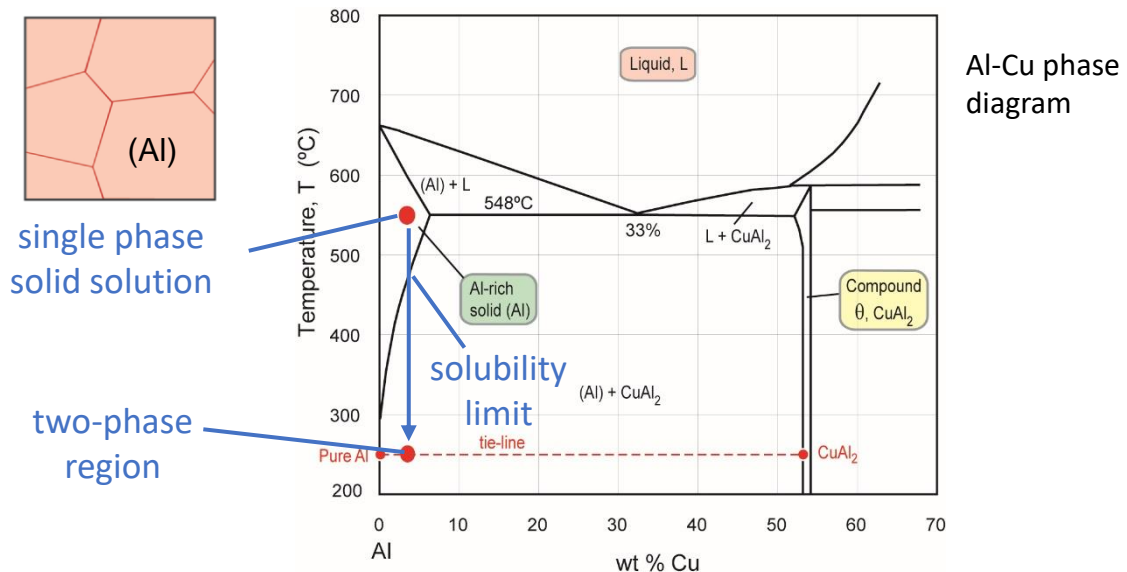


2.1 Composition range for heat treatable Al alloys

Aluminium can be combined with a variety of other elements, resulting in a large family of alloys. We will use Al-Cu alloys here as an example, as it is commonly heat treated to improve its strength.

The phase diagram can be used to identify suitable alloy compositions for heat treatment, and critical temperatures for the heat treatment process. The key requirements for heat-treatable alloys are:

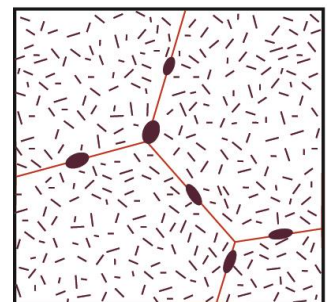
- At high temperature: **single phase solid solution** (high solubility of alloy additions)
- At low temperature: **two-phase region** (low solubility of alloy additions)
- A **solvus line** (solubility limit) is crossed on cooling, driving precipitation of the second phase, which is required for precipitation hardening.



The fall in solubility of the (Al) phase on cooling is the key feature of the phase diagram being exploited for precipitation hardened alloys. Recall from Teach Yourself Phase Diagrams that **slow cooling** allows time for the equilibrium microstructure to form:

- Below the solvus line, a two-phase mixture has the lowest Gibbs free energy, and so a phase transformation occurs:
 $(\text{Al}) \rightarrow (\text{Al}) + \text{CuAl}_2$
- Cu is rejected from the single phase (Al) solid to form CuAl₂ precipitates. The **driving force** for precipitation is the reduction in Gibbs free energy. **Diffusion** enables the transformation to occur.
- Precipitates nucleate most easily **heterogeneously** on grain boundaries (more space in the Al lattice, faster diffusion). The largest precipitates will occur here. Precipitates can also nucleate **homogeneously** within the grains.

Precipitates of CuAl₂ in (Al)



However, this slow-cooled microstructure provides ineffective precipitation hardening:

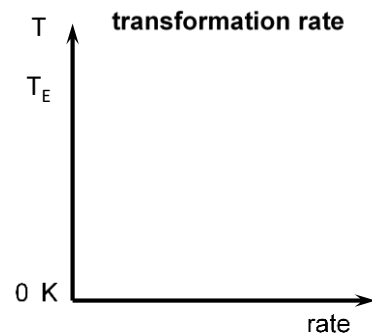
- Precipitates are large and spaced far apart. Precipitate coarsening is driven by Gibbs free energy, as it reduces the interface area (and interface energy penalty) per unit precipitate volume. Slow cooling gives time for this coarsening to occur.
- They provide ineffective obstacles to dislocations: $\sigma_y \propto 1 / \text{obstacle spacing}$

2.2 Rapid cooling of Al alloys (quenching)

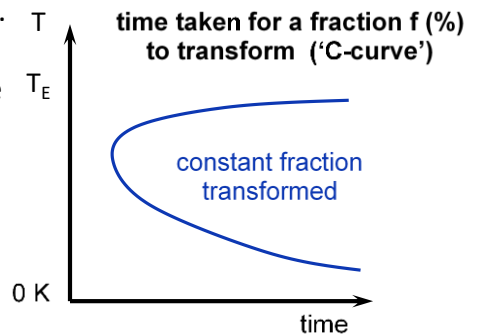
Consider next the effect of increasing the cooling rate of the alloy, from the single-phase solid solution. Recall from earlier lectures that phase transformation rate depends on **temperature** and **time**, as follows:

- The overall rate of transformation depends on the rates of **nucleation** and **growth**.
- This in turn depends on the **undercooling**:

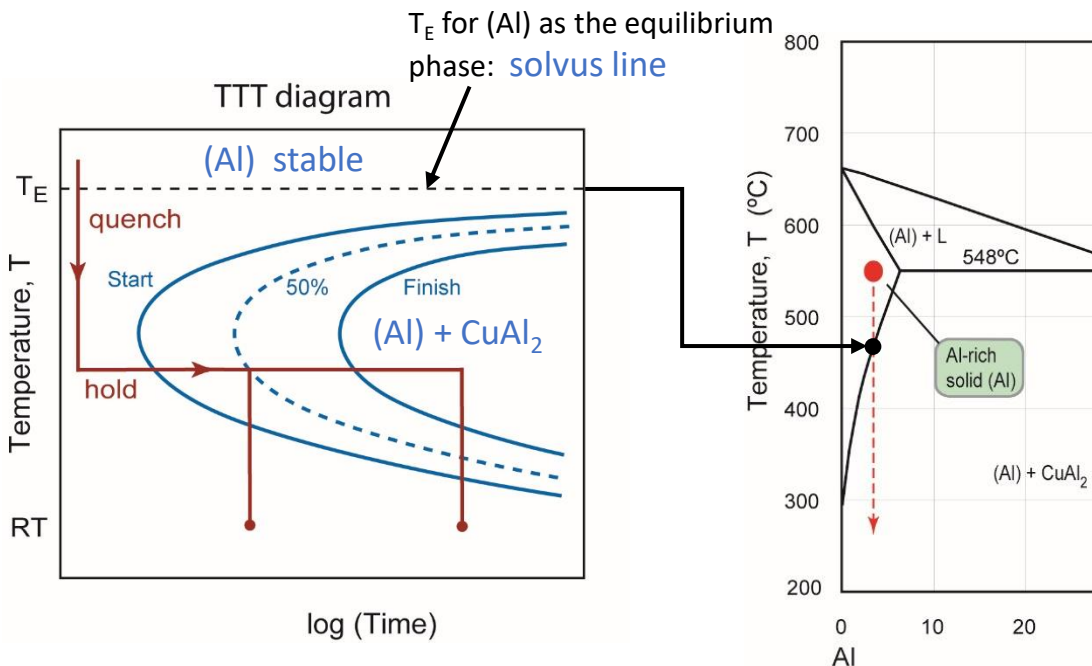
$$\Delta T = T_E - T$$
- Small $\Delta T \rightarrow$ small $\Delta G \rightarrow$ low thermodynamic driving force.
- Large $\Delta T \rightarrow$ low thermal energy \rightarrow rearrangement of atoms by diffusion is slow.
- The peak rate occurs at an intermediate temperature.



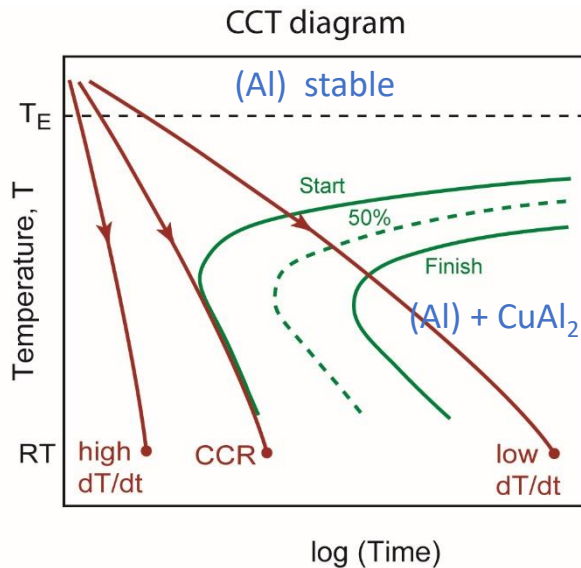
It is convenient in materials processing to invert the rate axis and show instead the **time taken** for a certain fraction to transform ('C-curve'). The plot of fraction transformed for a given temperature and time is known as a Time Temperature Transformation (TTT) diagram.



The same principles govern precipitation in the aluminium alloy:



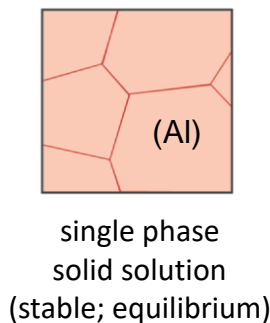
Note that TTT diagrams apply to **isothermal** transformations only (i.e. with the specimen held at a fixed temperature). In practical heat treatment processes, **continuous cooling** is more likely to occur. There is an analogous **continuous cooling transformation (CCT)** diagram, where the C-curves show the fraction transformed for a fixed cooling rate.



- A key piece of information shown by the CCT diagram is the **critical cooling rate (CCR)**.
- This is the slowest cooling rate that just avoids the C-curves.
- Cooling at this rate or faster means that **no precipitation phase transformation** occurs. There is insufficient time or temperature for nucleation of precipitates.

Material cooled faster than the critical cooling rate will therefore remain a single phase solid solution at room temperature:

Above T_E (above the solvus line):

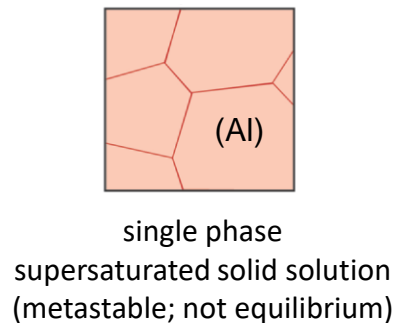


quench



$$\frac{dT}{dt} \geq \text{CCR}$$

Room temperature:



This is not the equilibrium state: it is a “metastable” micro-structure. There is more Cu trapped in the Al lattice than the equilibrium amount, and it is therefore known as a **supersaturated solid solution (SSSS)**.

This results in a material with effective **solid solution hardening**. It has a higher yield strength than the slow-cooled alloy with the coarse precipitates. However, this is still not the optimum microstructure for maximum strength.

2.3 Age hardening

A higher yield strength than either slow-cooled or quenched alloys can be achieved by a process known as **age hardening**. The aim of this heat treatment process is to achieve precipitation hardening, but compared to slow cooling we want:

- precipitates that are smaller and more closely spaced,
- more effective obstacles to dislocations.

The process consists of three steps:

(1) **solution heat treatment**

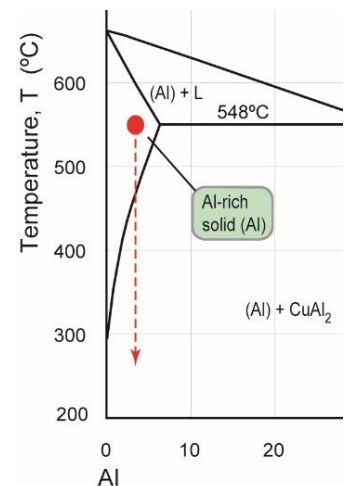
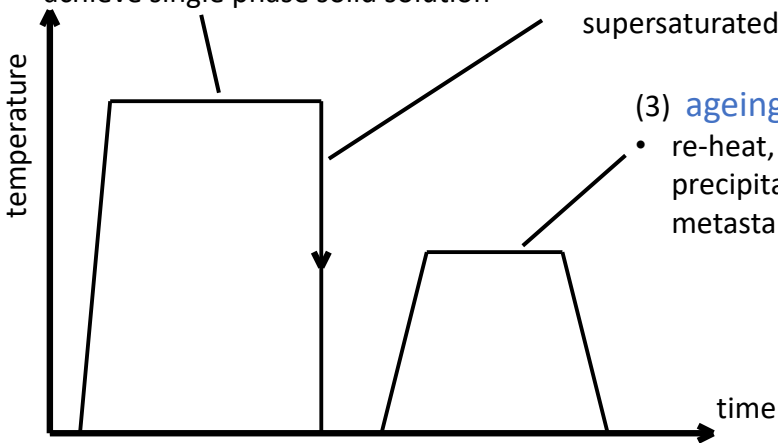
- dissolve alloying elements, to achieve single phase solid solution

(2) **quenching**

- cool faster than the CCR, forming a supersaturated solid solution (SSSS)

(3) **ageing**

- re-heat, allowing time for precipitation to occur from the metastable SSSS

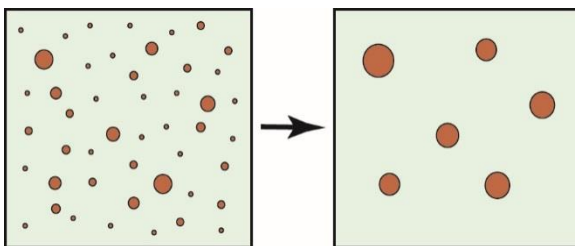


There are two options for the ageing step:

- **artificial ageing:** re-heat for a few hours at around 150-200°C (which still keeps the material within the two-phase region on the phase diagram),
- **natural ageing:** leave for several days at room temperature.

During the ageing step, precipitates nucleate and grow. The size and spacing of the precipitates can be controlled by varying the **ageing time and temperature**.

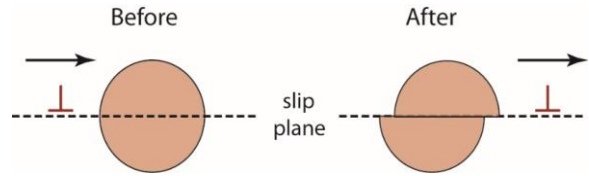
With increasing ageing time, the precipitates coarsen: **average size and spacing** ↑



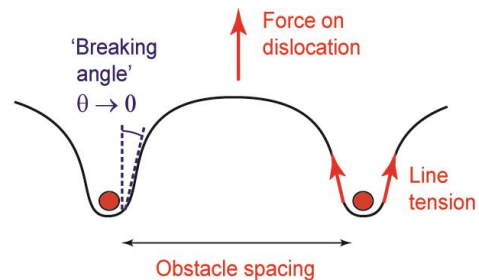
- Driven by Gibbs free energy: coarsening reduces the (Al) / precipitate interface area (interface energy penalty).
- Higher ageing temperature means:
 - more rapid coarsening
 - but a lower equilibrium fraction of precipitates (from the phase diagram).

As the precipitates grow, the effectiveness of the precipitation hardening changes:

- When the precipitates are small, dislocations easily shear through them. They are weak obstacles.
- As they grow, the shearing resistance increases with the radius of the precipitate, until the dislocation breaking angle falls to zero.
- Typically: **strength** \propto **radius**^{1/2}
- As the precipitates get large, the spacing also gets large (the volume fraction of precipitates initially increases but then remains fixed).
- Strength is now dominated by dislocations “bypassing” obstacles (breaking and reforming of the dislocation)
- **Strength** \propto **1 / spacing** \propto **1 / radius**

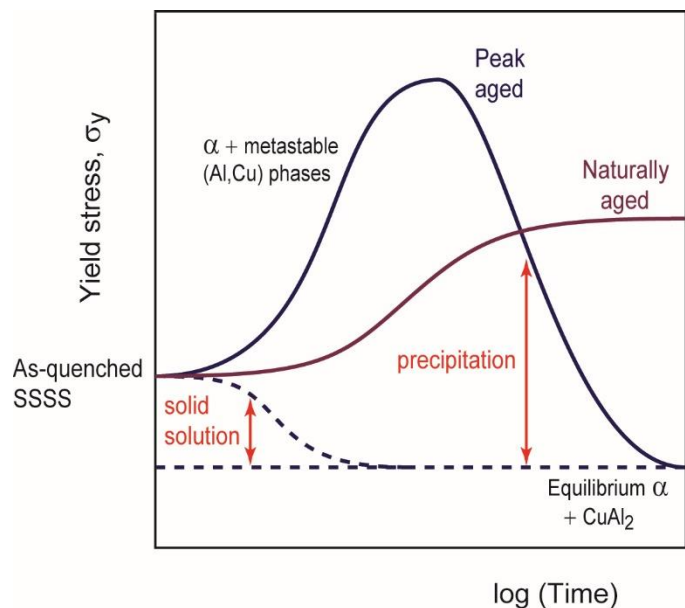
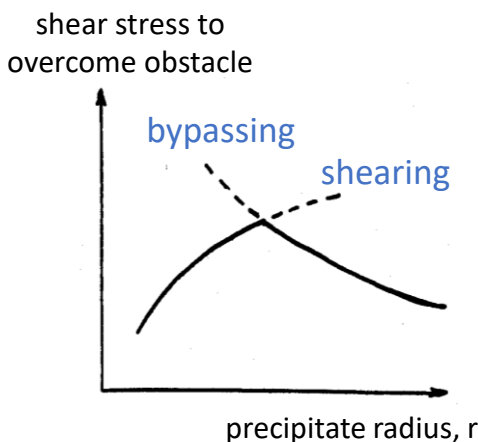


precipitate shearing
radius $\uparrow \Rightarrow$ strength \uparrow



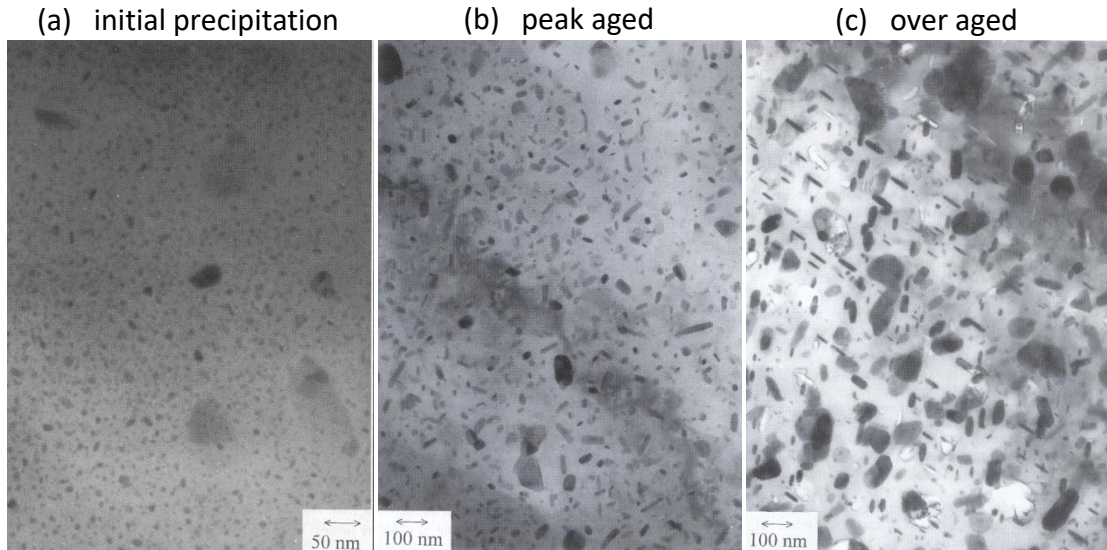
dislocation bypassing
radius $\uparrow \Rightarrow$ strength \downarrow

These two effects trade off as the precipitates grow: precipitate shearing dominates the strength at first, then bypassing. A peak in resistance is seen when the two mechanisms swap over. The strength of the material varies with ageing time as shown:



- **Artificial ageing:** yield stress rises to a ‘peak aged’ condition, and then falls to a soft ‘overaged’ state (which is similar to the slow cooled material).
- **Natural ageing:** the low temperature means slow diffusion, and precipitates remain small; yield stress rises more slowly, to an intermediate plateau value.

Experimental evidence from transmission electron microscopy (TEM) of high-strength aerospace Al-Zn-Mg-Cu alloy (artificially aged):



(note scale:
cf. diameter of Al atom = 0.28 nm)

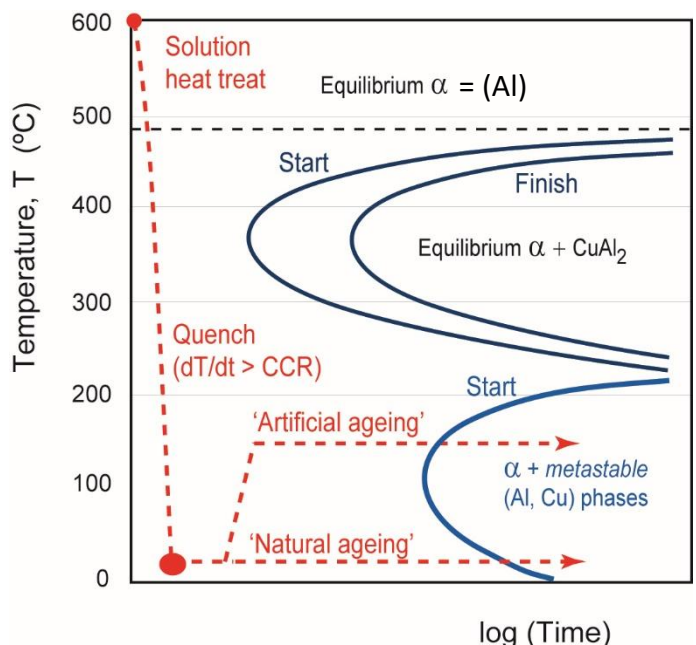
Source: Poole W.J., Shercliff H.R. and Castillo T.,
Mat. Sci. Tech. 13, Nov. 1997, pp.897-904

Note that in **natural ageing**, the microstructure evolution stops at a point similar to (a) above. There is insufficient thermal energy for ageing to continue, and the material remains “underaged” (but with useful strength, and with lower processing cost).

2.4 Age hardening: further microstructural details

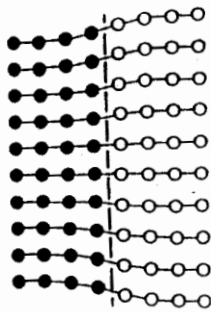
We will look more closely now at the details of this age hardening process. This is important to understand why some aluminium alloys age harden in this way, but some do not (the latter are known as “non-heat-treatable” alloys).

- A first look at the TTT diagram suggests there would be no precipitation during ageing – the time to produce CuAl_2 is very long at ageing temperatures.
- However: **metastable (non-equilibrium) precipitates** can form at these low temperatures (even at room temperature).
- There is another set of C-curves governing the precipitation of these metastable phases.



Metastable precipitates have a different crystal structure to equilibrium CuAl_2 :

Al lattice precipitate

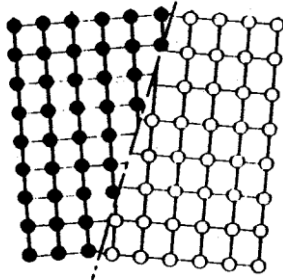


coherent

- The precipitate is **coherent**, i.e. its crystal lattice matches that of the Al closely. This reduces the **interface energy** penalty to nucleation.
- Because slip planes are continuous across the interface, dislocations easily cut through these precipitates (the “shearing” mechanism).
- They are weak obstacles, with a high dislocation breaking angle.

As coarsening proceeds, coherency increasingly strains the lattice:

Al lattice precipitate



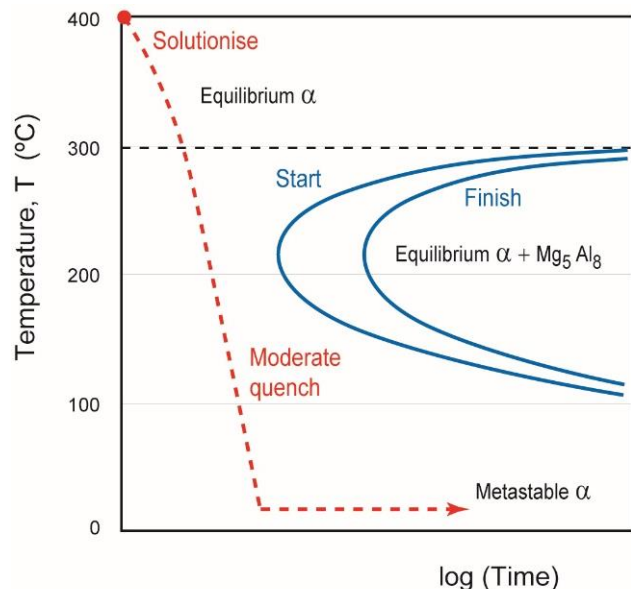
incoherent

- Overall, it becomes energetically favourable for the precipitates to transform through a whole **sequence of metastable phases**, eventually reaching equilibrium CuAl_2 , with a progressive loss of coherency at the interface.
- This is the result of a tradeoff between the interface energy penalty (coherent vs incoherent) and the volumetric Gibbs free energy penalty (of metastable precipitates vs equilibrium CuAl_2).

The precipitates at the peak-aged state will be fine metastable precipitates, with larger equilibrium CuAl_2 precipitates occurring in the over-aged material.

Non-heat-treatable Al alloys:

- Some alloys, due to their composition, do not form these metastable precipitates at lower temperatures.
- Precipitates only form with very slow cooling, which would give coarse precipitates, providing negligible hardening. Even a modest quench will retain a 100% super-saturated solid solution.
- So, they rely on solid solution and work hardening.
- Examples include: Al-Mg (‘5000 series’), Al-Mg-Mn (‘3000 series’).



2.5 Summary of the learning outcomes: heat treatment of Al alloys

After completing section 2 you will be able to do the following:

1. Use the phase diagram to identify suitable composition and temperature ranges for the heat treatment of an Al alloy.
2. Use TTT and CCT diagrams to explain the differences in microstructure and properties between slow cooled and quenched aluminium alloys.
3. Describe the evolution of the microstructure and properties during age hardening.
4. Explain the difference between heat treatable and non heat treatable Al alloys.

2.6 Quiz W5.1: heat treatment of Al alloys

Samples of a heat treatable aluminium alloy are initially held at high temperature until they become a single-phase solid solution.

Sample A: cooled slowly

Sample B: quenched

Sample C: quenched and aged

Which of the following statements are correct (more than one can be correct)?

1. B has a higher yield strength than A, because there is solid solution hardening instead of precipitation hardening.
2. C has a higher yield strength than B, because there is precipitation hardening instead of solid solution hardening.
3. C has a higher yield strength than A, because there is precipitation hardening instead of solid solution hardening

Additional worked examples: heat treatment of Al alloys

For further explanation, a video will be available with the following worked examples:

- Tripos Question 2016 Q3, which helps with Examples Paper 4 Q1.
- A discussion of Examples Paper 4 Q1(b-c), and non-heat-treatable alloys.

Now attempt: Examples Paper 4, Q.1

3. Heat treatment of steel

Steels (Fe-C alloys) are the most widely used class of engineering alloys. In this section we will consider how heat treatment can be used to manipulate their microstructure and mechanical properties. Steels are an important engineering alloy due to their stiffness, strength and low cost, though this comes with a high density:

$$\rho = 8000 \text{ kg/m}^3, \quad E = 210 \text{ GPa}$$

Mild steels (0.1-0.2 wt% C) are ubiquitous structural materials. Alloying and heat treatment can be used to produce extremely hard steels, useful for cutting tools, wear resistant gears etc.

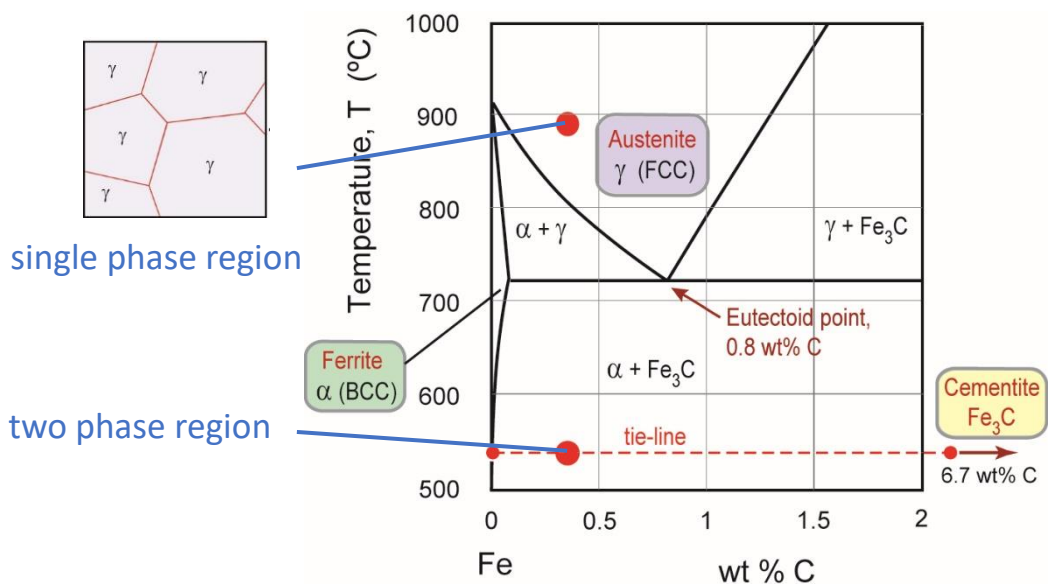
mild steel
 $\sigma_y \approx 300 \text{ MPa}$



alloy steel, heat treated
up to
 $\sigma_y \approx 2000 \text{ MPa}$

Images: Corus media gallery

The key region of the phase diagram for the heat treatment of steels is shown below. Typical steel compositions lie in the range ~0.1 - 2 wt% C. 'Mild steels' have a low C concentration, ~0.1-0.2 wt% C. In what follows, we focus on **hypo-eutectoid** steels: those with composition <0.8 wt %.



Like Al alloys, the heat treatment of steels involves moving between single and two-phase regions of the phase diagram. However, unlike the precipitation phase transformation in Al alloys, steel involves a **three-phase reaction**:

- FCC Austenite (γ) → BCC Ferrite (α) + Fe₃C

3.1 Slow cooled steel

The microstructures of slow cooled steels were introduced in Teach Yourself Phase Diagrams. A brief recap is provided here. Slow-cooled steels are referred to as **normalised**. Hot-rolled steel is often in this condition.

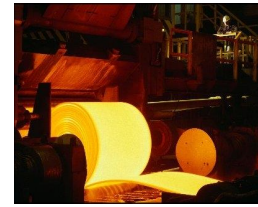
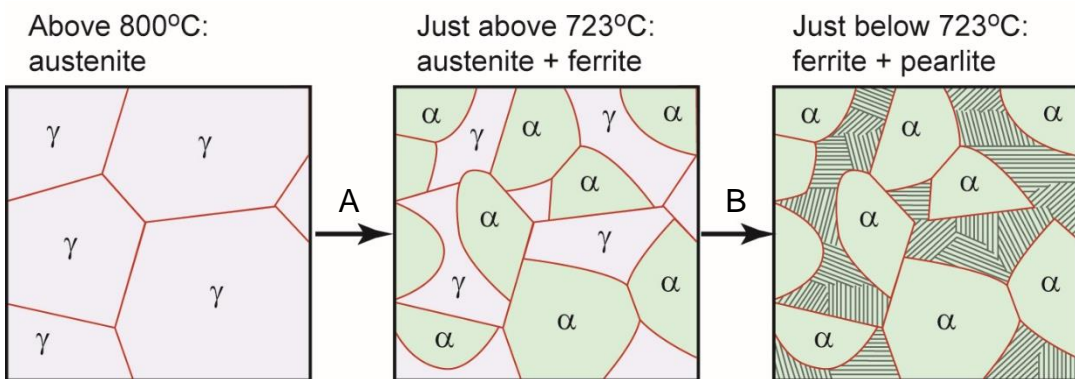
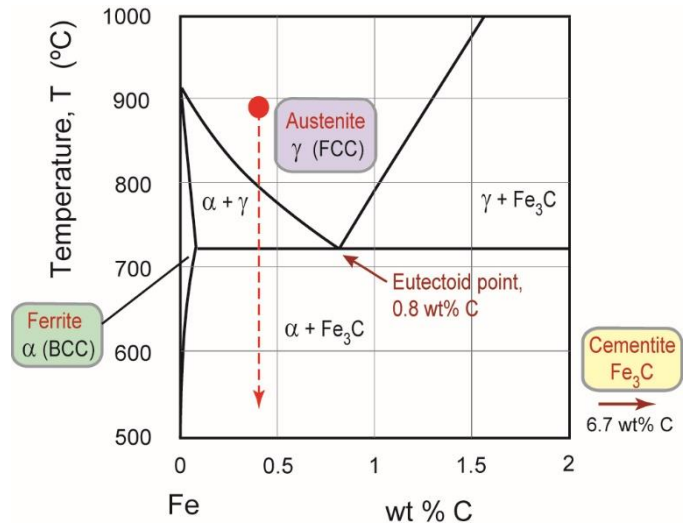


Image: Corus media gallery

Microstructure evolution on slow cooling for a Fe – 0.4 wt% C steel:

(A) the material enters the two-phase $\alpha + \gamma$ region at around 800°C;
– the ferrite α rejects carbon into the austenite γ ;

(B) at the eutectoid temperature, the austenite (now containing 0.8wt% C) transforms to the microstructure pearlite, containing the phases ferrite α + cementite Fe_3C .

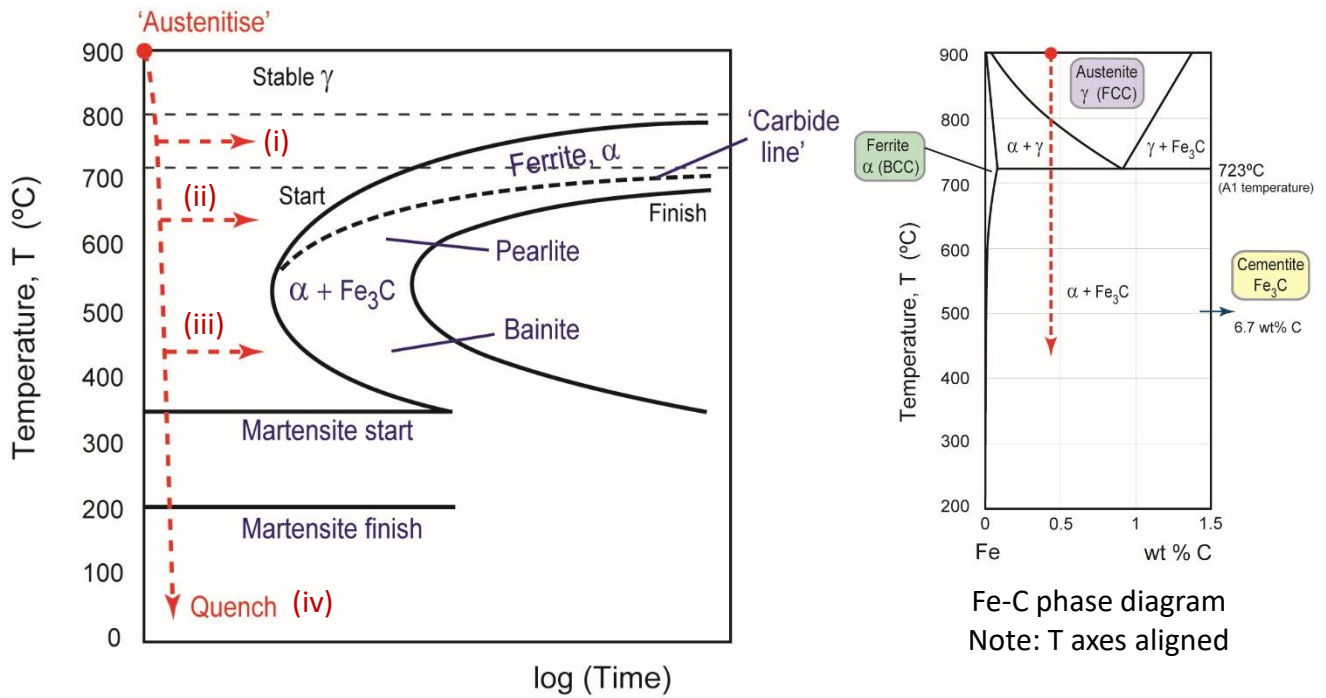


The properties of normalised hypo-eutectoid steels are determined by the **carbon content**:

- The carbon content affects the proportion of ferrite and pearlite: the level rule, applied just above the eutectoid temperature, gives the proportion of austenite, which transforms into pearlite on further cooling.
- Cementite is very hard, and the pearlite structure obstructs dislocation motion effectively. So, the higher the pearlite fraction, the harder the material.
- **Low carbon** steels have only a small proportion of pearlite, and have a yield stress around **200 MPa**, which is combined with high ductility. This is the lower end of the strength range.
- Normalised **eutectoid steel** (100% pearlite) has a yield stress around **450 MPa**, but with lower ductility. This is the upper end of the strength range.

3.2 TTT diagrams for hypo-eutectoid steels

Just like Al alloys, cooling rate has a significant effect on the microstructure and properties of steel. We can use the TTT diagram to assess the influence of **temperature and time** on the phase transformations. The TTT diagram for **0.4 wt% C, hypo-eutectoid steel** is shown below, alongside the phase diagram for comparison:



The various transformations (i)-(iv) shown on the TTT diagram are now described in turn:

(a) Diffusion-controlled transformations (higher temperatures):

austenite, $\gamma \rightarrow$ ferrite, α + cementite, Fe_3C (equilibrium phases)

TTT diagram has the conventional C-curve shape for diffusional phase transformations at higher temperatures, with the following details (for hypo-eutectoid steels):

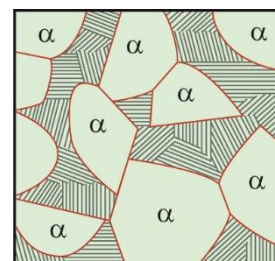
(i) **above** the “nose” of the C-curves, and **above** the “A1 temperature”, 723°C:

- ferrite forms first (from austenite grain boundaries)
- final microstructure: ferrite + austenite (proportions given by the tie line)

(ii) **above** the “nose” of the C-curves, and **below** the “A1 temperature”, 723°C:

- ferrite forms first (from austenite grain boundaries)
- transformation switches from ferrite to pearlite at the **carbide line**;
- final microstructure: ferrite + pearlite

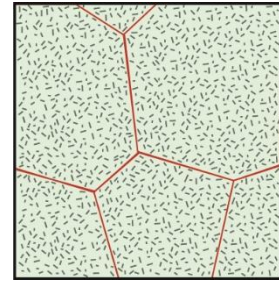
Microstructure: A quench-and-hold close to (and below) the A1 temperature is essentially very similar to **slow continuous cooling**, as discussed above. Shown right is the final microstructure for case (ii).



(iii) **below** the “nose” of the C-curves: diffusion is more inhibited

- austenite transforms directly to ferrite + iron carbide, in a fine-scale dispersion
- this microstructure is called **bainite**.

Microstructure: Bainite nucleates on the austenite grain boundaries, with simultaneous growth of ferrite and iron carbide, giving a **fine-scale dispersion** of iron carbide needles within a ferrite matrix (rather than the lamellar structure of pearlite).

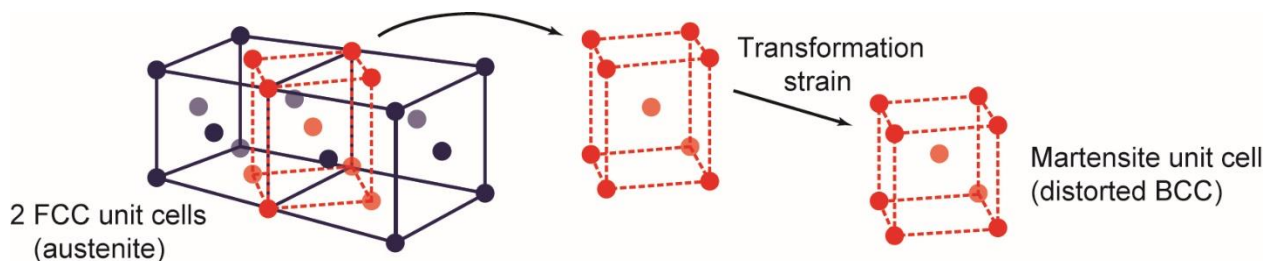


(b) Diffusionless transformation (lower temperatures):

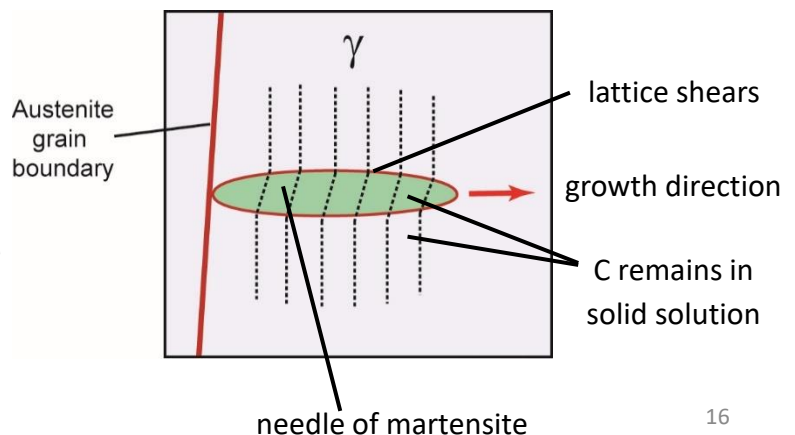
austenite, $\gamma \rightarrow$ martensite, α' (metastable phase)

Quenching carbon steels to bypass the nose of the C-curves (i.e. faster than the Critical Cooling Rate) prevents diffusive phase transformations from taking place. Instead there is a transformation to a metastable phase called **martensite (α')**: case (iv) .

- Quenching produces a **supersaturated solid solution** of C in Fe, i.e. there is more carbon trapped in the Fe lattice than the equilibrium amount (similar to the Al alloy case).
- However, in contrast to Al alloys, iron is FCC at high temperatures (austenite), but BCC at low temperatures (ferrite). Therefore the SSSS is also initially in the ‘**wrong**’ **atomic packing**, compared to equilibrium.
- To overcome this, the material can get closer to BCC **without diffusion**, by a modest distortion (straining) of the lattice. This is the **martensite phase transformation**.

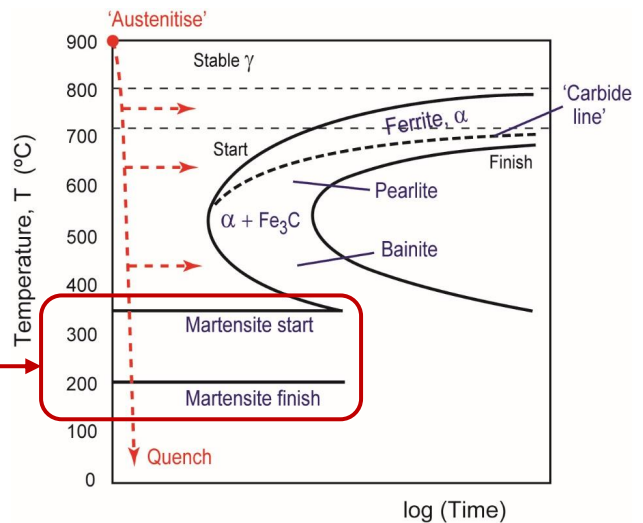


This lattice shape change is achieved by **shear** – narrow regions shear across the austenite grain (at the speed of sound in the material, effectively instantaneously), leaving a needle of the martensite phase within the austenite grain.



This transformation takes place **without diffusion**:

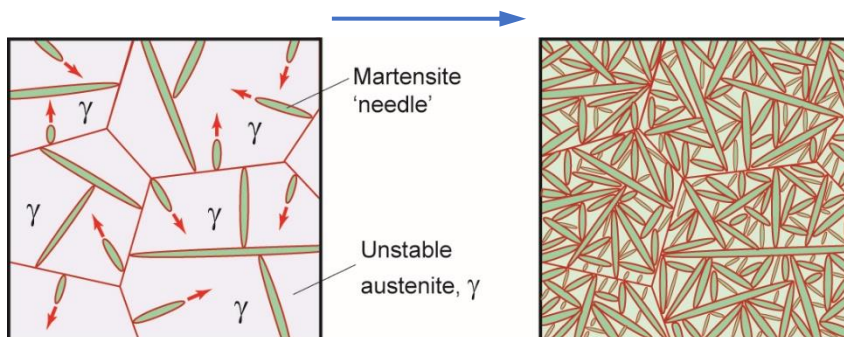
- there is **no time-dependence** on the TTT diagram,
- the contours of fraction transformed are horizontal lines.



However, the fraction transformed does depend on the **temperature**:

- Martensite begins to form at the “**martensite start temperature**”, M_s
- Reducing the temperature further increases the fraction of austenite that transforms to martensite.
- The transformation is complete at the “**martensite finish temperature**”, M_F

lower temperature: larger fraction transformed



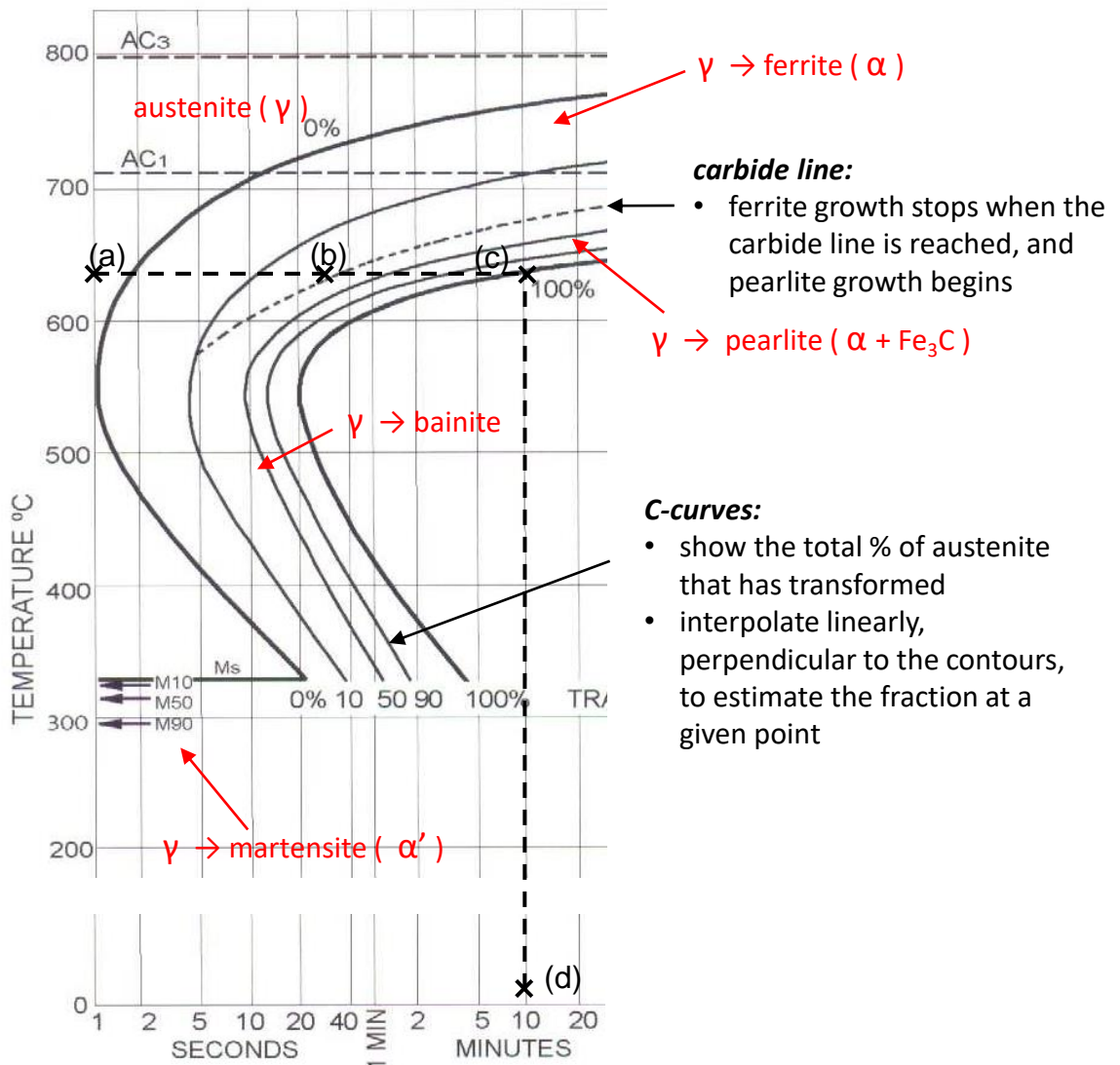
This is for thermodynamic reasons:

- As the temperature falls, at a temperature well below A_1 (see above), the Gibbs free energy of the martensite phase becomes lower than the austenite phase: there is a **thermodynamic driving force** (ΔG) for the martensite phase transformation.
- A certain degree of **undercooling** (and hence ΔG) is needed to start the transformation. This occurs at the martensite start temperature.
- At a given temperature, the transformation of a percentage of the austenite into martensite can **reduce the free energy** sufficiently to stop further transformation.
- The undercooling (and ΔG) must be increased further to induce further transformation. This completes at the martensite finish temperature.

Example: reading from the TTT diagram for a hypo-eutectoid steel

Estimate the final microstructure for the hypo-eutectoid steel with the TTT diagram shown below, subject to the following heat treatment:

- Austenitise (i.e. solution heat treat) for 30 minutes at 850°C
- Quench to 630°C, hold for 10 minutes, quench to room temperature.



Point	Total % transformed (from the C - curves)	Transformed phases	Balance
(a)	0 %	none	100% austenite
(b)	40 %	40% ferrite	60% austenite
(c)	100 %	40% ferrite + 60% pearlite	none
(d)	100 %	40% ferrite + 60% pearlite	none

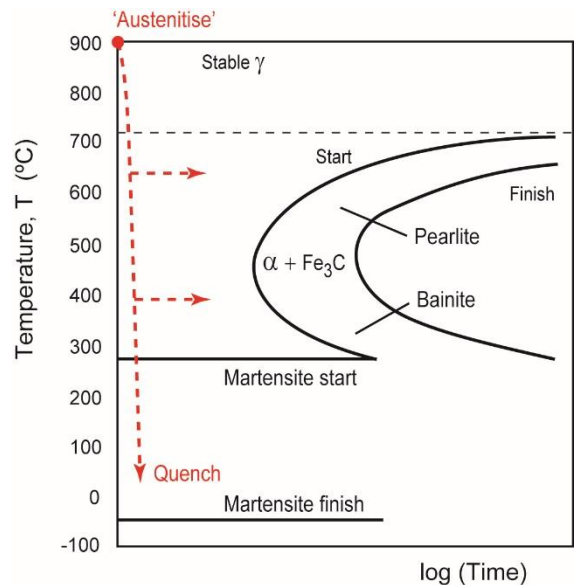
Note that no martensite transformation occurs between (c) and (d), as there is no austenite left at (c) to transform on quenching. It has all transformed to ferrite and pearlite, which is unaffected by the quench.

3.3 Effect of carbon content on the steel TTT diagram

As the carbon content of hypo-eutectoid steel **increases** (between ≈ 0.1 and 0.8 wt% C), there are systematic changes to the TTT diagram:

(1) The proportion of ferrite to pearlite decreases:

- This follows the phase diagram, and the lever rule applied just before the eutectoid transformation (see examples paper 1).
- At the **eutectoid composition**, the ferrite region has disappeared altogether: the carbide line on the TTT diagram merges with the curve for the start of transformation, which **goes straight to pearlite** above the nose.

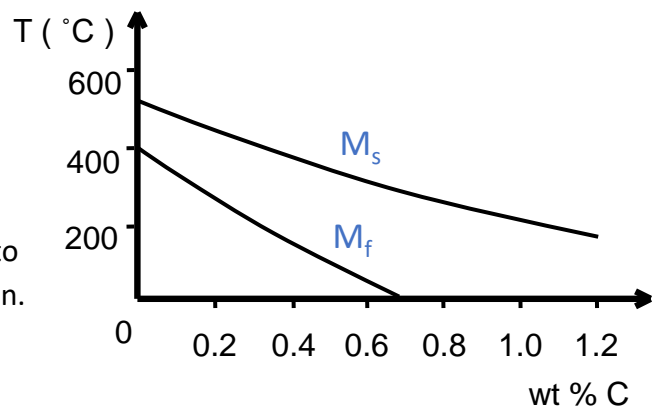


(2) The C-curves move to longer times:

- The greater amount of C to redistribute delays all of the diffusional transformations.

(3) The martensite start and finish temperatures decrease:

- More carbon in supersaturated solid solution means more lattice strain.
- This requires a greater undercooling to achieve the martensite transformation.

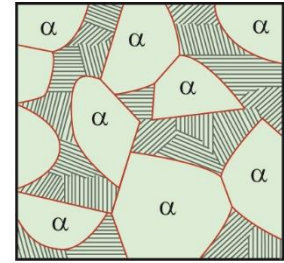


Note that for eutectoid steel, M_f is -50°C . At room temperature, a quenched specimen will therefore contain a fraction of retained austenite.

3.4 Properties of bainite and martensite

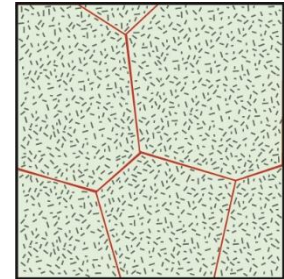
Recall that **slow cooled** ('normalised') hypo-eutectoid steels have a yield strength dependent on the carbon concentration (and hence pearlite fraction) in the range:

$$\sigma_y \approx 200 - 450 \text{ MPa} \\ (0.1 - 0.8 \text{ wt\% C})$$



Bainite has the ideal microstructure for effective precipitation hardening: a fine-scale dispersion of hard precipitates (Fe_3C). Also, all grains have the same microstructure and strength. Yield strengths are in the range:

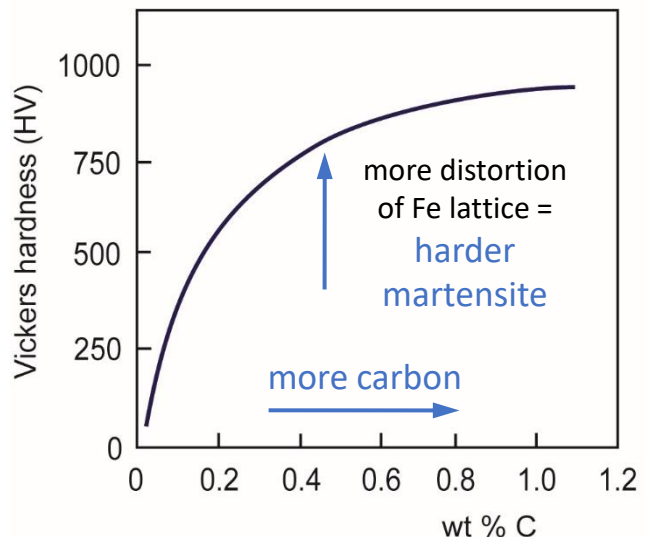
$$\sigma_y \approx 500 - 700 \text{ MPa}$$



Martensite has a very high yield strength (i.e. high hardness):

$$\sigma_y \approx 1000 - 3000 \text{ MPa}$$

- The BCC Fe lattice is heavily supersaturated with carbon. This gives **solid solution** hardening.
- This is further enhanced by the **distortion of the lattice**, as many interstitial holes contain C atoms that are too large to fit.
- The higher the C content, the greater the distortion of the lattice, and the higher the hardness.



It is also extremely brittle. For practical purposes, it can be considered to have **negligible fracture toughness** ($< 5 \text{ MPa.m}^{1/2}$).

3.5 Quenching and tempering of carbon steels

Martensite is rarely used in its as-quenched form: the low toughness means the component would shatter easily. Hence, it needs to be **tempered**: re-heated to a temperature of order $450\text{-}600^\circ\text{C}$ (still in the two-phase $\alpha + \text{Fe}_3\text{C}$ region on the phase diagram) to encourage diffusion.

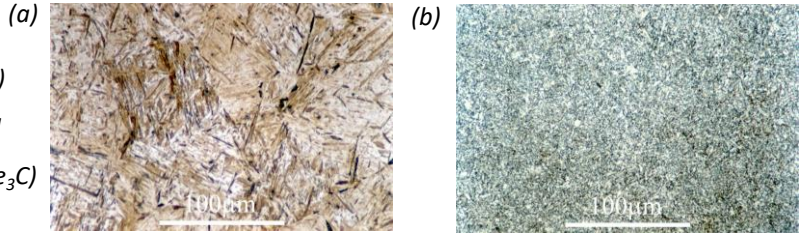
Tempering has the following effects:

- the yield strength reduces: after tempering $\sigma_y \approx 450 - 800 \text{ MPa}$
- the fracture toughness significantly increases.

This is due to the microstructural changes that takes place during tempering:

- The carbon in supersaturated solid solution diffuses to form Fe_3C precipitates.
- The Fe lattice changes from martensite to its equilibrium state: undistorted BCC.

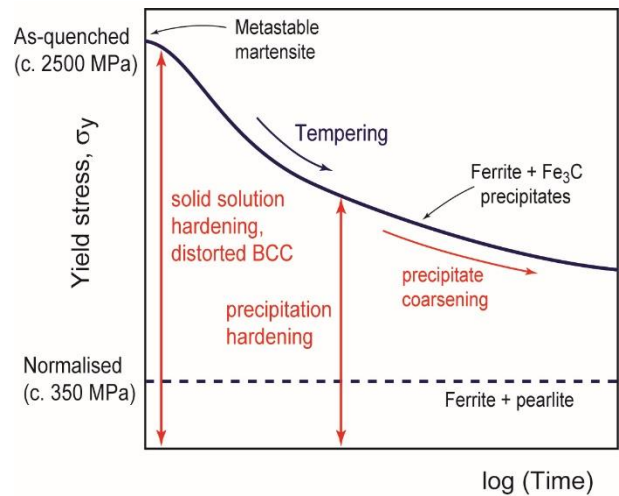
Fe – 0.9 wt% C steel:
 (a) quenched (martensite)
 (b) quenched & tempered
 (ferrite + cementite, Fe_3C)



Images: DoITPoMS micrograph library: https://www.doitpoms.ac.uk/miclib/full_record.php?id=318

As the tempering time increases, the Fe_3C precipitates coarsen, giving a steady fall in strength.

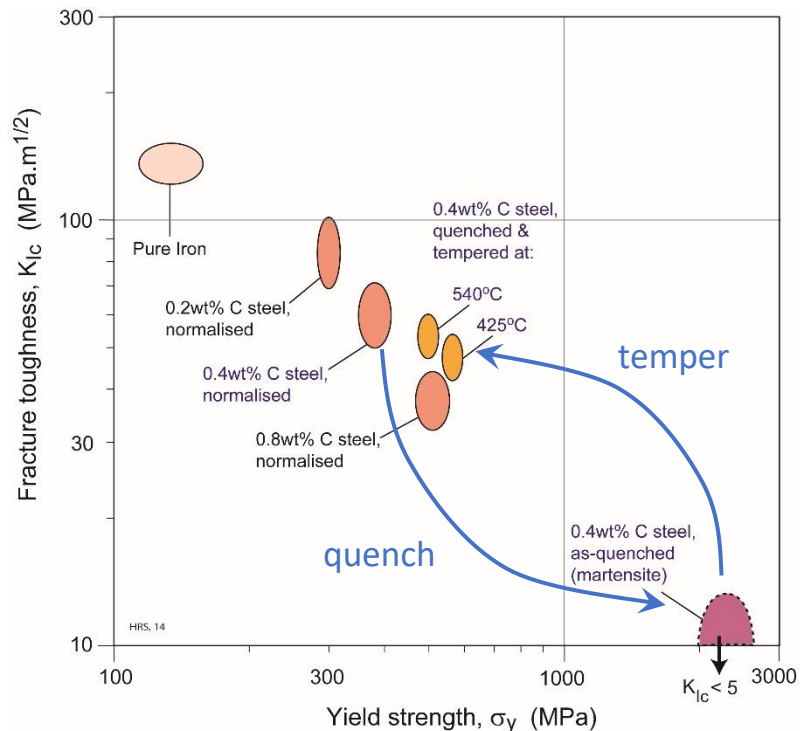
The tempering temperature also influences the softening rate (faster diffusion means faster coarsening), and the volume fraction of precipitates formed (from the phase diagram).



The fine-scale dispersion of carbides in tempered martensite provides excellent precipitation hardening. It results in a yield strength 2-3 times greater than slow cooled (normalised) steel, but with comparable fracture toughness.

Component cross-sections can therefore be reduced (saving weight), or design loads increased.

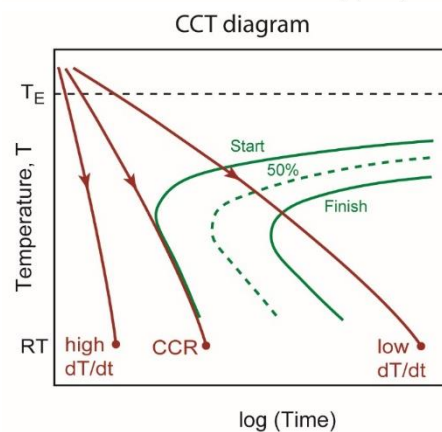
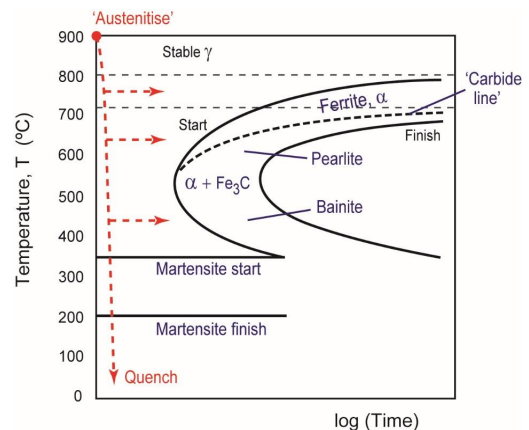
For further details see experiment M2.



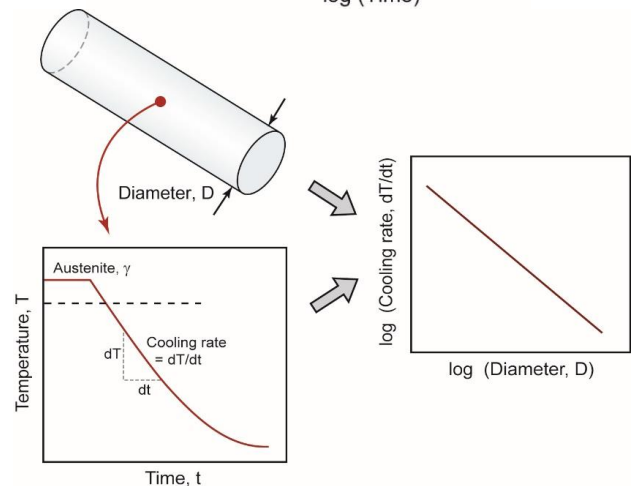
3.6 Hardenability

A key consideration for steels subjected to thermal cycles is the hardenability: how **easily a steel forms martensite** on cooling. Measures of hardenability:

- **TTT diagram:** the time taken for diffusive phase transformations to begin (e.g. ferrite, pearlite C-curves).
higher hardenability
= **longer transformation times**
- **CCT diagram:** the critical cooling rate, the slowest cooling rate that gives 100% martensite (i.e. just missing the nose of the C-curves).
higher hardenability
= **slower CCR**
- The largest **bar diameter** that will give 100% martensite at its centre after quenching:
higher hardenability
= **larger diameter**



Heat flow analysis is used to relate cooling rate and component geometry. Standard geometries are used to characterize the response of different steels: e.g. long cylinders, quenched in water, oil or air.



When do you want a steel with **high hardenability**?

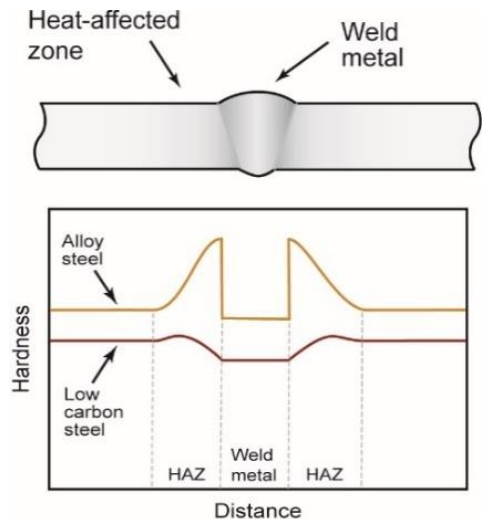
- When you want to form martensite easily, typically when you want to **quench and temper** the steel, e.g. for cutting tools (you need high hardness and toughness).
- High hardenability means a **larger component** can be “through hardened”, i.e. forming martensite through the whole cross-section that can then be tempered.
- High hardenability also means a component of a given size can be **cooled more slowly** (e.g. by air cooling) while still achieving 100% martensite. This gives much lower thermal stress, reducing thermal distortion and the risk of quench cracking (noting that martensite is brittle).

When do you want a steel with **low hardenability**?

- When you **do not** want to form martensite on cooling, for example: welding.
- Fusion welding involves traversing a heat source (flame, arc or laser) along the joint line between two components
- The thermal cycle will form austenite in the heat affected zone (HAZ) close to the weld metal (the region that melts); this could form martensite on cooling.
- In this context, forming martensite is undesirable – it is brittle, risking weld failure by fast fracture.

high hardenability

= poor weldability



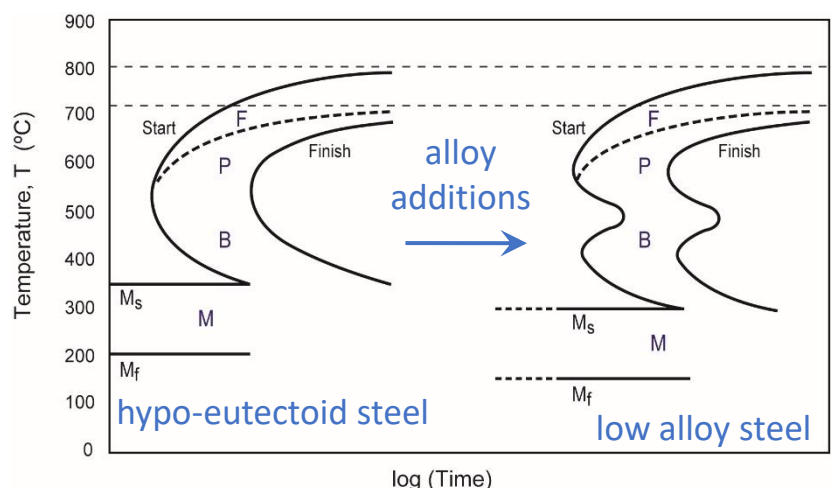
Factors affecting the hardenability of steels:

(1) Carbon concentration:

- Increasing the C content increases the hardenability, by delaying the diffusional phase transformations (see above).
- However, the effect is relatively weak: even eutectoid steel requires a bar diameter < 30mm (water quenched) to form 100% martensite in the centre. Heat-treatable steel components can be considerably larger than this.

(2) Further alloying:

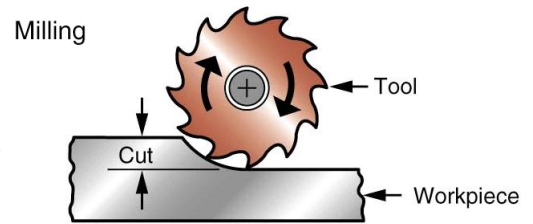
- This increases the hardenability by delaying the diffusional phase transformations.
- If up to 5 wt% of various alloying elements (Ni, Cr, Mo, V, W) are added, these are known as **low alloy steels**.



- For the $\gamma \rightarrow \alpha$ phase transformation to take place, these alloying elements need to be rearranged by diffusion (as they have a different solubility in FCC austenite vs BCC ferrite).
- This diffusion of substitutional solute elements takes time, and hence shifts the C-curves to longer times.

High alloy steels for cutting tools:

- As well as needing high hardenability (to allow quenching and tempering) tools for high-speed metal-cutting often operate at **high temperatures** (due to the heat generated by plastic deformation).
- In plain C steel, the Fe_3C precipitates may coarsen (or re-dissolve), leading to softening.



To prevent this, **high alloy steels** are used (containing Mo, W and V – up to 20 wt% in total). These elements perform multiple functions:

- increasing the hardenability;
- the quench and temper treatment also leads to the formation of **alloy carbides** (Mo_2C , W_2C , VC) – these are stable at high temperatures, retaining **precipitation hardening** in service;
- contribute to high temperature **solid solution hardening**.

3.7 Summary of the learning outcomes: heat treatment of steels

After completing section 3 you will be able to do the following:

1. Use the phase diagram to explain the microstructure, and hence properties, of slow cooled steel.
2. Use the TTT diagram to explain the effect of transformation temperature and time on the microstructure and properties of steel.
3. Describe the microstructure and properties that result from quenching and tempering steel.
4. Explain what is meant by the 'hardenability' of steel, why it is important in steel processing, and how it can be influenced.

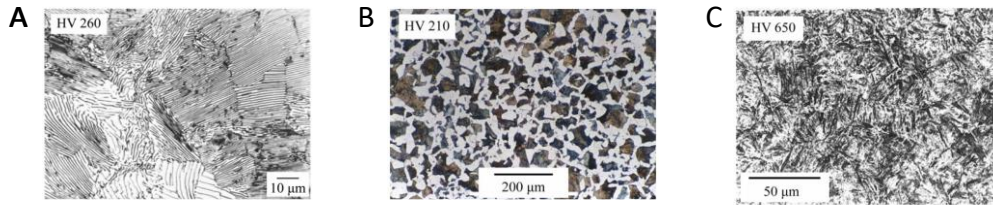
3.8 Quiz W5.2: heat treatment of steels

Three steel samples are compared:

Sample A: 100% pearlite, hardness HV 260

Sample B: 50% pearlite and 50% ferrite, hardness HV 210

Sample C: 100% martensite, hardness HV 650



Which of the following statements are correct (more than one can be correct)?

- 1) A is harder than B because it has been cooled more rapidly.
- 2) C is harder than A because it has a higher carbon concentration.
- 3) C has the highest hardness because it has undergone a displacive rather than a diffusive phase transformation.
- 4) A, B and C can be tempered to increase their ductility.

Additional worked examples: heat treatment of steels

For further explanation, a video will be available with the following worked examples, which help with Examples Paper 4 Q2-4:

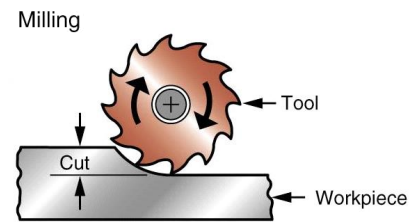
- Tripos Question 2008 Q2.
- Tripos Question 2016 Q4(d).

Now attempt: Examples Paper 4, Q.2-4

4. Diffusion in heat treatment processes

Diffusion plays an important role in heat treatment processes. Two specific examples will be considered in this section:

- **Modelling thermal history:** As noted in the previous sections, the heat treatment of metal alloys is dependent on thermal history, in particular the cooling rates. There are direct parallels between the diffusion of atoms (covered in earlier lectures) and the conduction of heat. Analogous solutions to the diffusion equations can therefore be applied.
- **Surface hardening:** In many practical heat treatment problems, we want to achieve different properties for the surface compared to the bulk of a component. For example, to deliver improved wear resistance, without compromising component toughness. Surface hardening processes depend on both the diffusion of atoms and the diffusion of heat.



Before proceeding, we will recap some key diffusion results from earlier lectures. The 1D flux of atoms ($\text{atoms s}^{-1} \text{m}^{-2}$) is given by Fick's first law:

$$J = -D \frac{\partial C}{\partial x}$$

where $C(x)$ is the concentration, and $D = D_0 \exp(-Q/RT)$ is the diffusion coefficient, which is dependent on the temperature, T . The governing equation for unsteady 1D diffusion is Fick's second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

which can be solved to find the concentration variation with position and time, $C(x, t)$.

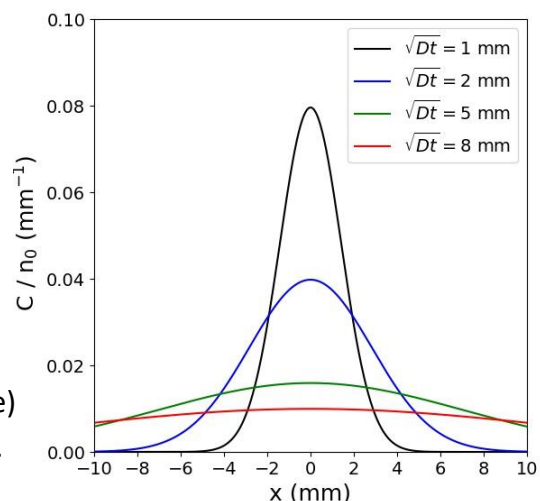
Two solutions have been presented so far.

(1) "Impulse response": normal (or Gaussian) distribution:

$$C(x, t) = \frac{n_0}{2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

This has the following properties:

- It tends to a delta function as $t \rightarrow 0$, and has a standard deviation $\sqrt{2Dt}$.
- The constant n_0 is set by the initial conditions: it is the total number of atoms per unit area (i.e. the area under the curve) which remains constant for all values of t .

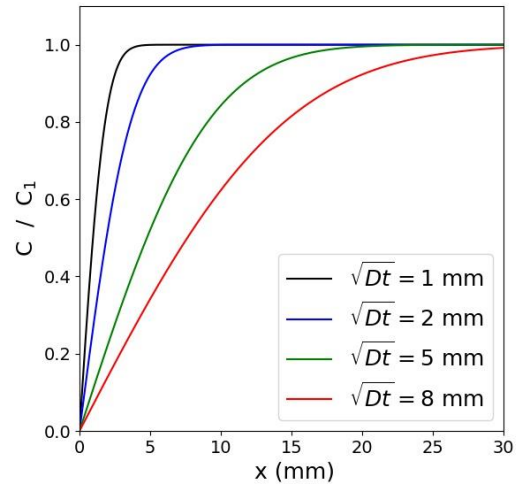


(2) “Step response”: error function (erf) distribution:

$$C(x, t) = C_1 \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

This has the following properties:

- The value of $\operatorname{erf}(\infty) = 1$ and $\operatorname{erf}(0) = 0$.
- $C(x, t)$ tends to a step function of amplitude C_1 as $t \rightarrow 0$, and tends to zero as $t \rightarrow \infty$.
- The ‘width’ of the step is of the order \sqrt{Dt} .
- Note that this solution can be re-scaled to the case with non-zero concentration at $x = 0$, i.e. $C(x = 0, t) = C_0$.



$$C(x, t) = C_0 + (C_1 - C_0) \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

In the following, we will make use of a third solution of the diffusion equation: when the initial conditions are a **sinusoidal function**.

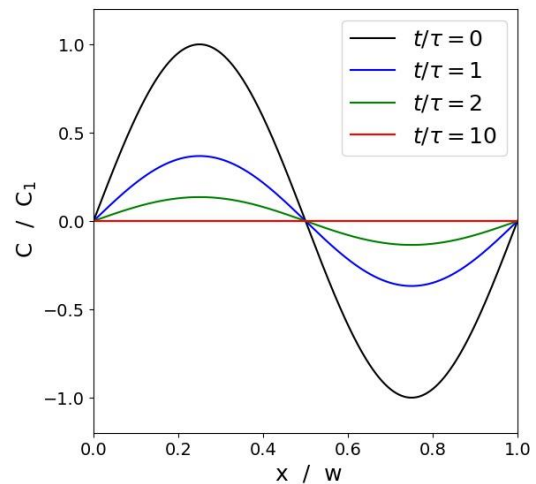
$$C(x, t = 0) = C_1 \sin\left(\frac{2\pi x}{w}\right)$$

To solve this, take a trial solution of the form:

$$C(x, t) = C_1 f(t) \sin\left(\frac{2\pi x}{w}\right)$$

Here, $f(t)$ is an unknown time-dependent amplitude. Substituting this trial solution into Fick’s second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \Rightarrow \frac{df}{dt} + D \left(\frac{2\pi}{w}\right)^2 f = 0$$



This has the solution: $f(t) = \exp(-t/\tau)$, $\tau = w^2/4\pi^2 D$

Therefore, a solution to the diffusion equation with sinusoidal initial conditions is:

$$C(x, t) = C_1 \sin\left(\frac{2\pi x}{w}\right) \exp\left(-\frac{4\pi^2 Dt}{w^2}\right)$$

This solution can also be rescaled for the case where $C(x = 0, t) = C_0$, i.e.

$$C(x, t) = C_0 + (C_1 - C_0) \sin\left(\frac{2\pi x}{w}\right) \exp\left(-\frac{4\pi^2 Dt}{w^2}\right)$$

4.1 Modelling thermal history

So far, we have looked at the diffusion of atoms. However, by comparing this with heat transfer by conduction, we can show that the governing equations are the same.

Therefore, the same solutions can be used, with a change of variables.

diffusion of atoms

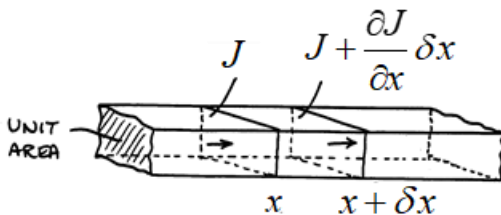
C = concentration (atoms m^{-3})

Fick's first law: $J = -D \frac{\partial C}{\partial x}$

J = atom flux (atoms $\text{s}^{-1} \text{m}^{-2}$)

D = diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)

Conservation of mass:



net flow of atoms in = change in concentration x volume

$$J \delta t - \left(J + \frac{\partial J}{\partial x} \delta x \right) \delta t = \delta C \delta x$$

$$\therefore \frac{\partial C}{\partial t} = - \frac{\partial J}{\partial x} = D \frac{\partial^2 C}{\partial x^2}$$

thermal conduction

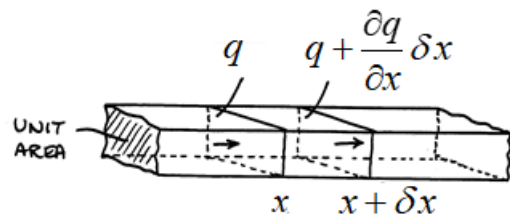
T = temperature (K)

Fourier's law: $q = -\lambda \frac{\partial T}{\partial x}$

q = heat flux (W m^{-2})

λ = thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)

Conservation of energy:



net flow of energy in = mass x specific heat capacity x change in temperature

$$q \delta t - \left(q + \frac{\partial q}{\partial x} \delta x \right) \delta t = (\rho \delta x) c \delta T$$

$$\therefore \frac{\partial T}{\partial t} = - \frac{1}{\rho c} \frac{\partial q}{\partial x} = \frac{\lambda}{\rho c} \frac{\partial^2 T}{\partial x^2}$$

c = specific heat capacity ($\text{J kg}^{-1} \text{K}$)

$\lambda / \rho c = a$ = thermal diffusivity ($\text{m}^2 \text{s}^{-1}$)

The governing equations for mass and thermal diffusion have the same form. The solutions are therefore interchangeable, with the change of variables:

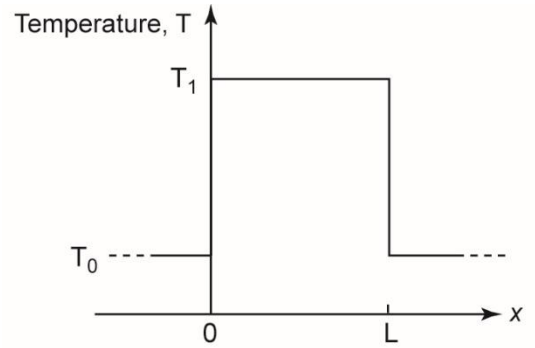
- concentration C for temperature T
- diffusion coefficient D for the thermal diffusivity a (note that these have the same units, $\text{m}^2 \text{s}^{-1}$)

4.2 Example: thermal history of a quenched plate

Consider quenching a steel plate of thickness L , from a uniform **initial temperature** T_1 , into a large bath of liquid at temperature T_0 .

- If we assume perfect heat transfer, the boundary condition at the surfaces is:

$$T = T_0 \text{ for } x = 0, L \text{ for all times } t \geq 0$$
- Also, assume the plate is large, so heat flow is 1D: $T(x, t)$.



The aim is to find a solution for $T(x, t)$. This in turn can be used to provide information on **cooling rates**, and hence the likely **phase transformations**.

Case 1 – thick plate limit

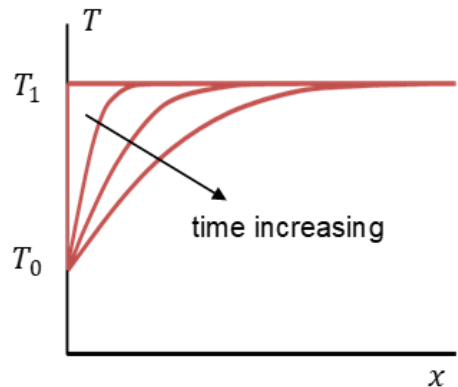
If we assume that dimension L is much larger than the distance over which heat can diffuse (i.e. for short times, a low thermal diffusivity material or a very thick plate), we can treat the plate as **effectively infinite** in thickness.

- Recall that a ‘representative’ diffusion distance for atoms in time t is given by: \sqrt{Dt}
- The equivalent distance for thermal diffusion is given by: \sqrt{at}
- So, the thick plate limit is reasonable when: $L \gg \sqrt{at}$

The initial conditions are therefore a step function, with amplitude $(T_1 - T_0)$, and $T(x = 0, t) = T_0$.

The correct solution for this problem is therefore the error function, scaled to these initial conditions:

$$T(x, t) = T_0 + (T_1 - T_0) \operatorname{erf}\left(\frac{x}{2\sqrt{at}}\right)$$

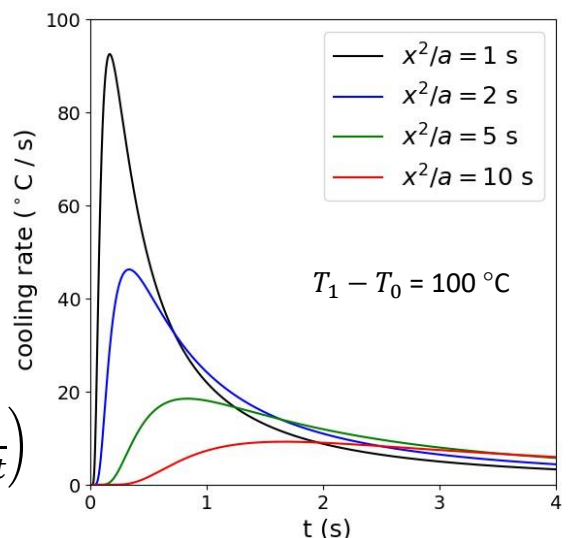


We can use this to calculate the cooling rates in the plate (e.g. to see where martensite may form). From the materials data book:

$$\frac{d}{dZ} [\operatorname{erf}(Z)] = \frac{2}{\sqrt{\pi}} \exp(-Z^2)$$

Taking $Z = x/2\sqrt{at}$ and $\frac{\partial}{\partial t} [] = \frac{d}{dZ} [] \frac{\partial Z}{\partial t}$:

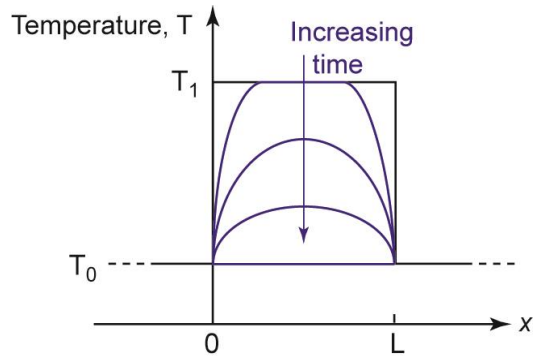
$$\frac{\partial T(x, t)}{\partial t} = -\left(\frac{T_1 - T_0}{t}\right) \left(\frac{x}{2\sqrt{\pi at}}\right) \exp\left(-\frac{x^2}{4at}\right)$$



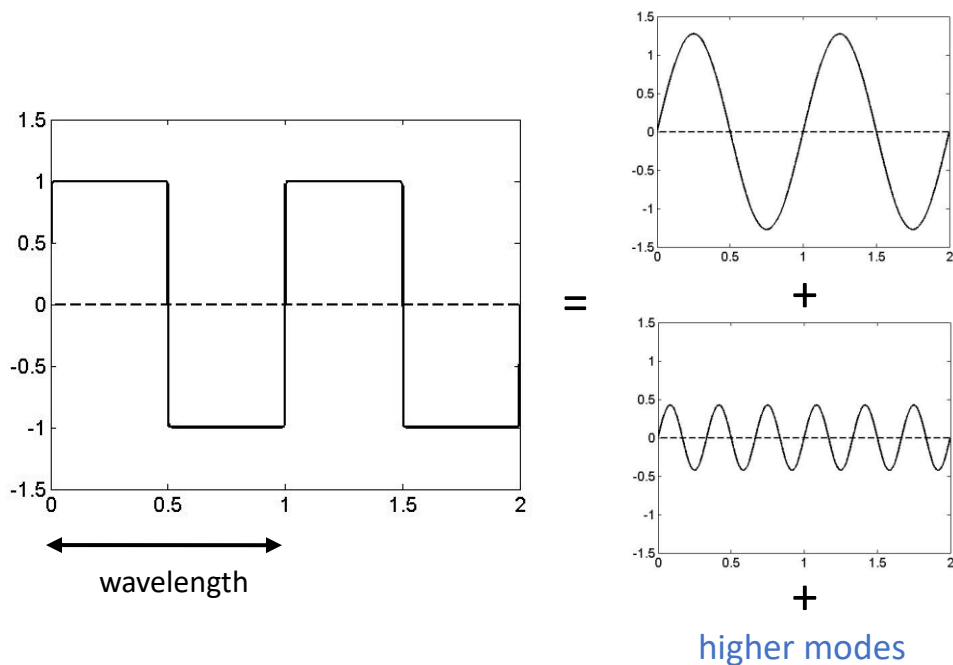
Case 2 – finite width plate

A different solution is required if the thermal diffusion distances are significant compared to the plate thickness:

$$L \sim \sqrt{at}$$



The way to solve this is to model the initial conditions as the first half wavelength of a **square wave** function. This can then be expressed as a **Fourier series**: a sum of sinusoidal functions. Each term in that sum can be solved using the sinusoidal solution outlined above.



The equivalent square wave parameters for the plate quenching problem are:

- wavelength $2L$ (but only over the domain of one half wavelength: $0 < x < L$),
- mean temperature of T_0 ,
- mean-to-peak amplitude scaled to the temperature difference $(T_1 - T_0)$.

Hence, the initial conditions can be described by the Fourier series in x :

$$T(x, t = 0) = T_0 + (T_1 - T_0) \sum_{n=1,3,5,\dots} \frac{4}{n\pi} \sin\left(\frac{n\pi x}{L}\right)$$

(Maths Databook – note the change of variable from time t to a Fourier series in x)

To find a solution to the diffusion equation for these initial conditions, consider each sinusoidal term in the summation separately. Term n has initial conditions :

$$T_n(x, t = 0) = (T_1 - T_0) \frac{4}{n\pi} \sin\left(\frac{n\pi x}{L}\right)$$

Next, find a solution that satisfies this initial condition. As before, take a trial solution:

$$T_n(x, t) = (T_1 - T_0) \frac{4}{n\pi} \boxed{f_n(t)} \sin\left(\frac{n\pi x}{L}\right)$$

Here, $f_n(t)$ is the unknown time-dependent amplitude of mode n . Substituting this trial solution into the diffusion equation:

$$\frac{\partial T_n}{\partial t} = a \frac{\partial^2 T_n}{\partial x^2} \Rightarrow \frac{df_n}{dt} + a \left(\frac{n\pi}{L}\right)^2 f_n = 0$$

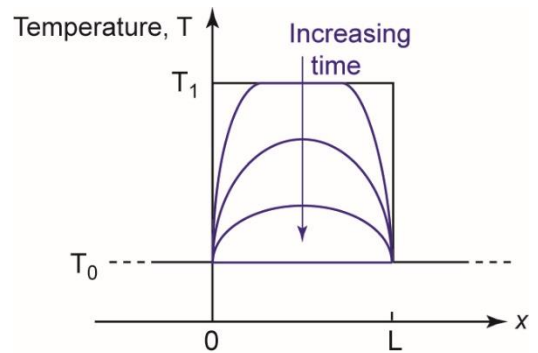
This has the solution: $f_n(t) = \exp\left(-\frac{t}{\tau_n}\right)$ $\tau_n = \frac{L^2}{n^2\pi^2 a}$

If each term is a solution to the diffusion equation, then the sum will also be a solution. The end result is therefore:

$$T(x, t) = T_0 + (T_1 - T_0) \sum_{n=1,3,5,\dots} \frac{4}{n\pi} \sin\left(\frac{n\pi x}{L}\right) \exp\left(-\frac{n^2\pi^2 at}{L^2}\right)$$

This result gives some insights into the plate quenching problem:

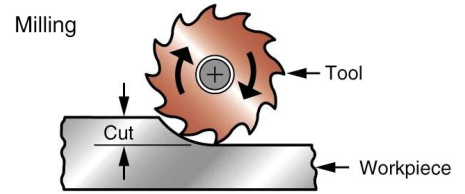
- (1) The time constant τ_n for each mode is dependent on the **parameter** L^2/a .
Therefore, reducing the plate thickness L will significantly increase cooling rates.
- (2) The time constant τ_n is also very sensitive to the **mode number** n (with $n = 1, 3, 5, \dots$).
The higher modes will decay much faster.
So, the solution can (after a short period) be well approximated by just the first term:



$$T(x, t) \approx T_0 + (T_1 - T_0) \frac{4}{\pi} \sin\left(\frac{\pi x}{L}\right) \exp\left(-\frac{\pi^2 at}{L^2}\right)$$

4.3 Surface hardening

Many steel components used in machinery (e.g. gears, bearings, tool edges) are subjected to **high surface stresses**, due to friction and sliding contact. Surface engineering is used to harden the surface of the component ('**case hardening**') to increase its hardness and wear resistance – without damaging the strength and toughness of the underlying steel

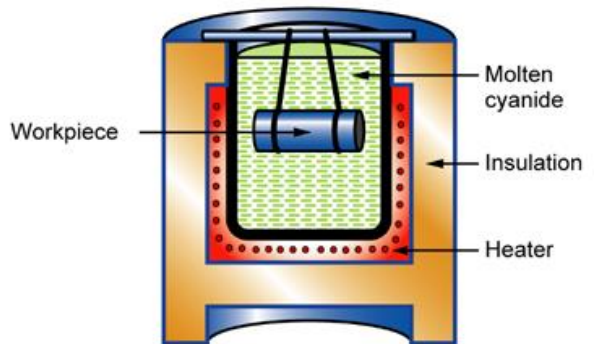


This can be achieved using a combination of the following two processes, which both rely on diffusion:

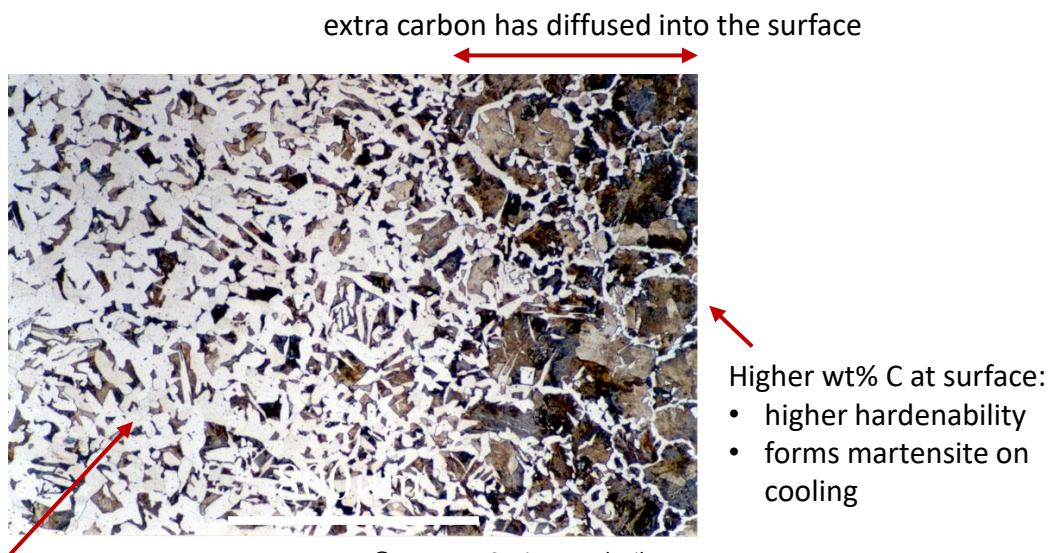
(1) Carburising:

This technique involves immersing the steel at high temperature in a carbon-rich atmosphere (such as molten cyanide or nitrate salts).

- Carbon diffuses into the surface of the component, prior to any heat treatment.
- The higher C content increases the **hardenability**, making it easier to form a surface layer of martensite, which may then be tempered.
- The higher C content will also make the martensite **harder**, due to the greater supersaturation with carbon.



The microstructure of a steel (0.15 wt% C) that has been carburised and then quenched is shown below:



Lower wt% C:

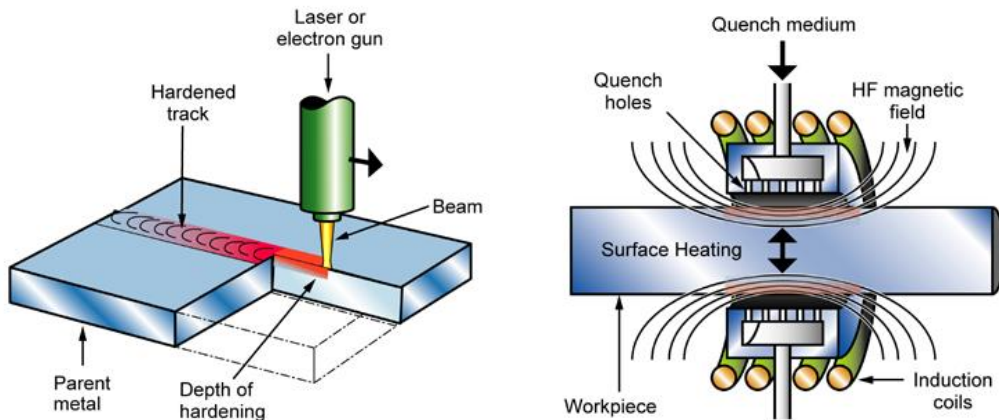
- low hardenability
- high proportion of ductile ferrite

Image: © DoITPoMS Micrograph Library,
University of Cambridge (Dr R F Cochrane)

(2) Transformation hardening:

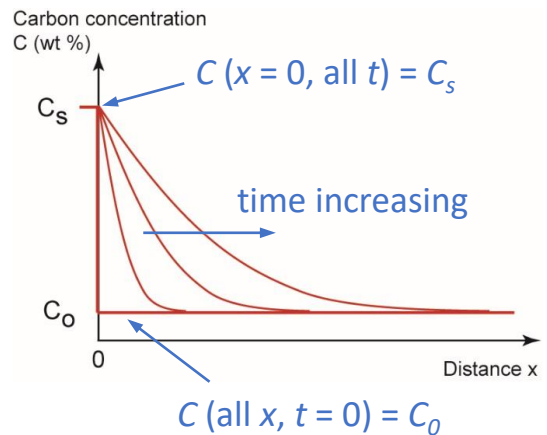
This involves imposing a heat source to the surface, such that a thin layer is austenitised, and then cooling it quickly to form a layer of martensite (which can then be tempered).

- Surface heating may use a traversing flame, laser, or electron gun; or high frequency induction coils are used to induce surface eddy currents.
- Air cooling may be sufficient to form martensite – or a water-quench can be used.



We will use the diffusion analysis to model process (1): carburising.

- Consider a steel component with initial carbon concentration C_0 .
- The component is placed in a carbon rich environment at high temperature, which results in a higher surface concentration, C_s .
- The surface concentration C_s is assumed to **remain constant** (i.e. large carbon supply).
- Carbon will diffuse into the surface of the steel component over time, at a rate dependent on temperature and time.



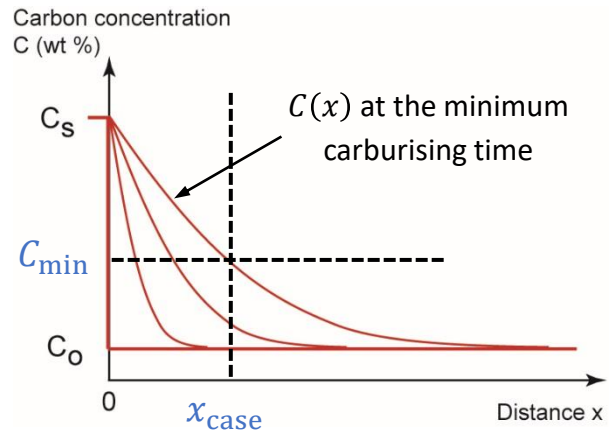
The initial conditions are therefore an inverted step function, with amplitude $(C_s - C_0)$, shifted by an initial concentration C_0 .

- The solution for these initial conditions was introduced earlier in the course (the pre-deposition stage in Si doping): $C(x, t)$ is a function of $1 - \text{erf}(x/2\sqrt{Dt})$.
- Adding the offset C_0 to that solution, and scaling the amplitude to $(C_s - C_0)$, gives:

$$C(x, t) = C_0 + (C_s - C_0) \left[1 - \text{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right]$$

We can use this solution to calculate the **time required** to achieve a particular '**case depth**' for the case hardening process, i.e. a particular thickness of hardened layer:

- The hardness of the steel will increase with the carbon concentration, C .
- Hence, for case hardening, it is necessary to specifying a **minimum concentration** C_{\min} at a specified depth into the material: the **case depth** x_{case} .
- This will set the depth and minimum hardness of the hardened layer.

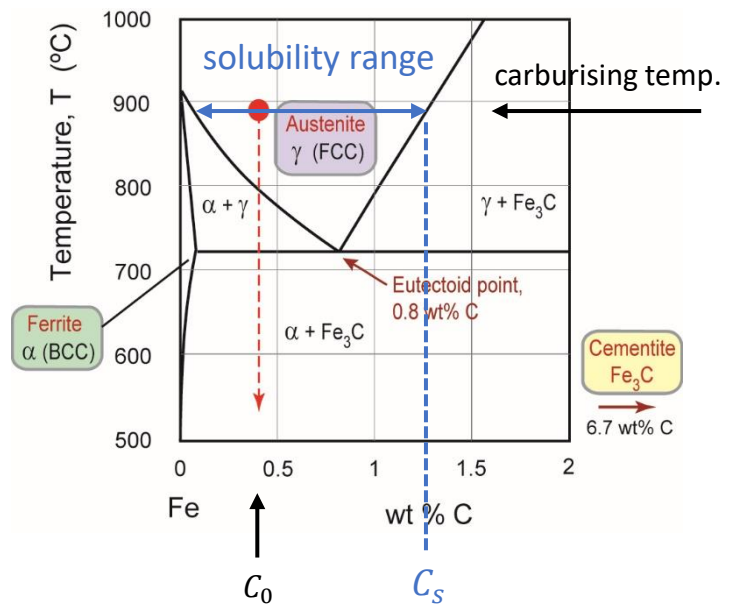


Substituting these values into the solution above, the time t_{case} to achieve this case depth is given by the relationship:

$$\operatorname{erf}\left(\frac{x_{\text{case}}}{2\sqrt{Dt_{\text{case}}}}\right) = 1 - \frac{C_{\min} - C_0}{C_s - C_0}$$

Before this can be solved for t_{case} , we need to evaluate the concentrations C_s and C_0 .

- The concentration C_0 is the initial composition of the steel being hardened.
- Assuming a carbon rich environment, C_s will be the **maximum** amount of carbon that can be accommodated in **solid solution** at the carburising temperature.
- This is set by the **solubility limit** of the steel at the carburising temperature, from the phase diagram.



The only unknown now is t_{case} . Tables in the Materials Data Book give values $\operatorname{erf}(Y)$ vs Y . Hence, $x_{\text{case}}/2\sqrt{Dt_{\text{case}}}$ can be evaluated. After working out the diffusion coefficient $D = D_0 \exp(-Q/RT)$ at the carburising temperature T , the time t_{case} can be found.

4.4 Summary of the learning outcomes: diffusion in heat treatment

After completing section 4 you will be able to do the following:

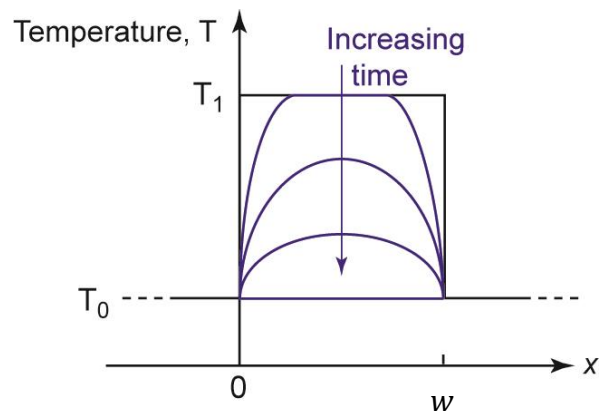
1. Describe the analogy between thermal and atomic diffusion, and how to switch diffusion equations and solutions from one to the other via a change of variables.
2. Compare characteristic diffusion distances and times for thermal and atomic diffusion.
3. Use appropriate solutions to the 1D diffusion equations to analyse thermal diffusion in heat treatment processes.
4. Describe the surface hardening processes of carburisation and transformation hardening, and analyse them using solutions to the 1D diffusion equations.

4.5 Quiz W6.1: diffusion in heat treatment

A large steel plate of thickness w is taken from a furnace and quenched in water. The steel has thermal diffusivity α and diffusion coefficient D for carbon in austenite.

Which of the following must be true in order to use the error function (erf) is to model the temperature vs depth below the surface, $T(x, t)$ (more than one can be correct)?

- 1) $w \approx \sqrt{at}$
- 2) $w \ll \sqrt{at}$
- 3) $w \gg \sqrt{at}$
- 4) $w^2/a \ll w^2/D$



Additional worked examples: diffusion in heat treatment

For further explanation, a video will be available with the following worked examples:

- Tripos Question 2017 Q5, which helps with Examples Paper 4 Q5.
- Tripos Question 2012 Q6, which helps with Examples Paper 4 Q6

Now attempt: Examples Paper 4, Q.5-6