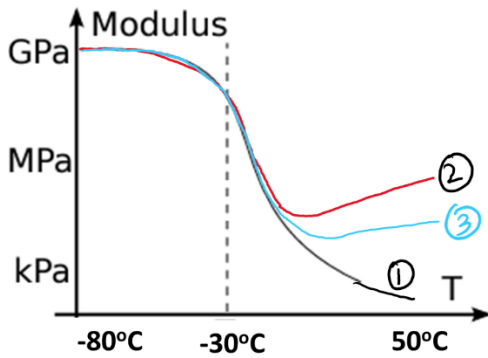


Question-1

(a)

(i)



Curve-1: No crosslinking, polymer chains flow above T_g and thus loss of elastic modulus. Curve-2 and Curve-3 are associated with a crosslinked elastomer, where the number of monomers between crosslinking points increases from Curve-2 to Curve-3. The form of the curves reflect that for an elastomer above the glass transition temperature, the elastic modulus (E) scales with T/n_c , where n_c is the number of monomers between cross-links.

Below $T_g = -30^\circ\text{C}$, the curves will overlap. The differences occur above T_g .

(ii)

$T = 20^\circ\text{C}$

$k = 10 \text{ N/m}$

$L_0 = 15 \text{ cm}$

$m = 50 \text{ g}$

$F = k \Delta L$ (Taking $g = 10 \text{ m/s}^2$)

At 20°C
SI unit: $0.05 \times 10 = 10 \times \Delta L_{20}$

$\Delta L_{20} = 0.05 \text{ m} = 5 \text{ cm}$

Large deformation ($\frac{\Delta L}{L} = \frac{5 \text{ cm}}{15 \text{ cm}} > 50\%$, assume linear elasticity)

Assume the stiffness is solely due to entropic forces and neglect effects of thermal expansion, $k \propto \frac{1}{T}$

$\therefore \Delta L_{50} = \frac{(20 + 273) \times 0.05}{(50 + 273)}$

$\approx 0.045 \text{ m} = 4.5 \text{ cm}$

$\Delta L_{50} - \Delta L_{20} \approx 0.045 - 0.05 = -0.005 \text{ m}$ (goes upwards by 5 mm)

Assumptions: (1) linear elasticity; (2) the elastomer stiffness is solely due to entropic forces; (3) negligible thermal expansion.

(iii)

Decreasing the degree of crosslinking density, is equivalent to increasing n_c , thus the stiffness of the elastomer will decrease.

$$k_{20} \Delta L_{20} = k_{50} \Delta L_{50}$$
$$\Delta L_{50} = \frac{k_{20} \Delta L_{20}}{k_{50}}$$
$$\Delta L_{50} - \Delta L_{20} = \Delta L_{20} \left(\frac{k_{20}}{k_{50}} - 1 \right)$$

magnitude

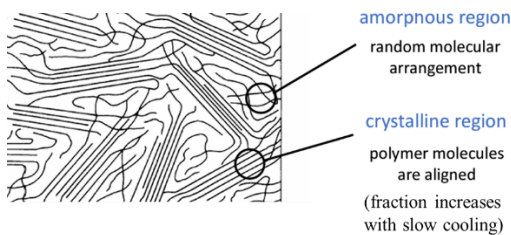
$$\Delta L_{20} = \frac{F}{k_{20}}$$

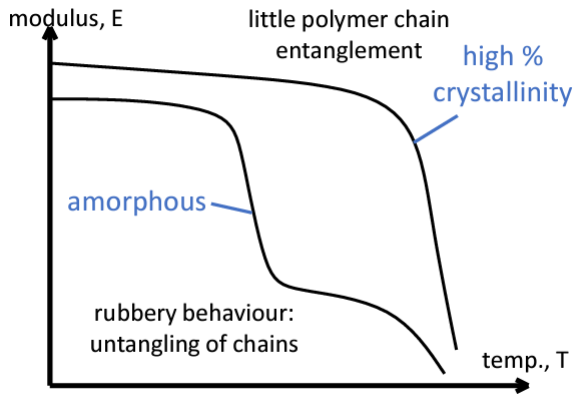
$\frac{k_{20}}{k_{50}} < 1$
this term negative
contraction

Re-analysing the experimental conditions in a(ii) as above, the weight will still go up (contraction), but the magnitude of displacement will be larger since the new k_{20} (the stiffness of the elastomer at 20°C) is smaller.

(b)

(i) Slow cooling increases crystallisation fraction. Thus, the filament will have increased opacity and possibly density as closer molecular packing of crystalline regions make them denser. The glass transition temperature of the filament will be increased due to the increased crystallisation fraction. The mechanical properties (strength and modulus) will increase, this is especially noticeable if the filament were to be used at a temperature at elevated temperatures below their glass transition temperatures.

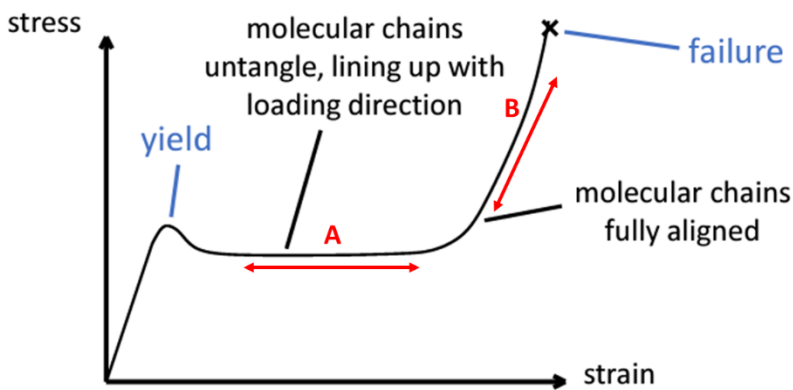




(ii)

Stretching will untangle, re-orient and possibly fully aligning the chains depending on the level of stretching (as shown in the graph below). The filament will have increased opacity, and could have increased density and glass transition temperature.

Depending on the amount of stretching, i.e. whether the stretch level lies in a region around A, or a region around B, the effect on the mechanical property of filament will be different. If stretch reaches region-A, the filament will have similar modulus and yield strength as the standard condition, but elongation to break will be reduced. If the stretch reaches region-B, the filament will have significantly higher modulus and yield strength compared to the standard condition, with reduced elongation to break.



[Examiner's comments: Q1 was about elastomers and polymer processing. It was poorly answered, with many students not completing all the question parts, resulting in a wider spread of marks. For a)i) Most knew that decreasing cross linking (increasing n_c) would decrease stiffness. Not all stated that this was only above T_g . Very few plotted the amorphous curve (lowest E) compared with the increased cross-link curves (higher E). for a)ii) Most could calculate the initial elongation at 20 °C, and knew intuitively that the elastomer would shrink at higher temperature. Many didn't attempt to calculate the new displacement at 50 °C, instead just estimating the upward displacement. Some students forgot to convert the from Celsius to

Kelvin and few remembered to state their assumptions, even though the question asked for this. For a)iii) Many students incorrectly stated that the stiffness of the elastomer would increase and the elastomer would extend. Few went back to the formulas to derive the increased uplift for a) ii). For b)i) Many students drew the TTT diagram for thermoplastic polymers, and showed that slow cooling leads to higher crystallinity. Marks were awarded for noting consequent increases in cloudiness, density, yield strength, stiffness, and glass temp, with a reduction in ductility. Few drew the graph of modulus versus temperature for amorphous and high crystallinity polymers, despite using this in a) i). Some students tried to apply mechanisms for metals to the polymer case! For b) ii) Most students knew that the chains would stretch and align, increasing the yield strength and the opacity of the filament. Some drew the graph of stress versus strain for a polymer undergoing orientation strengthening, but few identified the two regions (flat and rising stress).

Question-2

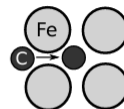
(a)

For atoms to diffuse (i.e. to move from one site), it needs to overcome an energy barrier. Atoms are constantly vibrating about their mean position, and the average energy per atom is given by k_bT (thermal energy). We would like to determine that probability that as the atoms vibrate at a temperature T , how likely atoms can move over the energy barrier. Arrhenius Law describes the probability of overcoming a barrier of activation energy by exponential temperature dependence.

(b)

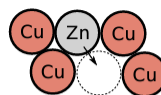
(1) **Bulk interstitial diffusion:** Small interstitial solute atoms move between the interstitial sites in a crystal lattice. The solute atom needs to have a sufficiently small atomic size compared to the bulk crystal. Example: C in Fe.

Diffusion rate: (large number of available adjacent sites)



(2) **Bulk vacancy diffusion:** Substitutional solute atoms exchange places with a vacancy in the crystal structure. Relevant to atoms of a similar atomic size. Example: Zn in Cu.

Diffusion rate: (number of free adjacent sites is relatively small)



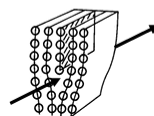
(3) **Short-circuit diffusion along a grain boundary:** Grain boundaries are areas where the crystal packing is more open, providing a faster route. This route is planar (2D).

Diffusion rate: (open crystal structure)



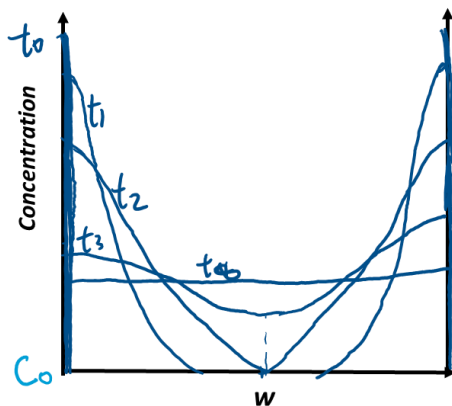
(4) **Short-circuit diffusion along dislocation cores:** The atom spacing around a dislocation core exceeds that in a perfect crystal. This route is linear (1D).

Diffusion rate: (open crystal structure)



(c)

(i)



C_0 - the baseline carbon concentration in the original steel plate

Assumptions: no edge effects 1-D diffusion. Homogenous diffusion constant.

(ii)

$$\langle x^2 \rangle \propto Dt$$

$$t \propto \frac{\langle x^2 \rangle}{D}$$

$$\frac{t_2}{t_1} = \frac{\frac{\langle x^2 \rangle}{D_2}}{\frac{\langle x^2 \rangle}{D_1}} = \frac{D_1}{D_2} = \frac{\exp\left(\frac{Q}{T_1}\right)}{\exp\left(\frac{Q}{T_2}\right)} = \exp\left(Q\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$

$$t_2 = t_1 \exp\left(Q\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$

Assume the diffusion process follows the Arrhenius law.

(iii)

Carbon can diffuse via interstitial diffusion (main route), or grain boundary diffusion in iron/steel; both are relatively fast process due to the small carbon atom compared to the Fe atoms. Increased grain size will decrease the amount of grain boundaries. However, due to small size of the carbon atoms, it is expected that the increase in grain size will have small effects on the diffusion routes of carbon. Thus Q will be the same or slightly larger. Thus, similar concentration profiles of b(i) will be resulted.

[Examiner's comments: Question 2 was on diffusion, which was a popular question and in general answered satisfactorily.

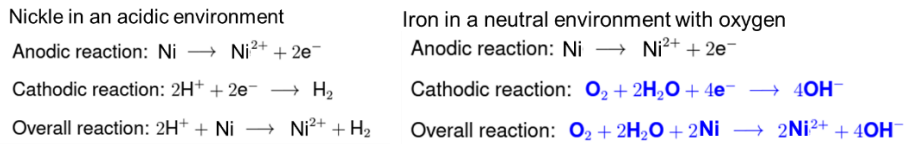
Questions (a) and (b) tested the students' ability to recall concepts in Arrhenius law and different diffusion mechanisms in solids. These questions were answered well overall, and full marks were given for the completeness of the answers.

Question (c) tested the students' ability to apply knowledge learnt in the course into a material processing scenario of 'carburisation'. The statement of 'carburisation process' would set the initial and boundary conditions of the diffusion. This part was answered satisfactorily. Marks were mainly lost in part-(c) which is to identify the main route of diffusion to determine whether the changes in microstructure would affect the diffusion constant.]

Question-3

(a)

(i)



(ii)

According to the Engineering databook, the free energy of oxidation for iron ($\text{Fe} \rightarrow \text{Fe}^{2+}$) is more negative than nickel ($\text{Ni} \rightarrow \text{Ni}^{2+}$). The formation of Fe_3O_4 is also more energetically favourable than NiO .

Oxidation reaction for solution of the metal	Normal hydrogen scale (volts)	Material	Oxide	Free energy (kJ/mol O_2)
$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$	-0.44	Iron	Fe_3O_4	-508
$\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$	-0.25	Nickel	NiO	-439

Thus the tendency for the oxidation of nickel will be lower than that of iron in most environmental conditions.

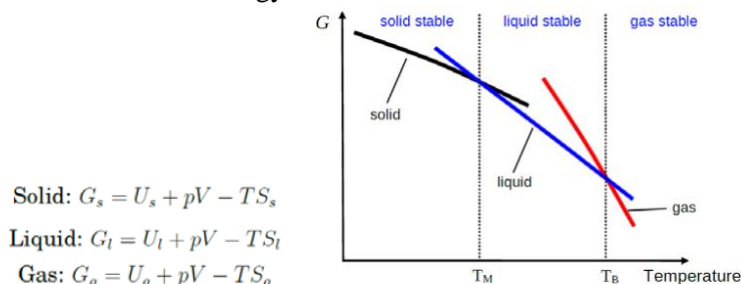
Additionally, once oxidised, nickel oxide has good stability, forming a good surface barrier which prevents further oxidation of nickel.

(iii)

In galvanic protection, a highly electro-potentially negative metal (such as zinc) is used to couple with a less electro-negative metal (such as iron), such that the electro-potentially negative metal is preferentially corroded. The galvanisation protection can be applied in the form of coating a layer of zinc (galvanization) on the surface of a metal structure. Coating the whole surface provides the best protection, but it is not required in many cases. Another method is to use a sacrificial metal (e.g. zinc as an anode), which is electrically connected to the steel structure. Both the sacrificial electrode and the steel structure need to be in the same electrolyte. When the life time of the steel structure needs to be longer than the life time of the coating, it is preferred to have a separate anode that can be replaced as often as required.

(b)

Consider the free energy functions of a material in its three different states:



Because atoms attract each other, the internal energy is lower when particles are closer to each other for a given temperature. So qualitatively we expect: $U_s(T) < U_l(T) < U_g(T)$

However, because entropy is a measure of disorder, it is expected that: $S_s(T) < S_l(T) < S_g(T)$

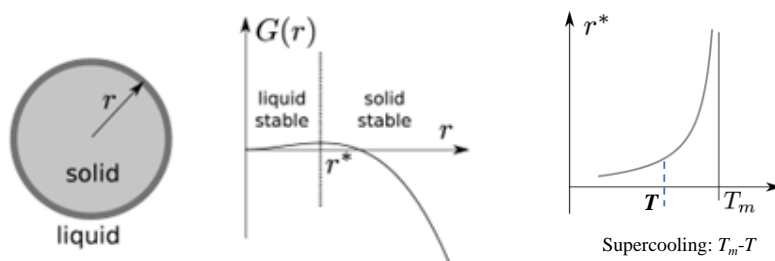
As a result, the Free Energy of a gas starts higher than the free energy of a liquid at high temperature, but should decrease faster with temperature. The curves are expected to cross. The same argument can be applied for solids and liquids. The crossing points represent the transition temperatures.

(c)

(i)

Liquid cooling period (A–B–C), at this stage the water (single liquid phase) is cooled until it reaches the nucleation point c. The temperature of the cooled water is lower than its freezing temperature ($0\text{ }^{\circ}\text{C}$), and the difference between them is called degree of supercooling.

Supercooling is required since the water is pure, and an interfacial energy associated with homogenous nucleation (to reach a critical size nucleus) needs to be overcome from B to C.

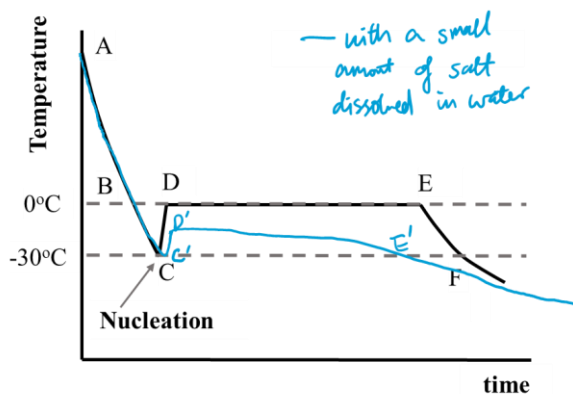


(ii)

The temperature at which nucleation starts is called nucleation temperature, i.e., the lowest temperature of liquid state (point C). From C to D, as water freezes, latent heat is released thus temperature of water gradually increases back to the freezing point. The existing nucleated ice crystals can also act as points for heterogenous nucleation (thus, requiring lower undercooling). For the phase transition period (D–E, mixture of liquid and solid phases), the nuclei grow to bigger ice crystals (i.e. more water turns into ice) at 0 degC (the freezing temperature). Since the water is pure (single component), the freezing temperature is kept constant (thus horizontal line for D-E). (E-F) Now solidification completes, where water is fully transformed into ice, freezing continues whereby the ice (single solid phase) temperature can drop further upon cooling.

(iii)

Dissolving salt in water (increased entropy of mixing, and decreased enthalpy of mixing) will decrease the freezing point (liquid to solid phase transition temperature); thus the line of D to E will be depressed overall. Adding salt promotes heterogenous nucleation (thus reducing the supercooling required (thus reduced temperature difference between C and D). This is a liquid solution (instead of single component liquid), thus solidification will take place across a range of temperatures instead of a single temperature (i.e. D-E lines will have a downward slop instead of being horizontal).



[Examiner's comments: Question 3 tested the students' thermodynamics knowledge, it was a popular question and overall was answered very well.

Part (a) examined students' knowledge in electrochemistry/oxidation/corrosion. The completeness of the answers determines whether full marks will be given.

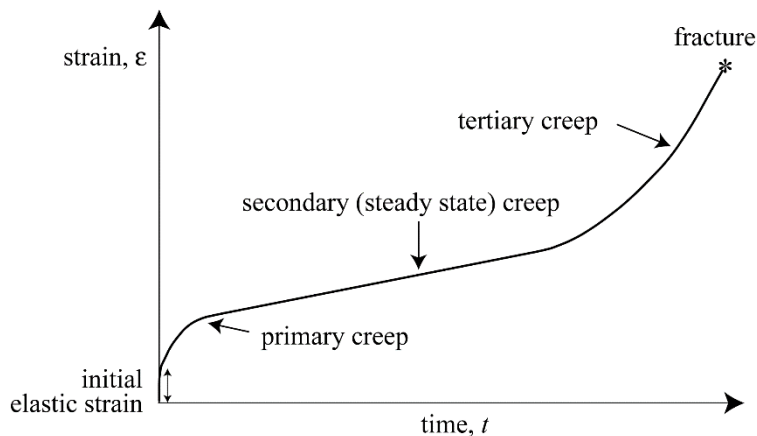
Part (b) was again very well answered, and again the completeness of the answers determines whether full marks will be given.

Part (c) tested whether the students can apply their knowledge learnt in metal solidification into the context of water. Marks were mainly lost in (iii) where adding salts could increase the complexity of the solidification process leading to many changes in the freezing curve of water.]

Section B (AE Markaki)

Question 4

(a) A schematic showing the three stages in a typical creep curve is shown below:



Three stages to the creep curve may be identified:

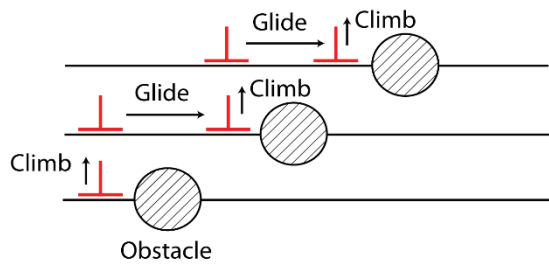
Stage I: Primary creep in which the creep resistance increases with strain leading to a decreasing creep strain rate – occurs over a short period.

Stage II: Secondary (Steady State) creep in which strain increases steadily with time (i.e. constant creep rate) – dominates creep life.

Stage III: Tertiary creep in which there is an accelerating creep rate due to the accumulating damage, which leads to creep rupture.

(b) Region I – Yielding. Deformation results from dislocation motion which resisted is by obstacles (e.g. solute atoms, precipitates and grain boundaries), leading to work hardening. Yield strength and hardening are determined by the type and number of obstacles to dislocation motion.

Region II - Power-law or dislocation creep involves climb and glide of dislocations to enable plastic strain. It essentially describes deformation produced by the movement (glide) of dislocation which is itself limited by the climb of those same dislocations around obstacles substantial enough to prevent plastic flow. At high temperatures, dislocations can escape from the obstacles by climbing out of the slip plane and thus continue to glide allowing further slip. After a little slip, the unlocked dislocations encounter the next obstacles, and the whole cycle repeats itself. This explains the progressive, continuous nature of creep. This creep mechanism depends on dislocation motion and dominates at higher temperatures. It has a creep exponent n between 3-8 ($\log \sigma$ vs $\log \dot{\epsilon}$) and is favoured at high applied stress.



Region III - Diffusion creep occurs by the redistribution of material by diffusion within the bulk and along the grain boundaries, enabling deformation in the direction of applied stress. For example, for a sample (and a grain) under tension, atoms migrate from the sides of the grain to its ends, so that it gets longer in the direction of the applied stress. Diffusion occurs throughout the material rather than locally at dislocations as in power-law creep. Grain boundary diffusion is easier (lower activation energy) and dominates at lower temperatures whereas bulk diffusion is more difficult and occurs at higher temperatures. Diffusion creep does not involve dislocation motion and is therefore less sensitive to the applied stress ($n \sim 1$). It depends on the grain size (creep rate is inversely proportional to the grain size).

(c) (i) If $L (=50 \text{ mm})$ is the length of the blade, and x is the distance from the tip, then we can define

$$\bar{x} = \frac{x}{L}$$

Transition occurs when

$$A \cdot (100\bar{x})^n = B \cdot 100\bar{x}$$

$$A \cdot (100\bar{x})^{n-1} = B$$

$$\begin{aligned} \Rightarrow (\bar{x})^{n-1} &= \left(\frac{B}{A}\right) \cdot \frac{1}{100^{n-1}} \\ &= \left(\frac{5 \times 10^{-12}}{5 \times 10^{-26}}\right) \cdot \frac{1}{100^{n-1}} \end{aligned}$$

For $n = 8$, we have

$$\therefore \bar{x} = (10^{14})^{1/7} \cdot (100^{-7})^{1/7} = 10^2 \cdot 0.01 = 1$$

Therefore transition occurs at the root of the blade and so the blade creeps by diffusional creep.

(ii) Hence, the steady strain rate of blade will be

$$\dot{\epsilon} = B\sigma = B \int_0^1 (100\bar{x}) d\bar{x}$$

Therefore the elongation of the blade will be

$$\begin{aligned}u &= (30000 \times 60 \times 60 \text{ s}) \cdot L \cdot \dot{\epsilon} = \\ &= (30000 \times 60 \times 60 \text{ s}) \cdot 50 \text{ mm} \cdot \int_0^1 B \cdot (100\bar{x}) d\bar{x} = \\ &= 108 \times 10^6 \cdot 50 \cdot \frac{(5 \times 10^{-12}) \cdot 100}{2} = \frac{108 \cdot 25 \cdot 10^{-3}}{2} = 1.35 \text{ mm}\end{aligned}$$

The blade extends more than 1 mm over its design life and therefore the current material is not suitable.

(iii) Creep resistance can be improved by increasing grain size. Since diffusional flow involves redistribution of material on the grain boundaries by diffusion, it is best to eliminate grain boundaries altogether and use a single crystal.

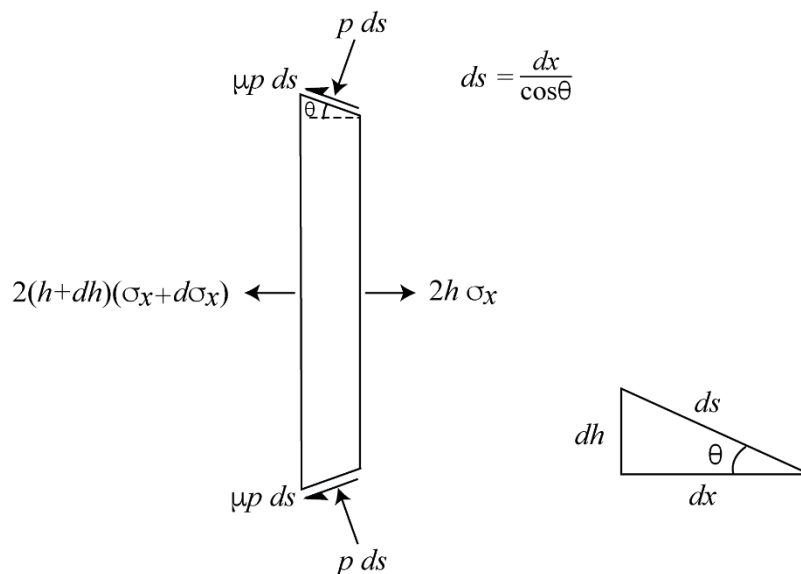
A single crystal can be produced using innovative processing: a spiral “pigtail” at the bottom of the mould permits the growth of just one grain with a specific crystal orientation.

By using a single crystal, we expect that the constant B will decrease, hence for a given stress the strain rate will decrease.

Comments: Part (a) was answered well, although several candidates could not name the different stages of creep. Part (b) was not answered less well. Most candidates did not name yielding as the mechanism in region I. A significant number of candidates identified region II as diffusion creep and III as dislocation creep. Nevertheless, they were able to describe reasonably well both mechanisms. The most significant loss of marks was in parts (c)(i) and (ii). Very few students equated the two mechanisms to identify which deformation mechanism(s) were active. Several candidates discussed the two mechanisms in the context of a turbine blade and were appropriately credited with marks. In part (c)(ii), a significant number of candidates derived incorrect, often unreasonable, values for the blade elongation (some didn't use the blade design life in their calculations). Part (c)(iii) was generally well answered. Full marks were given for describing how single crystals can be produced.

Question 5

(a) (i) For unit depth, the forces on an element strip of height $2h$ and width dx are shown in the figure below.



As illustrated in the figure above, dh , dx and ds are related to one another as follows:

$$dh = dx \tan \theta$$

$$dx = ds \cos \theta$$

(ii) Applying a force equilibrium in the x direction

$$2\mu p ds \cos \theta + 2p ds \sin \theta = 2h\sigma_x - 2(h+dh)(\sigma_x + d\sigma_x)$$

$$2\mu p dx + 2p \frac{dx}{\cos \theta} \sin \theta = 2h\sigma_x - 2h(\sigma_x + d\sigma_x) - 2dh(\sigma_x + d\sigma_x)$$

$$\therefore \mu p \frac{dh}{\tan \theta} + p dh = -h d\sigma_x - \sigma_x dh - (dh \cdot d\sigma_x)$$

Ignoring the second order term $(dh \cdot d\sigma_x)$ and dividing by dh gives

$$\therefore \mu p \cot \theta + p + \sigma_x + h \frac{d\sigma_x}{dh} = 0$$

(iii) For small values of θ and small coefficients of friction, μ , the principal axes of stress in the planes of the diagram will align vertically and horizontally to a good approximation. Assuming that the shear stress $\tau(x)$ is sufficiently small compared to the normal pressure $p(x)$ and the horizontal stress σ_x , then these may be treated as principal stresses. $p(x)$ and σ_x can be related by the Tresca yield criterion. σ_x is tensile and $p(x)$ is compressive. Hence to a good approximation, the Tresca yield condition can be written as

$$\sigma_x - (-p) = \sigma_y = 2k$$

$$\therefore \sigma_x + p = 2k$$

(b) (i) 1 mm of nickel is converted into oxide

$$8900 \times 0.001 \text{ kg m}^{-2} = \frac{8900 \times 0.001 \times 1000}{58.7} \text{ mol m}^{-2} \text{ Ni} = \text{no of moles of NiO}$$

$$\text{mass of NiO} = \frac{8900 \times 0.001 \times 1000 \times (58.7 + 16)}{58.7} = \frac{8900 \times 74.7}{58.7} \text{ g m}^{-2} = 11.3 \text{ kg m}^{-2} \text{ NiO}$$

$$m^2 = kt \Rightarrow 11.3^2 = 3 \times 10^{-5} t$$

$$\therefore t = 4.25 \times 10^6 \text{ s} = 49.2 \text{ days}$$

(ii) oxide thickness = $\frac{11.3}{6670} \text{ m} = 1.69 \text{ mm}$

Comments: This was a popular question on the paper and was generally well answered. A surprisingly high number of candidates didn't draw a free-body diagram despite fully answering part (a)(ii). Instead several candidates reproduced Fig. 3(b) showing stresses rather than forces. Also, several candidates used $2h$ instead of $2(h+dh)$ for the length of the slab on the left-hand side. In part (b)(ii), several students resorted to various artifices in order to obtain the required answer. In part (a)(iii), a large number of candidates described the Tresca yield criterion instead of outlining the assumptions for the approximation and also commenting on the signs of the principal stresses. Part (b) was well answered, although several students used the mass of nickel instead of the mass of the nickel oxide to work out the time in part (b)(i).

Question 6

(a) X: L + α , Y: α + β and Z: L + β

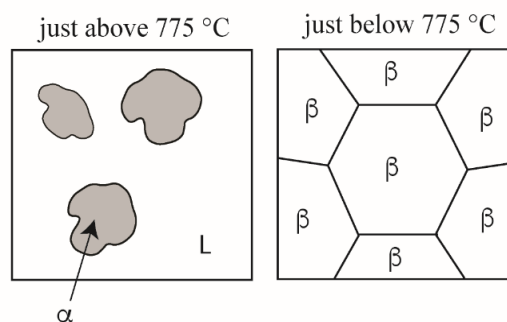
There is one peritectic point at 775 °C, Liquid (72% wt.% B) + α (14% wt.% B) \rightarrow β (50% wt.% B)

(b) (i) Just above the peritectic temperature, the phases present are α and liquid. The α phase is a solid solution based on A with around 14 wt.% B. The liquid is around 72 wt.% B.

Using the lever rule we can calculate the proportions of each:

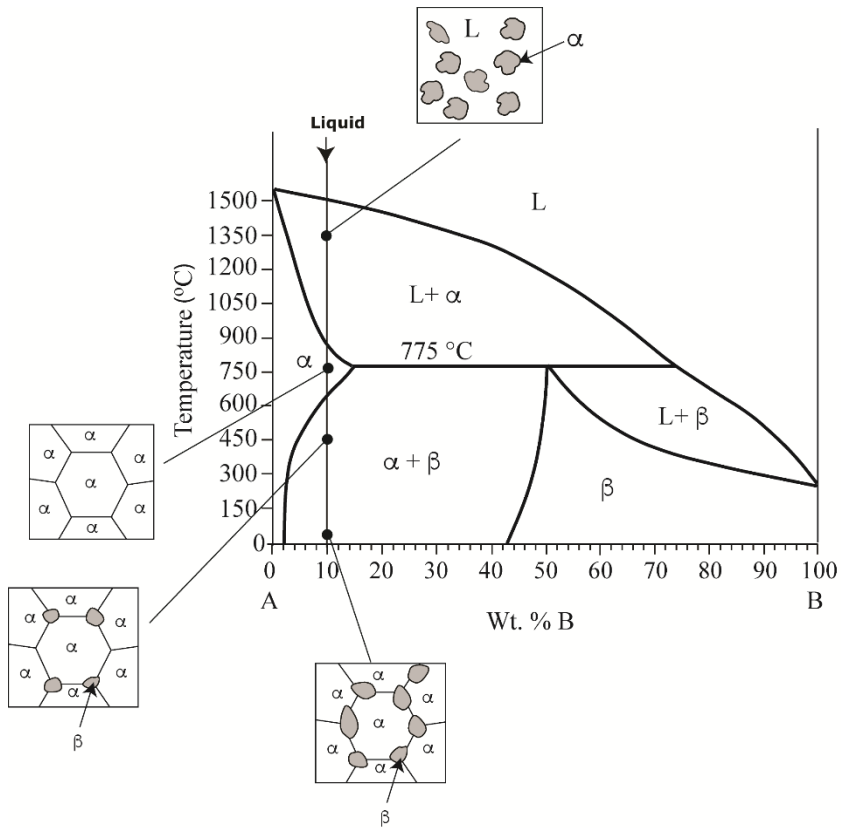
% Weight fraction of α = $\frac{72 - 50}{72 - 14} = 38\%$, so weight fraction of L of 62%.

(ii) Just below the peritectic temperature, only β (50 wt.% B) is present, so we have 100% β .



(c) The energy barrier to homogeneous nucleation is high, as there is a significant surface energy cost of making small nuclei of the new solid β phase in the liquid. Hence the critical radius is likely to be large. Heterogeneous nucleation on a pre-existing surface will be easier. As stated in the question, no other heterogeneous nucleation sites are available at the centre of the melt, so the α phase is the obvious place.

(d) On cooling (see schematic below), the first solid to form at the liquidus temperature ($\sim 1500^\circ\text{C}$) is the α phase which will have a composition of ~ 1 wt.% B. The composition of the liquid and solid becomes richer in B following the liquidus and solidus lines respectively. At the temperature of the solidus ($\sim 870^\circ\text{C}$), only the α phase is present. The α phase will then cool down until it reaches $\sim 570^\circ\text{C}$, at which point some β phase will start to precipitate. At this temperature, the β phase will have a composition of ~ 50 wt.% B, and will probably nucleate heterogeneously on the grain boundaries of the α phase as explained above (see also sketch below). On further cooling, the quantity of β phase will increase (the proportions of the two phases will be given by the lever rule at any temperature), and the solute content of B will drop (the composition is given by the tie-line crossing the phase boundary at any temperature).



1350°C

Two-phase field

Phases	Composition (wt.% B)	Proportion (wt.%)
α	2	$\frac{34-10}{34-2} \times 100 \approx 75$
L	34	25

750°C

A single-phase region (100% α), the phase composition and alloy composition coincide (10 wt.% B, 90 wt.% A)

450°C

Two-phase field

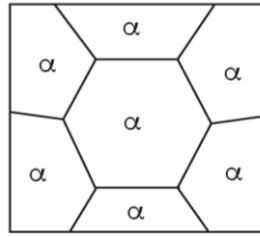
Phases	Composition (wt.% B)	Proportion (wt.%)
α	5	$\frac{49-10}{49-5} \times 100 \approx 89$
β	49	11

Room temperature

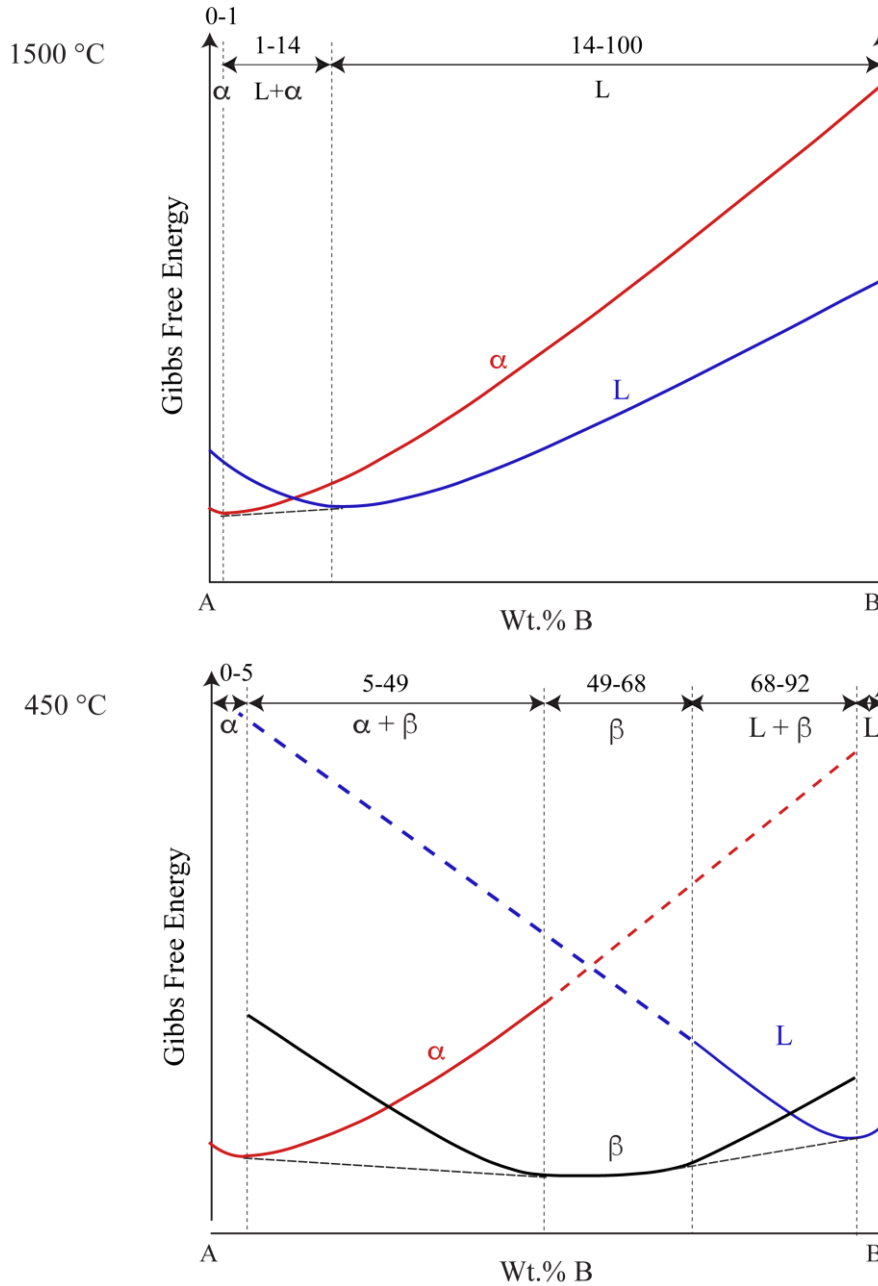
Two-phase field

Phases	Composition (wt.% B)	Proportion (wt.%)
α	4	$\frac{44-10}{44-4} \times 100 \approx 85$
β	44	15

For very fast cooling, the solid state diffusion required to form the β precipitates will not have time to occur, so a supersaturated solid solution will be retained, and the microstructure observed will consist of 100% α grains.



(e)



Comments: This was the most popular question on the paper. In part (a), several candidates incorrectly identified the 3 phase reaction as a peritectoid or eutectoid. Very few students wrote down the wt.% of the L and α phases, which was required for full marks. In part (b), microstructure sketches could have been more precise. Part (c) required a discussion of homogenous and heterogeneous nucleation. In part (d), marks were awarded for clear diagrams, quantitative detail of the wt% and proportions of phases, nucleation of β on the grain boundaries and clear descriptive text. Some students incorrectly cooled at 90 wt.% B, rather than 90 wt.% A. Part (e) was well answered. Marks were given for identifying the stable phases and their percentages, and also clarity of their schematic plots.