2016 1B Materials Paper Crib

Q1) "Entropic Forces"
a) i) If heated up to a moderate temperature above a certain level of strain new crystals grow in the material replacing the original strained grains. By growing un strained crystals containing fewer dislocations the free energy of the system is reduced.

ii) If a semi-permeable membrane separates a less concentrated and more concentrated solution the solvent will tend to flow through the membrane so as to increase the pressure on the initially more concentrated side. This process is driven, in the dilute limit, by the change in the entropy of mixing as solvent flows across the membrane. As the solution becomes more dilute the system becomes more disordered as there are more ways of arranging the solute in the solvent.

iii) In over aging the precipitates tend to become larger and less numerous. This is driven by the reduction in free energy observed by minimising the surface energy, this occurs for larger precipitates as the surface energy varies as the square of precipitate size whereas the volume free energy which is opposite in sign goes as the cube.

iv) Displacive transformation of austenite to martensite driven by the relative free energies of γ and α' at room temperature.

b)
i)[Non Derivation] When we stretch the spring we reduce the number of possible configurations and thus reduce the entropy of the system. We can restate the first law as

$$TdS = dU - fdr$$

so ds/dr is negative which means f is positive

$$f = -T\frac{\partial S}{\partial r}$$

Which implies that reducing the entropy of the system must imply an increase in force.

[Derivation – not asked for but accepted] We can rewrite the 1st law as:

$$TdS = dU - fdr$$

and from this write an equation for the force on the polymer chain as U does not depend on r.

$$f = -T\frac{\partial S}{\partial r}$$

From reasoning for the previous question

$$\ln \Omega_c \approx -\frac{r^2}{2na^2} + n\ln 2$$

and

$$S = k_B \ln \Omega_c$$

so

$$f = \frac{k_B T}{na^2} r$$

ii) The U and PV terms in the free energy will remain more or less constant. Consequently most of the change in the free energy comes form change in the entropy of the system as the number of available arrangements changed. This is multiplied by the temperature in the TS term Consequently a higher temperature will result in a quicker change in free energy and thus larger slope and larger restoring force.

iii) Joints between elements are not pin joints – some elastic energy from deforming the chain. Side chains can cause steric hindrance and reduce the number of configurations available. Real case is 3D – more possible configurations.

[This question, reflecting new material this year, was both not popular and very poorly attempted with the exception of parts (a i,ii and iv). A small minority of candidates, however, provided excellent solutions. Answers to part (a,ii) indicated that most candidates did not understand the entropic origin of osmosis and thought it was driven by equalisation of concentration.
In part (b,i) many candidates referred to bond stretching or change in internal energy rather than change in configurations on stretching. In (b,ii) a very large number of candidate confused a single polymer chain's properties with the young's modulus of a bulk polymer. Part (b,iii) was much better answered with most candidates providing reasonable answers, although again many were confused and talked about interactions between multiple chains.]

2) "Corrosion"

a) i) Aluminium is more electronegative but this does necessarily affect reaction rate. In damp conditions iron reacts with oxygen and water to form a porous oxide that does not prevent further oxidation. In contrast aluminium rapidly forms a thin layer of alumina. As the diffusion rate of oxygen in alumnia is very low this protects against further corrosion.

ii) The three modes are linear loss where oxide formed is removed, linear gain where oxide formed but does not prevent further oxidisation and parabolic where the growing oxide prevents oxygen reaching the metal. Consequently as time goes on the reaction rate slows due to lack of oxygen. Aluminium follows the parabolic model as the oxide is impermeable. Iron follows the linear gain model.

iii) Methods for protecting steel need to disrupt some part of the electrochemical reaction. Coatings such as paint or plastic prevent oxygen and water from reaching the steel. There are also electrochemical approaches that use a sacrificial material to reduce the effective electrochemical potential of the steel, or indeed an impressed current can be used to achieve this. Steel can be galvanised with a material which is sacrificial such as zinc. Alternatively can alloy with, say, chromium which forms a hard oxide like that in aluminium. This is self-healing which is a significant advantage. Steel can also be passivated by using conditions that encourage a hard oxide to form magnetite – although oil is also required for full protection. Other chemical coating methods exist for steel. It cannot – however – be anodised as anodization is the growth of a thicker native oxide. In the case of steel this would not be a good thing.

b)i) Stainless steel – the Ni is there to stabilise the gamma phase and the Cr reacts quickly to form an impermeable Cr_2O_3 layer that protects from rust. The Cr is more reactive than the iron or Nickel so the Cr_2O_3 forms first.

ii) Fresh SS the oxygen can freely reach the surface so we have linear gain rate is limited by reaction rate. After the oxide layer has reached a certain thickness the mass gain model changes to parabolic as now the diffusion of oxygen through the chromium oxide film is the rate limiting step.

iii) Relationship is parabolic so (al little simplistically) $h(t)=Ct^{1/2}$ note similarity to diffusion result where diffusion depth is sqrt(Dt). Indeed in practice the C here would be found to be D^2 where D is the diffusion rate of oxygen in Cr_2O_3 (very low !). Using the given conditions of 7 days and 2nm we can determine D. From this we can then work out what h(t) will be after a year. In this case C=2nm/(7*24*60*60)^2 which is 2.57×10^{-12}. So ~14nm. In reality the growth of the oxide layer is more complex than simple parabolic and the layer thickness may be less.

[This question was generally well answered, especially (a,ii), with the exception of (b,iii) where a significant minority of candidates having correctly identified the parabolic nature of the time dependence of the thickness of the oxide layer then failed to apply this a relatively simple calculation.]

3) "Phase Diagrams and Al age hardening"

Ai) Point A. One phase present 100% alpha. Composition is 3% Cu.
Point B two phase alpha (4%) and Liquid (15%). Composition is 10% Copper. Proportions from lever rule is ~ 2/3rds alpha and 1/3 liquid.
Point C is Liquid single phase 33% copper.

ii) A: Sketch should show alpha matrix and $CuAl_2$ inclusions

B: Sketch should show combination of alpha primary grains with $CuAl_2$ inclusions. Should also contain smaller number of grains showing eutectic composition (which formed from the liquid present just above the eutectic temperature)
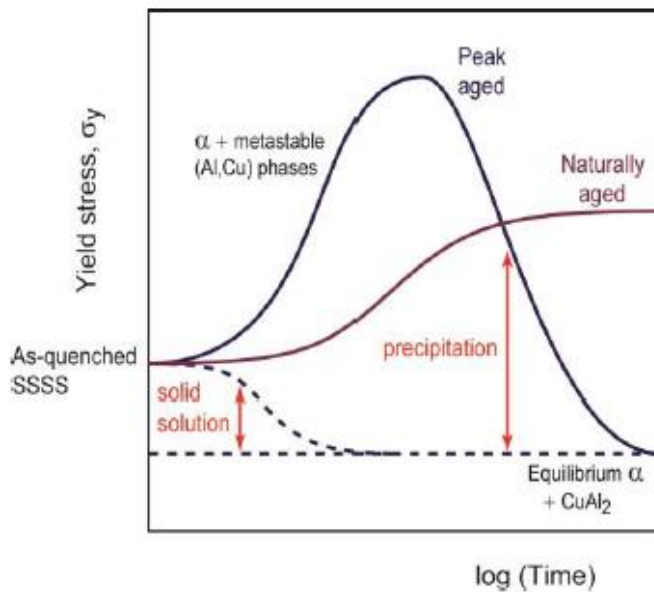

C) Purely Eutectic microstructure showing lamellae of alpha phase and $CuAl_2$
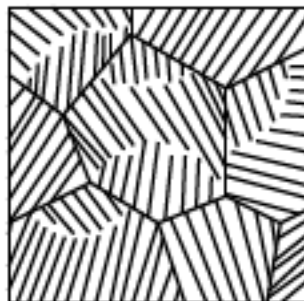
b) i) The slow cooled sample reaches equilibrium As at RT the solubility of $CuAl_2$ in alpha phase Al is very low the $CuAl_2$ initially present in the solid solution precipitates out. The fast cooled sample has no time for $CuAl_2$ to precipitate out before diffusion slows too much for this to happen. Result is a supersaturated solid solution.

ii)

Yield stress, σ_y

Peak aged

α + metastable (Al,Cu) phases

Naturally aged

As-quenched SSSS

precipitation

solid solution

Equilibrium α + CuAl$_2$

log (Time)

Slow cooled sample is lower dotted behaviour. You can't get any more equilibriated than equilibrium. In the SSSS first G-P zones form this reduces SS hardening but adds precipitate hardening. Initially the precipitates are coherent and can't be bypassed. As they grow this increases the pining. Eventually the precipitates become incoherent and bypassing becomes possible/preferable. As the precipitates gets larger yet fewer in number the resultant contribution to precipitation hardening reduces.

[Generally well answered although a significant minority of candidates applied the lever rule to single phase fields in (a,i). In (a,ii) many candidates thought that the CuAl$_2$ would form entirely at the grain boundaries and many sketches were poor and unlabelled. There were confusions with the Fe-C system in many answers. In (b,ii) a significant proportion of candidates thought that equilibrated aluminium would still age harden significantly.]

Section B
4. "Metal and polymer processing and microstructure"
(a) Correct: segregation is the non-uniform distribution of solute in a casting.
Incorrect: that it is due to faster nucleation nearer the mould walls (which is the explanation for formation of a fine-grained chill zone).

Correct interpretation: the "partition" of the liquidus and solidus lines means that when a given alloy composition solidifies into the two phase solid+liquid region, the first solid to nucleate is purer than the alloy average composition. Equilibrium requires that the concentration of the solid rises as temperature falls, but diffusion is too slow in the solid for diffusion to occur back to the centre of the growing grains. A concentration gradient forms, rising from the centre as solidification proceeds outwards. This applies at both grain scale within the casting (microsegregation) and on the scale of the casting itself (macrosegregation).

(b) Correct: as-quenched non-heat-treatable Al alloys are of average strength
Incorrect: that a quench leads directly to an equilibrium microstructure; recovery is irrelevant in this context.

Correct interpretation: quench avoids any equilibrium precipitation of non-hardening phases, leaving a metastable supersaturated solid solution (of average strength, due to solid solution hardening). No metastable precipitation occurs subsequently at room temperature (which is only the case for heat-treatable Al alloys).

(c) Incorrect: corrosion is irrelevant in this context (it is stainless steels that are made corrosion resistant using Cr).

Correct interpretation: Ni and Cr increase the hardenability of carbon steel, meaning that martensite may form readily on cooling after welding, leading to failure by brittle fracture.

(d) Correct: the cooling rate is lower in the larger bar, and the hardness will be higher – but not for the reason given.
Incorrect: the quench will not lead to alloy carbides, but the formation of martensite in the low alloy steel.

Correct interpretation: low alloy steel is a carbon steel (of similar wt% C to the medium C steel) but has higher hardenability than the plain C case, i.e. martensite forms readily, and can subsequently be tempered. This is in spite of the fact that the cooling rate at the bar centre is slower than in the (smaller diameter) medium carbon steel. In the medium carbon steel, the faster cooling rate leads to ferrite and pearlite at the bar centre, which cannot be tempered, giving a lower hardness. Alloy carbides will form, together with iron carbide, during tempering of the low alloy steel, enhancing the tempered hardness.

(e) Correct: Stretch blow moulding of thermoplastics does increase the strength (and the thinner section will cool faster – but this has no effect on strength). It is also true that the explanation given does not apply to fibre drawing.
Incorrect: Strengthening does not come from spherulite formation (crystalline regions).

Correct interpretation: Strengthening comes from alignment of the polymer molecules during moulding ("orientation strengthening"), utilizing the covalent backbone of the long-chain molecules. Thin sections give faster cooling which avoids or minimizes spherulite formation (crystalline regions requiring slower cooling rates, and these are often deliberately minimized in stretch blow moulding where the amorphous structure is needed for transparency). The same applies to fibre drawing – molecular alignment of molecules is the main source of strengthening. There a cooling effect due to the section being thin – to "lock in" the alignment of the molecules.

[A different question structure was trialled: statements were given with errors to identify, explain and correct (aiming to reduce pure recall, but increase interpretation). The average mark was much the same as usual, but it did produce more high quality answers. Low quality answers were characterised by: (i) simple failure to do what the question asked; (ii) parroting long answers to (different) past paper questions; (iii) inability to distinguish between material classes; (iv) poor knowledge of nomenclature/basic physics (e.g. "low alloy" taken to mean "low carbon", "supersaturated" not considered to be metastable, "diffusion of precipitates" etc).]

5.   "Composite failure"

(a) Uniaxial:

- parallel to fibres: strong direction, but weaker in compression (fibre buckling) than tension (fibre failure);
- perpendicular to fibres: much weaker than parallel to fibres, with matrix fracture in tension (from flaws or fibre-matrix interface), and somewhat stronger crushing/yielding in compression.
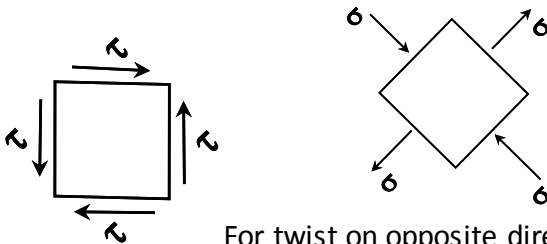
Biaxial:

- same strength in 2 perpendicular directions; tensile failure dominated by fibre strength (now in only half the cross section); compressive failure determined by buckling of fibres (ditto). Transverse plies make little contribution, cracking in tension and carrying negligible load.

(b) (i)   Structures Databook: $q = \tau t = \dfrac{T}{2A_e}$ where $A_e = \pi r^2$. Hence $\tau = \dfrac{T}{2\pi r^2 t}$

(Alternatively, use $\dfrac{\tau}{r} = \dfrac{T}{J}$ with $J = 2\pi r^3 t$ for a thin-walled cylinder).

(ii)   Pure shear, aligned with shaft axis: Biaxial tension/compression at 45°:

For twist on opposite direction, reverse shear stresses, and exchange tension and compression in the biaxial case at 45 °. Hence fibre winding at ±45° aligns the fibres with pure tension and compression, the strong orientations of the composite, maximizing the failure torque.

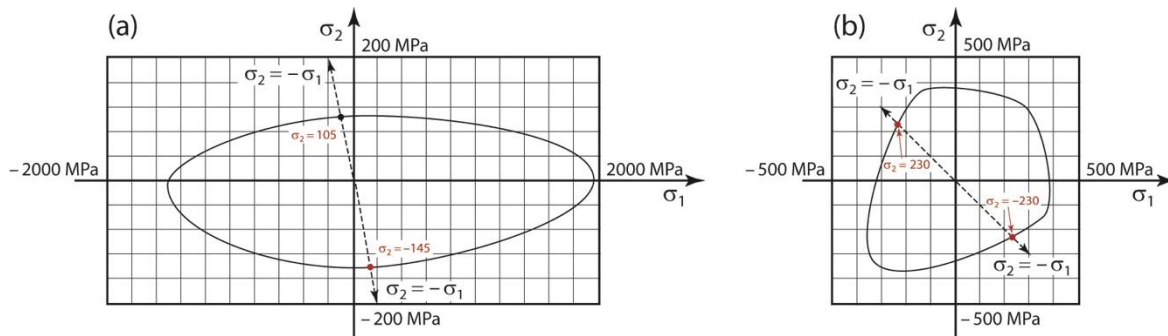(iii) For unidirectional case, from Fig (a) below:
Failure stresses σ_2 = 105 or −145 MPa. Hence the magnitude of the shear stress for twisting in each of the 2 directions are τ = 105 and 145 MPa.
Substituting r = 40mm, t = 4mm and rearranging, failure torques = 4.2 and 5.8 kNm (2 s.f.'s)

(iv) For biaxial case, from Fig (b) below:
Failure stress is the same in both directions of twist: $\sigma_2 = \tau$ = 230 MPa.
Substituting r = 40mm, t = 4mm and rearranging, failure torque = 9.2 kNm (2 s.f.'s)

(a) Failure envelope, axes σ_1 (−2000 MPa to 2000 MPa) and σ_2 (−200 MPa to 200 MPa), with lines $\sigma_2 = -\sigma_1$, and points $\sigma_2 = 105$, $\sigma_2 = -145$.

(b) Failure envelope, axes σ_1 (−500 MPa to 500 MPa) and σ_2 (−500 MPa to 500 MPa), with lines $\sigma_2 = -\sigma_1$, and points $\sigma_2 = 230$, $\sigma_2 = -230$.

(v) Bending generates axial tension and compression. Include fibres oriented parallel to the shaft axis (not very easy in filament winding). Alternatively, if the torque and bending scale together, then a new optimum fibre orientation could be found, more closely aligned with the shaft axis.

[Students described composite failure well (though many omitted to discuss the biaxial case). Most managed the basic stress analysis reasonably well, but not use of the failure surface: for the biaxial case $\sigma_1 = -\sigma_2$, more than half took the failure stresses in pure tension and compression and said the lower magnitude was limiting (i.e. completely missed the point of the failure surface). More nomenclature issues: "fibres" discussed as if they were polymer molecules (blurred with "fibre drawing" in Q4), and composite failure referred to in terms of "yield stress", "yield surface".]

6. "Forging analysis"
 (a) (i)   For either half of the block, resolve forces horizontally (for unit depth):

$$\sigma_{max} \times 2h = 2 \times k \times w$$

Hence $\sigma_{max} = k\,w/h$

(b) Assume σ and p are principal stresses (i.e. ignore effect of $\tau = k$ on size of Mohr's circle).
Also assumes plane strain (zero out-of-plane strain, and corresponding stress intermediate).
Then by Tresca criterion: $\left| p - \sigma \right| = Y = 2k$

Hence at $x = 0$, $p_{max} = k(2 + w/h)$ (where $\sigma_x = \sigma_{max} = k\,w/h$),
and at $x = \pm w$, $p_{min} = 2k$ (as at free surface $\sigma_x = 0$).

(c) With linear "friction hill" between these extreme values of pressure:
$$p_{average} = (p_{max} + p_{min})/2 = k(2 + w/2h) = Y(1 + w/4h)$$

(d)   The longest dimension = 120mm is the out-of-plane dimension, so the in-plane dimensions are 2w = 60mm, 2h = 1mm.   Substituting for w and h:

$$p_{average} = 50 \times (1 + 30/4 \times 0.5) = 800 \text{ MPa} \text{ (16 times the yield stress)}$$

The average pressure is more than an order of magnitude greater than the uniaxial yield stress – the load is unnecessarily high, requiring a very large machine (or risking failure of the forging dies).

Fabrication from cold rolled sheet has several advantages:
- viable process route: rolling sheet to 1mm is routine, and easy to cut blanks to size, and form to shape;
- lower cost, as standard thickness sheet produced in bulk, and case blanks stamped out of sheet at speed;
- cold rolling enables work hardening to be used to strengthen the alloy, compared to softer hot forged state (potentially allowing thinner case to be manufactured);
- cold forming will give better accuracy and surface finish;
- cold forming avoids energy cost of hot forming processes.

(e)   The forging analogy with rolling shows that the friction hill (and thus pressure distribution) increases strongly with friction coefficient. Lubrication reduces friction between the rolls and the foil, reducing the friction hill and thus the rolling loads, torques and power.

Rolling two sheets simultaneously halves the aspect ratio w/h of the deforming region, reducing the pressure (as indicated by the factor $1 + w/4h$ in the analysis above), and hence also reducing the rolling load, torque and power. Also doubles the production rate from the last rolling pass.

[Not expected in exam, but note that this also explains why foil has a shiny side – the side in contact with the smooth rolls – and a matt side – the contact face between the two sheets, which are easily peeled apart after passing through the roll gap].

[Parts (a) to (c) sorted out those that understand concepts (here yield criteria) from those that just do maths without thinking – many students re-derived the full differential solution from the notes, when the question had deliberately prompted the simple thinking needed to produce the results in a few lines. These students also tended to integrate to find the average value of a linear variation between two known end values. Generally good discussion of rolling practicalities in parts (d, e).]