ENGINEERING TRIPOS   PART IB

Tuesday 5 June 2007   9.00 to 11.00

Paper 3

MATERIALS SOLUTIONS

1 (i) A medium carbon steel, Fe-0.4 wt.% C, cooled from 850 °C to room temperature.

(a) The steel begins as austenite at 850 °C.
Ferrite grains begin to nucleate on the austenite grain boundaries at 800 °C (very low C content) and grow as the temperature falls to 723°C, increasing the carbon content of the austenite.
A eutectoid transformation takes place at 723 °C. The remaining austenite (at 0.8 wt. % C) transforms to pearlite (i.e. a mixture of ferrite and iron carbide (cementite), 6.7 wt. % C). There is no significant change with further cooling.
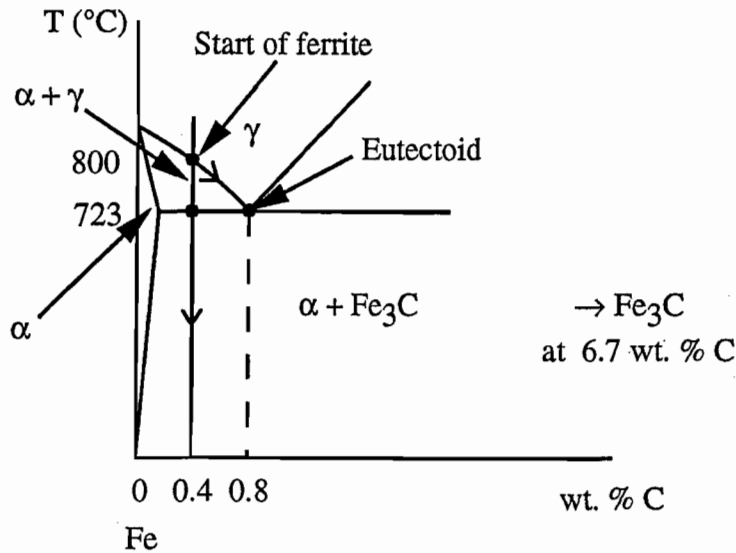
[4]

(b)
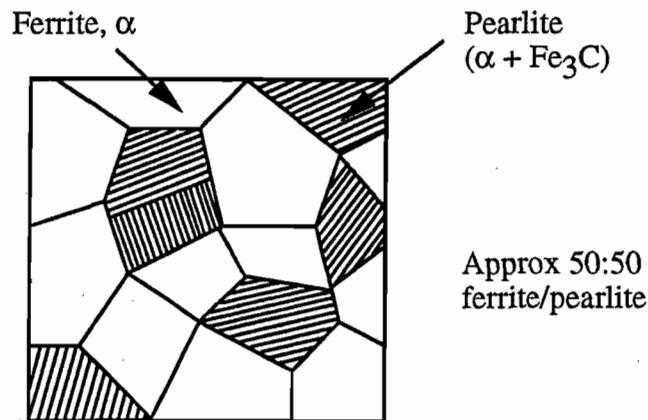
Ferrite nucleates on austenite grain boundaries: grain boundary size is determined by the size of prior austenite and the number of nuclei per grain.
Pearlite structure is lamellar (i.e. fine-scale plates of alternating ferrite and carbide). The growth of pearlite requires carbon diffusion to separate the material into high and low carbon-containing phases. The growth of plates enables the interface between austenite and pearlite to traverse austenite grains without long-range diffusion of carbon. [4]

(c) Applications of medium carbon steel, Fe-0.4 wt.% C, cooled from 850 °C to room temperature include tools, fasteners (nuts/bolts/screws etc.) bearings and gears. Improved properties are achieved by quenching and tempering. [2]

(ii) An aluminium casting alloy, Al-12 wt.% Si, cooled from 600 °C to room temperature.

(a) The material begins as a liquid.
A eutectic transformation occurs at 557 °C. Here the liquid transforms isothermally to a two-phase solid of Al-2wt. % Si solid solution containing a dispersion of Si plates.
Cooling to room temperature has little effect on the overall microstructure, but more Si will diffuse out of the matrix to enlarge the Si plates.
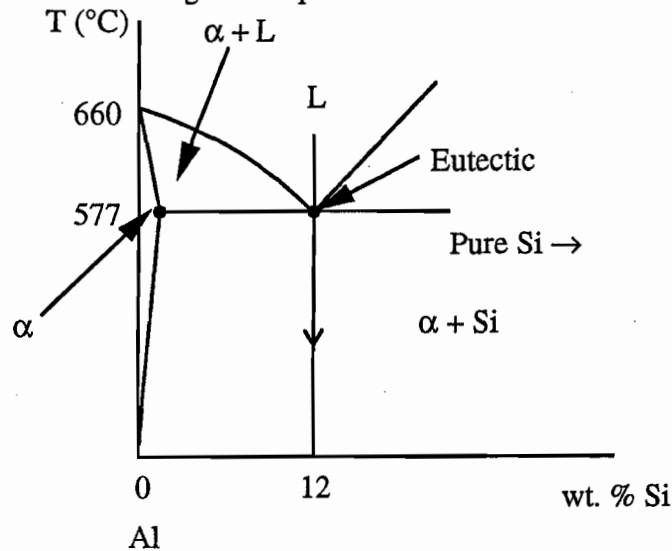
[4]

(b) On solidification. the solution of Al and Si separates into almost pure Al and Si. A plate-like microstructure of Si in an Al matrix minimises diffusion distances, enabling the change to take place.


[4]

2
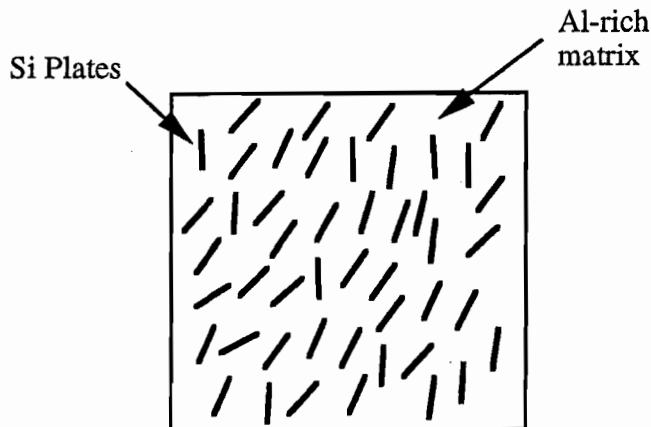
(c) Applications of an aluminium casting alloy, Al-12 wt.% Si, cooled from 600 °C to room temperature include automotive parts (e.g. cylinder blocks/heads). The casting of eutectic alloys produces essentially the microstructure described in (b). Al-Si alloys are not subsequently heat-treated. [2]

2(a) *The following gives more algebraic detail than is required for full marks.* A new phase forms 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 in 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 $r < r^*$.
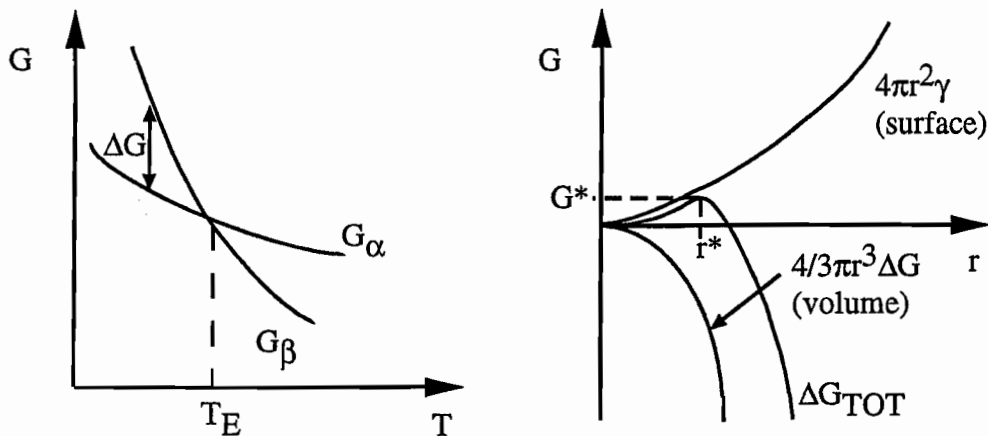

Heterogeneous nucleation is more common than homogeneous nucleation. Heterogeneous nucleation is the formation of a solid phase on a surface which is determined by different energy balance criteria than homogeneous nucleation. An approximately spherical cap forms in heterogeneous nucleation, which effectively 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.

3

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. [5]

(b)(i) Suppose a substrate exists;
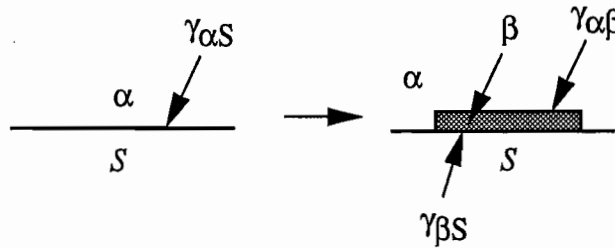
Upon nucleation, the interface energy $\gamma_{\alpha S}$ is replaced by $(\gamma_{\alpha b} + \gamma_{\beta S})$. Hence, if the disc is thin (so that the areas of the untransformed and transformed phases are equal), the change in surface energy is given by;

$$\gamma_{EFF} = \gamma_{\alpha\beta} + \gamma_{\beta S} - \gamma_{\alpha S}$$

(compared to $\gamma_{\alpha\beta}$ for homogeneous nucleation).

γ_{EFF} may be less than $\gamma_{\alpha\beta}$, resulting in easier heterogeneous β phase nucleation. [2]

(ii) For the thin disc shown in Fig. 1;

$$\Delta G_{tot} = \pi r^2 \gamma_{\alpha\beta} + 2\pi r h \gamma_{\alpha\beta} + \pi r^2 (\gamma_{\beta S} - \gamma_{\alpha S}) + \pi r^2 h \Delta G_{\alpha\beta}$$ [3]

(iii) Minimise free energy;

$$\frac{d\Delta G_{tot}}{dr} = 2\pi r \gamma_{\alpha\beta} + 2\pi h \gamma_{\alpha\beta} + 2\pi r (\gamma_{\beta S} - \gamma_{\alpha S}) + 2\pi r h \Delta G_{\alpha\beta}$$

Set $\dfrac{d\Delta G_{tot}}{dr} = 0$, $r = r^*$

$$r^* = \frac{-h\,\gamma_{\alpha\beta}}{\gamma_{\alpha\beta} + \gamma_{\beta S} - \gamma_{\alpha S} + h\Delta G_{\alpha\beta}}$$ [5]

(c) The overall grain nucleation rate depends both on the size of the thermodynamic barrier to be overcome (i.e. ΔG_{tot}) and on the rate of diffusion of the molecules {proportional to $\exp(-Q/RT)$}. The key point is that these effects work in opposition. If there are n atoms, then the number of critical nuclei at low temperature (where there is sufficient undercooling) is given by n* where;

$$n^* = n \exp\left[\frac{-\Delta G_{tot}}{kT}\right] \exp\left[\frac{-Q}{kT}\right]$$

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 (*graphs not required for full marks*);
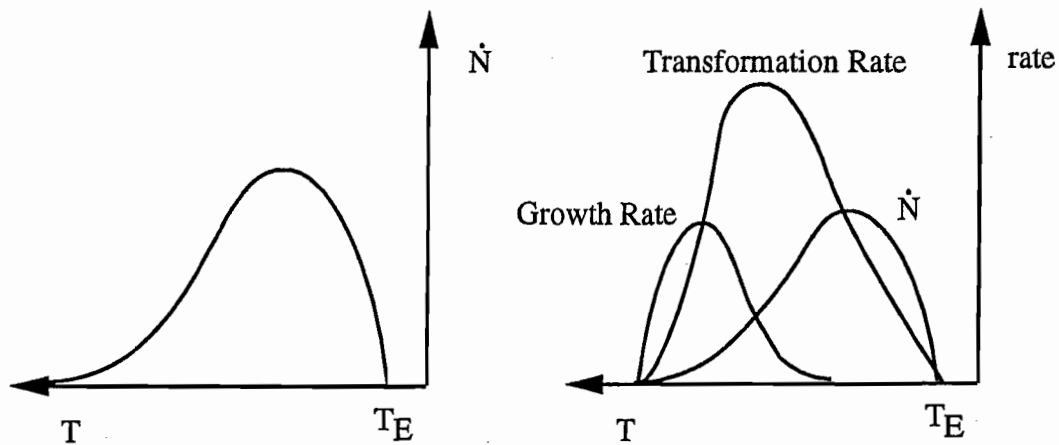
The growth rate of stable nuclei ($r > r^*$) depends on the driving force (proportional to ΔT) and the molecule diffusion rate. The overall transformation rate, therefore, is determined by the growth rate and the nucleation rate and is maximum for temperatures intermediate between those corresponding to maximum growth rate and maximum nucleation rate.

[5]

3(a) The strength of glass is controlled by surface defects (microscopic flaws or cracks). There are some important ways of in which the strength of glass can be increased; by inhibiting the growth of flaws, or by preventing the introduction of new flaws. Freshly-formed glass can be extremely strong (with only surface flaws present of atomic dimensions), but even exposure to the atmosphere, which contains dust, etc., causes a rapid deterioration in strength. The surface can be protected, as with optical glass fibres, which are coated with a polymer immediately after drawing from the melt.

[5]

(b) Consider an unconstrained bar of original length L_0, heated through a temperature ΔT. The new length of the bar is; $L_0 + \Delta L = L_0 (1 + \alpha \Delta T)$.

But the bar is constrained to have length L_0, so it must be under compressive elastic strain;

$$\frac{\Delta L}{L_0} = \frac{\alpha L_0 \Delta T}{L_0} = \alpha \Delta T$$

Hence the stress in the bar is compressive and is given by $\sigma = E \alpha \Delta T$.

If a material is exposed to a temperature gradient (e.g. due to localised heating or cooling sources), then some regions will clearly be constrained by the thermal contraction of others, leading to thermally-induced stresses. [5]

(c) In thermal toughening, glass sheet (at a temperature at which it can flow significantly) is cooled rapidly by cold air jets on the surfaces of the sheet. This locally increases the viscosity/flow stress to effectively prevent flow in the surface layers and, as the core of the sheet then cools more slowly, a compressive stress is induced in the surfaces, balanced by a tensile stress in the core.

The compressive residual stress in the surface suppresses crack growth until a much higher external stress is reached. However, the combination of surface compressive stress and the balancing internal tensile stress gives a large amount of stored elastic strain energy. When toughened glass does fracture it does so explosively, producing a large number of small fragments. Note that the glass is not really toughened at all; the fracture toughness stays the same. However, the process does increase the fracture stress.

The stress in the surface could be estimated using the method in (b) because once again a stress is induced in a region that is constrained against thermal contraction. The applicable value of ΔT will be influenced by the cooling rates, the thermal conductivity of the glass and the variation in the flow stress with temperature.

A thermoplastic polymer can not be thermally toughened because it would creep significantly after cooling, reducing the residual stress, and also because the flaws responsible for fracture in polymers are internal, whereas those in glass occur at the surface. [6]

(d) For glass without thermal toughening, the strength may be estimated from;

$$K_c = \sigma_f (\pi a)^{1/2}$$

From the data given and assuming $a = 100 \; \mu m$, $\sigma_f = 33.9$ MPa

Thermal toughening adds compressive stress - $E \alpha \Delta T = 189$ MPa, so that the new fracture stress is $34 + 189 = 223$ MPa. [4]

4.(a) Examples of material properties that are important in determining the processibility of engineering materials;
Yield strength; Determines ease of metal forming processes (i.e. forming load) such as forging, extrusion, rolling and sheet forming.
*Ductility*; Limits tensile strain achievable in metal forming, which is why most processes are compressive in nature. The exceptions are sheet-forming and deep drawing.
Viscosity; In metals, eutectic compositions are optimum for casting (metal flows easily into fine features in the mould). In polymers, higher viscosity means that pressure must be applied to fill complex shapes (e.g. in injection moulding).
Thermal conductivity (thermal diffusivity); Determines the cooling rate through the thickness of components in quenching processes such as the quenching of heat-treatable steels prior to tempering, or the quenching of heat-treatable aluminium alloys prior to age hardening. [6]

(b) Grain size is controlled in solid state by recrystallisation at temperature following hot or cold deformation. Deformation stores dislocations (work hardening). Annealing at an elevated temperature triggers recovery - dislocations rearrange into sub-grains. A small number of sub-grains then act as nuclei for new grains. In this case the boundaries migrate across the deformed grains, replacing them with softer grains with low dislocation density.
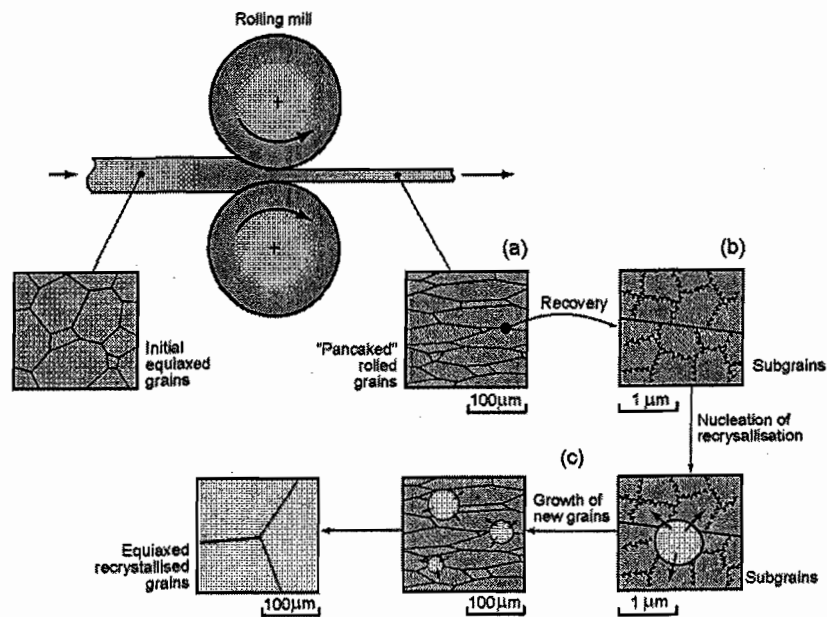

The recrystallised grain size is determined by the deformation strain, the temperature-dependent strain rate and the annealing temperature.   [4]

(c) Inter-phase coherency describes the degree of crystal matching across the boundary between two different solid phases. If the crystal structure is the same and the atomic spacing is similar, the close-packed planes can run continuously from phase to phase, with some mis-fit strain between the phases. This is a coherent boundary, for which the boundary energy is low. If there is no crystallographic lattice match, then the boundary is incoherent. An incoherent boundary is essentially the same as a grain boundary, but with different phases on either side. In this case the boundary energy is higher, but the strain energy is released.
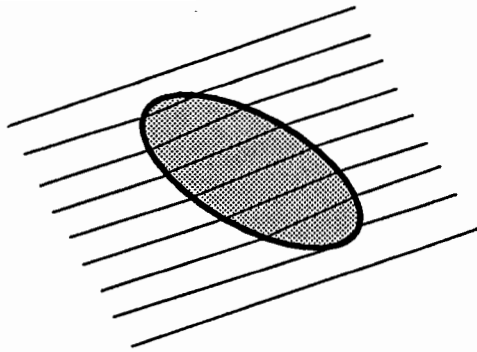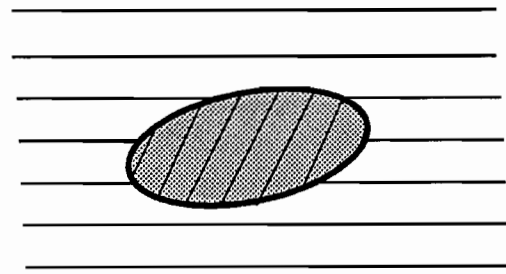
Phase coherency   Phase incoherency

In age hardening of aluminium alloys, the early stages of precipitation produce very large numbers of small precipitates, favouring the formation of coherent boundaries due to the increasing strain energy around the precipitates. This leads to a switch in dislocation interaction with the precipitates from shearing (when they are small) to by-passing (when they are large). This is a key factor in the yield strength (or hardness) rising initially during ageing for precipitate-hardened alloys, but going through a peak at a critical precipitate spacing (in contrast to alloys hardened by the formation of solid solution).
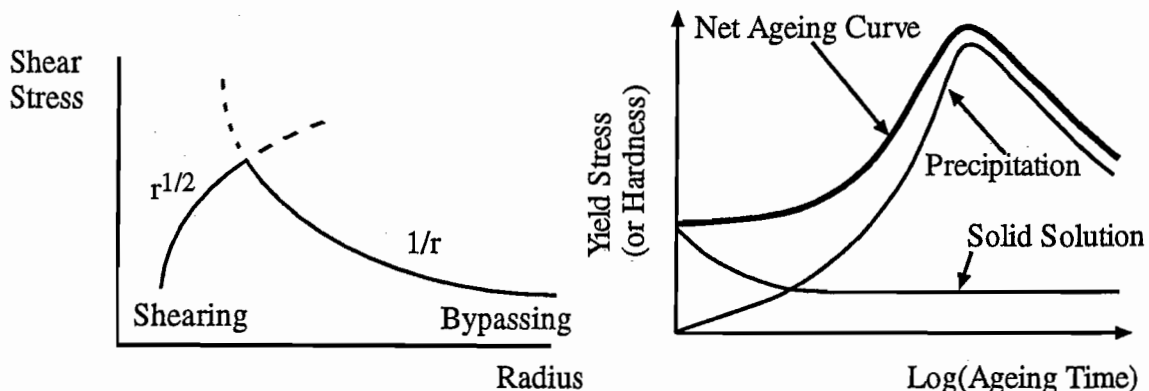
[6]

(d) Similarities;
In age hardening, aluminium alloys are first solutionised and then quenched rapidly to form a supersaturated solid solution. The alloy is then re-heated in the two-phase region to form a controlled fine-scale dispersion of precipitates.
Quenching and tempering of steels is essentially the same; solutionise as austenite to dissolve the carbon, quench to avoid ineffective precipitation and retain a super-saturated solid solution, then precipitation of fine-scale iron-carbide.

Differences;
Aluminium alloys remain FCC during the quench, giving a soft condition after quenching; in steels FCC austenite transforms to martensite (distorted BCC with C in supersaturated solution), which is very hard and brittle.
Aluminium alloys go through a complex sequence of precipitation of metastable phases, progressing towards equilibrium, and with strength rising to a peak with an optimum precipitate type and size; in steels, equilibrium iron carbide forms directly, softening continuously with time from the initial martensite state.

[4]

8

5(a) Amorphous polymers contain randomly oriented molecular chains, whereas semi-crystalline polymers contain regions in which the chains are packed together into regular (crystalline) regions, separated by amorphous regions.

Sketch of chain alignment

A polymer molecule is usually very stiff when it is strained parallel to the molecular backbone. If the molecules are oriented randomly, however, as in an isotropic amorphous polymer, the behaviour is dominated by the weak inter-chain bonds. A much greater stiffness can be achieved by aligning the molecules parallel to the applied stress. Maximum stiffness would result from a high proportion of crystallinity and alignment of the chains parallel to the direction of applied stress. [5]

(b) Processes for the manufacture of containers from a thermoplastic polymer:
(i) *Rotational moulding*. In rotational moulding, thermoplastic granules are placed in a closed metal mould which is then rotated simultaneously about three axes and heated. The granules bond by inter-diffusion but do not fully melt. No molecular alignment results, and the product is rather weak with poor control of the wall thickness.

(ii) *Blow moulding*: In blow moulding (also used for glass), the polymer is placed into the top of a mould and then inflated with air pressure to conform with the internal shape of the mould. Shape control is good and the polymer is fully molten, but there is no molecular alignment, which limits strength.

(iii) *Stretch blow moulding*: In stretch blow moulding a pre-form is made by injection moulding, which is then heated and placed in a mould. It is then inflated with air and also stretched longitudinally with a rod, to give good control of extension in the hoop and longitudinal directions. By carrying this out at the right temperature, significant molecular alignment can be achieved and hence strengthening and stiffening of the wall.

This is the main advantage of stretch blow moulding over blow moulding for the manufacture of internally pressurised bottles. [6]

(c) Hoop stress in a thin-walled cylinder $= \sigma_h = \dfrac{Pr}{t} = \dfrac{0.4 \times 30}{0.3} = 40 \, \text{MPa}$

9

Longitudinal stress $= \sigma_1 = \dfrac{Pr}{2t} = \dfrac{0.4 \times 30}{2 \times 0.3} = 20$ MPa

So minimum yield stress required is $2.5 \times 40 = 100$ MPa in the hoop direction and 50 MPa in the longitudinal direction. [4]

(d) From (b), need to increase the yield stress of PET by at least a factor of $100/50 = 2$ in the hoop direction to achieve the desired strength. This is achieved in stretch blow moulding by a combination of molecular alignment and partial crystallisation.
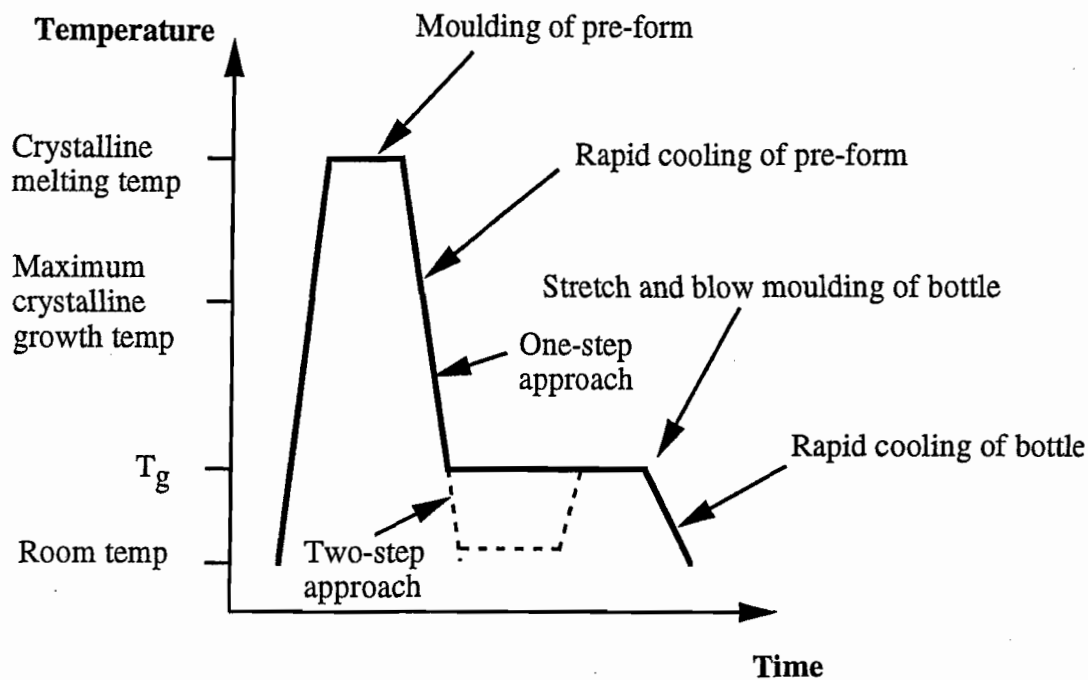
The injection moulding of the pre-form is carried-out with fully molten polymer (T > 250 °C). Stretch blow moulding needs to be carried out above T_g so that molecules can align, but not at too high a temperature, which will produce a large amount of crystallisation and the bottle will no longer be transparent (a temperature of around 85 °C - 100 °C is reasonable). [5]

6 (a) The Fourier series representation from page 17 of the Mathematics Data Book is

$$f(t) = \frac{1}{2} a_0 + \sum_{n}^{\infty} \left(a_n \cos \frac{2\pi n t}{T} + b_n \sin \frac{2\pi n t}{T} \right) \quad \text{for } 0 \le t \ge T$$

here, $t \to x$ and $T \to 2h$

Choice of origin for x in Fig. 2 implies that the cosine terms vanish, so $a_n \equiv 0$ for $n > 0$

10

Also; $\frac{1}{2} a_0$ = mean signal = 0.1, so a_0 = 0.2. <u>Hence first term = 0.1</u>.

Obtain coefficients b_n by integrating. For b_1; $b_1 = \frac{1}{h} \int_0^{2h} f(x) \sin\left(\frac{\pi x}{h}\right) dx$

where $f(x)$ is a square wave of amplitude 0.2 (i.e. a_0).

$$b_1 = \frac{1}{h} \int_0^{2h} 0.2 \sin\left(\frac{\pi x}{h}\right) dx = \frac{-0.2}{\pi} \left[\cos\frac{\pi x}{h}\right]_{x=0}^{x=2h}$$

Hence; $\qquad b_1 = \frac{0.4}{\pi}$

$\qquad\qquad b_2 = 0$

$$b_3 = \frac{1}{h} \int_0^{2h} 0.2 \sin\left(\frac{3\pi x}{h}\right) dx = \frac{b_1}{3}$$

$b_3 = \frac{0.4}{3\pi}$

In general, therefore, $\underline{b_n = \frac{1}{n}\frac{0.4}{\pi}}$ for n = 1, 3, 5, 7, ...etc.

Therefore, $C(x, t=0) = 0.1 + \sum_{n=1,3,5,..}^{\infty} \frac{0.4}{n\pi} \sin\left(\frac{\pi n x}{h}\right)$, as required $\qquad$ [6]

(b) Use Fick's second law given in the Materials Data Book; $\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial t^2}$

For the first (constant) term in the series try C(x) = 0.1 at t = 0.

i.e. C(x,t) = A, where $\underline{A = 0.1}$

For the second term (i.e. n=1) try $\qquad C(x) = \frac{0.4}{\pi} \sin\left(\frac{\pi x}{h}\right)$ at t=0

$$C(x,t) = g_1(t)\frac{0.4}{\pi} \sin\left(\frac{\pi x}{h}\right) \text{ for } t \geq 0$$

Differentiate w.r.t., x and t and substitute into diffusion equation;

$$\frac{dg_1(t)}{dt} = -D\left(\frac{\pi}{h}\right)^2 g_1(t) \qquad\qquad \Rightarrow \qquad \frac{1}{D}\left(\frac{h}{\pi}\right)^2 \frac{dg_1(t)}{dt} + g_1(t) = 0$$

11

Put $\tau_1 = \frac{1}{D}\left(\frac{h}{\pi}\right)^2$ (1)   hence $g_1(t) = \exp\left(-\frac{t}{\tau_1}\right)$

Check general trend by determining third term (not required for full marks);

For the third term (i.e. n=3) try $C(x) = \frac{0.4}{3\pi} \sin\left(\frac{3\pi x}{h}\right)$ at t=0

$$C(x,t) = g_3(t)\frac{0.4}{3\pi} \sin\left(\frac{3\pi x}{h}\right) \quad \text{for } t \geq 0$$

Differentiate w.r.t, x and t and substitute into diffusion equation;

$$\frac{dg_3(t)}{dt} = -D\left(\frac{3\pi}{h}\right)^2 g_3(t) \quad \Rightarrow \quad \frac{1}{D}\left(\frac{h}{3\pi}\right)^2 \frac{dg_3(t)}{dt} + g_3(t) = 0$$

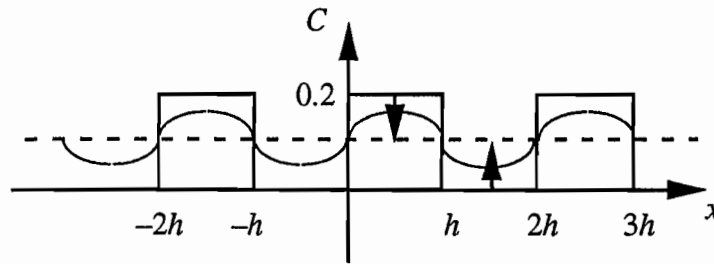Put $\tau_3 = \frac{1}{D}\left(\frac{h}{3\pi}\right)^2$ hence $g_3(t) = \exp\left(-\frac{t}{\tau_3}\right)$

So, first three terms are given by;

$$C(x,t) = 0.1 + \exp\left[-\frac{t}{\tau_1}\right]\frac{0.4}{\pi}\sin\left(\frac{\pi x}{h}\right) + \exp\left[-\frac{t}{\tau_3}\right]\frac{0.4}{\pi}\sin\left(\frac{\pi x}{h}\right)$$

Only the first two terms are required.

From (1), $\tau_1 = \frac{1}{D}\left(\frac{h}{\pi}\right)^2$. Physical significance of τ_1; the time for diffusion on a length scale of $h \sim h^2/D$.   [8]

(c)

At $x = h/2$ we have; $C(x=h/2,t) = 0.1 + \frac{0.4}{\pi}\exp\left[-\frac{t}{\tau_1}\right]$

From (b), $\tau_1 = \frac{h^2}{D\pi^2}$ and solution to the diffusion equation; $D = D_0 \exp\left(\frac{-Q}{RT}\right)$

Put in values;   h = 1 μm
$D_0 = 2.0 \times 10^{-4}\ m^2 s^{-1}$
$Q = 280\ kJ\ mol^{-1}$
$R = 8.314\ J\ mol^{-1}$

$$D = 2 \times 10^{-4} \exp\left(\frac{-280 \times 10^3}{8.314 \times 1273}\right) = 6.48 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$$

Hence $\tau_1 = 156$ s

In one hour, $t = 3600$ s so;

$$C = 0.1 + \frac{0.4}{\pi} \exp\left(\frac{-3600}{156}\right) = 0.1 + 1.2 \times 10^{-11}$$

Exponential term is negligible. Therefore, homogenisation is complete within 1 hour.

Alternatively, as a rule of thumb, diffusion distance with time, $x(t) = \sqrt{Dt}$. Hence can estimate diffusion distance in 1 hour from $\sqrt{6.48 \times 10^{-16} \times 3600} = 1.53$ μm (i.e. homogenisation is complete). Either method OK for full marks.   [6]