IB Paper 3: Materials

Materials Processing:
Handout 3, Lectures 15-16
Polymer Processing, Creep

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Michaelmas 2023

Contents:

8. Polymer processing

This section of the course will switch attention from metals to the processing of polymers. Polymers have a wide variety of molecular structures and properties. They are extensively used, for a number of reasons:

(a) Relatively low cost (per unit volume):

Mild steel:	~ £5000 / m³
Aluminium alloys:	~ £6000 / m³
Polyethylene:	~ £1000 / m³

(b) Low density: ρ ~ 1000 kg / m³

(c) Reasonable mechanical properties, on a unit mass basis.
(d) Low melting temperature: easy (therefore cheap) to process.
(e) Environmental and corrosion resistance
    (but bringing problems with disposal, end of life).
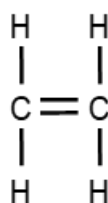
Images: DuPont Media Gallery

Molecular structure of polymers

The molecular structure plays an important role in their response to processing. This was covered in Part IA, but is briefly revised here.
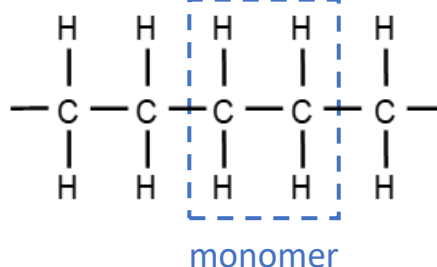
Consider first the simplest polymer structure: polyethylene (PE).
- The basic unit cell of polyethylene is a **monomer** of hydrogen and carbon atoms.
- These monomers link together to form **polymer** chains.

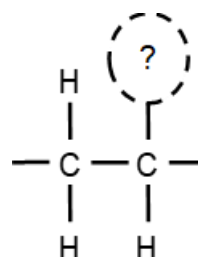ethylene molecule (C_2H_4)   polyethylene chain

monomer

A wide range of polymers are obtained by varying aspects of this basic structure:

(1) Replace some of the H atoms with other atoms or molecules: **side-groups**. The four most common (thermoplastics) are:

1. Polyethylene (PE) -   ? = H
2. Polypropylene (PP) -   ? = CH_3
3. Polyvinylchloride (PVC) -   ? = Cl
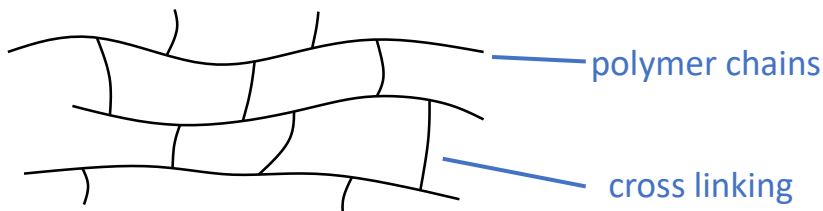4. Polystyrene (PS) -   ? = C_6H_5

2

(2) Add **branches** to the polymer chains. For example, low density polyethylene (LDPE) is a PE structure with chain branching.
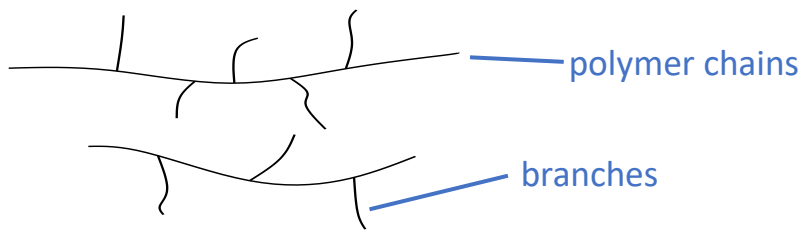
(3) **Cross-linking** between polymer chains:

- **Thermosets** and **elastomers** consist of polymer chains with a high and low degree of covalent cross-linking, respectively.

- Their molecular structure is fixed at the point of polymerisation:
  mould once-only, cannot be softened, reshaped, recycled

- **Thermoplastics** have no cross-links: only weak van der Waals bonds between polymer chains. These bonds break down through the glass transition temperature T_g, with viscous flow above the melting point (typically 1.5 x T_g):
  easy to mould, re-melt, recycle

This section will focus on two aspects of the processing of **thermoplastics**:
- Moulding: solidification, and control of crystallinity.
- Deformation processing: use of orientation strengthening.

8.1 Moulding thermoplastics

Injection moulding is a common technique for shaping thermoplastics:
- Polymer granules are heated until they become a viscous liquid.
- The polymer is then squeezed under pressure into a two-part mould.
- When solidification is complete, the mould is separated and the component removed.

Controlling **crystallinity** on solidification is an important consideration in moulding processes.
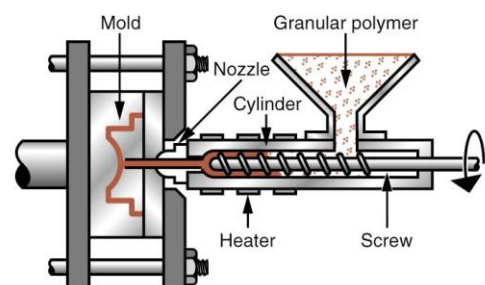
A characteristic of thermoplastics is that they can be **semi-crystalline**, solidifying to a mixture of crystalline and amorphous regions:
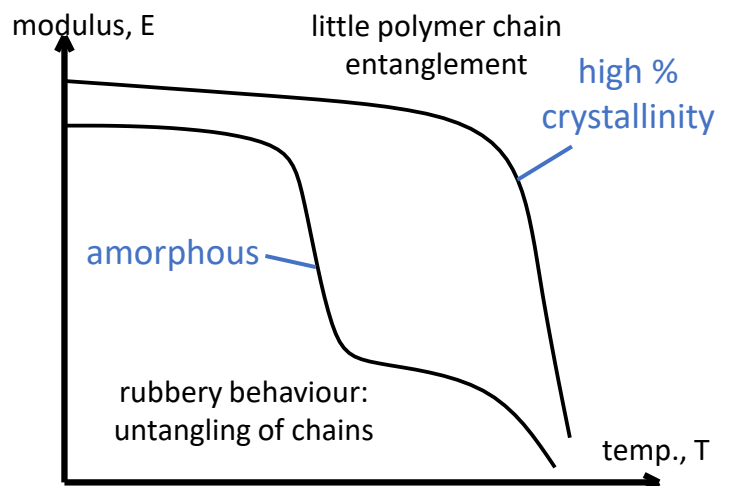

amorphous region
random molecular arrangement

crystalline region
polymer molecules are aligned
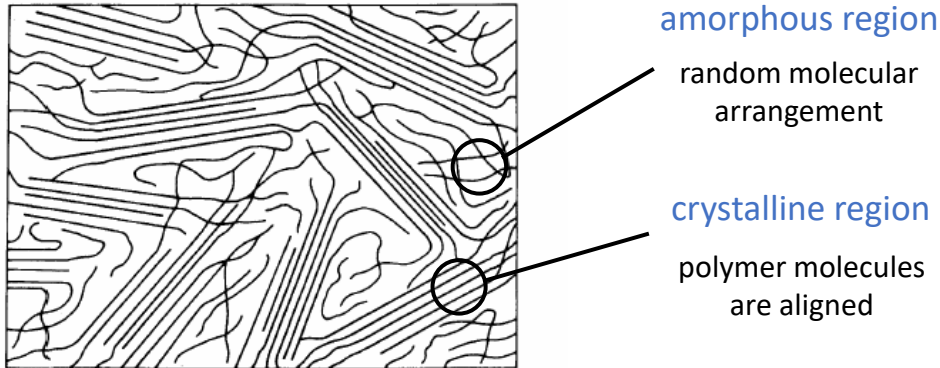
The properties of a thermoplastic are affected by the degree of crystallinity:

(1) Density
- The closer molecular packing of crystalline regions makes them **denser** than the amorphous equivalent.
- If the densities in the fully crystalline and fully amorphous states are known, the density of a semi-crystalline polymer can be estimated by a **rule-of-mixtures** based on volume fractions.
- Note also that crystallisation leads to **shrinkage**, so has to be considered in maintaining dimensional precision in moulded semi-crystalline polymer parts.

**(2) Young's modulus**
- Young's modulus **increases** with crystallinity.
- For a highly crystalline polymer, E **remains high** through the glass transition temperature, until the temperature is sufficient to break down the van der Waals bonds in the crystalline regions.

modulus, E
little polymer chain entanglement
high % crystallinity
amorphous
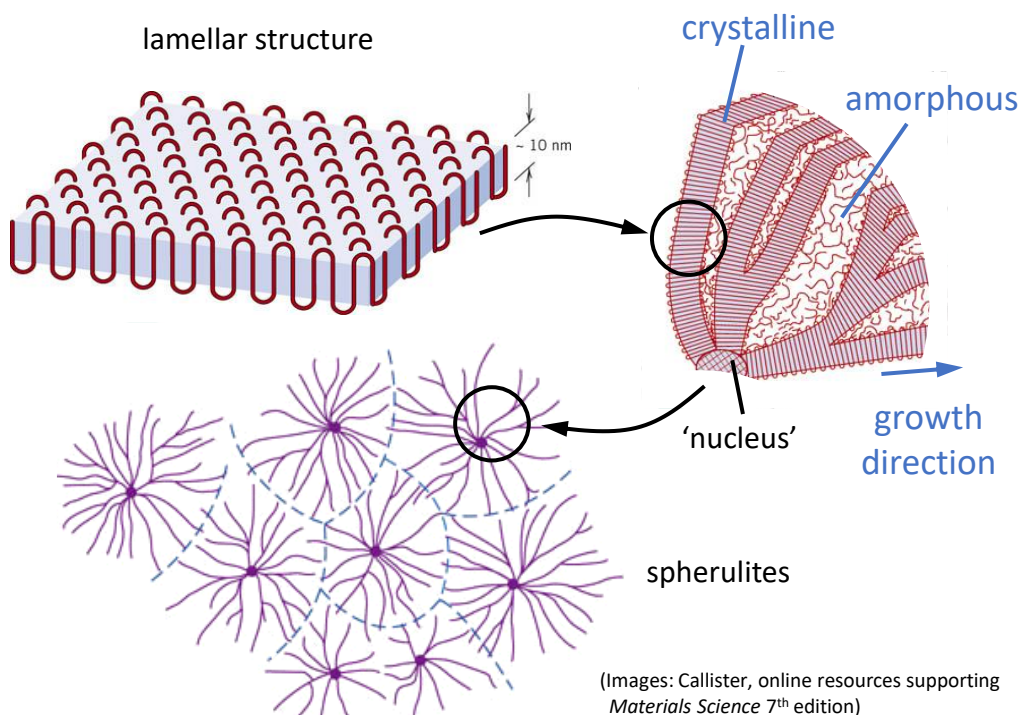rubbery behaviour: untangling of chains
temp., T

Polymer crystallisation is dependent on temperature and time in a similar way to diffusion-dependent phase transformations in metals. Crystallisation follows **C-curves**, and has a similar TTT diagram:

- Above the melting temperature (T_m) the amorphous state of the polymer is stable: it is a viscous liquid with randomly orientated molecules.

- Below T_m, the difference in free energy between the amorphous and crystalline states provides a **driving force** for crystallisation, increasing with **undercooling** ($T_m - T$).

temperature

amorphous (stable)

T_m

amorphous (unstable)

crystalline

T_g

log (time)

- However, to crystallise, the polymer chains have to **rearrange by diffusion**. The rate of diffusion reduces as the temperature reduces. This trade-off leads to the C-curves.

- Below the glass transition temperature (T_g), the van der Waals bonds become stronger, and chain mobility is inhibited, restricting further crystallisation.
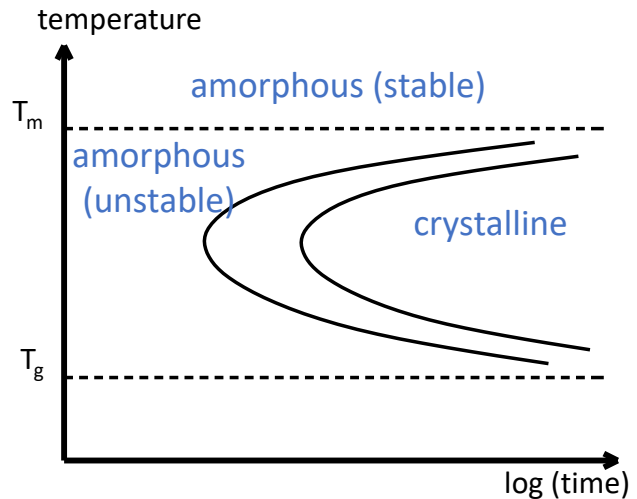
Crystallisation occurs by the **nucleation and growth** of plate shaped 'lamellar' crystallites within the amorphous regions. Radially arranged lamellar crystallites form structures called 'spherulites'.
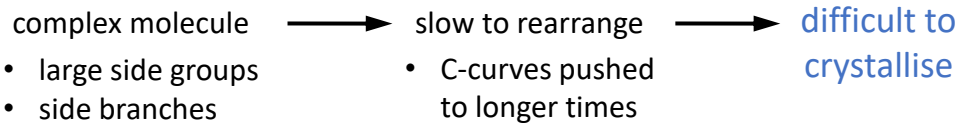

lamellar structure

~ 10 nm

crystalline

amorphous

'nucleus'

growth direction

spherulites

(Images: Callister, online resources supporting *Materials Science* 7th edition)
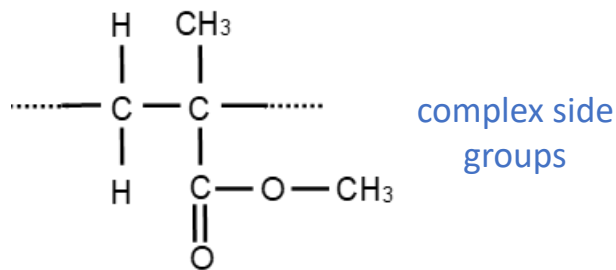
Controlling crystallisation

In applications where transmission of light is important (such as lenses for spectacles and polymer screens and windows), avoidance of crystallinity is a critical part of the processing route. **Large crystallites** will scatter light and make the polymer appear cloudy, so it's necessary to avoid crystallisation, or keep the crystallites small.

(1) Choice of polymer

The times taken for crystallisation to start and complete (i.e. the position of the C-curves) depends on the **molecular structure** of the polymer:

complex molecule $\longrightarrow$ slow to rearrange $\longrightarrow$ difficult to
- large side groups   • C-curves pushed   crystallise
- side branches   to longer times

Example: PMMA ('Perspex'). Complex molecule has poor mobility, so crystallisation is minimised.


complex side groups

(2) Controlling cooling rates

Because crystallisation follows C-curves, as with metals there is a **critical cooling rate** that is just fast enough to miss the C-curves, avoiding the onset of crystallisation.

High cooling rates can be achieved in injection moulding processes as follows:
- **Small section thickness:** This avoids slow cooling in the centre (which may crystallise), but requires a high injection pressure to force the viscous polymer into a mould with narrow sections.
- **Chill the mould:** This can be achieved by using a metal mould (high thermal conductivity) which is cooled internally by a flow of water.

8.2 Deformation processing of thermoplastics

Plastic deformation of a polymer can be used both for shaping purposes, and to alter properties. Amorphous or semi-crystalline thermoplastics near to T_g have an elastic-plastic tensile response as shown below:
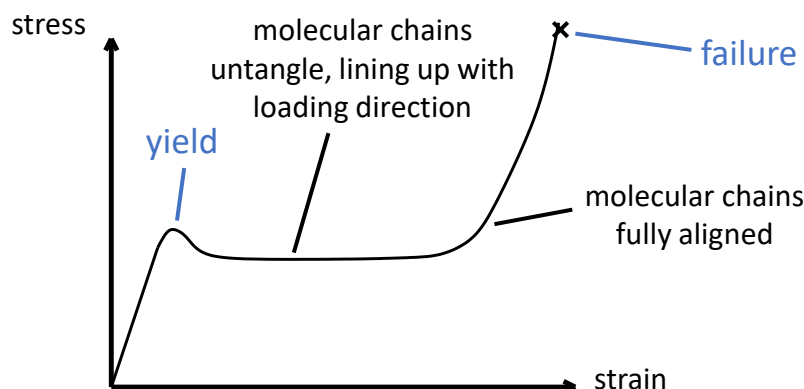
Stretching the polymer to align the molecular chains, which significantly increases the strength and stiffness, is known as **orientation strengthening**. Two processes which exploit this behaviour are **fibre drawing** and **blow moulding**.

Fibre drawing

The fibre drawing process uses a screw extruder to produce a polymer filament which is then drawn out, aligning the molecular chains, by applying tension:
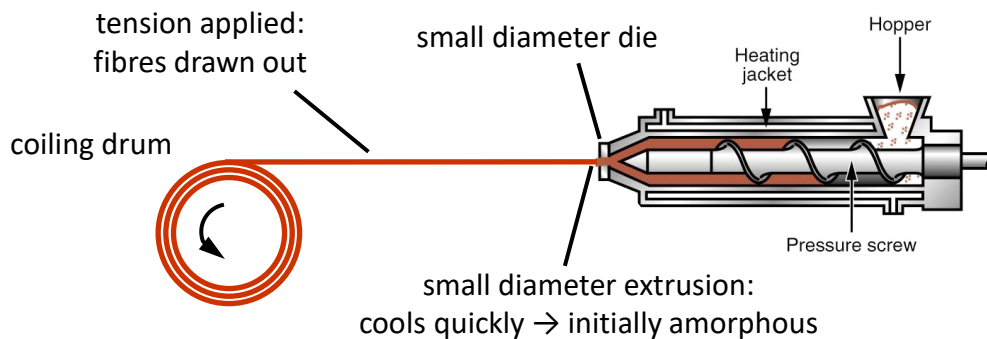
By orientation strengthening, polymer fibres have a high strength and stiffness:

polyethylene, 40% crystallinity -	*E* = 0.2 GPa
polyethylene, 80% crystallinity -	*E* = 0.7 GPa
polyethylene, drawn fibre -	*E* = 170 GPa

Unlike bulk polymers, the strength and stiffness of polymer fibres can outperform all metals and some composites on a per **unit weight basis** (i.e. σ_f/ρ and E/ρ).
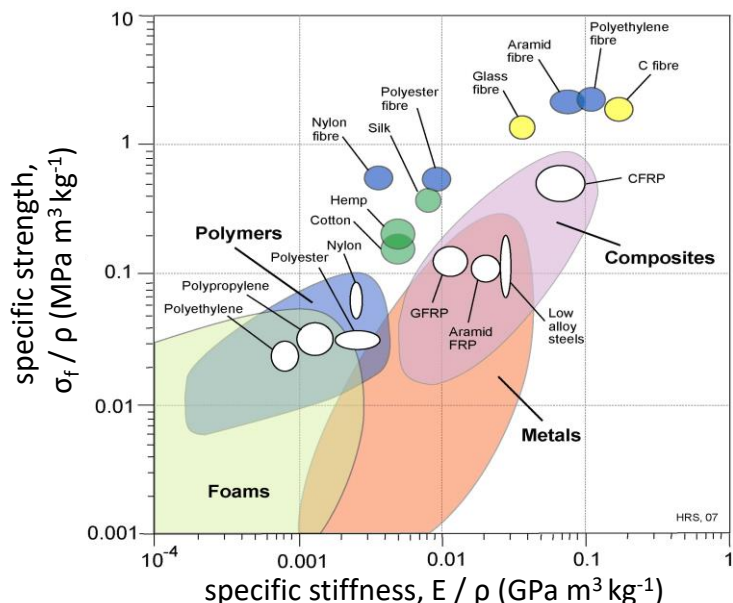
To exploit these properties in products, the drawn polymer fibres are used in yarns and woven textile products: fabrics, clothing, ropes, geotextiles, sails, parachutes, etc.

e.g. Kevlar fabric body armour


woven aramid fibres

(Images: DuPont media gallery)

Stretch blow moulding

Another polymer shaping process utilising orientation strengthening is stretch blow moulding, illustrated below.

(1) An injection moulded polymer preform called a 'parison' is pre-heated and transferred to a mould.

(2) A stretch rod elongates the preform.

(3) Compressed air inflates the preform to fill the mould.

(4) The mould is separated and the component ejected.
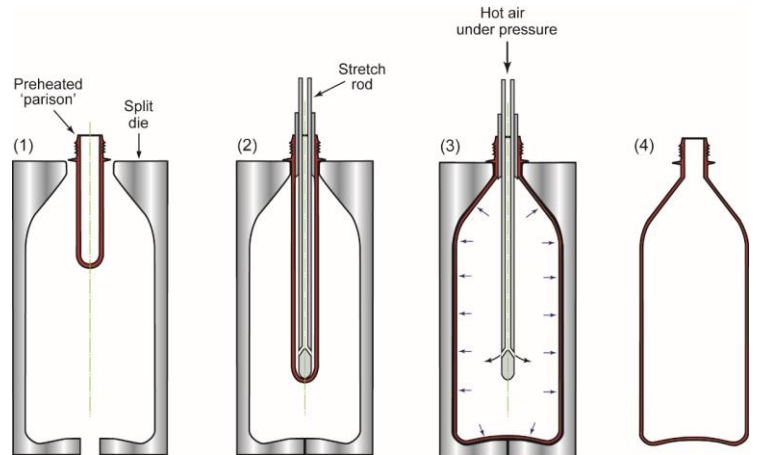
The elongation and inflation stages provide different molecular alignment in the **longitudinal** and **hoop-wise** directions (recall that the stress is twice as great in the hoop direction):
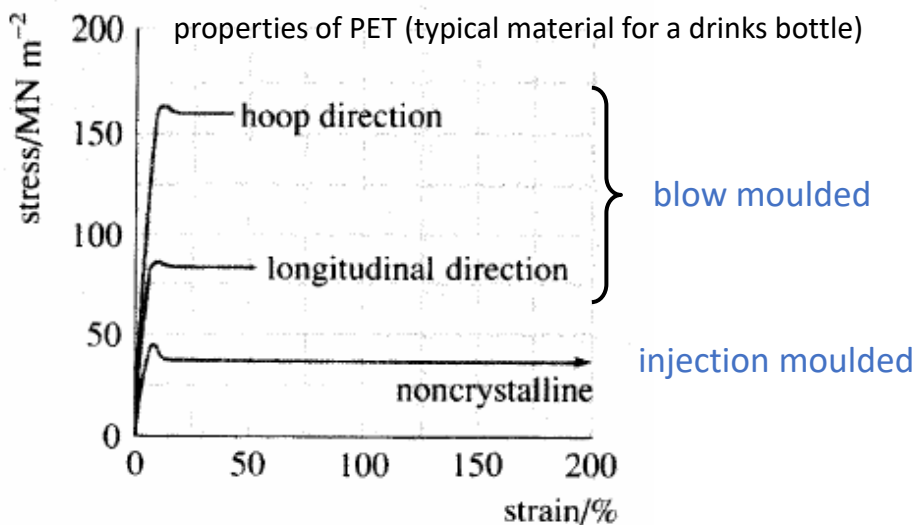
Example: fizzy drinks bottle

Internal pressure: $p \approx 0.4$ MPa

Radius: $R \approx 50$ mm

Wall thickness: $t \approx 0.3$ mm

Longitudinal stress: $pR / 2t \approx 33$ MPa
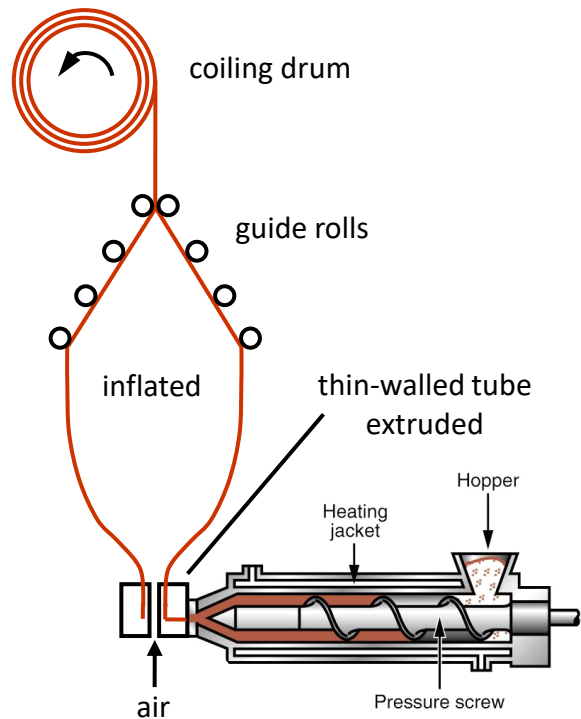
Hoop stress: $pR / t \approx 66$ MPa

- Stresses are high: some crystallinity and molecular alignment is desirable. Stretch blow moulding is suitable.
- The moulding temperature is kept just above T_g to restrict crystallinity to about 20%. Otherwise, it reduces the optical transparency of the bottle.

Film blowing

Film blowing is another type of blow moulding: extruded polymer is inflated by internal pressure, cooled and wound onto a drum.

The inflation produces polymer films with some alignment in the molecular structure. This alignment improves the mechanical properties of the film, minimising the weight (and cost) of material, e.g. for packaging applications, shopping bags.

coiling drum

guide rolls

inflated

thin-walled tube extruded

Hopper

Heating jacket

Pressure screw

air

8.3 Summary of the learning outcomes: polymer processing

After completing section 8 you will be able to do the following:

1. Explain how the molecular structure of a polymer affects its response to processing.
2. Describe the crystallisation of thermoplastics, the effect of crystallinity on properties, and how it can be controlled.
3. Describe how control of molecular alignment during processing can be used to manipulate the mechanical properties of polymers.

A thermoplastic polymer and moulding process are to be chosen to produce a final product with a high degree of crystallinity.

Which of the following material and process attributes would increase crystallinity (more than one may be correct)?

1. Slow cooling.
2. Fast cooling.
3. Polymer molecules with no chain branching.
4. Polymer molecules with extensive chain branching.

Additional worked example: polymer processing

For further explanation, a video will be available with the following worked example:
- Tripos Question 2013 Q5, which helps with Examples Paper 5 Q4.

Now attempt: Examples Paper 5, Q.4

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9. Creep: materials at high temperatures

We switch attention back to metals now, to consider their behaviour at high temperatures. Metals can undergo deformations at high temperatures during shaping processes, such as hot rolling. Components can also experience high temperatures in service: we will consider the example of turbine blades.

The models for metal plasticity encountered relate yielding to the applied stress, but are time independent. At high temperatures **"creep" deformation** occurs:

- Plastic deformation depends on the applied stress, but also temperature and time:

$$\varepsilon = f(\sigma, T, t)$$

  We will consider models relating the creep strain rate $\dot{\varepsilon} = d\varepsilon/dt$ to (σ, T).

- Creep also enables plastic straining to occur at applied stresses that would be **too low** to cause yielding at room temperature.

Consequences of creep

The response to creep shares many parallels with viscoelasticity, encountered in IA (which is the time-dependent equivalent of linear elasticity).

(1) Continued straining (i.e. non-zero strain rate) at a **constant applied stress**.
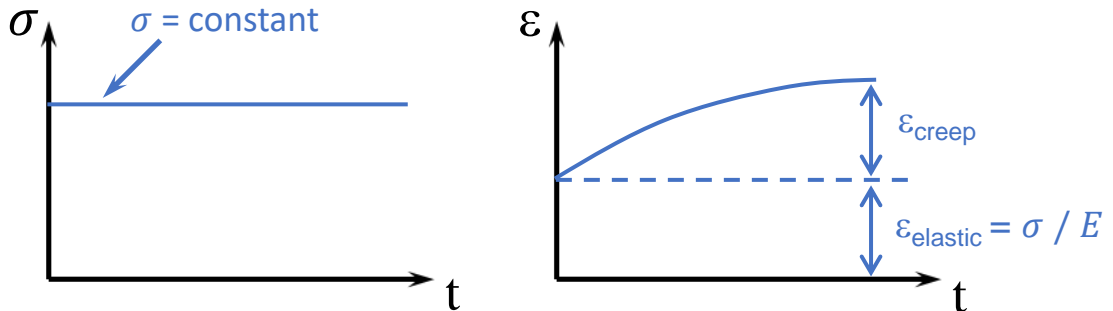
- For room temperature plasticity, an increase in stress is necessary to cause a further increase in strain.
- Excessive creep straining can lead to component contacts (e.g. turbine blades touching the engine housing), or necking and tensile failure ("creep rupture").

(2) Stress relaxation at a **constant applied strain**:

$$\varepsilon_{total} = \varepsilon_{elastic} + \varepsilon_{creep}$$
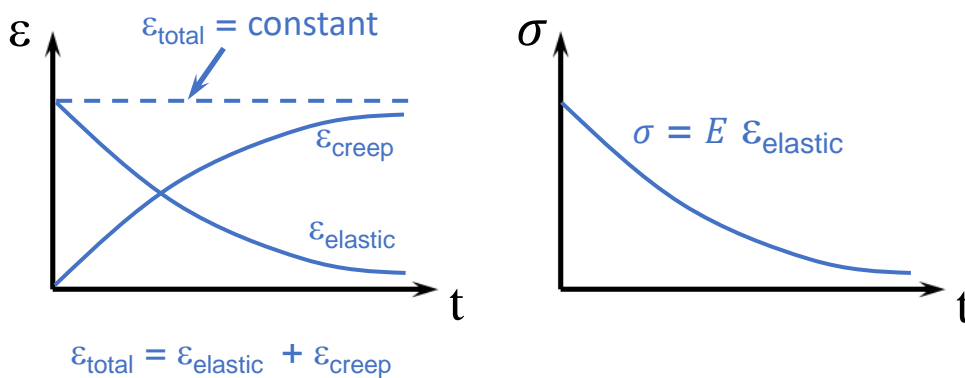
- An example of stress relaxation is bolts slackening over time at high temperatures.

At what temperatures does creep occur?

For crystalline materials (metals and ceramics), this depends on the ratio of the temperature to the melting temperature, T/T_m (both in Kelvin). Creep becomes significant at $T/T_m \approx 0.5$.

	T_m	$T \approx 0.5\, T_m$	
lead	600 K	30°C	pipes, cladding
low alloy steels	1780 K	617°C	power plant
ice	273 K	-137°C	glaciers
alumina (Al$_2$O$_3$)	2325 K	890°C	

9.1 Modelling creep deformation

The time-dependent strain of a material undergoing creep at constant applied nominal stress (i.e. constant applied load) and constant temperature shows three stages of behaviour:
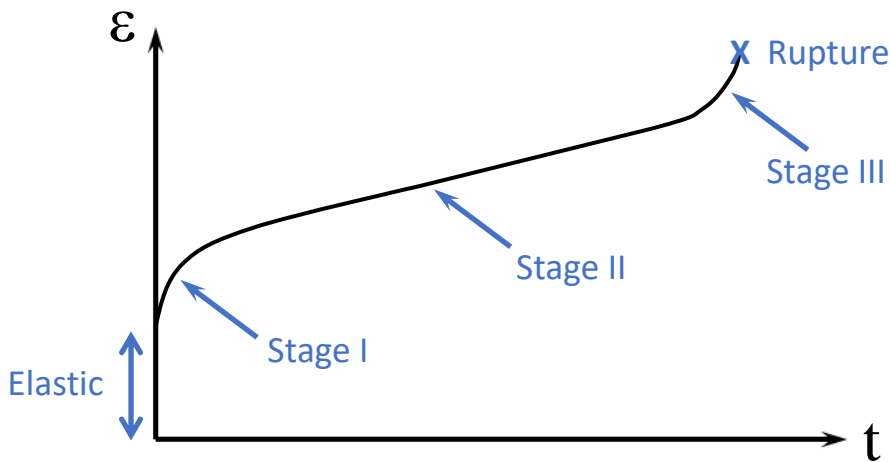
- Stage I: Primary creep – occurs over a short time period
- Stage II: Steady-state creep - **dominates creep life**
- Stage III: Tertiary creep – leads up to rupture

Design against creep generally focusses on Stage II.

- Typical creep strain-rates (s^{-1}): 10^{-10} → 10^{-5}

- Time taken for 10% creep strain: 32 years   3 hours

The steady-state creep rate in Stage II is well modelled by a **power law** dependence on the applied stress, at fixed temperature:

$$\dot{\varepsilon}_{ss} \propto \sigma^n$$

This can be verified experimentally, by plotting $\log \dot{\varepsilon}$ against $\log \sigma$. This should give a straight line with gradient n .

Furthermore, if creep experiments are performed at a range of temperatures, the constant of proportionality in this relationship is seen to obey the **Arrhenius law**:

$$\dot{\varepsilon}_{ss} = A \exp\left(-\frac{Q}{RT}\right) \sigma^n \qquad (1)$$

Here, Q = activation energy (J / mol), n = creep exponent (no units), A = the creep constant (a material parameter). To determine the activation energy, plot:

$$\ln \dot{\varepsilon}_{ss} \quad \text{vs} \quad \frac{1}{T} \quad \text{at constant stress}$$

Note that an alternative form of equation (1) is sometimes used, replacing the creep constant A with material parameters $\dot{\varepsilon}_0$ and σ_0 :

$$\frac{\dot{\varepsilon}_{ss}}{\dot{\varepsilon}_0} = \exp\left(-\frac{Q}{RT}\right)\left(\frac{\sigma}{\sigma_0}\right)^n$$

9.2 Creep mechanisms

The fact that the creep strain rate is found to follow the Arrhenius law indicates that atomic diffusion plays a role in creep. Recall that the diffusion coefficient follows the same relationship: $D = D_0 \exp(-Q/RT)$.

There are two important creep mechanisms, that both depend on atomic diffusion:

(1) Power-law (or dislocation) creep

In conventional yielding, dislocation motion is resisted by obstacles (precipitates, other dislocations etc.), leading to work hardening. An increase in the stress is required for further straining to occur.

Power-law creep is the mechanism of dislocations **escaping from obstacles** at high temperatures by local diffusion of atoms:

- Diffusion allows **dislocation climb** to occur.
- A segment of the dislocation line moves onto an alternative slip plane, and glide of the dislocation continues.
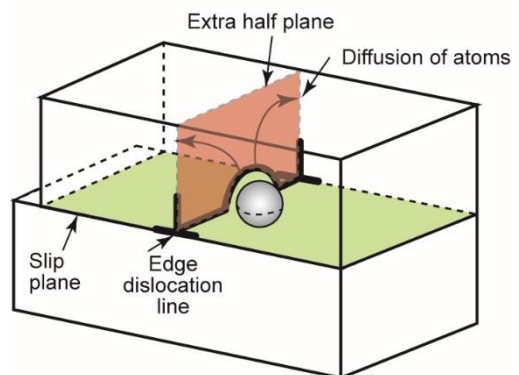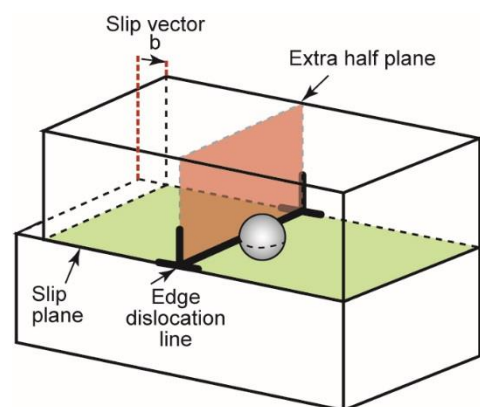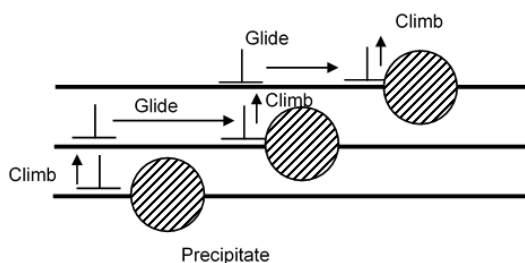
(Images: Ashby, Shercliff, Cebon)

The steady state creep rate during power law creep is given by equation (1), with the creep exponent:

$$n = 3 - 8$$

Because the exponent applies to the stress term in equation (1), this mechanism is therefore sensitive to the applied stress.

(2) Diffusion creep (or "diffusional flow")

In diffusion creep, grains elongate in the direction of applied tensile stress by the diffusive rearrangement of atoms throughout the material (rather than just locally at dislocations, as in power law creep).

Atoms can diffuse along two routes:
- **along grain boundaries** (easier, occurs at lower temperatures),
- bulk diffusion **through the crystal** itself (more difficult, occurs at higher temperatures).
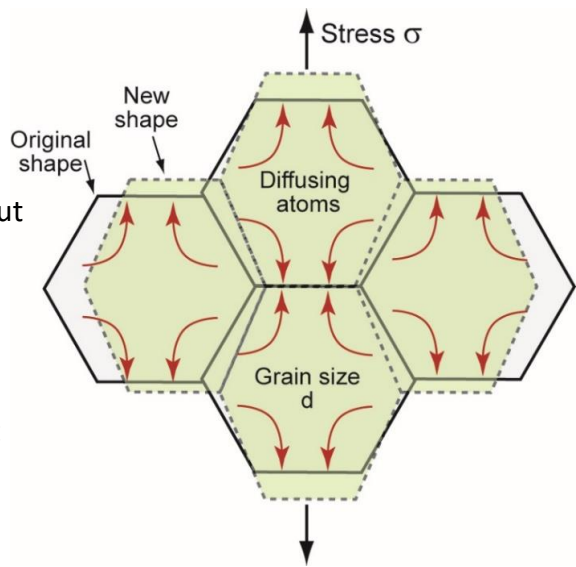
The steady state creep rate during diffusion creep is given by equation (1), with the creep exponent:

$$n = 1$$

It is therefore sometimes known as 'linear viscous creep'. This mechanism doesn't depend on dislocation motion, and is therefore less sensitive to the applied stress.

However, diffusion creep is sensitive to the **grain size**:
- large grains $\implies$ larger diffusion distances required, lower grain boundary area
  $\implies$ slower creep
- small grains $\implies$ larger grain boundary area, giving rapid diffusion pathways
  $\implies$ faster creep

Note that the 'dislocation creep' mechanism is not sensitive to grain size: it is dependent on atomic rearrangement locally at dislocations.

Failure during creep: creep rupture

Creep failure begins with the **nucleation of voids** on the grain boundaries.
- Eventually, growth of voids leads to a reduction in the load-bearing cross-section, **increasing the stress**.
- The creep rate accelerates in the damaged section (particularly for power-law creep, with large exponent n), giving the transition to tertiary creep, and creep rupture.
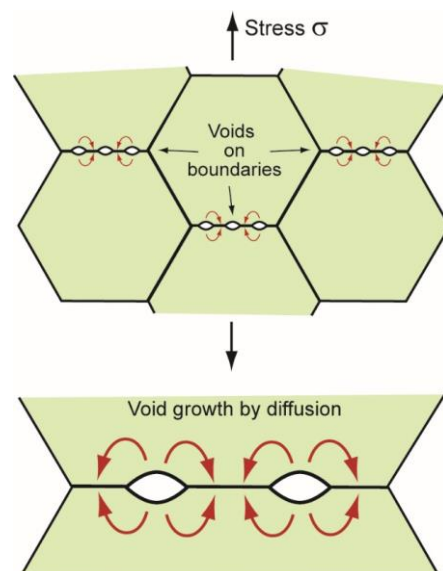
The overall time to failure t_f at a given stress often follows the empirical Monkman-Grant relationship:

$$t_f \dot{\varepsilon}_{ss} = C$$

Here, the material constant C represents a critical strain at failure.

Example: A stainless steel component was designed to operate at a stress of $\sigma_1 = 180$ MPa, at a temperature in the power law creep regime, for which $n = 7.5$.
- If the stress is reduced to $\sigma_2 = 150$ MPa, by how much would the creep failure time increase?

Taking ratios at constant temperature:

$$\frac{\dot{\varepsilon}_2}{\dot{\varepsilon}_1} = \left(\frac{\sigma_2}{\sigma_1}\right)^n = \left(\frac{150}{180}\right)^{7.5} = 0.255$$

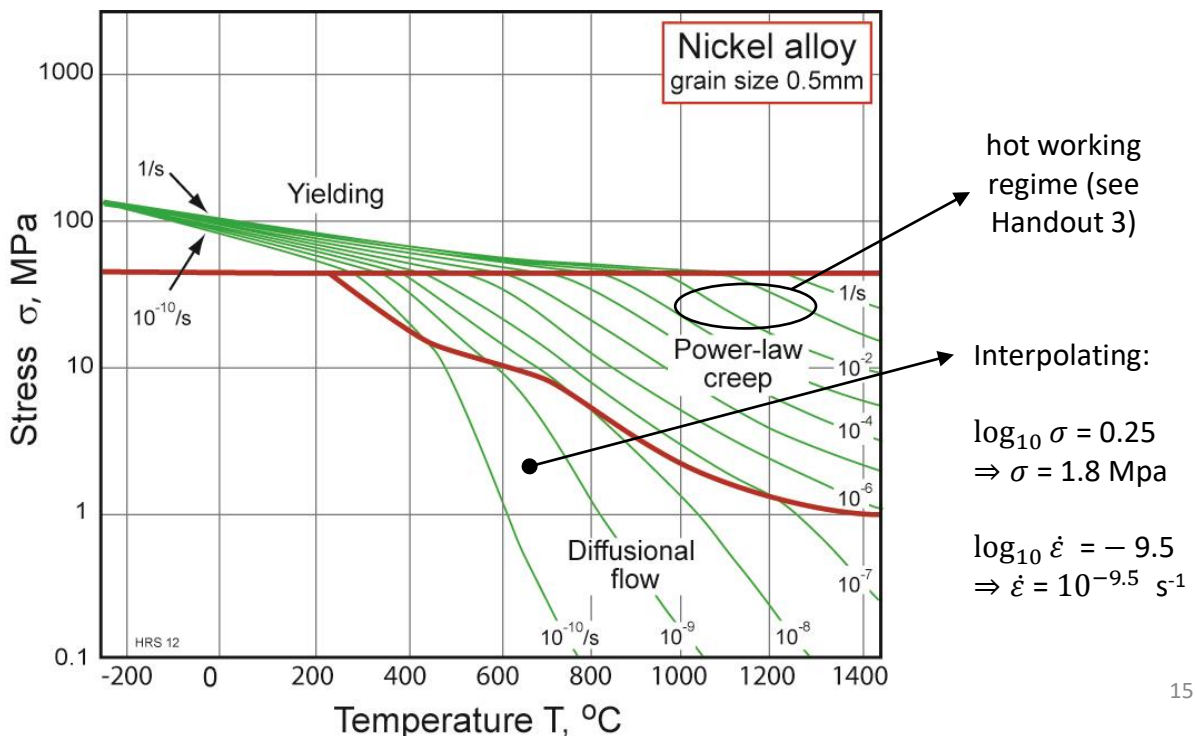Assuming failure occurs when: $t_f \dot{\varepsilon}_{ss} = C$

$$\frac{t_{f2}}{t_{f1}} = \frac{\dot{\varepsilon}_1}{\dot{\varepsilon}_2} = \frac{1}{0.255} = 3.9$$

A 17% reduction in the applied stress therefore results in nearly a 400% increase in component creep life.

Creep mechanism maps

The dominant creep mechanism depends on both the temperature and the applied stress. This is encapsulated in a creep mechanism map for steady state creep:
- axes of log (stress) and temperature, contours of constant strain rate
- boundaries separate regions where a particular mechanism dominates.

hot working regime (see Handout 3)

Interpolating:

$\log_{10} \sigma = 0.25$
$\Rightarrow \sigma = 1.8$ Mpa

$\log_{10} \dot{\varepsilon} = -9.5$
$\Rightarrow \dot{\varepsilon} = 10^{-9.5}$ s^{-1}

The creep mechanism map can be used to calculate the value of the creep exponent n :

- At **a fixed temperature**, read off the change in stress between a pair of strain rate contours:
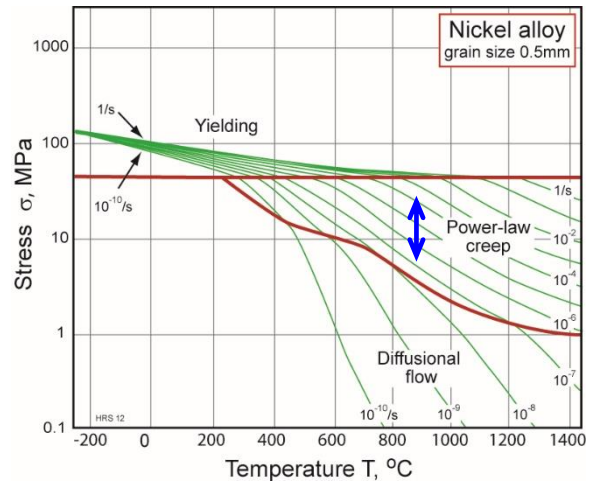
  $$\Delta[\,\log_{10}\sigma\,]\,,\ \ \Delta[\log_{10}\dot{\varepsilon}_{ss}]$$

- Choose an interval of strain rates within a single creep regime.

- Taking $\log_{10}$ of equation (1), and noting that T is constant:

  $$\log_{10}\dot{\varepsilon}_{ss} = n\log_{10}\sigma\ +\left[\,\log_{10}A - \frac{1}{\ln 10}\frac{Q}{RT}\,\right]$$

  $$\therefore\,\Delta[\log_{10}\dot{\varepsilon}_{ss}] = n\ \Delta[\,\log_{10}\sigma\,]\quad\rightarrow\quad n$$

Note that the spacing of the strain rate contours (and therefore the creep exponent) changes across the map. Care has to be taken over the range of strain rates spanned when determining a value for n.

9.3 Case study: processing for creep resistance

This case study will look at the creep resistant design of jet engine turbine blades:

Example of a turbofan engine: Rolls-Royce Trent
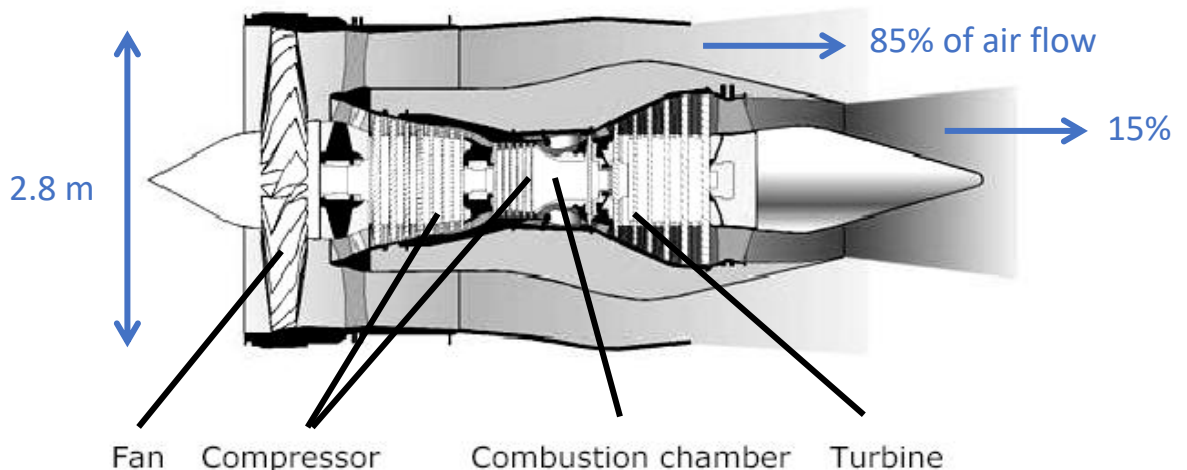
Source for case study: Michael Cervenka, Rolls-Royce plc

The most critical component for creep resistant design is the first stage turbine blade, which follows the combustion chamber:

- it experiences the highest temperatures,
- high longitudinal stresses (typically **250 MPa**) result from the high rotational speed: 10,000 rpm in the Rolls Royce Trent 800.

turbine

high pressure stage: compressor
10,000 rpm
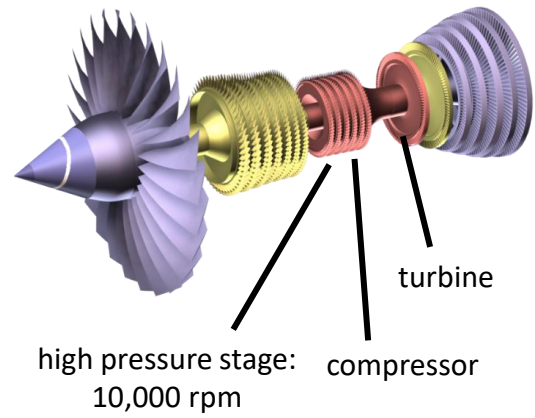
Increasing the combustion temperature (the 'turbine entry temperature') leads to increased efficiency:

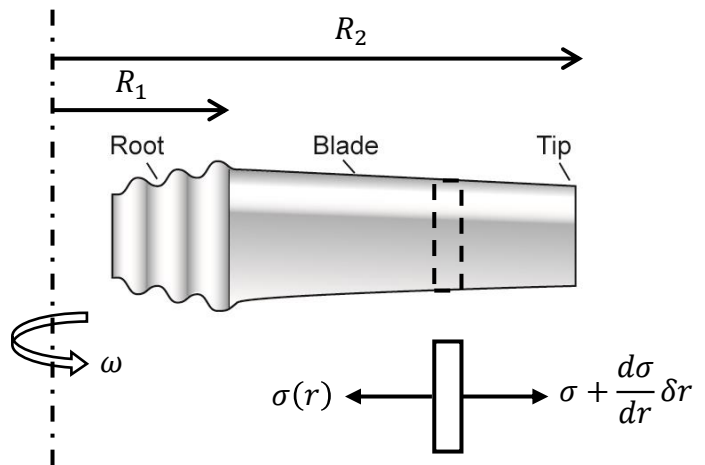- Turbine entry temperatures **>1500 °C** are now used.

Rate of elongation of a turbine blade

For the turbine blade, the stress varies with position along the blade:

- centripetal self-loading due to the angular velocity
- root has a higher stress than the tip.

Writing F = ma for a small element of turbine blade gives:

$$\frac{d\sigma}{dr} = -\rho\omega^2 r \quad \rightarrow \quad \sigma(r)$$

R_2

R_1

Root   Blade   Tip

ω

$\sigma(r) \longleftarrow \qquad \longrightarrow \sigma + \dfrac{d\sigma}{dr}\delta r$

The rate of elongation of a small element of length δr is: $\dot{\varepsilon}_{ss}(r)\,\delta r$

The overall rate of elongation must therefore be found by integrating the local strain-rate (which depends on the local stress) over the length:

$$\frac{dL}{dt} = \int_{R_1}^{R_2} \dot{\varepsilon}_{ss}(r)\,dr$$

The full calculation is covered in Examples Paper 5. The life of the turbine blade is improved by reducing the creep strain rate $\dot{\varepsilon}_{ss}$. Different processing strategies to achieve this are discussed next.

Strategy 1: creep resistant alloy

Current engines make extensive use of **nickel-based alloys** (more than 40% by weight in a modern engine):

- High **melting temperature**:

  reduces T/T_m

- Note that $T_m = 1453°C$ for pure Ni, but blade cooling maintains $T/T_m \approx 0.7$

- High alloy content gives **solid solution** and **precipitation** hardening:

  reduces dislocation creep

Titanium
Nickel
Steel
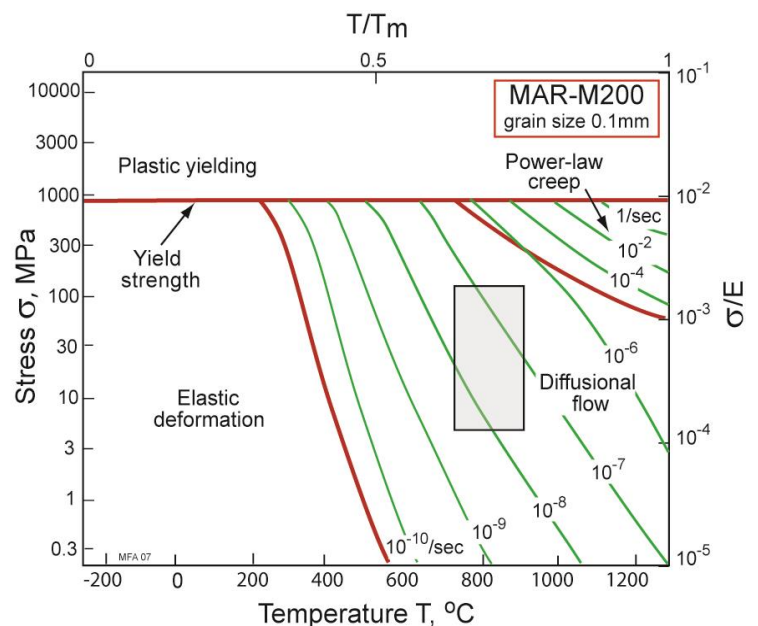Aluminium
Composites
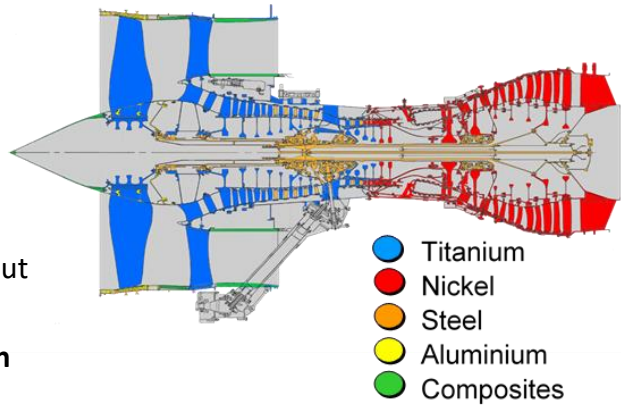
Deformation mechanism maps:

(a) Pure Ni:

- The grey box indicates typical blade operating conditions:

  $\dot{\varepsilon}_{ss} \sim 10^{-1} \text{ s}^{-1}$

- Blade would double in length in 10 seconds!

- Power law creep regime: creep is due to dislocation motion. Alloying is needed to stop this (see above).
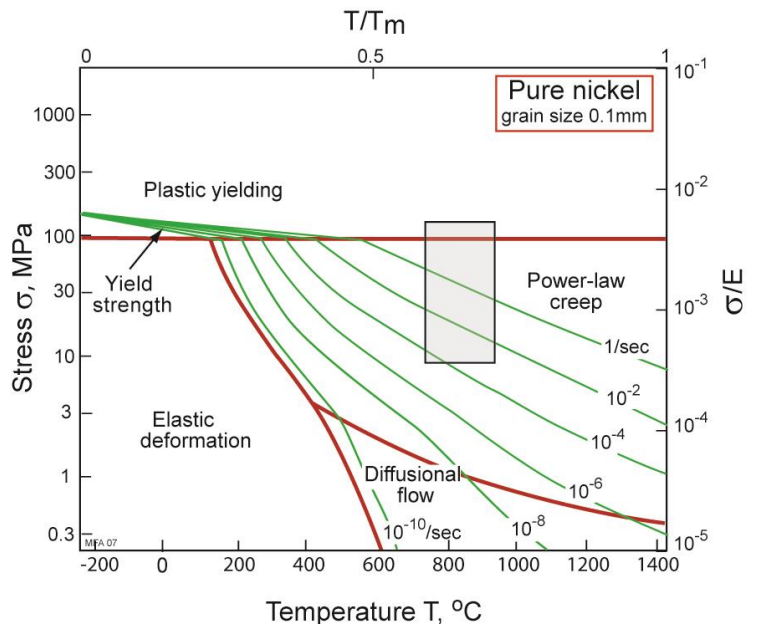
(b) Ni superalloy MAR-M200:

- Ni plus 10% Co, 12% W, 9% Cr, 5% Al, 2% Ti.

- Now, at the blade operating conditions:

  $\dot{\varepsilon}_{ss} \sim 10^{-7} \text{ s}^{-1}$

- By increasing the resistance to dislocation motion, alloying reduces the power law creep regime.

- Operating point moves into the **diffusional flow** regime, and strain rates reduce by 6 orders of magnitude.
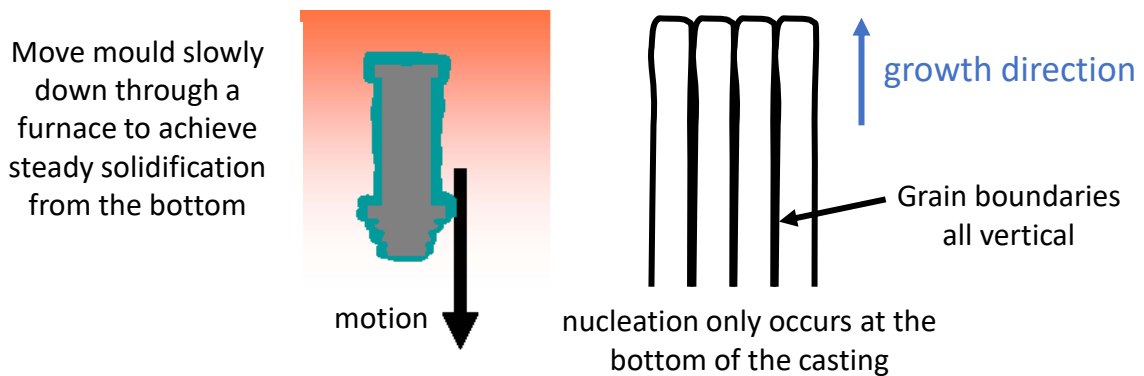

Deformation-Mechanism Maps: The Plasticity and Creep of Metals and Ceramics, Frost and Ashby, Pergamon Press, 1982

Strategy 2: grain size control during casting

Alloying has moved the blade operating point into the diffusional flow creep regime. Recall that grain size and grain boundary area influences the rate of diffusion creep:

- atoms diffuse most easily along grain boundaries.

Further improvement in life results if blades are **cast with only columnar grains** (see earlier lectures) running along the axis, known as 'directional solidification':

- the diffusion distances required to elongate the grain become large.

Move mould slowly down through a furnace to achieve steady solidification from the bottom

motion

growth direction

Grain boundaries all vertical

nucleation only occurs at the bottom of the casting

The creep life can be improved further if grain boundaries are eliminated altogether:

- The whole blade is cast as one **single crystal**.
- This requires innovative processing: a spiral "pigtail" at the bottom of the mould permits the growth of just one nucleus with a specific crystal orientation.

Evolution of turbine blade casting technology:

Equiaxed crystal structure

Directionally solidified

Single crystal
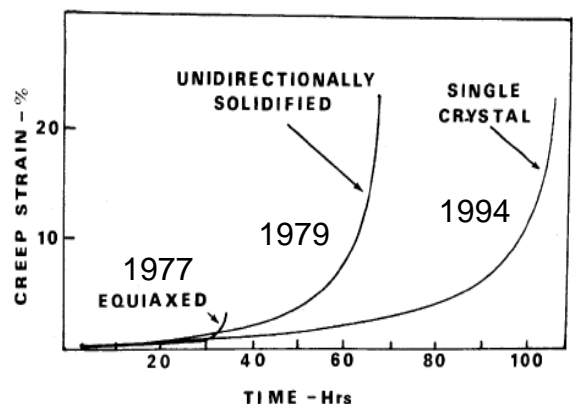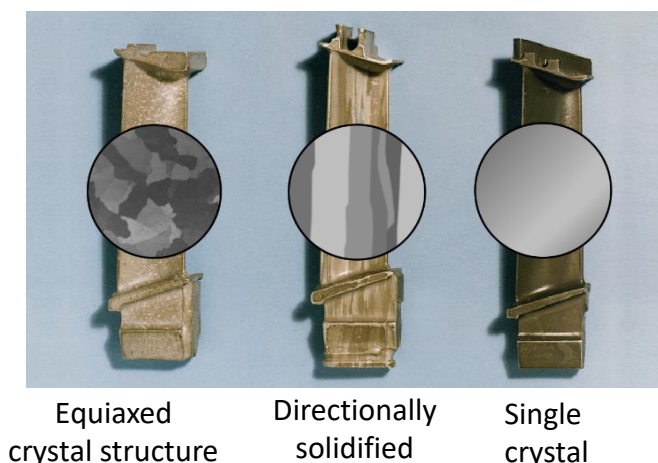
Accelerated lab creep tests of MAR-M200

[Source: CH White, chapter 4 in *The development of gas turbine materials*, GW Meetham (ed.), Applied Science Publishers, 1981]
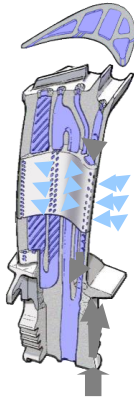
Strategy 3: blade cooling

A negative consequence of alloying is to reduce the melting temperature, and hence increase T/T_m, for a fixed turbine entry temperature (>1500°C)

- Pure Ni: T_m = 1453°C
- Ni superalloy: T_m = 1280°C

Blade cooling strategies are needed to maintain $T/T_m \approx 0.7$:

(a) Cooling the blade from the inside. A flow of **cooling air** reduces the surface temperature by >200°C .

(b) A zirconia (ZrO_2) ceramic **thermal barrier coating** provides an insulating layer between the hot gasses and the Ni superalloy.
- A coating 150 μm thick reduces the surface temperature by a further 170 °C.

9.4 Summary of the learning outcomes: creep

After completing section 9 you will be able to do the following:
1. Describe the mechanisms of power law creep and diffusion creep, and identify them on a creep mechanism map.
2. Use a model for steady state creep to predict the creep life of components.
3. Explain how alloying, processing and component design can influence creep life.

9.5 Quiz W8.2: creep

A weight hangs from the end of a cantilevered metal strut within a furnace. Which of the following strategies will increase the creep life of the strut (more than one may be correct)?

1. Reduce the grain size, in order to increase the yield strength.
2. Increase precipitation and solid solution hardening.
3. Reduce the cross-sectional area, to reduce the total grain boundary area.
4. Use a low melting temperature alloy, in order to reduce casting defects.

Additional worked example: creep

For further explanation, a video will be available with the following worked example:
- Tripos Question 2015 Q5, which helps with Examples Paper 5 Q5-8.

Now attempt: Examples Paper 5, Q.5-8