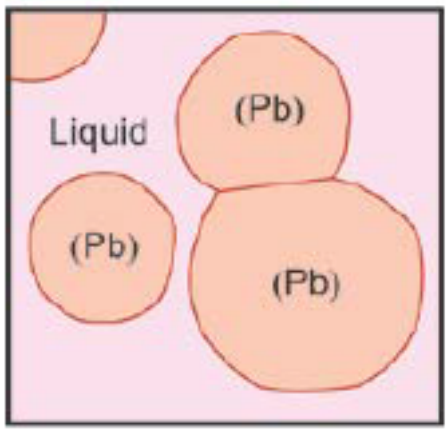
2017 1B Paper 3 Crib V3.1

Q1 Phase diagrams and nucleation

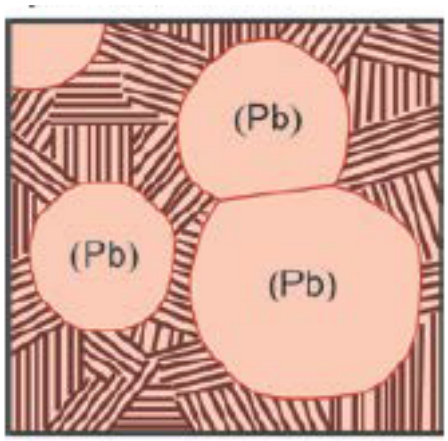
1) ii) At 275C and 10% the phases present are Liquid and (Pb) rich solid. (Pb) is ~8wt%Sn and Liquid is ~23wt%Sn. Tie line is thus 23-8= 15 long and 1/14 is liquid and 13/14 (Pb).
   At 200C and 10% the phases present are just (Pb) of 10wt%Sn composition.
   At 100C and 10% the phases present are (Pb) and (Sn). The (Pb) phase is 3wt%Sn and the (Sn) phase is 99wt%Sn. Tie line is thus 101 long and proportions are 7/101 and 94/101.

   ii)
   At 225



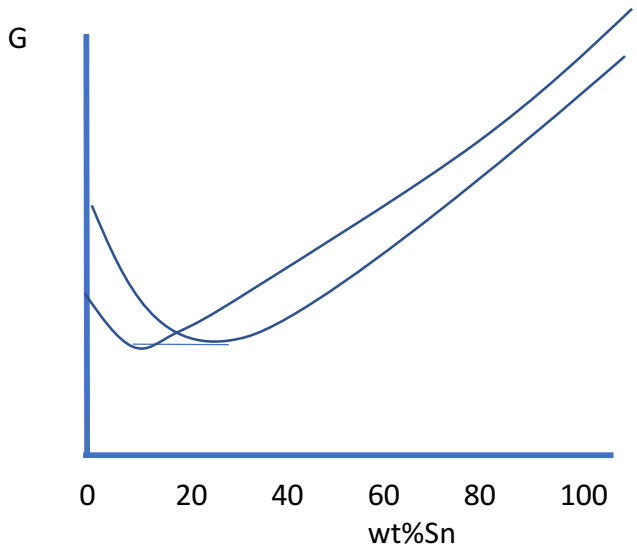
   Roughly 40% Liquid looking at the tie-line (by weight)

At 180, the Pb grains will have grown somewhat and then any remaining liquid will have undergone a eutectic reaction.



At 25 - as diagram for 180 but with small dots representing precipitation of Sn in (Pb) primary grains.

iii) At 250 the two-phase region should extend from ~12wt%Sn to 35wt%Sn. A plot where the common tangent region is between these two points is representative of this behaviour. The plot for Sn –rich could be drawn but this is not required as it will always be higher in energy (no Sn-rich region forms at this temperature for any wt% Sn.



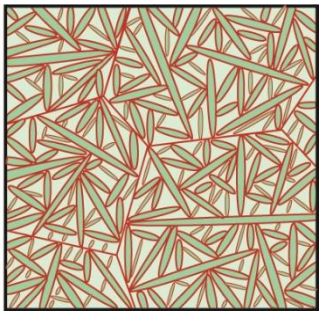
b) a) During solidification the region of the casting near the mould wall is cooled quickly leading to a large undercooling. In addition, heterogenous nucleation occurs on the mould wall. This means nucleation is easy and multiple small grains are formed.
As the depth in the casting increases, the undercooling drops and the rate at which a grain grows becomes faster than the rate of nucleation of new grains leading to columnar grain growth. As the whole casting cools the solidification front moves in towards the centre. Finally, in the centre large equiaxed grains are obtained as they have nucleated in a region where undercooling was small and thus the nucleation rate low. Typically, nucleation is heterogeneous on impurities, the impurity concentration in the remaining melt will rise as they are not included in the columnar grains)

b) The addition of TiO powder provides multiple sites for heterogeneous nucleation. The resultant grain structure will, therefore, be a more even distribution of small grains rather than the grain structure in the diagram.

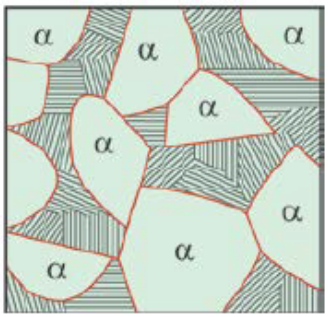
On the whole a very well answered question. Good quality, labelled where appropriate, diagrams were required for full marks. Most marks were lost by candidates who, in part b), simply described the features of the diagram they were given rather than explaining why it occurred.

2) Thermal Processing of Materials - Steel

i) Would expect just martensite – at the temperature given the material will be entirely gamma phase which will all transform to alpha prime on cooling.



ii) Would expect mixture of Ferrite and Pearlite.



b) i) Overall provides a hard surface while retaining a tough core without requiring more expensive alloy steels. In addition the pre-processed cylinder can be machined before hardening. It is also difficult to through harden large pieces of non-alloy steel. There can be issues with thermal cracking with a water quench.

Increasing the C content in the surface means on quenching the steel is easily transformed in to martensite. The tempering retains much of the hardness of the martensite while restoring some fracture toughness.

Deeper in the cylinder the combination of slower cooling and lower carbon content means that martensite is not formed, indeed at the centre the cooling may be slow enough that F+P is formed as for slow cooling. In intermediate regions, a split transformation may be observed with the formation of bainite.

Consequently, the final article has a hard, and somewhat tough, surface with the core of the cylinder retaining the touchness and crack resistance of mild steel.

ii) For this problem can write than C(x,t)-Co/Cs-Co=1-erf() . Need to remember that Cs is 1.6% as that is the maximum amount of C that can be dissolved into the gamma phase at the carburising temperature (see Fe-C phase diagram in databook). Co is 0.2%. So Cs-Co is 1.4 and C(t) is 0.6 consequently we have 1- 0.4/1.4 = 0.715 = erf() .

We are probably ok using the erf(X)=X approximation (just!) so now we have that x/2√Dt is 0.715. Squaring and rearranging we have that x^2/4D(0.715)^2 is t . So we have (5e-4)^2/4*6.68e-11*0.511 which is 2.5e-7/1.36e-10 =1838s i.e. 30min.

iii) A complex shape will lead to stress concentrations on cooling due to differing cooling rates. This, combined with hard but brittle martensite can lead to cracking. This could be avoided by quenching into oil, rather than water. Consideration would need to be given to the resultant cooling rate to ensure that it is fast enough that martensite is formed.

Alternatively, an alloy steel could be used that forms martensite at the surface even with a relatively slow air cool. – this would also eliminate the need for the carburising step.

The question was not badly answered on the whole, but many candidates lost marks by not considering the difference between surface carburising and generic quenching and tempering. High quality and clear sketches, coupled with clear explanations, were required for full marks. Relatively few candidates remembered to work out the maximum solubility of C in austenite from the phase diagram in the data book. Candidates who used incorrect values but had otherwise correct answers were not heavily penalised.

3) Free energy and nucleation

a) From the information given G=U+pV-TS. Differentiating this leads to :

dG=TdS-pdV-TdS$_{irrev}$+pdV+VdP--dTS-TdS

Cancelling terms gives:

dG=VdP-dTS-TdS$_{irrev}$

Which leads to the standard result that at constant T and P dG only depends on the change in the irreversible component of entropy.

iii) At a particular pressure and temperature VdP=SdT=0 so changes in the Gibbs free energy are entirely due to irreversible changes in entropy which are always greater than zero. Consequently, changes in G will always be negative. The most stable state will therefore be that with the minimum of Gibbs free energy. For full marks students needed to talk about the suitability of Gibbs for reversible transformations at constant T and P as opposed to simply stating that it is minimised.

b)

I) While the water is cooled below its thermodynamic freezing point if the container is clean there will not be sufficient heterogeneous nucleation sites to initiate the freezing process. When the water is poured onto a surface it can freeze and as fresh super-cooled water is added it also freeze instantly.

To maximise the chances of successful super-cooling you need pure water free of dirt and contaminants in a clean container that is, ideally, not very wettable (large contact angle). Need to cool slowly.

ii) The critical radius is at the maximum in G_{tot} arising from forming the sphere. So we can calculate:

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

and take the derivative:

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

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

note that this is –ve as delta G should be negative for the cooling process leading to a positive radius.

iii)

$$\text{Substituting for } \Delta G = \Delta H \Delta T / T_E: \quad r^* = \frac{2\gamma T_E}{\Delta H_v (T - T_E)}$$

Consequently, the critical radius is 2.275 nm. Note that delta H is negative for formation of ice. As delta H is positive and ($T-T_e$) is also negative thie correct equation should result in a positive r^*.

This question was generally well answered. Marks were lost in part a by candidates who forgot that differentiation of a product results in two terms. A small number of candidates correctly derived the relationship between change in G and irreversible entry in part i) but then provided an entirely different erroneous explanation of the importance of G in part ii). Some descriptions of why super-cooled water freezes on pouring made rather strained appeals to increase in overall kinetic energy rather than the rather more likely situation of initial heterogeneous nucleation on the surface poured onto followed by homogenous nucleation on the subsequently formed ice. A surprisingly large number of candidates attempted to argue that lower temperature let to increased kinetic energy and thus a higher likelihood of nuclei formation.

4) Polymers and processing

a) Possible answers (any three accepted):

Different polymers are formed when some or all of the H atoms are replaced with other atoms or molecules (side-groups). This affects interactions between polymer chains.

One can add side branches of the same polymer –e.g. LDPE. Side branches affect the ability of chains to pack close each other and affects crystallisation.

One can control the level of crystallinity which affect the strength of inter-chain attraction. The ability to crystallise depends also on the side chains and side groups. The presence of crystallinity will lead to a reduced effect of Tg .

Cross linking – can join chains with covalently bonded chains rather than relying on van-der waals forces or hydrogen bonding. Unlike VdW forces, these are not turned off at Tg.

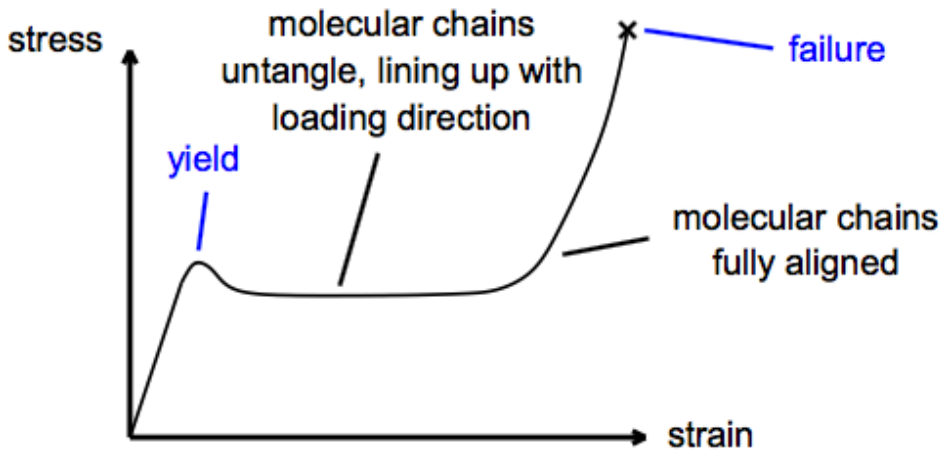
In terms of properties (only one required):
Side groups and chains strongly affect the ability to crystallise. A crystalline polymer has a higher modulus and, at very high crystallinity, the modulus remains high through the glass transitions temperature. A complex polymer will find it difficult to crystallise.

Crystallinity (and the side groups and chains associated with a polymer) will also affect the density. If the crystallinity changes through a machining process, dimensional control may be affected.

b)i) For the proposed application, the material required should be both tough and transparent. Hardness is also potentially a desirable property. As it is an aircraft it should be lightweight.
Polymer choice is large but essentially need one that is complex so crystallisation is slow. PMMA would be a good choice. Polycarbonate would also be a good choice and has good scratch resistance. There are more obscure choices such as Butyrate or PETG that students are unlikely to suggest but should be accepted if given.

ii) Injection moulding of a polymer allows production of a polymer that is shaped. If the mould is cooled the polymer can be quickly cooled thus aiding the production of an amorphous part.
High injection pressure allows the use of thin sections that cool quickly although this may result in a part that does not satisfy the mechanical requirements.

c)



The initial regime is the linear, and the deformation is elastic. The level of forces applied can reversibly pull the neighbouring chains apart, by acting against the van der Waals inter-chain attraction.
After the applied force exceeds a certain level (i.e. the yield point), the van der Waals attraction within chains is overcome, causing the chains to permanently displaced against each other. The chains are able to slide over each other, and start to re-orient and align with respect to the loading direction. Very little force increase is resulted over a large strain during this alignment regime.
When the chains are fully aligned, the applied force is now stretching the covalent bonds of the polymer chains. Hence, there is steep increase in stress versus strain.
Finally, the applied force exceeds the covalent bonding strength and the polymer fractures.

[On the whole, this is a well answered question. Most marks are lost by the candidates in the following aspects: In part b i), blow moulding is stated as the manufacturing method instead of injection moulding. Blow moulding is for thin sections which will produce insufficient thickness to withstand the impacts and pressure difference incurred for an airplane. Also in part c), the yield point is often missed on the graph drawing. Some candidates were also confused this question with the Young's modulus against temperature graph for thermoplastic polymers.]

5) Heat Transfer

a) I)

$\frac{T-T_0}{T_1-T_0} = \text{erf}(\frac{x}{2\sqrt{at}})$ for one surface close to 0; and $\frac{T-T_0}{T_1-T_0} = \text{erf}(\frac{\delta-x}{2\sqrt{at}})$ for the other surface close to δ.

(ii)

The above solution is only true when considering the plate thickness as semi-infinite (when the thickness of the plate >> $2\sqrt{at}$), where the bulk temperature of the plate remains at T_0. However, beyond early stages of the cooling, the centre of the plate temperature will drop below T_0.

(b)

Note that the assumption that g(0)=1 for this Fourier term is only valid when considering large T where the other Fourier terms have become negligible.

$\frac{\partial T}{\partial t} = (T_1 - T_0)\frac{4}{\pi}\sin(\frac{\pi x}{\delta})\frac{\partial g}{\partial t}$ [eq.1]

$\frac{\partial T}{\partial x} = a(T_1 - T_0)\frac{\pi}{\delta}\frac{4}{\pi}\cos(\frac{\pi x}{\delta})g$

$\frac{\partial^2 T}{\partial x^2} = -a(T_1 - T_0)\frac{4}{\pi}\frac{\pi^2}{\delta^2}\sin(\frac{\pi x}{\delta})g$ [eq.2]

$\frac{\partial T}{\partial t} = a\frac{\partial^2 y}{\partial x^2}$

Thus, $(T_1 - T_0)\frac{4}{\pi}\sin\left(\frac{\pi x}{\delta}\right)\frac{\partial g}{\partial t} = a(T_1 - T_0)\frac{\pi^2}{\delta^2}\frac{4}{\pi}\sin(\frac{\pi x}{\delta})g$

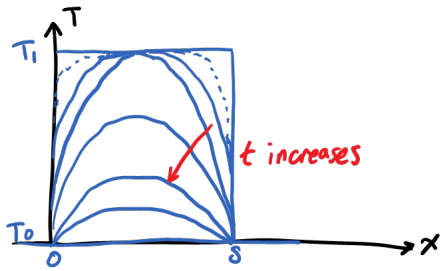
$$\frac{\partial g}{\partial t} = a\frac{\pi^2}{\delta^2}g$$

$\int_{g(0)}^{g(t)}\frac{dg}{g} = \int_0^t -a\frac{\pi^2}{\delta^2}dt$

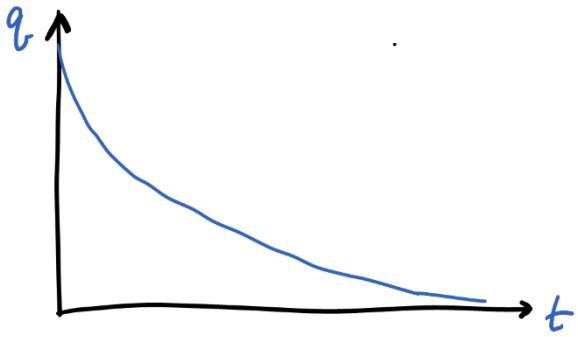
$\ln(g)_{g(o)}^{g(t)} = -a\frac{\pi^2}{\delta^2}t$

$g(t) = g(0)\exp(-a\frac{\pi^2}{\delta^2}t) = \exp(-a\frac{\pi^2}{\delta^2}t)$

(c) i)



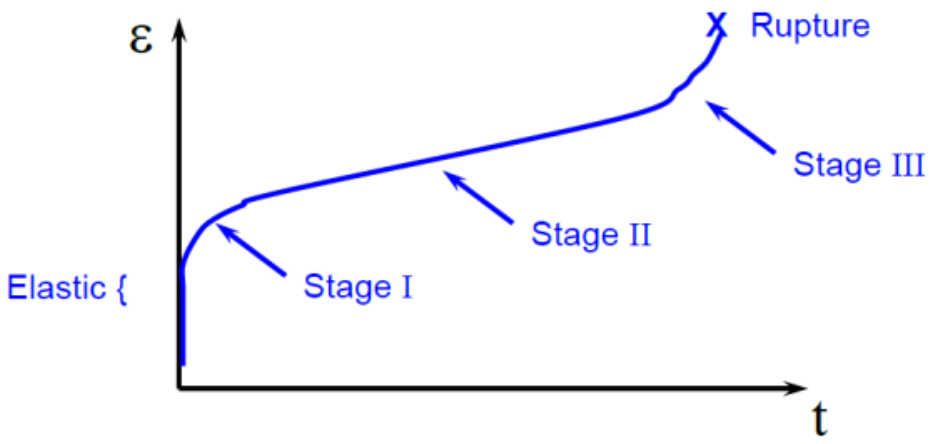
(ii)



[On the whole this is a reasonably well-answered question, for the candidates who attempted it. Common mistakes include the following. In a(i), only one surface temperature equation is stated instead of two. In b, some candidates did not remember to use Fick's law for the derivation. In c(i), the drawing did not clearly show the transition between error-function for the early stages, to the half sine function in the later stages. In c(ii), at time 0, the heat flux q will be very sharp but cannot be infinity in real life.]

6) Creep and Failure

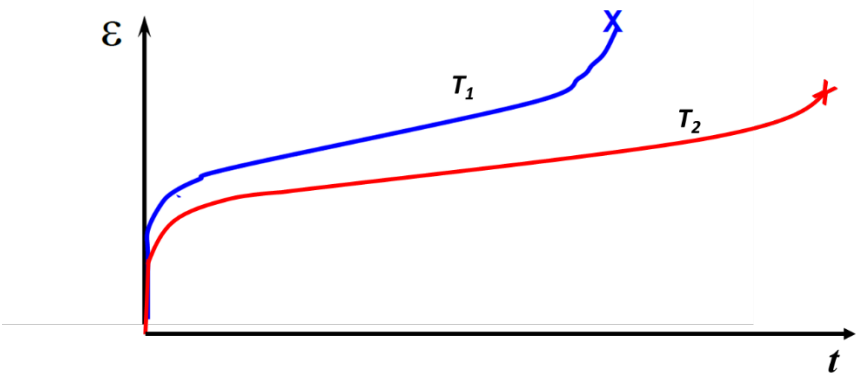
(a) (i)



Stage I: Primary Creep
Stage II: Secondary Steady-state Creep ← dominates creep life
Stage III: Tertiary Creep

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. Little contribution to creep life.
Stage II: Secondary (Steady State) creep in which strain increases steadily with time (i.e. constant creep rate). This stage 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. Little contribution to creep life.

(ii)



The key differences include:

- Lowered ε at the turning point between the elastic deformation and the Stage I creep.
- The stage II creep which dominates the creep life will proceed for longer periods, with a shallower gradient. This is due to the thermally activated nature of the creep deformation (i.e. $\dot{\varepsilon} \propto \exp\left(-\frac{Q}{RT}\right)$).

- Stage III creep will have a shallower upturn for ε vs. time. The strain at failure is also reduced.

(b) i)

Mass of the bar ~ π(2.5)^2*30*10^-9*8900~0.005 kg

Thus the mass of the bar is negligible.

$$\sigma = \frac{F}{A} = \frac{1000}{\pi(0.0025)\text{^}2} \sim 5.1\times10^{7} Pa$$

Assume stead state creep dominates creep life:

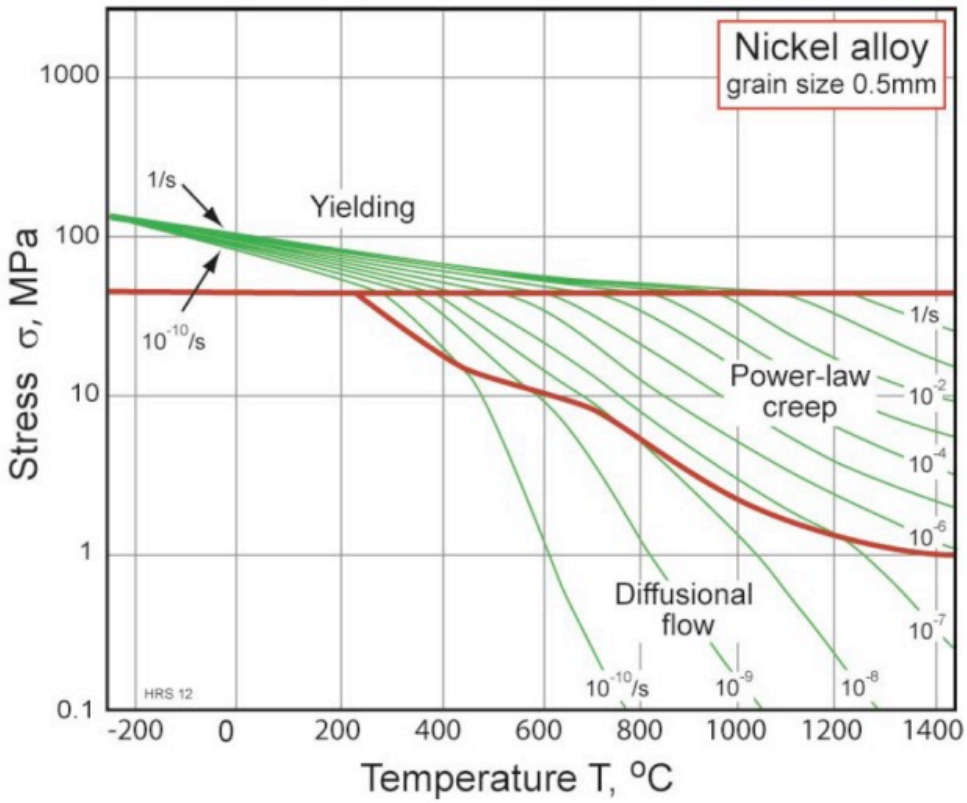
$$\dot{\varepsilon} = 4\times10^{-11}\times5.1\times10^{7}\times \exp\left(-\frac{135\times10^{3}}{8.3\times1273}\right) \sim 5.7\times10^{-9} s^{-1}$$

t= 20,000 hrs = 7.2x10^7 s.

$$\varepsilon_{tot} = \dot{\varepsilon}\times t = \ 5.7\times10^{-9}\times7.2\times10^{7} \sim 0.41 \sim 41\%$$

Thus, the bar will not fulfil the creep test requirement.

(ii)



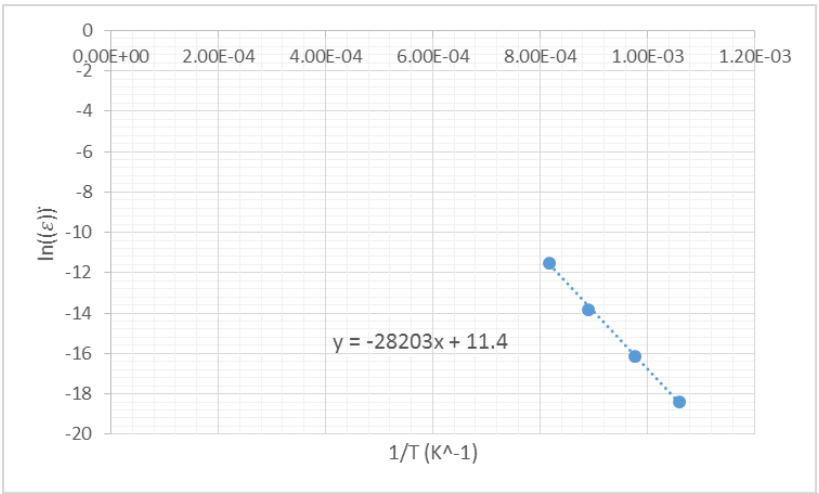
$$\ln(\dot{\varepsilon}) = \ln(A) + n\ln(\sigma) - \frac{Q}{RT}$$

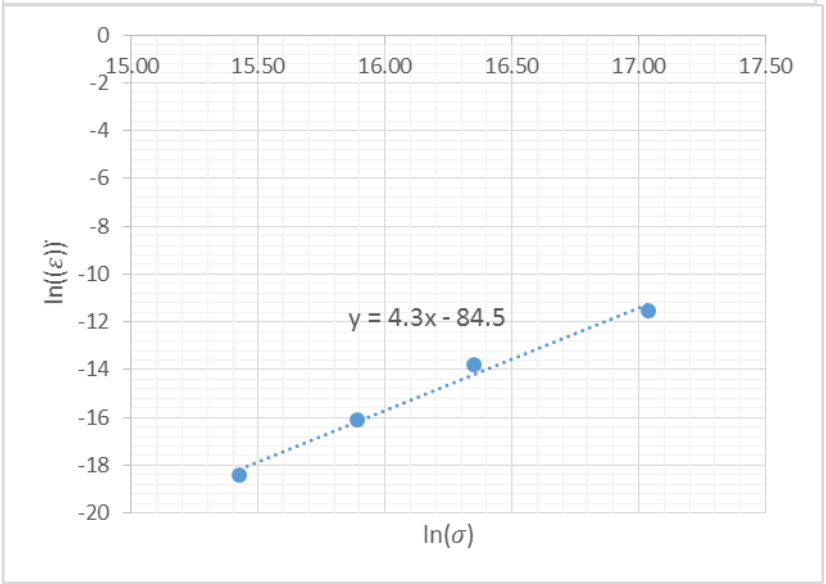
At constant T=800 degC, plotting $\ln(\dot{\varepsilon})$ *vs.* $\ln(\sigma)$, the slope will equal to the exponent *n*.

n~ 4.2

At constant σ=10 MPa, plotting $\ln(\dot{\varepsilon})$ *vs* 1/T, the slope will equal to –Q/R.
-Q/R~-28200 → Q~235 kJ/mol

log(σ) MPa from graph	σ (MPa)	ln(σ/ Pa)		$\dot{\varepsilon}$	ln($\dot{\varepsilon}$)		T (°C)	T (K)	1/T
0.7	5.01	15.43		1.E-08	-18.4207		670	943	1.06E-03
0.9	7.94	15.89		1.E-07	-16.1181		750	1023	9.78E-04
1.1	12.59	16.35		1.E-06	-13.8155		850	1123	8.90E-04
1.4	25.12	17.04		1.E-05	-11.5129		950	1223	8.18E-04





[A surprisingly large number of candidates were confused with the axes labels for the creep curve in a(i), with e.g., stress versus strain, strain rate versus time, or strain versus stress. Even though the forms of the curve may look similar to a creep curve; in those cases, marks are only given to the description of the curve life but not the curve drawing itself. In a(ii), few candidates were able to draw all features of the creep curve at a lowered temperature. In b(i), this part is generally well-attempted, though some candidates did not realise that the weight of the bar was negligible compared to the load, leading to complicated integrations for the calculations. Finally in b(ii), marks are lost mainly due to the candidates running out

of time, mistakes in the calculation, or the answers not being sufficiently precise. In order to achieve full marks in b(ii), at least three points should be plotted with a best fitted line drawn across the three points on a graph paper.]

JHD (Sec A)/YYSH (Sec B) June 2017