SECTION A Question 1

(a) Dislocation creep operates at high stresses and temperatures in excess of half the absolute melting temperature $0.35T_{\rm m}$ ($T_{\rm m}$ is the absolute melting temperature). 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.





To resist dislocation creep, it is important to choose a material with a high melting point (creep scales with T / T_m) and a microstructure that obstructs dislocation motion through alloying to give a solid solution or precipitate particles.

An engineering material in which this type of creep is suppressed is superalloys. They are based on iron, nickel or cobalt and are heavily alloyed with aluminium, chromium and tungsten.

(b) If the creep rupture life is inversely proportional to the creep rate, the coefficient can be absorbed into the constant of the creep equation. Hence

$$\left(\frac{1}{t}\right) = A'\sigma^{n} \exp\left(-\frac{Q}{RT}\right)$$

Hence if you plot log(1/t) against $log\sigma$, the gradient will be equal to the stress exponent.



The stress exponent is 5.3728.

To determine the activation energy Q, you can plot the $\ln(1/t)$ against 1/T, the gradient will be equal to -Q/R.



Using $R = 8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$, from the plot 33,634 × 8.3143 ≈ 280 kJ mol⁻¹

(c) $\left(\frac{\left(\frac{1}{t_1}\right)_{700}}{\left(\frac{1}{t_2}\right)_{700}}\right) = \frac{t_2}{t_1} = \left(\frac{\sigma_1}{\sigma_2}\right)^n$ $\therefore t_2 = 400 \times \left(\frac{157}{200}\right)^{5.37} = 109 \text{ hours} \approx 4.5 \text{ days}$

Hence 316 austenitic stainless steel would not be acceptable for such an application.

2. (a) From the Fe-C equilibrium phase diagram (Materials data book, pg 30), at $0.85T_m$, the steel is in the austenite phase field (γ). Hence the microstructure will be consisting of equiaxed grains of austenite. On quenching, there is no sufficient time for diffusion-controlled nucleation and growth. Instead, martensite forms by a shear transformation. Martensite is a metastable supersaturated, interstitial solid solution of C in steel with a bct (body centred tetragonal) structure. So the resulting microstructure will be martensite with some retained austenite. Martensite has high hardness (yield strength) and low ductility.

From the Al-Cu equilibrium phase diagram (Materials data book, pg 30), at $0.85T_m$, the alloy is in the α phase field (Al-rich solid solution). On quenching, there is no sufficient time for diffusion-controlled nucleation and growth. Instead, the Cu solute is trapped in the solid solution producing a supersaturated solid solution. The alloy in the as-quenched condition will be stronger than pure Al but not at its peak strength.

Before quenching





austenite (γ) (equiaxed grains) α phase (Al-rich solid solution) (equiaxed grains)

After quenching





martensite (black) and retained austenite (white) (equiaxed grains)

supersaturated solid solution (equiaxed grains)

(b) Fe-0.6%wt C

On re-heating (tempering) to a temperature less than the eutectoid temperature, precipitates of cementite Fe_3C will nucleate and grow. Their shape is spheroidal (to minimise surface energy) and the residual matrix will be ferrite. Since the alloy has not been through the eutectoid temperature, no pearlite can form. This will restore ductility and toughness although the yield strength will decrease. The tempering time and temperature can be adjusted to optimise the cementite precipitates' spacing and size for the desired properties.

Al-4 %wt Cu

On re-heating (ageing) to a temperature sufficient to allow diffusion (in practice to around 180°C), the nucleation and growth of a series of metastable precipitates will commence. The first to form with be GP zones followed by θ ", θ ' and, finally, the equilibrium phase θ (CuAl₂).



A few students will know this, but the precipitates in Al - 4%wt Cu will be considerably finer than the cementite in the steel

(c) The GP zones are fully coherent with the aluminium matrix, so interfacial energy is low Because the GP zones are coherent with the matrix, and nucleation occurs readily. dislocations are able to cut through the GP zones. The cutting stress varies with \sqrt{r} (r is the mean precipitate radius). As r increases with ageing, the stress required for cutting increases. The final θ is completely incoherent (bct structure). Dislocation may overcome obstacles, even coherent ones, by bowing around them. This occurs when the stress required for cutting exceeds that for bowing. On the other hand, the bowing stress is inversely proportional to r. As the precipitates coarsen, the stress required for bypassing decreases. The maximum resistance to dislocation motion occurs when the mechanisms switch (peak). The varying coherence from coherent (GP zones) to partial $(\theta^{"}, \theta^{'})$ to fully incoherent (θ) , plus control of the precipitates' spacing to simultaneously restrict dislocations either cutting coherent precipitates or bowing around incoherent precipitates, will ensure optimum strength. This will give a maximum yield strength and also reasonable ductility and toughness. The tempering time and temperature would need to be adjusted to optimise the precipitates' type, spacing and size for the desired properties.

Solid solution strengthening provided by the solute still trapped in solid solution (not yet precipitated out) also contributes to the yield stress/hardness. At the instant of quench, this provides 100% of the hardening effect. As the solute precipitates out of solid solution, this contribution falls. The overall ageing curve is sketched below:

The maximum yield strength usually occurs when one of the intermediate phases is present. At the optimum ageing time and temperature there will be a fine dispersion of Al-Cu precipitates.



3. (a) Viscoelasticity is a combination of elastic and viscous response exhibited in polymers. Hookean springs are used to simulate the elastic response in polymer deformation: f = kx, where k is the elastic constant of the spring. As indicated in the lectures, f and x represent stress and strain, rather than force and extension. Springs store energy and respond instantaneously.

Dashpots are used to model the viscous (time-dependent) response in polymer deformation: $f = \eta \dot{x}$, where η is viscosity and \dot{x} is the strain rate. Dashpots dissipate energy in the form of heat, characterise retarded nature of response.

Springs and dashpots can be used to produce simple and tractable models that reproduce empirical results. The predictions of the simple model can be tested against empirical results and if they hold to sufficient accuracy, the parameters for the model can be used for computational purposes ("curve fit").



Spring and dashpot in series: The first part is the instantaneous elastic response while the second part is the viscous retarded response.

Spring and dashpot in parallel: The strain reaches a limiting value at very long times (retarded elastic behaviour).

(b)

(i) The displacement x is the sum of the displacement in the spring 1 and the viscous strain in the dashpot

$$x(t) = x_{spring1}(t) + x_{viscous}(t)$$
$$x(t) = \frac{f}{k_1} + x_{viscous}(t)$$

where f(t) is the force carried by the spring.

Since the force within the spring is also that on the dashpot (and equal to the imposed force), we can differentiate the previous equation with respect to time

$$\dot{x}(t) = \frac{f}{k_1} + \dot{x}_d$$
$$\therefore k_1 \dot{x} = \dot{f} + \frac{k_1}{\eta} f$$

Assume harmonic response

$f = Fe^{i\omega t}, x = Xe^{i\omega t}$ Substitute in the governing equation to get $i\omega k_1 X = \left(i\omega + \frac{k_1}{\eta}\right)F$

$$\frac{X}{F} = \frac{\left(i\omega + \frac{k_1}{\eta}\right)}{i\omega k_1} = \frac{i\omega + \frac{1}{\tau}}{i\omega k_1} = \frac{i\omega\tau + 1}{i\omega\eta}$$

or

$$f = k_{1}(x - y)$$

$$f = \eta \dot{y}$$

$$\therefore \dot{f} = k_{1}\dot{x} - \frac{k_{1}f}{\eta}$$

$$f = Fe^{i\omega t}, x = Xe^{i\omega t}$$

$$i\omega F + \frac{k_1}{\eta}F = i\omega k_1 X$$

$$i\omega F + \frac{1}{\tau}F = i\omega k_1 X$$

$$\therefore \frac{X}{F} = \frac{i\omega + \frac{1}{\tau}}{i\omega k_1} = \frac{i\omega\tau + 1}{i\omega\eta}$$
(ii)

Imaginary (loss) modulus

$$E'' = \frac{k_1 \omega \tau}{1 + \omega^2 \tau^2}$$



The $T_{\rm g}$ is at: $\omega \tau = 1$

Note that ω is in radians per second, hence $\omega = 2\pi$ at 1Hz

 $\therefore 2\pi \frac{\text{rad}}{\text{s}} \cdot \frac{6 \times 10^8}{T \cdot 10^7} \frac{\text{Pa s}}{\text{Pa}} = 1$ $\therefore T = 377 \text{ K} = 104 ^{\circ}\text{C}$ (c) "Resistance": Spring 1: $\frac{1}{k_1}$ Dashpot: $\frac{1}{i\omega\eta}$ Spring 2: $\frac{1}{k_2}$ First branch (spring 1 and dashpot in series): $\frac{1}{k_1} + \frac{1}{i\omega\eta} = \frac{k_1 + i\omega\eta}{k_1i\omega\eta}$ Total "resistance" $\frac{1}{1/k_2} + \frac{1}{\left(\frac{k_1 + i\omega\eta}{k_1i\omega\eta}\right)} = k_2 + \frac{k_1i\omega\eta}{k_1 + i\omega\eta} = \frac{k_2(k_1 + i\omega\eta) + k_1i\omega\eta}{k_1 + i\omega\eta}$

$$\therefore \frac{X}{F} = \frac{k_1 + i\omega\eta}{k_2(k_1 + i\omega\eta) + k_1i\omega\eta}$$

4 (a) A eutectic reaction in a binary alloy is the reversible transformation upon cooling of a liquid phase (L) into two solid phases, $\alpha + \beta$, at a well-defined, or eutectic, temperature T_E (note that eutectic means "easily melted");

Heating

$$L(C_E) \leftrightarrow \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$
Cooling

 C_E is the eutectic concentration of the liquid phase.

A peritectic reaction in a binary alloy is the reversible transformation upon cooling of a liquid phase (L) and a solid phase (α) into a second solid phase (β) at a well-defined, or peritectic, temperature T_p (note that eutectic means "partially melted");

Heating

$$L(C_{p}) + \alpha(C_{\alpha p}) \leftrightarrow \beta(C_{\beta p})$$
Cooling

- (i) Eutectic point; this is the point by the intersection of the two liquidus lines on the composition-temperature phase diagram at which the eutectic reaction occurs (i.e. a liquid phase transforms incongruently into two solid phases). Example; 60 wt % Sn, 40 wt % Pb, 183 °C in the Pb-Sn system.
- (ii) Eutectoid point; (Eutectoid means "eutectic-like"). This is the point formed by the intersection of two solidus lines on the composition-temperature phase diagram at which a single solid phase transforms incongruently and reversibly into two solid phases. Example; 75 wt % Zn, 25 wt % Cu, 560 °C in the Zn-Cu system and 0.8 wt % °C, 723 °C in the Fe-C system.
- (iii) Hypereutectic region; the high temperature region to the right of the eutectic point. The composition of the liquid tends towards that of the eutectic as the β phase precipitates out on cooling. Example; > 60 wt % Sn, < 40 wt % Pb, up to 230 °C.
- (iv) Hypoeutectic region; the high temperature region to the left of the eutectic point. The composition of the liquid tends towards that of the eutectic as the α phase precipitates out on cooling. Example; < 60 wt % Sn, > 40 wt % Pb, up to 320 °C.



(b) The lever rule is used to calculate the mass (or weight) fraction of one particular phase in a two phase alloy of known net composition at a given temperature (i.e. constitution point) and is applied as follows;

A tie line is constructed across the two-phase region at the temperature of the alloy;
 The overall alloy composition is located on the tie line;

3. The fraction of the phase at one end of the tie line is calculated by taking the length of the tie line from the overall alloy composition to the phase at the other end of the tie line and dividing by the total length of the tie line. The distance from where the lines meet to the phase boundary (R and S) can be regarded as a lever arm, and the weight of the phase at the boundary balances the weight of the phase at the other boundary;

4. This method is only applicable for a phase diagram with weight or mass fraction on the abscissa scale.



The lever rule is based on two conservation of mass expressions:

1. The sum of mass fractions must be unity;

 $W_a + W_b = 1$

2. The total mass of either component present in both components must be equal to the mass of that component in the total alloy;

 $W_a C_a + W_b C_b = C_0$

Hence;

$$W_a = \frac{C_b - C_0}{C_b - C_a}$$
$$W_b = \frac{C_0 - C_a}{C_b - C_a}$$

[4]

(c) From Figure 6.2 in the Materials Data Book, the phases present at a constitution point of 40 wt % Sn, 60 wt % Pb and 150 °C are the α phase (Sn) and the β phase (Pb). Plot this composition/temperature point on the phase diagram. The composition of each phase determined by constructing a tie line across the $\alpha + \beta$ phase field at 150

°C. The composition of the α phase corresponds to the tie line intersection with the $\alpha/(\alpha+\beta)$ phase boundary - about 11 wt % Sn and 89 wt % Pb (denoted as C_{α}).

Similarly the liquid phase has composition approximately 99 wt % Sn and 1 wt % Pb.

The mass fractions W_{α} and W_{β} at a composition of 40 wt % Sn, 60 wt % Pb and 150 °C can be determined using the lever rule as follows;

$$W_a = \frac{C_b - C_0}{C_b - C_a} = \frac{99 - 40}{99 - 11} = 0.67 = 67 \text{ wt\%}$$

$$C_0 = C_a = 40 - 11$$

$$W_b = \frac{c_0 - c_a}{c_b - c_a} = \frac{40 - 11}{99 - 11} = 0.33 = 33 \text{ wt\%}$$

Conversion of mass fraction into volume fraction requires knowledge of the density of each phase, which is assumed to be constant for each phase (note that volume and mass fractions only differ significantly when the densities of the two phases vary by a large amount).

Knowledge of phase volume fractions is useful because they may be determined directly by examining the sample microstructure using EM or (less commonly) optical microscopy. In addition, the mechanical properties of an alloy may be predicted from phase volume fractions.

(d) 60 wt % Sn, 40 wt % Pb corresponds to the eutectic composition and, prior to 2006, was used for solder. It worked well for this application because it has a low eutectic temperature, which minimized the potential for heat damage to electronic circuits and components during soldering. On July 1, 2006, however, the European Union Waste Electrical and Electronic Equipment Directive (WEEE) and Restriction of Hazardous Substances Directive (RoHS) came into effect prohibiting the intentional addition of lead to most consumer electronics produced in the EU.

[5]

5 (a) Polymers are used widely in the manufacture of products for the following reasons:

1. Relatively low cost per unit volume compared to metals and metal alloys (mild steel: ~ $\pounds 5000 / \text{m}^3$, aluminium alloys: ~ $\pounds 6000 / \text{m}^3$, polyethylene: ~ $\pounds 1000 / \text{m}^3$)

2. Low density: $\rho \sim 1000 \text{ kg/m}^3$

- 3. Reasonable mechanical properties, on a unit mass basis
- 4. Low melting temperature: easy (therefore cheap) to process
- 5. Environmental and corrosion resistance

(b) Thermoplastics, Thermosets and Elastomers contain different amounts of crosslinking between the polymer molecules, which accounts for their different mechanical properties.

Thermoplastics have only weak van der Waals bonds between polymer chains. These bonds begin to break down at the glass transition temperature T_G (the covalent bonds forming the 'backbone' of the polymer chains remain intact up to higher temperatures).

Thermosets consist of polymer chains that are extensively cross-linked via strong covalent bonds. The molecular structure is fixed at the point of polymerisation: they can't be softened or reshaped. The properties are much less sensitive to temperature.

Elastomers have chains that are less extensively cross-linked than thermosets. The stiffness of elastomers is less than thermosets, but the covalent cross-links will restore the original shape when the elastomer is stretched.

Thermoplastics are particularly useful for practical manufacturing processes because they can be melted and solidified repeatedly (which is not the case for thermosets). This makes them easy to shape using moulding processes.

(c) Thermoplastics contain both amorphous and crystalline regions, which are engineered by processing.



The key properties of a polymer affected by the degree of crystallinity are *density* and *Young's modulus*.

Density: The closer molecular packing of crystalline polymers makes them more dense 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 used to interpolate the % crystallinity.

Young's Modulus (E): This increases with crystallinity. For a highly crystalline polymer, E remains high until the temperature is sufficient to completely break down

[4]

[4]

the van der Waals bonds:



The crystallisation of polymers shares many parallels with phase transformations in metals: crystallisation follows c-curves, with the rate dependent on temperature and time.



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 crystallization, which increases with undercooling (T_M -T). The degree of crystallinity, therefore, is determined by the nucleation of crystalline regions (determined primarily by undercooling) and their subsequent growth (determined primarily by time). This yields the characteristic c-curve structure.

(d) **Stretch blow moulding** is used to manufacture a drinks bottle polyethylene terephthalate (PET). The key steps in this process are;

(1) The injection moulded polymer preform is heated;

- (2)-(3) The hot preform is transferred to a mould;
- (4) A stretch rod elongates the preform;
- (5) Compressed air inflates the preform to fill the mould;
- (6)-(7) The mould is separated and the component ejected.

The elongation and inflation stages provide some molecular alignment in the longitudinal and hoop-wise directions. This provides extra strength compared to the non-crystalline regions:



Although some crystallinity is needed for mechanical properties, it reduces the optical transparency of the bottle, which is undesirable. The degree of crystallinity is limited to about 20%, therefore, by maintaining the moulding temperature at just above T_G (i.e. below the nose of the c-curves).

(e) Perspex (PMMA) is used for aircraft windows because it is tough and transparent. High-density polyethylene (HDPE) is used for water pipes because it is cheap and easy to extrude. [4]

[3]

A new phase forms (both heterogeneously or homogeneously) initially by nucleation and then by growth. There exists an energy barrier, ΔG_{tot} , to nucleation.

Homogeneous nucleation involves the spontaneous formation of nuclei of a second phase within the body of an initial phase. The extent to which a phase transforms homogeneously to a second phase depends on the thermodynamics and kinetics of the phase transformation (i.e. nucleation and growth). In general these are determined by the difference in the Gibbs free energy per unit volume, ΔG , between the phases, which is known as the driving force of the transformation. This subsequently determines the undercooling, $\Delta T = T_E - T$. The net total change in free energy ΔG_{tot} is given by ΔG (=4/3 $\pi r^3 \Delta G$), which is a volume term and is negative, and the surface energy associated with creating new surface between phases α and β (=4 $\pi r^2 \gamma_{\alpha\beta}$), which is an area term and is positive. $\Delta G_{tot}(r)$ therefore goes through a maximum, with this maximum value $\Delta G_{tot}(r)^*$ representing the thermodynamic barrier to nucleation of the solid. The value of r at $\Delta G_{tot}(r)^*$ (i.e. r^{*}) corresponds to the critical size for phase growth. The nuclei will re-dissolve in the liquid if r < r^{*}.



Heterogeneous nucleation is more common than homogeneous nucleation. Heterogeneous nucleation is the formation of a solid phase on a surface, which is determined by different energy balance criteria than homogeneous nucleation. An approximately spherical cap forms in heterogeneous nucleation, which effectively achieves the critical radius for growth with fewer atoms and hence decreases the degree of undercooling required. As a result, the energy barrier ΔG_{tot} is lowered when nucleation occurs on a pre-existing substrate and the effective γ is reduced.

Examples of heterogeneous nucleation are;

1. The addition of Ti to steel to promote heterogeneous nucleation, and to produce a fine grain size with minimal segregation;

2. The formation of new phases at austenite grain boundaries during the heat treatment if steels;

3. The preferential nucleation of ice at the edges of a pond, rather than at its centre.

The overall grain nucleation rate depends both on the size of the thermodynamic barrier to be overcome and on the rate of diffusion of the molecules. At high temperature, therefore, the rate of grain nucleation is low since there is insufficient undercooling. At low temperatures the rate of grain nucleation is limited by a low diffusion rate {proportional to exp(-Q/RT)}. Both effects are strongly temperature-dependent and act in opposition. As a result the rate of grain nucleation exhibits a maximum at a given temperature.

[Half marks available for brief outline of hetero and homogeneous nucleation. Graphs with limited supporting discussion (less detailed than that given) required for full marks].

(b) The net total change in free energy ΔG_{tot} is given by [see part (a)];

$$\Delta G_{tot}(r) = 4/3\pi r^3 \Delta G + 4\pi r^2 \gamma$$

This has a maximum value $\Delta G_{tot}(r)^*$ at $r = r^*$, corresponding to the thermodynamic barrier that has to be overcome for stable growth of the nucleus. Therefore, differentiate $\Delta G_{tot}(r)$ to determine its maximum value;

$$\frac{d}{dr} \left(\Delta G_{tot} \right) = 4\pi r^2 \Delta G + 8\pi r \gamma = 0$$

Therefore, $r^* = -\frac{2\gamma}{\Delta G}$

But
$$\Delta G = \frac{|\Delta H|\Delta T}{T_E}$$

Hence

$$r^* = \frac{2\gamma}{|\Delta H_V|(7)|}$$

(c)
$$\Delta T = \frac{2\gamma T_E}{|\Delta H_V| r^*_{hom}} = \frac{2 \times 0.025 \times 273}{0.92 \times 10^3 \times 335 \times 10^3 \times 1 \times 10^{-9}} \approx 44 \text{ K}$$

$$V_{hom}^* = \frac{4}{3}\pi (r_{hom}^*)^3$$
$$V_{het}^* = \frac{2}{3}\pi (r_{het}^*)^3 \left(1 - \frac{3}{2}\cos\theta + \frac{1}{2}\cos^3\theta\right)$$

$$V_{hom}^* = V_{het}^*$$

$$\frac{4}{3}\pi (r_{hom}^*)^3 = \frac{2}{3}\pi (r_{het}^*)^3 \left(1 - \frac{3}{2}\cos\theta + \frac{1}{2}\cos^3\theta\right)$$

Hence

$$r_{het}^* = \frac{r_{hom}^*}{(\frac{1}{2}\{1 - \frac{3}{2}\cos\theta + \frac{1}{2}\cos^3\theta\})^{1/3}}$$

Therefore $r_{het}^* = 18.1 r_{hom}^*$ for $\theta = 10^\circ$

[4]

$$\frac{2\gamma T_E}{\Delta H_V (T_E - T_{het})} = 18.1 \times \frac{2\gamma T_E}{\Delta H_V (T_E - T_{hom})}$$

So $\Delta T_{het} = \frac{\Delta T_{hom}}{18.1} \approx \frac{44}{18.1} \approx 2.4 \text{ K}$

Hence, ice always nucleates heterogeneously on the walls of the beaker, and not homogeneously in the body of the water. This explains why ponds freeze first at surface/bank.

(d) 1. Casting (liquid-solid phase transformation); fine, high melting point, chemically compatible powders (inoculants) are added to melt to provide heterogeneous nucleation sites, leading to rapid nucleation. This produces a fine grain size, which is good for strength and toughness, and minimises segregation.

2. Solid-solid phase transformations; Ferrite phase nucleates on austenite grain boundaries to produce a fine grain size on cooling.

3. Seeded growth of silicon in single crystal fabrication.

4. Nucleation of growth at tip of turbine blade using controlled thermal gradient.

[2]

[6]