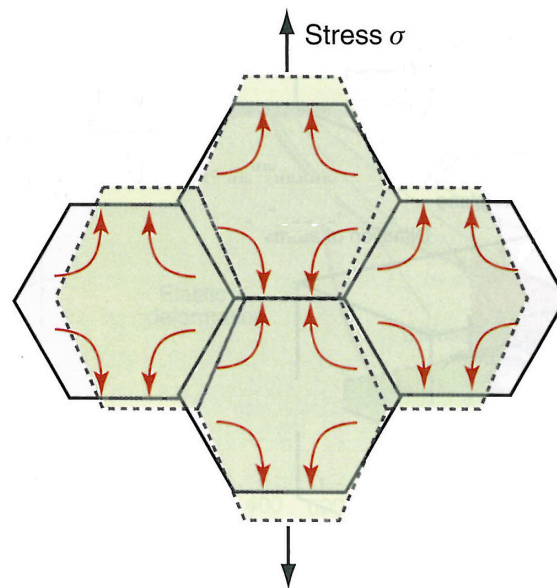


**CRIBS****SECTION A****Question 1****(a)**

Diffusion creep (or also known as diffusional flow) occurs when the component is subjected to high temperatures at low loads (too low for dislocation motion to be activated). It occurs by the redistribution of material by diffusion within the bulk and along the grain boundaries, enabling deformation in the direction of applied stress. A polycrystal can respond to the applied stress by grain elongation – see schematic below. Atoms diffuse from one set of grain faces to the other, and dislocations are not involved. At high  $T / T_m$ , this diffusion takes place through the crystal itself (*bulk diffusion*). At lower  $T / T_m$ , when bulk diffusion is slow, *grain boundary diffusion* takes over (the activation energy for grain boundary diffusion is considerably less than that for bulk diffusion).



To avoid diffusion creep, it is important to choose a material with a high melting point (creep scales with  $T / T_m$ ) and a large grain size, so that diffusion distances are large. Diffusion creep is suppressed in single crystals (no grain boundaries). Grain boundaries act as sites for void formation leading to tertiary failure.

An engineering application in which this type of creep is suppressed is single-crystal turbine blades in jet engines. Nickel-based super alloys are used.

**(b)** If Coble and Herring- Nabarro creep have the same creep rate, it follows that

$$\dot{\epsilon} = \frac{D_{gb}\sigma b^4}{kTd^3} = \frac{D\sigma b^3}{kTd^2}$$

$$\therefore \frac{D_{gb}}{D} = \frac{d}{b} = \frac{100 \times 10^{-6}}{2.5 \times 10^{-10}} = 4 \times 10^5$$

$$D = D_o \exp\left(-\frac{Q}{RT}\right), \text{ where } D_o = 2 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}, Q = 280 \text{ kJ mol}^{-1} \text{ and}$$

$$R = 8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$D_{gb} = D_{ogb} \exp\left(-\frac{Q_{gb}}{RT}\right), \text{ where } D_{ogb} = 5.7 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \text{ and } Q_{gb} = 140 \text{ kJ mol}^{-1}$$

Hence

$$\frac{D_{gb}}{D} = \frac{D_{ogb} \exp\left(-\frac{Q_{gb}}{RT}\right)}{D_o \exp\left(-\frac{Q}{RT}\right)} = 4 \times 10^5$$

$$\ln D_{ogb} - \frac{Q_{gb}}{RT} = \ln(4 \times 10^5) + \ln D_o - \frac{Q}{RT}$$

$$\frac{Q - Q_{gb}}{RT} = \ln(4 \times 10^5) + \ln\left(\frac{D_o}{D_{ogb}}\right)$$

$$\therefore T = \frac{Q - Q_{gb}}{R} \cdot \frac{1}{\ln(4 \times 10^5) + \ln\left(\frac{D_o}{D_{ogb}}\right)} = \frac{(280000 - 140000)}{8.3143} \cdot \frac{1}{\ln(4 \times 10^5) + \ln\left(\frac{2}{5.7}\right)} = 1421 \text{ K}$$

$$(c) \quad \dot{\epsilon} = B\sigma \exp\left(-\frac{Q}{RT}\right)$$

where  $B = 4.0 \times 10^{-11} \text{ N}^{-1} \text{ m}^2 \text{ s}^{-1}$ ,  $Q = 135 \text{ kJ mol}^{-1}$ ,  $R = 8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $T = 1173 \text{ K}$  (900+273)

The mass of the bar itself is negligible  $m = 8900 \cdot 0.04 \cdot \pi(2.5 \times 10^{-3})^2 = 0.007 \text{ kg}$  (0.014% of load). Therefore the stress in the bar is given by

$$\sigma = \frac{F}{A} = \frac{50 \times 9.81}{\pi(2.5 \times 10^{-3})^2} = 2.5 \times 10^7 \text{ Pa}$$

$$\dot{\epsilon} = B\sigma \exp\left(-\frac{Q}{RT}\right) = 4 \times 10^{-11} \cdot 2.5 \times 10^7 \cdot \exp\left(-\frac{135000}{8.3143 \cdot 1173}\right) = 9.7 \times 10^{-10} \text{ per second}$$

$$(= 3.5 \times 10^{-6} \text{ per hour})$$

If the maximum total creep strain is 0.05 (5%), then the time taken to elongate would be

$$\frac{0.05}{3.5 \times 10^{-6}} \sim 14278 \text{ hours}$$

Hence, the nickel alloy would not fulfill the requirement.

**Question 2****(a)**

A: Liquid + solid solution

B: solid solution

C: (Au) +(Ni)

1200°C – two-phase field

Phases	Composition (wt% Ni)	Proportion (wt%)
L	14	$\frac{52 - 30}{52 - 14} \times 100 \approx 58$
Solid solution	52	42

900°C

A single-phase region (solid solution), the phase composition and alloy composition coincide (30 wt% Ni, 70 wt% Au)

600°C

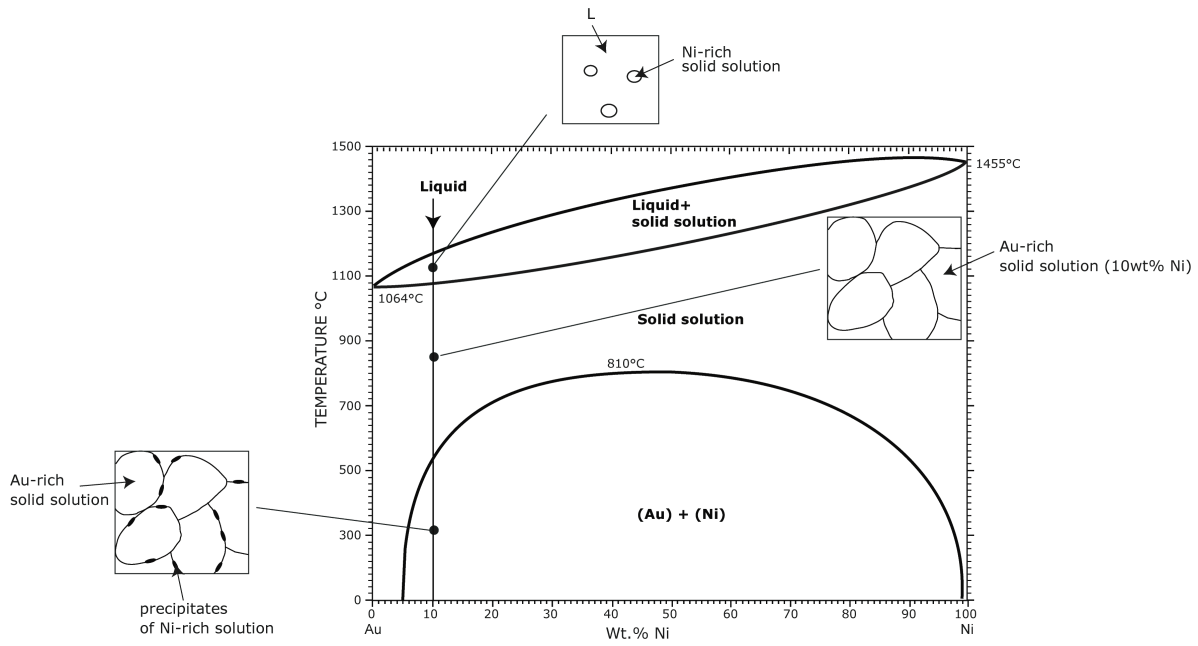
Phases	Composition (wt% Ni)	Proportion (wt%)
(Au)	13	$\frac{86 - 30}{86 - 13} \times 100 \approx 77$
(Ni)	86	23

**(b)**

**(i)** On cooling (see schematic below), the first solid to form at the liquidus temperature (~1170°C) will have a composition of 45 wt% Ni. The composition of the liquid and solid becomes richer in Au (i.e. Ni is rejected) following the liquidus and solidus lines respectively. At the temperature of the solidus (1080°C), a uniform 10%Ni solid solution (Au-rich solid solution) will form. The solid solution will then cool down until it reaches 540°C, at which point some Ni-rich solution will start to precipitate. At this temperature, the Ni-rich solid solution will have a composition of 10 wt% Au, and will probably precipitate at the grain boundaries of the Au-rich solid solution (see sketch). On further cooling, the quantity of Ni-rich precipitate will increase (the proportions of the two phases will be given by the lever rule at any temperature), and the solute content of each solid solution will drop (the composition is given by the tie-line crossing the phase boundary at any temperature).

At 300°C, the system will consist of Au-6.5 wt% Ni and Au-98 wt% Ni. The proportions will be

$$\frac{98 - 10}{98 - 6.5} \times 100 \approx 96\% \text{ of Au-6.5 wt\% Ni and } 4\% \text{ Au-98 wt\% Ni.}$$



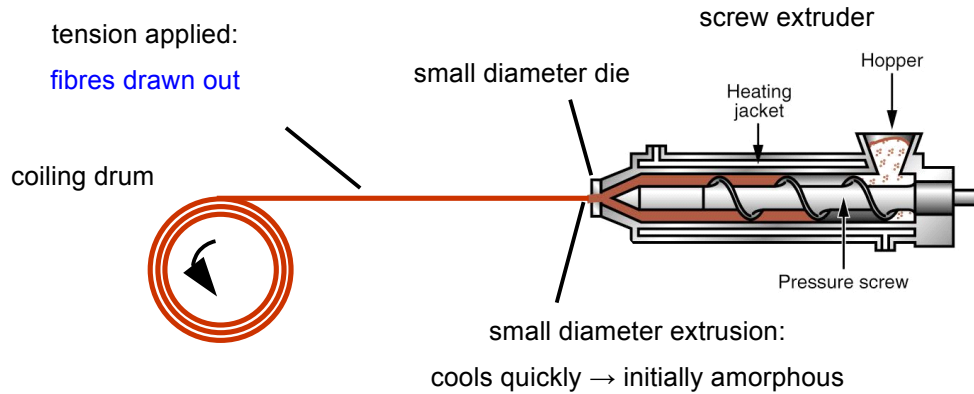
**(ii)** If cooling is fast we may expect “segregation gradients” in the solid. If the cooling rate is not slow enough to allow diffusion to take place, the composition of the solid won’t follow the solidus line during cooling through the 2-phase region (i.e. Ni won’t diffuse out and Au won’t diffuse in). As a result of this there will be a composition gradient in the grains, with the final solid having Ni-rich inner cores to the grains.

Segregation gradients are difficult to eliminate completely but can be reduced by holding the casting at relatively high temperature to allow for some redistribution of solute by diffusion (this is known as “homogenisation”).

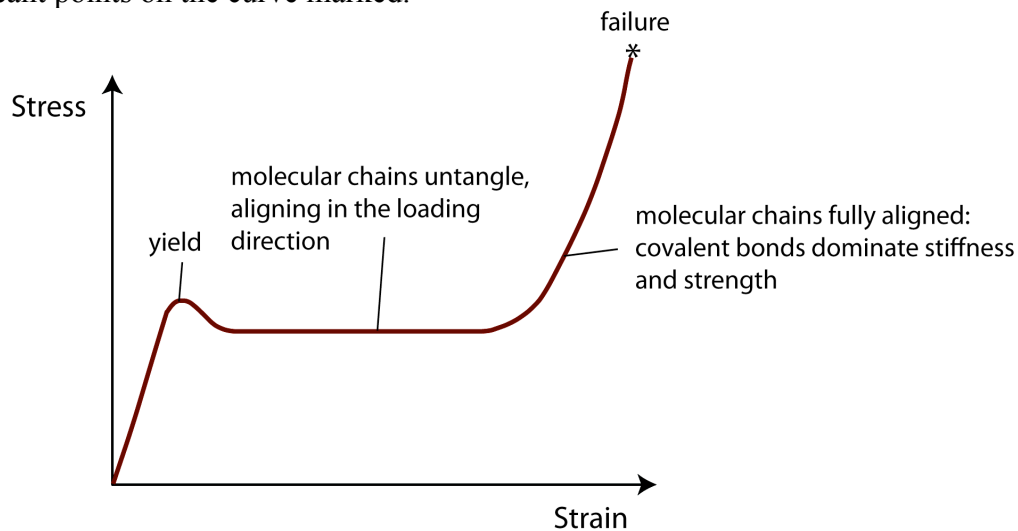
**Question 3**

(a) This process is known as fibre drawing. Stretching the polymer to align the molecular chains significantly increases the strength of the fibre (this mechanism is also known as orientation strengthening). The conditions necessary for this process to take place: the material should be a thermoplastic with temperature close to  $T_g$ .

A schematic illustration of the process is shown below:



A typical (tensile) stress-strain response is illustrated in the schematic below, with the significant points on the curve marked.



(b) (i)

$$\frac{T(t) - T_0}{T_m - T_0} = \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 at}{4h^2}\right)$$

$$T(t) = T_0 + (T_m - T_0) \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 at}{4h^2}\right)$$

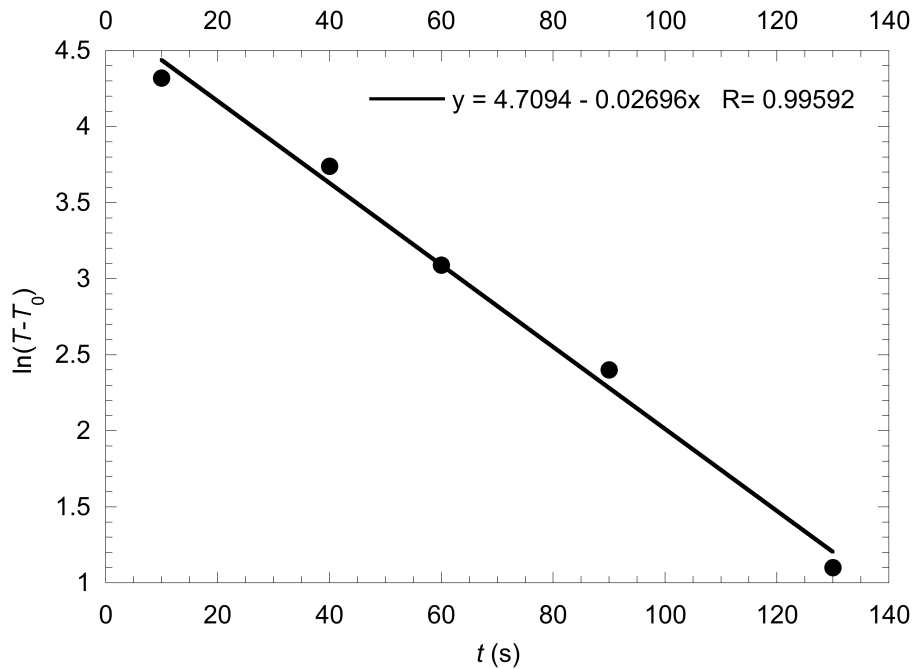
$$\frac{dT}{dt} = (T_m - T_0) \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 at}{4h^2}\right) \left(-\frac{\pi^2 a}{4h^2}\right)$$

Substituting back from the original solution gives:

$$\frac{dT}{dt} = (T_m - T_0) \left(\frac{T(t) - T_0}{T_m - T_0}\right) \left(-\frac{\pi^2 a}{4h^2}\right) = (T - T_0) \left(-\frac{\pi^2 a}{4h^2}\right)$$

The high heat transfer away from the sheet surface will inhibit the formation of a crystalline region on the outside of the moulding – the polymer chains will not have enough time to rearrange themselves by diffusion and the time needed for rearrangement will increase as the temperature decreases. When the cooling rate at the sheet mid-thickness is slow, the interior of the moulding is likely to be crystalline containing either plate-shaped lamellar crystallites or radially-arranged lamellar crystallites (the latter are also known as spherulites). When the cooling rate at the sheet mid-thickness is fast, the microstructure of the whole moulding is likely to be amorphous.

(ii) Plotting the logarithm of  $T-T_0$  as a function of  $t$  gives a straight line with a slope of  $\pi^2 a / 4h^2$ .



Hence

$$a = \frac{0.02696 \times 4 \times 0.0015^2}{\pi^2} = 2.45 \times 10^{-8} \text{ m}^2\text{s}^{-1}$$

(iii) The thermal diffusivity  $a$  is related to the thermal conductivity  $\lambda$  using this relationship

$$a = \frac{\lambda}{\rho c} \Rightarrow \lambda = a\rho c$$

$$\therefore \lambda = 2.45 \times 10^{-8} \frac{\text{m}^2}{\text{s}} \cdot 900 \frac{\text{kg}}{\text{m}^3} \cdot 1100 \frac{\text{J}}{\text{kg K}} = 0.024 \text{ W m}^{-1}\text{K}^{-1}$$

**SECTION B**

**Question 4**

(a) *Hardenability* is a measure of ease of forming martensite when quenching steel from austenite. A steel with a high hardenability is one which has a low critical cooling rate, so that even slow cooling will lead to a martensitic structure. The higher the hardenability, the larger is the component that can be hardened in depth on quenching.

(b)

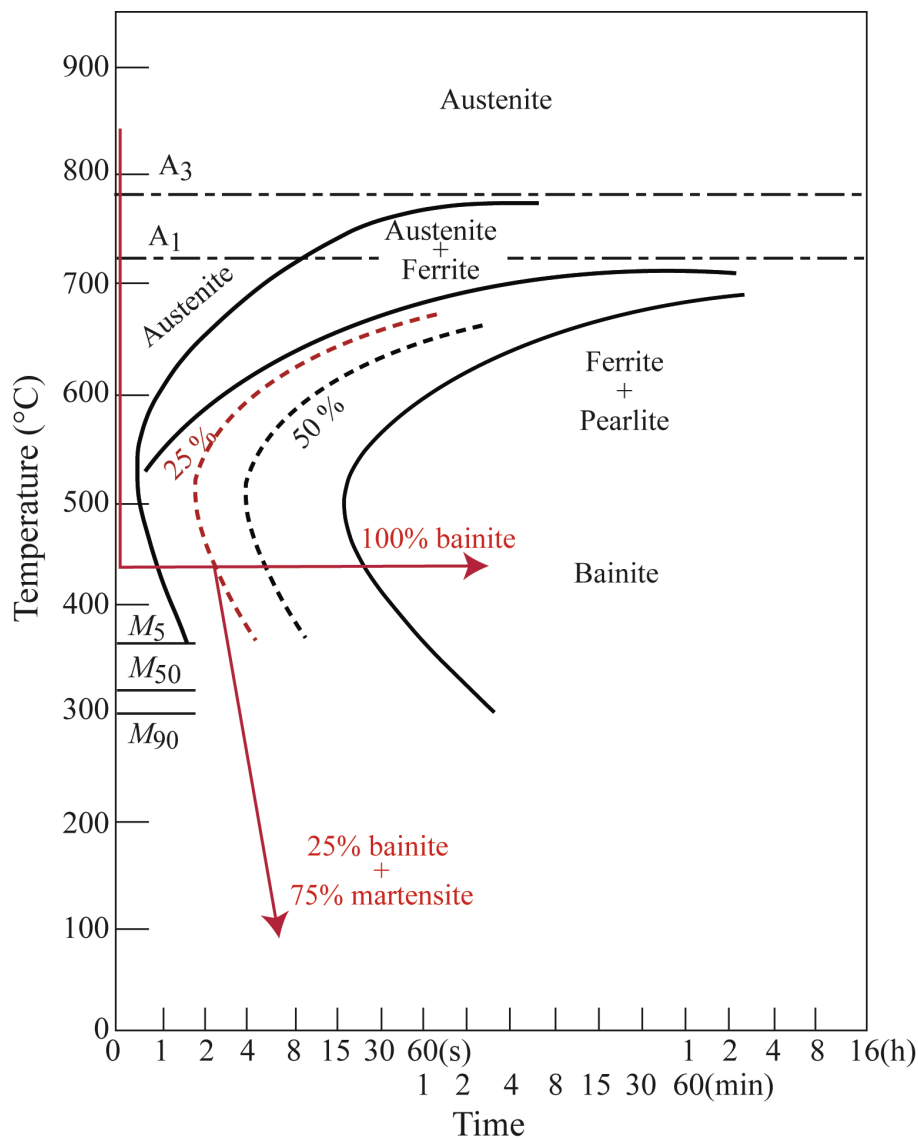
(i) The contours of constant fraction transformed have a C-shape characteristic for diffusional transformations. At low temperatures, nucleation is fast but growth is slow, while at high temperature nucleation is difficult but growth is fast. Thus on a plot of % transformed against time and temperature, there will be a C-curve such that the fastest transformation occurs at an intermediate temperature.

$A_3$  refers to the equilibrium temperature at which austenite transforms to ferrite, the  $\gamma/\gamma+\alpha$  boundary.

$A_1$  refers to the equilibrium temperature of the eutectoid reaction for the steel.

A: austenite, B: ferrite, C: pearlite, D: bainite

(ii)



100% bainite: Cool rapidly below 500 °C, but above the martensite start temperature, hold for ~ 4 min, then cool (cooling rate is not important).

25% bainite - 75% martensite: Cool below 500 °C, but above the martensite start temperature, hold for ~ 3 s, then quench to room temperature.

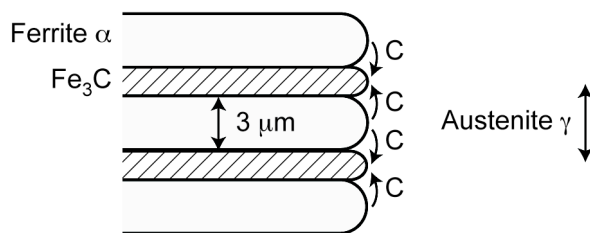
See also annotated sketch for time-heat treatments.

Critical cooling rate from 840 °C:  $(dT/dt)_{\text{crit}}: (840-550)/0.5 \text{ °C s}^{-1} = 580 \text{ °C s}^{-1}$

(c) An estimate of the diffusion time  $t$  is given by

$$t = \frac{x^2}{D} \quad (\text{from } x = \sqrt{Dt}) \quad \text{where } D \text{ is the diffusion coefficient and } x \text{ is the diffusion distance}$$

If the cementite plates are 3  $\mu\text{m}$  apart then the maximum diffusion distance will be 1.5  $\mu\text{m}$ .



*Plain carbon steel: Carbon diffuses ahead of the interface*

The diffusion coefficient  $D$  is given from

$$D = D_o \exp\left(-\frac{Q}{RT}\right), \quad \text{where } D_o = 2 \times 10^{-6} \text{ m}^2\text{s}^{-1}, \quad Q = 110 \text{ kJ mol}^{-1}, \quad R = 8.3143 \text{ J mol}^{-1} \text{ K}^{-1},$$

$$T = 923 \text{ K } (650+273)$$

$$\therefore D = 1.19 \times 10^{-12} \text{ m}^2\text{s}^{-1}$$

$$\text{Using } t = \frac{x^2}{D} = \frac{(1.5 \times 10^{-6})^2}{1.19 \times 10^{-12}} = 1.89 \text{ s}$$

*Chromium steel: Chromium diffuses ahead of the interface*

$$D = D_o \exp\left(-\frac{Q}{RT}\right), \quad \text{where } D_o = 1 \times 10^{-4} \text{ m}^2\text{s}^{-1}, \quad Q = 260 \text{ kJ mol}^{-1}, \quad R = 8.3143 \text{ J mol}^{-1} \text{ K}^{-1},$$

$$T = 923 \text{ K } (650+273)$$

$$\therefore D = 1.93 \times 10^{-19} \text{ m}^2\text{s}^{-1}$$

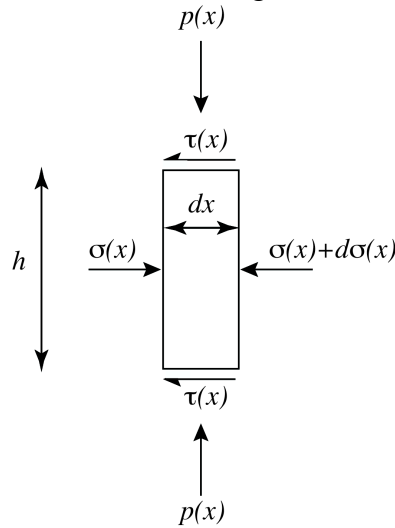
$$\text{Using } t = \frac{x^2}{D} = \frac{(1.5 \times 10^{-6})^2}{1.93 \times 10^{-19}} = 1.16 \times 10^7 \text{ s} = 3235 \text{ hr}$$

The latter time is extremely long suggesting that it is unlikely that chromium diffuses in the austenite. This is unsurprising, as chromium is substitutional on Fe lattice and diffuses much more slowly than interstitial carbon.



**Question 5**

(a) For  $x > 0$ , consider the equilibrium of an element of height  $h$ , width  $dx$  and unit depth normal to the cross-section. Taking compressive stresses as positive, the equation of static equilibrium in the  $x$ -direction, after converting the stresses to forces, is given by



$$d\sigma(x) \cdot h \cdot 1 + 2\tau(x) \cdot dx \cdot 1 = 0$$

$$\Rightarrow \frac{d\sigma(x)}{dx} = -\frac{2\tau(x)}{h} \quad (1)$$

(b) Assuming that the frictional shear stress  $\tau(x)$  is small in comparison to  $p(x)$  and  $\sigma(x)$ , then the last two can both be treated as principal stresses. Using the von Mises yield criterion

$$p(x) - \sigma(x) = 2k = \frac{2Y}{\sqrt{3}} \quad (2)$$

where  $Y$  is the uniaxial yield stress of the slab material. We assume that  $Y$  is constant i.e. does not work harden once yielding has occurred.

Differentiation of the above equation with respect to  $x$  gives

$$\frac{dp(x)}{dx} - \frac{d\sigma(x)}{dx} = \frac{2}{\sqrt{3}} \frac{dY}{dx} = 0 \quad (3)$$

as the yield stress is position-independent. From Equations (1) and (3), we can write

$$\frac{dp(x)}{dx} = -\frac{2\tau(x)}{h} \quad (4)$$

Using Coloumb's friction law

$$\frac{dp(x)}{dx} = -\frac{2\mu}{h} p(x)$$

$$\therefore \frac{dp(x)}{p(x)} = -\frac{2\mu}{h} dx$$

The general solution for the above equation is

$$\ln p(x) = -\frac{2\mu}{h} x + C \quad (5)$$

where  $C$  is a constant of integration. Applying the boundary conditions,  $x = b/2$ ,  $p(x) = 2k$  (the stress  $\sigma(x)$  is zero at the edge)

$$\ln 2k = -\frac{2\mu}{h} \frac{b}{2} + C$$

$$\therefore C = \ln 2k + \frac{2\mu}{h} \frac{b}{2}$$

Using the above, we can rewrite equation (5)

$$\ln p(x) = -\frac{2\mu}{h} x + \ln 2k + \frac{2\mu}{h} \frac{b}{2}$$

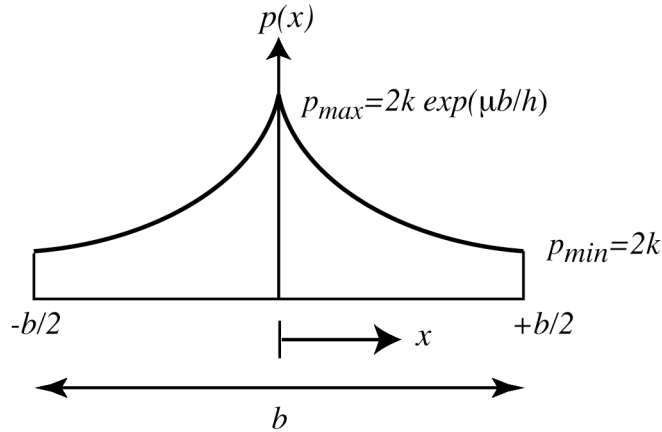
$$\ln p(x) - \ln 2k = -\frac{2\mu}{h} x + \frac{2\mu}{h} \frac{b}{2}$$

$$\therefore p(x) = 2k \exp\left(\frac{2\mu}{h} \left(\frac{b}{2} - x\right)\right) \text{ for } 0 < x \leq \frac{b}{2}$$

Obviously the solution will be

$$\therefore p(x) = 2k \exp\left(\frac{2\mu}{h} \left(\frac{b}{2} + x\right)\right) \text{ for } -\frac{b}{2} \leq x < 0$$

The pressure distribution (also known as “friction hill”) is plotted below



(c) The average pressure for  $0 < x \leq b/2$  is given by

$$\begin{aligned} p_{av} &= \frac{1}{b/2} \int_0^{b/2} p(x) dx = \frac{2}{b} \int_0^{b/2} 2k \exp\left(\frac{2\mu}{h} \left(\frac{b}{2} - x\right)\right) dx = \frac{4k}{b} \exp\left(\frac{\mu b}{h}\right) \int_0^{b/2} \exp\left(\frac{2\mu x}{h}\right) dx = \\ &= \frac{4k}{b} \exp\left(\frac{\mu b}{h}\right) \left[ -\frac{h}{2\mu} \exp\left(-\frac{2\mu x}{h}\right) \right]_0^{b/2} = \frac{4k}{b} \exp\left(\frac{\mu b}{h}\right) \left[ -\frac{h}{2\mu} \exp\left(-\frac{\mu b}{h}\right) + \frac{h}{2\mu} \right] \\ &= \frac{2kh}{\mu b} \exp\left(\frac{\mu b}{h}\right) \left[ 1 - \exp\left(-\frac{\mu b}{h}\right) \right] = \frac{2kh}{\mu b} \left[ \exp\left(\frac{\mu b}{h}\right) - 1 \right] \end{aligned}$$

Expressed in terms of the uniaxial yield stress  $Y$ , the above equation becomes

$$p_{av} = \frac{2Yh}{\sqrt{3}\mu b} \left[ \exp\left(\frac{\mu b}{h}\right) - 1 \right]$$

For a low carbon steel ( $Y = 300$  MPa,  $b = 150$  mm,  $h = 20$  mm) and  $\mu = 0.1$  the average pressure is going to be

$$p_{av} = \frac{2Yh}{\sqrt{3}\mu b} \left[ \exp\left(\frac{\mu b}{h}\right) - 1 \right] = \frac{800}{\sqrt{3}} \left[ \exp(0.75) - 1 \right] = 516 \text{ MPa}$$

**Question 6**

(a) During transformation hardening, the steel surface is subjected to rapid heating and quenching. Heating the surface (with a flame, laser, electron gun or induction coils), austenite forms which when cooled sufficiently fast (either by conduction into the underlying material or by water quench) forms martensite. The depth of hardening will depend on the heating and cooling rates and also the hardenability of the steel. Another surface hardening process is carburising. Both processes involve diffusion. The main difference between the two processes is that in carburising, hardening occurs by modifying the surface composition whereas in transformation hardening, hardening takes place by a phase transformation (no change in surface composition).

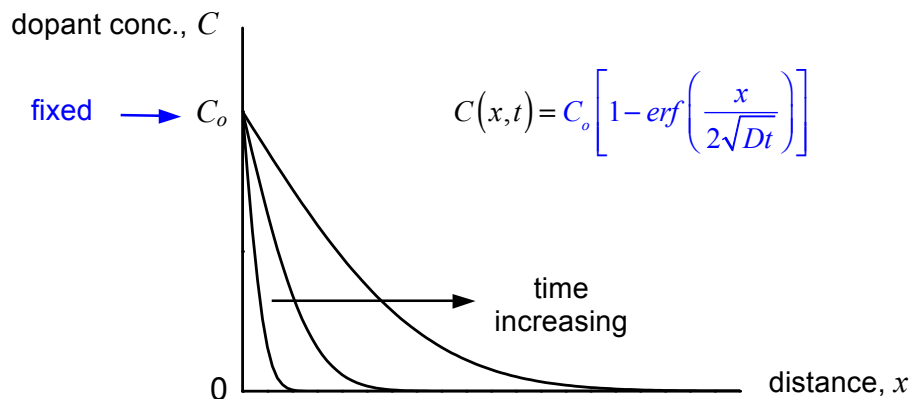
(b)

(i) Pre-deposition

A thin layer of dopant is diffused into the surface of the semiconductor, by maintaining a high concentration of dopant at the surface. The surface concentration is constant during the process and will be determined by the solubility of the dopant in the semiconductor at the doping temperature. The initial concentration of dopant within the solid is zero. Therefore the boundary conditions are:

$$C(0, t) = C_0; \quad C(x, 0) = 0; \quad C(\infty, t) = 0$$

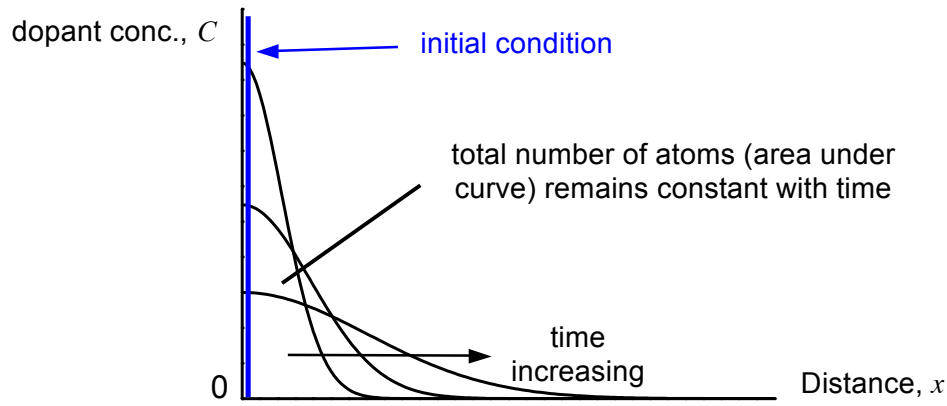
Diffusion depths are small compared to the treated area, so the diffusion process obeys the 1D unsteady diffusion equation. As the source of solute at  $x = 0$  is constantly replenished, the result is the equivalent of adding together lots of exponential functions with different width. The resulting profile can be described by the error function as illustrated below:

Drive-In

In drive-in diffusion, the source of dopant is removed, and the dopant diffuses a much greater distance in the semiconductor. The aim is to give an approximately uniform distribution of dopant. It is assumed that as time increases, the total amount of dopant is fixed.

$$C(x, 0) = 0; \quad C(\infty, t) = 0; \quad \int_0^{\infty} C(x,t) dx = \text{constant} = K$$

The solution, which satisfies both Fick's 2nd law and also the third boundary condition, is illustrated below:



A Gaussian distribution, delta function when  $t \rightarrow 0$ .

(ii) Pre-deposition:

The diffusion coefficient at 1000 °C is given by

$$D_{1273} = D_o \exp\left(-\frac{E}{kT}\right) = 5.42 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}, \text{ where } D_o = 3.7 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}, E = 3.5 \text{ eV} = 3.5 \times 1.6 \times 10^{-19} \text{ J atom}^{-1}, k = 1.381 \times 10^{-23} \text{ J K}^{-1}, T = 1273 \text{ K (1000+273)}$$

The total number of atoms per unit area after pre-deposition is given by

$$K = \frac{2}{\sqrt{\pi}} C_o \sqrt{Dt_{PD}}$$

where  $C_o = 1.1 \times 10^{21} \text{ atom cm}^{-3}$ ,  $t_{PD} = 15 \times 60 = 900 \text{ s}$ ,  $D_{1273} = 5.42 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ . This gives  $K = 8.67 \times 10^{14} \text{ atom cm}^{-2}$ .

Drive-In:

The diffusion coefficient at 1100 °C is given by

$$D_{1373} = D_o \exp\left(-\frac{E}{kT}\right) = 5.52 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}, \text{ where } D_o = 3.7 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}, E = 3.5 \times 1.6 \times 10^{-19} \text{ J atom}^{-1}, k = 1.381 \times 10^{-23} \text{ J K}^{-1}, T = 1373 \text{ K (1100+273)}$$

To find the depth at which the boron concentration will be 1% of the initial surface concentration ( $C_o / 100 = 1.1 \times 10^{19} \text{ atom cm}^{-3}$ ), the Gaussian solution below needs to be solved in terms of  $x$

$$C(x,t) = \frac{K}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \Rightarrow \frac{C\sqrt{\pi Dt}}{K} = \frac{1}{\exp\left(\frac{x^2}{4Dt}\right)}$$

$$\Rightarrow \exp\left(\frac{x^2}{4Dt}\right) = \frac{K}{C\sqrt{\pi Dt}} \Rightarrow \frac{x^2}{4Dt} = \ln\left(\frac{K}{C\sqrt{\pi Dt}}\right)$$

$$\therefore x = \sqrt{4Dt \ln\left(\frac{K}{C\sqrt{\pi Dt}}\right)} \text{ where}$$

$C = C_o / 100 = 1.1 \times 10^{19} \text{ atom cm}^{-3}$ ,  $K = 8.67 \times 10^{14} \text{ atom cm}^{-2}$ ,  $D_{1373} = 5.52 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$   
and  $t = t_{DI} = 1 \text{ hr} = 3600 \text{ s}$ . This gives  $x \sim 0.000014 \text{ cm}$  ( $0.14 \mu\text{m}$ ).

For the analysis to be reasonable (the dopant distribution at the start of the drive-in process may be treated as a thin layer at the surface), the diffusion distance during drive-in must be greater than the pre-deposition distance

$$x_{\text{drive-in}} \gg x_{\text{pre-deposition}} \quad \text{i.e.} \quad (\sqrt{Dt})_{\text{drive-in}} \gg (\sqrt{Dt})_{\text{pre-deposition}}$$

which is true as  $4.5 \times 10^{-6} \text{ cm} \gg 7 \times 10^{-7} \text{ cm}$