

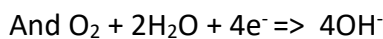
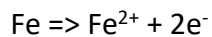
Question 1 (Corrosion)

259 attempts, average 68%

This question was very well answered, although many responses slavishly followed the notes. In Qai) many candidates did not provide an explicit discussion as requested and simply quoted half reactions. In Qaii) many candidates did not note both the difference in electrochemical potential between the steels and that sea water is an effective electrolyte. Many candidates incorrectly asserted that seawater is acidic (global warming notwithstanding it is in fact slightly alkaline). Part b was well answered, although several candidates asserted that the free energy and the electrochemical potential were independent, whereas they are simply proportional. Part c was very well answered.

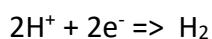
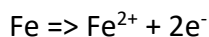
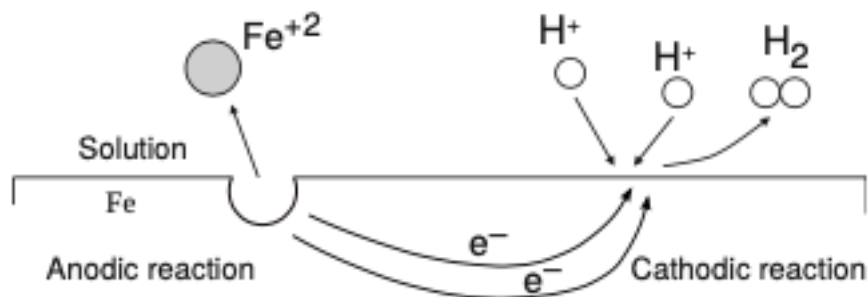
1)i) In a neutral environment Iron only reacts if oxygen is present:

So the reactions are:



Overall reaction is oxygen, water and iron generating Fe^{2+} and OH^{-} ions. This further reacts to form the flaky hydrated iron hydroxide we know as rust.

In an acidic environment H^{+} ions are present in excess, so no oxygen is required the following reactions can take place:



Overall reaction is H^{+} ions and Iron generating Fe^{2+} and hydrogen.

ii) An explanation is that mild steel and stainless steel have rather different electrochemical potentials (which they do), the high conductivity seawater leads to the generation of an effective electrochemical cell and galvanic corrosion where the metals touch.

iii) Painting – cheap, not so durable. Galvanising, more durable but when fully removed corrosion will start. Alloying with an element that forms a self passivation layer – expensive but self healing. Sacrificial anode – effective but more complex and needs ongoing maintenance. Deliberately forming a passivation layer – “blueing” of iron in an alkaline solution, adonisation.

b) i) The difference in free energy does not control the kinetics of the reaction consequently there is no *a priori* reason why the amount of energy released should control the rate of reaction. In addition, in many systems the overall corrosion rate is controlled not by reaction rate but by the rate of diffusion of species through a self-passivation layer

ii) Linear Gain – continues reaction – layer formed does not block further diffusion, but resultant corrosion product remains attached.

Linear Loss – as linear gain but flaky corrosion product is removed, or corrosion product soluble and dissolved.

Parabolic gain corrosion product inhibits required species from reaching the surface of the metal so as the corrosion layer thickens overall rate becomes controlled by diffusion through the corrosion layer.

C i)

We can rearrange the rate equation given in the question $\Delta m = \sqrt{tk}$ to give:

$$k = \frac{\Delta m^2}{t}$$

We know that the change in mass is 0.005 kg and the time is 3.153×10^7 s. So the rate constant, k is thus $7.93 \times 10^{-13} \text{ kg}^2 \text{ m}^{-4} \text{ s}^{-2}$ which, from literature, is a reasonable value for corrosion of Cr at the temperature given.

ii) Using the rate equation, we now have that $\Delta m = \sqrt{tk} = \sqrt{7.93 \times 10^{-13} \times 6.306 \times 10^7}$ which gives 0.007 kg i.e. 7g. As expected from the parabolic model the weight gain in year 2 is less than that in year 1.

The weight gain is purely oxygen, the chromium is still present, it has just reacted. The number of moles of oxygen gained is $7/16$ as oxygen's atomic weight is 16 g/mol. As the chemical formula has 2 moles of Chromium to 3 moles of Oxygen the number of moles of Chromium that have reacted is $2/3 \times 7/16 = 7/24$. The total mass of Chromium metal that has reacted is thus $7/24 \times 52 = 15.2$ g.

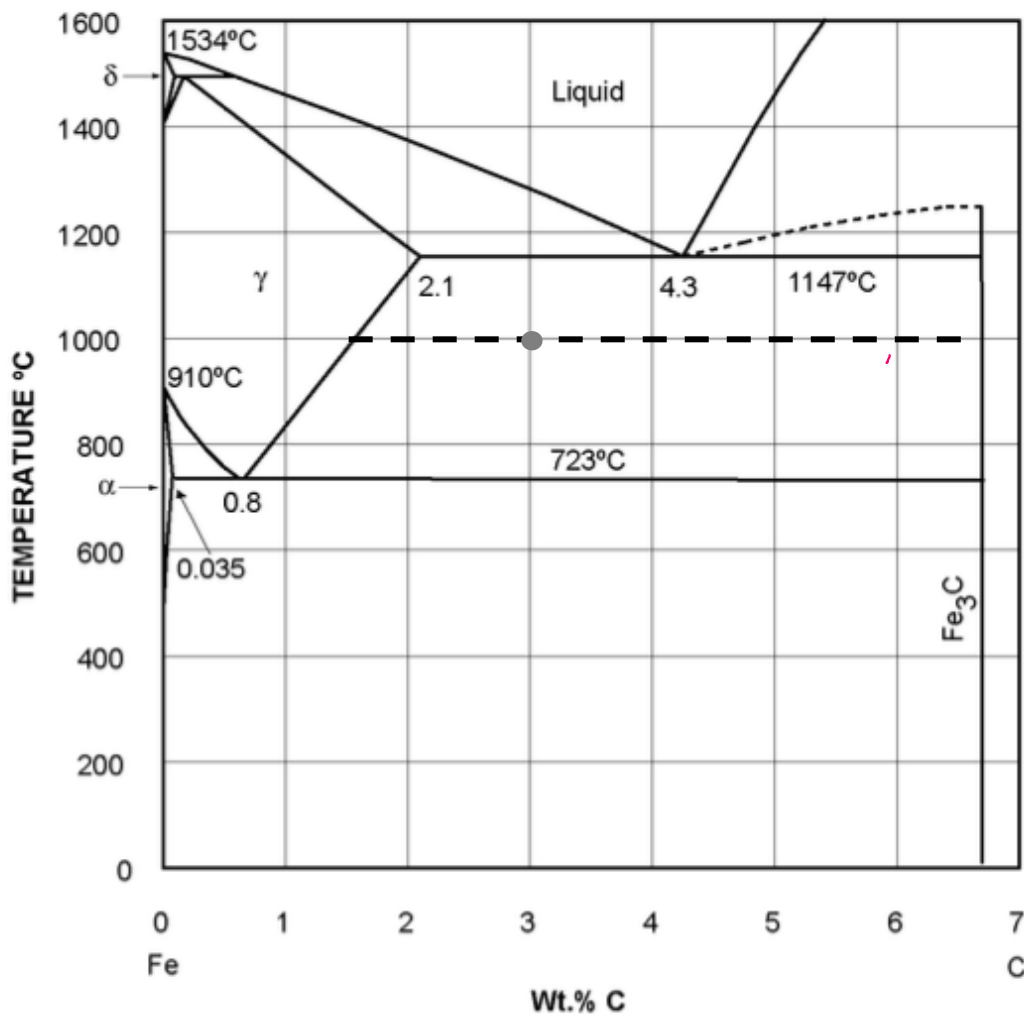
Volume is mass / density, so the volume of Chromium removed is $0.0152 / 7150 = 2.13 \times 10^{-6} \text{ m}^3$.

As the area in question is 1 square metre the thickness of chromium metal that has corroded is thus $2.13 \text{ } \mu\text{m}$.

294 attempts, average 66%

Generally, well answered. Very few diagrams were well drawn and labelled clearly, and this is where most marks were lost by candidates. Many explanations were overly wordy and unclear. There was again a tendency to 'dump' irrelevant sections of notes into answers.

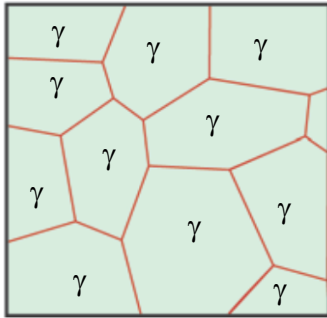
- 2) i) On the version of the Fe-C diagram in the data book we see a eutectoid at 0.8% and 723 degrees C, a eutectic at 4.3% and 1147 degrees C and a peritectic (delta and liquid) at 1500 degC and 0.3 %.
- ii) Draw a tie line at 3% and 1000



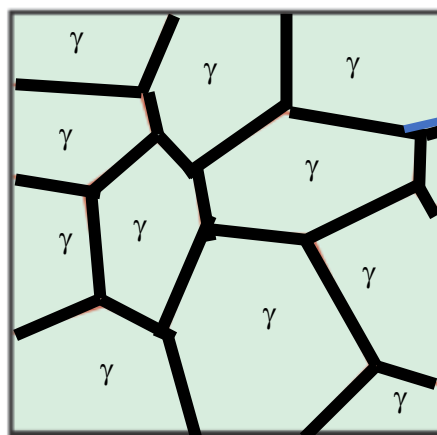
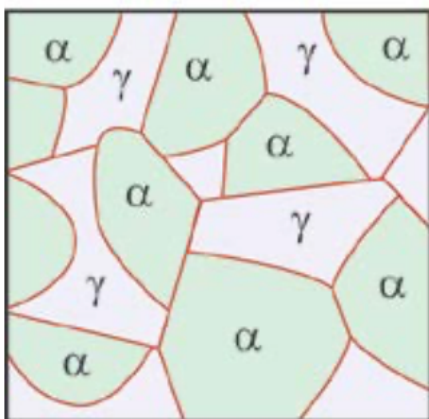
Looking at the tie-line drawn on the phase diagram. The total length is 5%. So proportion of austenite is $3.6/5 = 72\%$ and that of Fe₃C is 28%. The Fe₃C is 6.8% carbon and the austenite is ~1.5% carbon (from the point the tie line touches the edge of the phase).

From lectures candidates will know that in reality cast iron contains non equilibrium graphite inclusions.

b) i) The two steels are hypo – and hyper- eutectoid so they behave differently on cooling. However initially at 1000 deg C the microstructure is purely austenite in both cases.

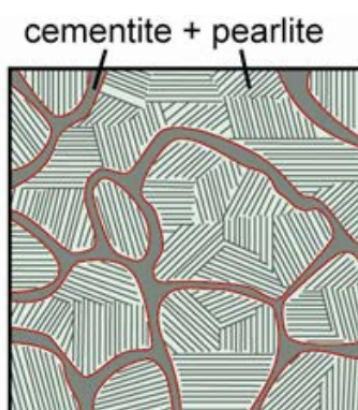
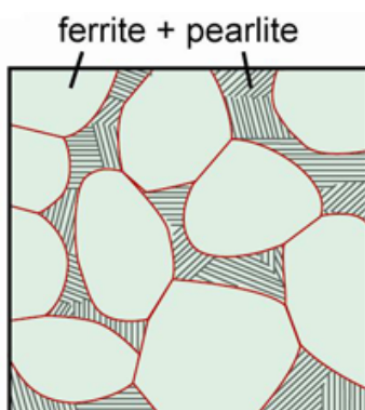


As the temperature drops in the 0.4% case ferrite grains start to form, in the 0.9% case Fe_3C starts to form. As the tie lines are rather different rather larger ferrite grains are formed in the 0.4% case than the size of the grains of cementite .

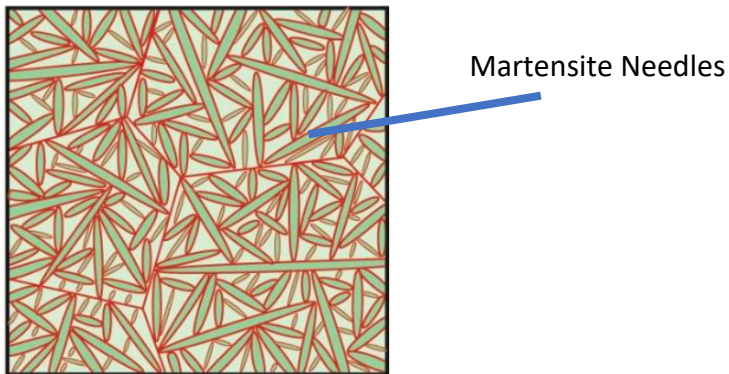


Fe_3C forming at γ grain boundaries

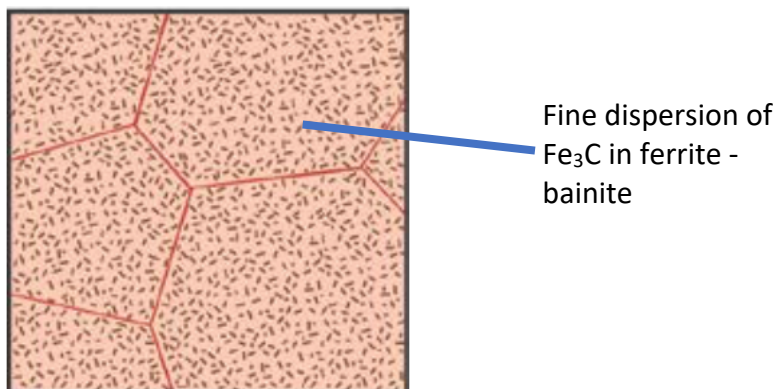
Finally, as we drop through the eutectoid temperature any remaining austenite forms pearlite. There is then very little change to room temperature, any ferrite present rejects a small amount of carbon. We are left with ferrite and pearlite for the hypo-eutectoid case and pearlite and cementite for the hyper-eutectoid case.



ii) Quenching – no time for diffusions – displacive martensitic transformation to give lenticular martensite. The transformation for 0.4% steel is complete as the martensite finish temperature is above room temperature, although candidates won't necessarily know this. When C concentration increase candidates should know that the martensite finish temperature drops so the likelihood of there being retained austenite increases.



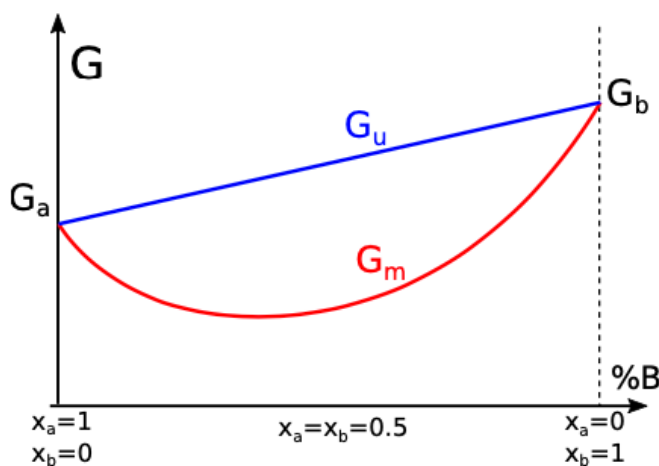
iii) From knowledge of the course, or refreshing memory from TTT diagrams in the databook for the steel given the temperature given is going to be below the start of the carbide line so bainite will form. This is a fine dispersion of Fe_3C in ferrite since diffusion is too inhibited to permit formation of the pearlite microstructure.



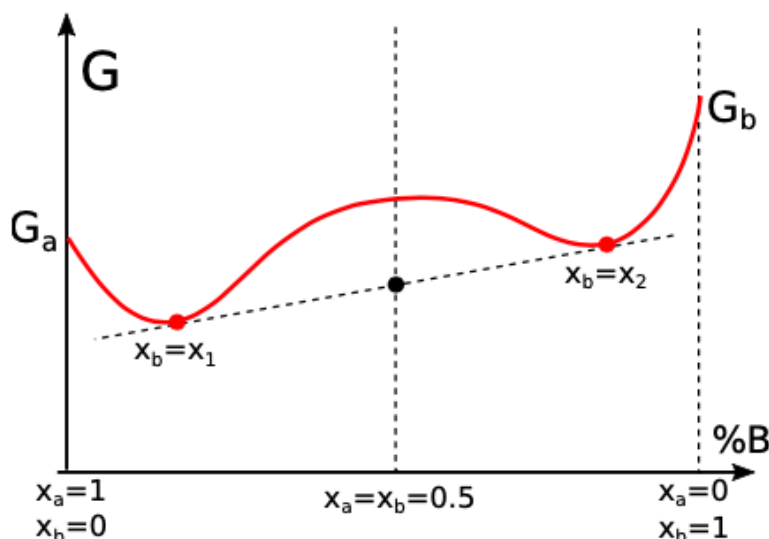
3) 53 attempts, average 62%

Part ai) challenged many candidates who failed to clearly explain the contribution of enthalpy of mixing acting in opposition to the effect of the entropy inherent in the mixing of non-interacting particles. Part aii) was generally well answered although many diagrams were poor and did not clearly identify clear features. Responses to part b were mixed. Some candidates had clearly thought through the scenario carefully and had good explanations. Other candidates struggled to answer this scenario based question as, rather than thinking through the question, they attempted to identify chunks of notes to reproduce. Suggestions for how the metal disk caused nucleation which were incorrect but plausible and showed understanding received full marks.

For non-interacting materials the free energy purely depends on entropy – $S = k \ln \Omega$. The number of ways of ordering is maximised for equal mixing (all other factors being equal) so something like the below would be expected:

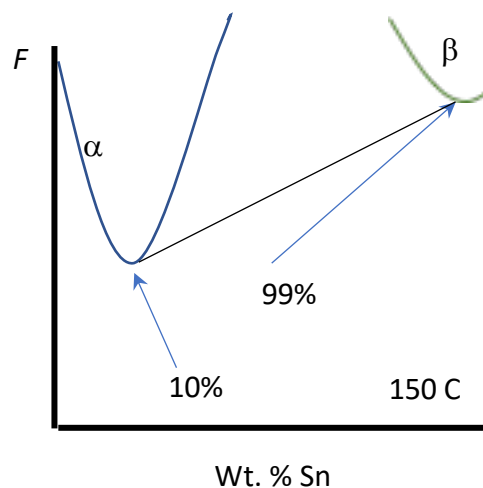
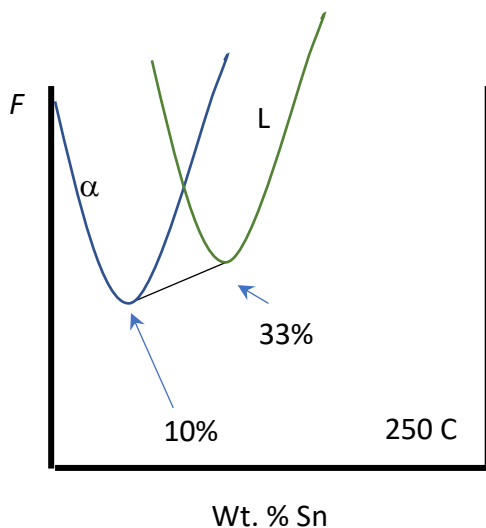
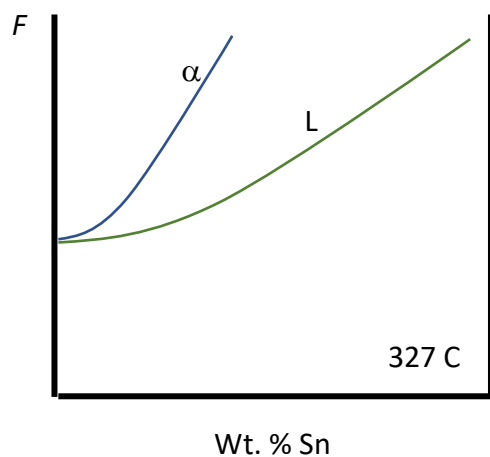


Where G_m is the free energy of the mixture. A complication arises, since when some substances interact there can be an interaction. This gives rise to an “enthalpy of mixing” term in the free energy leading to a double minimum.



Here the overall free energy is minimised for compositions between x_1 and x_2 by having a mixture of phases of the x_1 and x_2 compositions, in this case the overall free energy follows the common tangent.

ii) At each point a correct answer has curves that will reproduce the observed behaviour of the phase diagram. At 327 C the curve for alpha and liquid should meet but the liquid line should then be lower. At 250 C there are two phases present, the beta phase can be drawn with a free energy above the liquid and the alpha, or omitted. The tangent should join the curves at ~12 wt% and ~33 wt. % to reproduce the observed two-phase region. At 150 the 2 phase region between alpha and beta is more larger so the common tangent should run from 10 wt% to ~99 wt. %.



b) This question requires no previous knowledge of how the item described works. It can fully understand by reading the description of the behaviour and applying knowledge of nucleation.

i) We are told that heat is emitted as the liquid solidifies. The liquid is therefore in an undercooled state, when nucleation is triggered it starts due to the shock waves generated by the disc and slowly proceeds through the material. As the liquid is viscous the kinetics of the process is slow. The energy released is the heat of crystallisation of the material from liquid to solid. Once all the liquid has solidified there is no more free energy available to emit as heat.

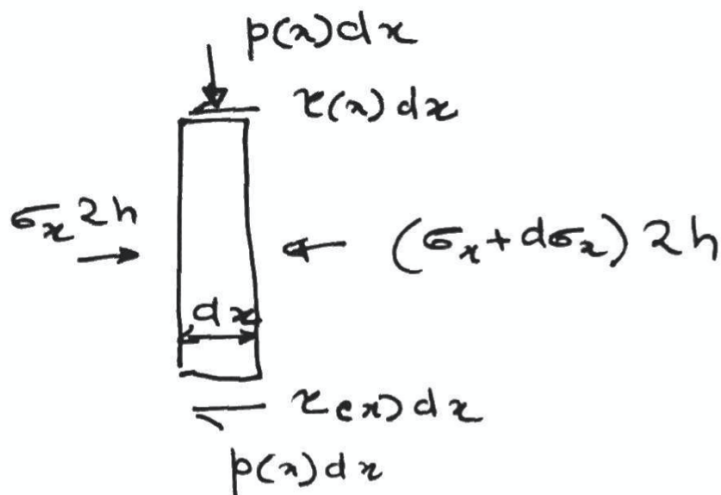
- ii) The material is originally supercooled, it can only remain liquid due to the lack of a homo- or hetero- genous nucleation centres. Once the disc generates nucleation there are plenty of homogenous nucleation sites available, these can't be removed so the solidification process must proceed.

- iii) To reset we need to warm above the melting point of the solid (or more correctly the point at which the contents dissolves in its own liquid of crystallisation – knowing this distinction is not required for full marks). It is critical that no small elements of solid remain otherwise on cooling the handwarmer will immediately trigger. The warmer therefore needs to be thoroughly warmed through.

- iv) Full marks for any two . If there is an impurity in the liquid, such as dust etc, this could act as a heterogenous nucleation centre without the metal disc being triggered. This could also apply if the plastic or metal contents were not smooth and themselves provided nucleation sites. Another issue would be if the manufacturer had got the composition of the filling wrong such that at room temperature the critical radius is small enough for spontaneous homogenous nucleation to occur.

4) 231 attempts, average 62%

The analysis of forging loads was done well by most candidates. This calculation is familiar from the lecture notes, so almost all got the steps entirely correct. More discriminating was the critical discussion on model validity and assumptions. This made the question sufficiently challenging in an open book context. A major source of lost marks was poor or absent discussion on these points. Part (d) didn't score well overall. Many candidates reproduced standard points on the general features of the forging process (or even rolling processes, not covered here), or annealing of metals, rather than addressing the specific question on the suitability of the model.



For $x > 0$ $(\sigma_x + d\sigma_x)2h - \sigma_x 2h + 2 \tau dx = 0$. Thus: $d\sigma_x/dx = -\tau/h$ and therefore: $d\sigma_x/dx = -m\sigma_y/2h$

b) By the Tresca criterion: $p - \sigma_x = \sigma_y$, so $dp/dx - d\sigma_x/dx = 0$. Using the equilibrium equation we then have that $dp/dx = -m\sigma_y/2h$

The boundary condition is that $\sigma_x = 0$ at $x = w$ so given the yield criterion $p - \sigma_x = \sigma_y$ we have $p = \sigma_y$ at $x = w$

So

$$\int_{p(x)}^{\sigma_y} dp = \int_x^w -\frac{m\sigma_y}{2h} dx$$

Solving:

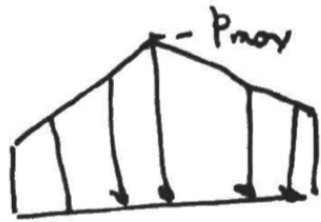
$$p = \sigma_y \left[1 + \frac{m}{2} \left(\frac{w-x}{h} \right) \right] \text{ for } x \geq 0$$

And similarly:

$$p = \sigma_y \left[1 + \frac{m}{2} \left(\frac{w+x}{h} \right) \right] \text{ for } x \leq 0$$

The assumption that σ_x is uniform is indeed valid in the centre of the bar when $w \gg h$. However, this breaks down near the surfaces as we would expect a bulge to form.

c)



$$P_{max} = \sigma_y \left(1 + \frac{mw}{2h}\right)$$

$$p_{average} = \frac{1}{2w} \int_{-w}^w p(x) dx$$

So

$$p_{average} = \sigma_y \left[1 + \frac{mw}{4h}\right]$$

So Force per unit depth is

$$F = 2wp_{average} = 2h \left(\frac{w}{h}\right) \sigma_y \left[1 + \frac{mw}{4h}\right]$$

As w/h is 6 and $m=0.1$ $F = 13.8 h \sigma_y = 276 \times 10^6$ N/m

d) The above analysis assumes an ideally plastic solid with no work hardening. Annealed Cu will strongly work harden and thus the analysis will significantly underestimate the forging force.

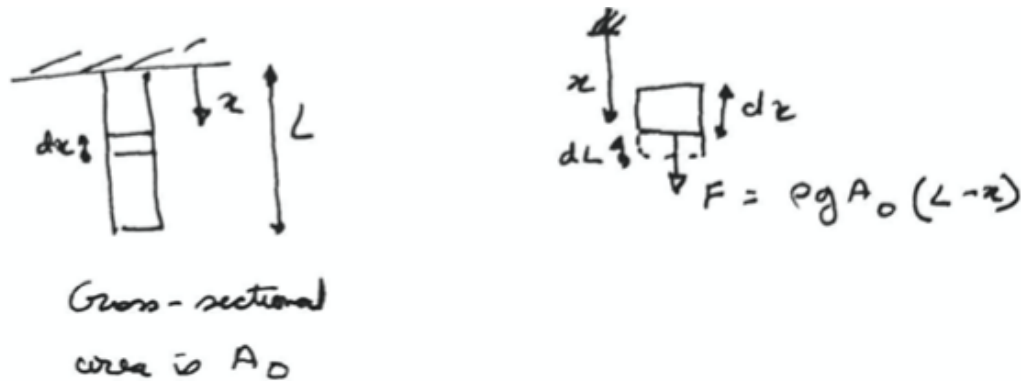
5) 222 attempts, average 61%

The analysis of the creep of a hanging rod due to self-weight loading was done well by most. A common error was to neglect the fact that the stress varies along the rod. Many could also answer the discussion on creep mechanisms well. It was perhaps too conventional in an open book context. A tough mark scheme was therefore required, with fully accurate and detailed answers needed for full marks. Lost marks were most often due to missing one of the two creep mechanisms. The discussion in part (c) on adapting the model to longer creep times was more discriminating, with many not providing much in the way of detail.

a) At low stress, atoms diffuse from grain boundaries parallel to grain boundaries perpendicular to applied stress resulting in grain and specimen elongation. The diffusion can be either along the grain boundaries or through the bulk.

b) Alloying elements such as Co, W, Cr, Al and Ti give solid solution and precipitation hardening impeding dislocation motion and thus reducing power-law creep. Processing by casting as a single crystal means there are no grain boundaries to allow diffusional flow.

c)
i)



$$\sigma = F/A_0 = \rho g(L-x)$$

$$\begin{aligned} \dot{\epsilon} &= \dot{\epsilon}_0 \left(\frac{\sigma}{\sigma_0} \right)^n \\ &= \dot{\epsilon}_0 \left(\frac{\rho g(L-x)}{\sigma_0} \right)^n \end{aligned}$$

$$E = dL/dx \text{ and } \dot{\epsilon} = dL/(dt \, dx)$$

So:

$$\begin{aligned} \frac{dL}{dx} &= \int_0^L \dot{\epsilon}_0 \left[\frac{\rho g(L-x)}{\sigma_0} \right]^n dx \\ &= \dot{\epsilon}_0 \left(\frac{\rho g}{\sigma_0} \right)^n \int_0^L (L-x)^n dx \\ &= \left[-\frac{\dot{\epsilon}_0}{(n+1)} \left(\frac{\rho g}{\sigma_0} \right)^n (L-x)^{n+1} \right]_0^L \end{aligned}$$

$$= -\frac{\dot{\epsilon}_0}{(n+1)} \left(\frac{\rho g}{\sigma_0}\right)^n (L)^{n+1}$$

ii) As the bar creeps the cross-sectional area changes. Necking may occur, creep rupture may also occur.

Not required but in terms of fixing the up the equation - incompressibility means $A=A_0(1+\epsilon)$ and we will need to modify σ to $\sigma = \rho g(1+\epsilon)(L-x)$ and repeat analysis.

6) 151 attempts, average 60%

This question, although less analytical than Q4 and Q5, worked well in an open book context as there were non-standard discussion questions applying knowledge from across the course to unfamiliar contexts (for example the aircraft skin, and the accidentally over-aged rivets). It also spanned topics, touching on polymers and heat treatment of metals. This challenged many candidates, with a lot of short or incomplete answers. Many also padded their answers with a lot of correct but irrelevant details from the notes. Most candidates could discuss the key features of thermosets and elastomers. A common mistake was to talk about thermoplastics instead. Marks were also lost by confusing concepts in the heat treatment of aluminium alloys and steels. A more generous mark scheme was introduced, but the average remained on the low side.

i) For an elastomer the value of 3 GPa at -200 degC results from van der Waals bonds since -200 degC is well below T_g . Above T_g at room temperature these van der Waals bonds “melt” and elasticity is mainly associated with entropic forces that tend to keep the polymer chains coiled. These entropic forces are small, hence the much lower modulus.

By contrast the elasticity of a thermoset is mainly due to cross linking (covalent bonds) and the van der Waals bonds that “melt” at T_g contribute little to the overall modulus. Thus, the Young’s modulus of a thermoset is weakly dependent on temperature.

ii) The high-strength of cold drawn Cu is caused by a high dislocation density resulting from work-hardening. Annealing results in recrystallisation and a reduction in dislocation density and hence a reduction in yield strength.

b) Al-Cu alloys strengthen by a precipitation process where a 2nd phase of finely spaced particles forms. Holding the alloy at a fixed elevated temperature is referred to as ageing of the alloy. First, solute atoms of the Al-Cu solid solution begin to cluster by diffusion forming nuclei of the 2nd phase. The strength increases are modest as the small precipitates offer little resistance to dislocation motion. As the number and size of these precipitates increases the force required to move dislocations past these precipitates increases and consequently yield strength increases with ageing time. Eventually it becomes easier for dislocations to bypass precipitates. Further ageing then causes precipitate growth which reduces spacing and thus strength falls. An alloy that has been aged beyond the peak strength is “over-aged” and below that “under aged”.

Aircraft skins operate for extended periods above 100 degC, and supersonic aircraft experience more skin heating due to air friction as speed increases. This heating can result in over-aging and strength decrease. Using under-aged material prevents this from occurring.

c) Heating, to sufficiently high temperature, of the rivets can dissolve the theta phase precipitates in the Al alloy and give a single phase solid solution. Hence rivets should be heated to 550 degC (see Al/Cu phase diagram in databook) and quenched to form a supersaturated solid solution. They can then be appropriately aged.