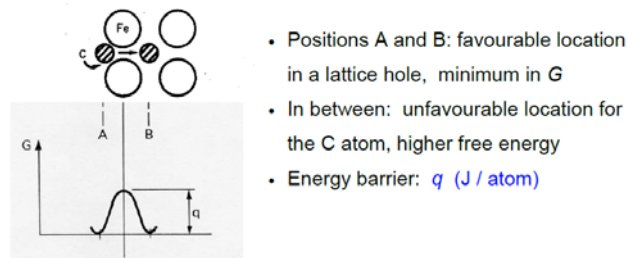


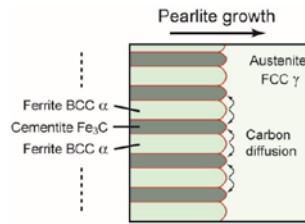
Question 1

(a) Particle diffusion is due to the random motion of particles caused by thermal fluctuation. In solids, diffusion follows Arrhenius law: $\text{rate} \propto \exp\left(-\frac{Q}{RT}\right)$, where Q is the activation energy, R is the gas constant and T is the temperature (in Kelvin). The physical basis of Arrhenius law is such that, atom vibrate at high frequency about equilibrium locations (A and B in the diagram below) where their free energy G is minimum. Atomic ‘jumps’ between locations must overcome a free energy barrier, q (J/atom). There is a statistical distribution in the energy per atom, such that the probability p of an atom having an energy greater than q is: $p = \exp\left(-\frac{q}{kT}\right)$. This temperature-dependence controls the rate of diffusion. $Q \sim N_a \cdot q$, where N_a is the Avogadro constant.



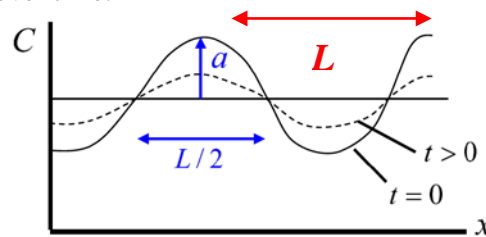
(b)

- (i) Polycrystalline nickel alloy has a high density of grain boundaries whereas nickel alloy single crystal does not have any grain boundaries. Grain boundaries have loose packing of atoms (thus a high density of vacancies) which allow faster atomic diffusion than other diffusion mechanisms within the grain.
- (ii) Carbon has a much smaller atomic size than iron, while nickel has a similar atomic size to iron. Thus, carbon diffuses *via* interstitial diffusion, while nickel diffuses *via* substitutional diffusion. Thus less activation energy, is required for carbon to diffuse than nickel in the iron lattice.
- (iii) The oxide thickness of a surface oxidised silicon varies linearly with time at the short time scale, and \sqrt{t} at the longer time scale. Once an initial oxide is form, the rate limiting factor becomes the diffusion of oxygen from the external atmosphere through this oxide layer (which acts as a barrier), to the ‘fresh’ silicon underneath the oxide for further oxidation. With the diffusion rate-limiting factor at longer times, the square root time dependence is as a result of the boundary conditions of constant oxygen concentration at the surface, zero oxygen concentration in the bulk of the silicon, and the assumption of 1D diffusion.
- (iv) The whole FCC lattice in the austenite regions (with 0.8wt% C in solution) has to transform into two new phases with different crystal structures and different carbon contents: ferrite (≈ 0 wt% C) and cementite (≈ 6.7 wt% C). Nucleation occurs from grain boundaries, with growth of the new lattice structures occurring simultaneously with the associated redistribution of carbon. The inter-lamella, plate-like microstructure of pearlite achieves this with minimum diffusion distances. The eutectic microstructure is finer-scale, since the temperature is now lower, atomic mobility is reduced, and the microstructural scale is strongly influenced by the kinetics of inter-diffusion of Fe and C, enabling transformation into two phases of widely different C contents. This process also allows to accommodate the phase transformation across large areas effectively.



(c)

- (i) Assumption: the segregated microstructure occurs similarly throughout the alloy; 1-D diffusion is used to simulate the change in solute concentration over time. Thus, one can model the homogenisation process using a sinusoidal distribution of solute, with time-dependent amplitude (i.e. amplitude ' a ' decreases with increased time). The wavelength L is an indication of the mean grain size. Area under the curve (i.e. total number of atoms) stays constant over time.



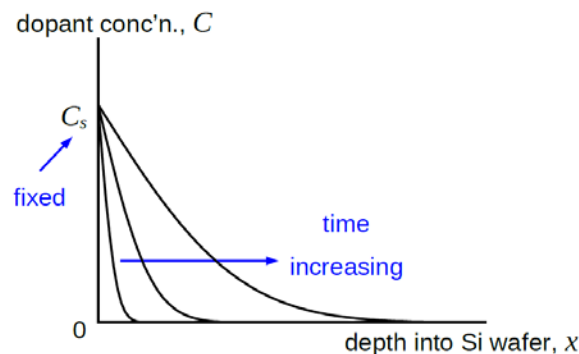
- (ii) In both cases, assumption of 1-D diffusion into the thickness of the film is made.

Pre-deposition: Dopant is diffused into the surface by maintaining a high concentration of dopant at the surface (from a gas, or a surface deposit).

Boundary conditions: fixed surface concentration thus $C(x=0,t) = C_s$; silicon wafers are hundreds of micron thick, doping depths of interest are typically less than several μm , thus $C(x \rightarrow \infty, t) = 0$.

Initial condition: $C(x, t=0) = 0$, assuming there is no diffused dopant in the substrate at time 0.

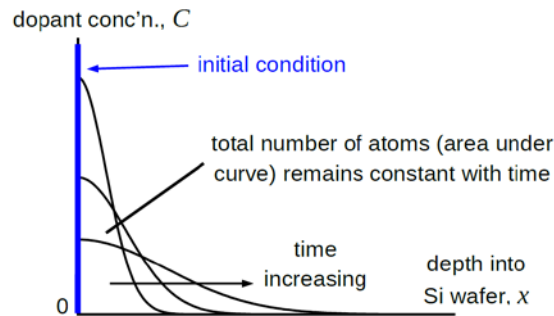
Over time, diffusion depths are small compared to the treated area (i.e. \sqrt{Dt} small). Total number of atoms increases over time.



Drive-in: the surface supply of dopant is removed, and the temperature is increased, to diffuse the pre-deposited atoms much further into the material.

Boundary conditions: $C(x \rightarrow \infty, t) = 0$; $\left. \frac{dC}{dx} \right|_{x=0} = 0$ (no diffusion flux in/ out of the Si surface)

Initial condition: $C(x, t=0)$ approximated with a δ -function.



[Examiner’s comments: Question 1 was answered well overall. In part (a), many answers did not define the terms Q or R , or show the correlation between activation energy (Q) and the atomic jump energy barrier (q). In (c), most students could state some but not all the initial and boundary conditions. The time-dependent concentration distribution graphs should be sketched properly to reflect the corresponding solutions in order to score full marks.]

Question 2

(a) Consider the free energy functions of a material in its three different states:

$$\text{Solid: } G_s = U_s + pV - TS_s$$

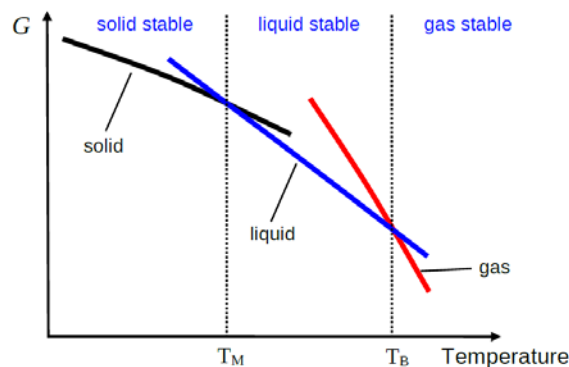
$$\text{Liquid: } G_l = U_l + pV - TS_l$$

$$\text{Gas: } G_g = U_g + pV - TS_g$$

Because atoms attract each other, the internal energy is lower when particles are closer to each other for a given temperature. So qualitatively we expect: $U_s(T) < U_l(T) < U_g(T)$

However, because entropy is a measure of disorder, it is expected that: $S_s(T) < S_l(T) < S_g(T)$

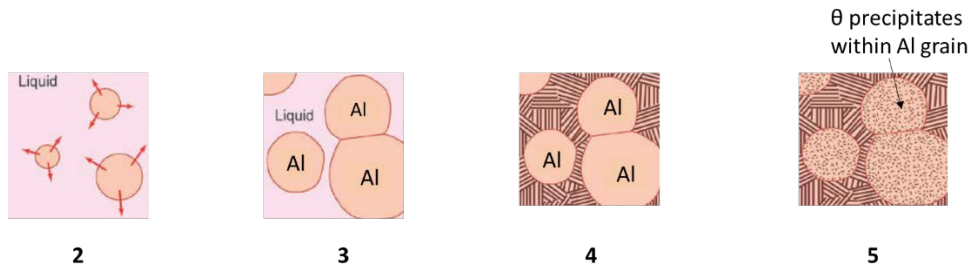
As a result, the Free Energy of a gas starts higher than the free energy of a liquid at high temperature, but should decrease faster with temperature. The curves are expected to cross. The same argument can be applied for solids and liquids. The crossing points represent the transition temperatures.



(b)(i) One can describe the phase change process by the following five steps. The corresponding microstructure diagrams associated with each step are also shown below.

1. Above $\sim 610^\circ\text{C}$, single-phase liquid, no phase reactions.
2. From $\sim 610^\circ\text{C}$ to 548°C : Nuclei of Al-rich solid solution appear. The composition of the liquid moves along the liquidus line, that of the solid along the solidus line.
3. This regime ends when the temperature reaches 548°C . Note that the alloy composition in weight (wt%, 15) will result in about ~ 60 wt% solid, with the remaining being liquid.

4. At 548°C: the remaining liquid has reached the eutectic point, and this liquid undergoes solidification. Note that the proportions of primary (Al) and eutectic microstructure are exactly the same as the solid-liquid proportions just above the eutectic temperature.
5. From 548°C to 500°C, the primary Al-rich solid becomes unstable and θ phase precipitates within the Al-rich grain. At 500°C, only a very small amount of θ phase is precipitated.



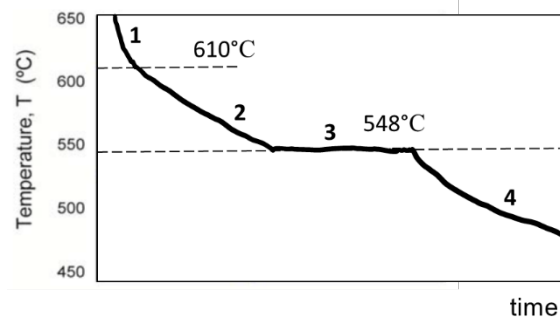
(ii)

Al phase $\approx (53-15)/53 \approx 72$ wt%

θ phase $\approx 15/53 \approx 28$ wt%

As temperature decreases, the solubility of Cu in Al decreases to 0, while the solubility of Cu in θ phase is relatively unchanged over the temperature range. Thus, there will be higher number of θ phase precipitates appearing within the main (Al) grains as (Al) grains become purer. One also expects slight increased θ phase in the eutectic /lamella structure.

(iii)



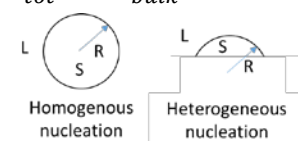
(1) Liquid (L) cools

(2) $L \rightarrow L+(Al)$, the slope of the cooling curve is reduced compared to (1), as latent heat is released progressively.

(3) At 548°C, the eutectic temperature, the remaining liquid solidifies at this temperature ($L \rightarrow$ eutectic). The duration of the arrest is similar to the cooling duration of (2), as the proportion of eutectic is $\sim 60\%$. At the end of the plateau, transformation completes.

(4) Solid cools.

(c) A nucleation process will include the transformation of an existing phase to a new phase (ΔG_{bulk}), and the creation of new interfaces (ΔG_{inter}) between the new phase and the existing phase. This applies to the nucleation of a new solid phase within a liquid, as well as the nucleation of a new solid phase within an existing solid phase. The total free energy for nucleation is $\Delta G_{tot} = \Delta G_{bulk} + \Delta G_{inter}$. With ΔG_{bulk} a negative term, and G_{inter} a positive term. With the balance of these two terms, a critical nucleation radius is required for both homogenous and heterogeneous nucleation. Homogenous nucleation



assumes a spherical nucleus formed in isolation. Heterogeneous nucleation takes place on an existing surface. Since the critical nucleus is the same for both processes, a lower number of atoms is required to form a critical nucleus (or smaller under-cooling) for heterogeneous nucleation than homogenous nucleation.

For the case of Al-15wt% Cu in the question, it first forms primary grains of Al-rich solid in liquid. Spontaneous nucleation of Al-rich solid in the liquid takes place (i.e. homogeneous nucleation). At just below 548°C, the remaining liquid transforms to a eutectic mixture of (Al) and CuAl₂. Nucleation takes place on the surfaces of existing Al-rich grains (i.e. heterogeneous nucleation). As temperature decreases further, the solubility of Cu in the Al decreases. Notably, the microstructure of the primary Al-rich grains will see the precipitation of CuAl₂, through a homogenous nucleation process within the Al grains, or heterogeneous nucleation on any defects.

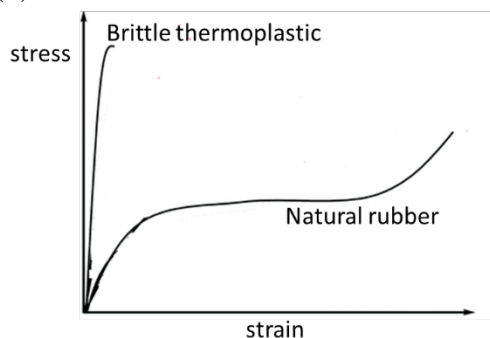
[Examiner’s comments: In part (a), many answers failed to address the internal energy differences between solid, liquid and gas. Part (bi) should distinguish stages (3)&(4), and also should expect the precipitation of small amount of θ phase in the end product; good diagrammatic sketches of the microstructures should reflect the approximate proportion of different phases for a particular stage. Part b(iii) were answered relatively poorly: some answers confuses between the continuous temperature decrease versus temperature arrest regimes; some answers also provide a C-curve instead of a temperature-time curve requested by the question. For part (c), most students can provide some descriptions for the difference between homogenous and heterogeneous nucleation; however, answers for explaining how these two nucleation mechanisms can account for the final distribution of phases for the alloy of part (b)(i) are less well provided.]

Question 3

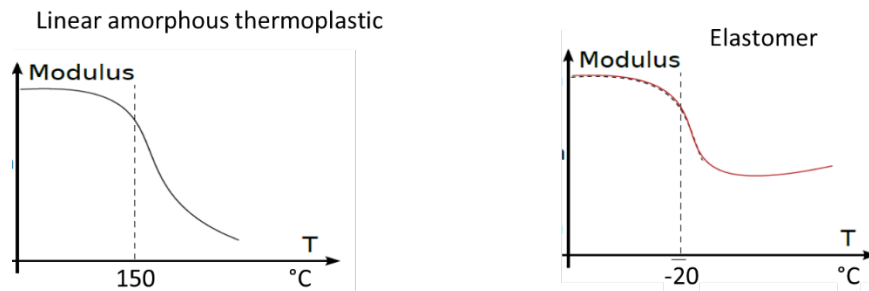
(a)(i)



(ii)



(iii)



Linear amorphous polymer (thermoplastic): below T_g , the thermal energy is too weak to allow the chains to slide past each other. The stiffness therefore relates to the rigidity of the polymer chains, typically of the order of GPa. Above T_g , the chain is flexible and fluctuates due to thermal agitation. On short time scales, polymer chains are entangled and can store deformation, leading to a transient elastic response. Under steady load, polymers are however liquid and flow above T_g .

Elastomer: elastomers are loosely crosslinked networks of polymer chains. These materials also experience a glass transition associated with a significant drop in the Young modulus, but remain solid above T_g . The normal room temperature operating conditions are above T_g for most elastomer chains. Above T_g , The elastomers' elasticity increases with temperature.

(iv) [answer for *either* case]

If the polymer were an elastomer, under a constant load, the elastomer will most likely extend, i.e. the length of the polymer will increase, as the elastomer's elasticity is expected to decrease for the temperature range stated in the question. The amount of extension is likely to be compensated by effects due to the thermal contraction, but the effects due to entropic elasticity should dominate over the thermal effects.

If the polymer were a thermoplastic with property in a(iii), there should be slight decrease or very small change in displacement (negligible contraction in comparison to magnitude of extension in the elastomer case). This is due to the fact that the operating temperature range is sufficiently far below $T_g=150^\circ\text{C}$ for the linear amorphous polymer, and hence the elastic modulus is only slightly increased. Note that there will also be effects arisen from thermal contraction. This will also make the thermoplastic polymer contract slightly.

(b)(i) The properties required are a good degree of transparency (for aesthetic reasons), and good mechanical properties, including strength to withstand the internal pressure of the drink, and toughness for withstanding knocking during e.g. transportation.

Plastic bottles are usually made of PET, which have adequate strength and toughness. Stretch blow moulding is used. The moulding temperature is kept just above T_g to restrict crystallinity to about 20%. The deformation and elongation provides differential molecular alignment, providing higher strength in the hoop stress direction.

(ii) The film material should have good tear strength, tensile strength and should be relatively low cost. Polyethylene is a popular material used for packing. Film blowing will be the manufacture method of choice. Extruded polymer is inflated by internal pressure, cooled and wound onto a drum. The inflation produces polymer films with some alignment in the molecular structure. The alignment improves the mechanical properties of the film, giving better strength per unit weight (and cost) of material.

(iii) A sail is made of a fabric consisting of woven fibres. The material needs to have high strength, high Young's modulus (and perhaps toughness), and should be light. It should also be resistant to environmental degradation (e.g. from sun light and sea water corrosion). The material of choice could be Kevlar fibres, which are then woven into a fabric. Fibre drawing is the material process method. During this process, the molecular chain are being aligned along the fibre axis during the fibre drawing process. The specific mechanical properties thus depend on the drawing ratio of the fibre.

(c) The main considerations are that the resting shape of an elastomer is fixed by adding a crosslinker (i.e. a chemical process). In comparison, during manufacturing of thermoplastics of small thicknesses, the shape of a thermoplastic is fixed by cooling the material below T_g , and then by plastic deformation beyond the yield point (i.e. a thermo- and mechanical process). The glove also has a more complex shape than a film packaging. Thus for a latex glove, a moulding process is required similar to how a thermoset is commonly shaped. To form a very thin layer, one would dip coat a hand shape mould into a sink of pre-crosslinked liquid polymer, such that a thin layer of liquid polymer will adhere to the mould surface. The object is subsequently dipped into a sink of solution of crosslinker for crosslinking. Post-crosslinking, the glove is then removed from the mould.

[Examiner's comments: In part (a)(ii), the stress-strain graph should reflect the overall shape of the deformation profile, as well as the relative difference in e.g. Young's modulus, breaking strength, and elongation to break, between typical thermoplastics and elastomers. In part (a)(iii), some answers give a drawing associated with a semi-crystalline thermoplastic rather than an amorphous thermoplastic. Part(b) questions are generally answered well. For part (c), most answers can address the fact that the main difference is due to the crosslinker addition; descriptions along the line of a 'moulding' process is required to achieve full marks.]

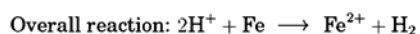
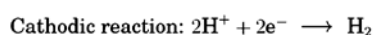
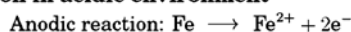
Question 4

(a) (i) Conditions required for aqueous corrosion include:

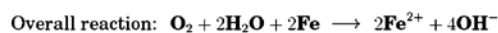
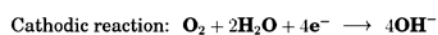
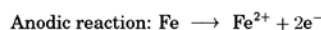
- an anodic reaction,
- a cathodic reaction,
- a conductive path between the anodic and cathodic sites,
- a solution containing ions in order to transport charges (an electrolyte).

(a)(ii)

Iron in acidic environment



Iron in a neutral environment with oxygen



(b) In galvanic protection, a highly electro-potentially negative metal (such as zinc) is used to couple with a less electro-negative metal (such as iron), such that the electro-potentially negative metal is preferentially corroded.

The galvanisation protection can be applied in the form of coating a layer of zinc (galvanization) on the surface of a metal structure. Coating the whole surface provides the best protection, but it is not required in many cases. Another method is to use a sacrificial metal (e.g. zinc as an anode), which is electrically connected to the steel structure. Both the sacrificial electrode and the steel structure need to be in the same electrolyte. When the life time of the steel structure needs to be longer than the life time of the coating, it is preferred to have a separate anode that can be replaced as often as required.

(c) (i)

$$\Delta m = 10^{-4} \sqrt{t}$$

$$10 \text{ years} \rightarrow t = 3.08 \times 10^8 \text{ s}$$

$$\Delta m = 10^{-4} \sqrt{3.08 \times 10^8} = 1.75 \text{ kg per m}^2$$

Δm is due to the addition of oxygen. Since FeO (the dominate oxide component) is formed with the molar ratio of Fe and O being 1:1, the total Fe metal loss to the oxide is (*this part not always done well*):

$$\Delta m_{Fe} = \frac{M_{Fe}}{M_{O}} \times \Delta m = \frac{0.056}{0.016} \times 1.75 = 6.13 \text{ kg per m}^2$$

$$\text{Thus the wall thickness reduction is } d_{reduction} = \frac{\Delta m_{Fe}}{7870} = 7.8 \times 10^{-4} \text{ m}$$

$$\text{Remaining wall thickness would be, } d = 0.005 - 7.8 \times 10^{-4} \text{ m} = 4.22 \times 10^{-3} \text{ m}$$

$$\text{Hoop stress, assuming thin-wall theory: } \sigma_{\theta} = \frac{Pr}{d} = \frac{10^6 \times 0.25}{4.22 \times 10^{-3}} = 0.059 \times 10^8 = 59 \text{ MPa.}$$

No failure.

Or approach this by looking at the time needed to reach a critical stress associated with loss of mass (178 years, for a critical thickness of 1.67 mm).

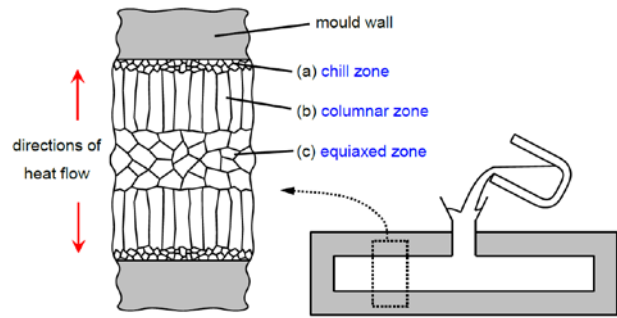
(c) (ii) Creep may need to be considered since the operation temperature would be above half the melting points of common alloys like that of mild steel. The material's microstructure can be improved by either alloying, or reduced the grain boundaries present, for example, by forming a large grain size especially along the circumferential direction with maximum stress. Forming a single crystal will theoretically provide the optimum creep resistance, however, it is impractical to be made into a cylinder for a pressure vessel.

[Examiner's comments: The descriptions were mostly well done. The numerical part was done less well than expected, with people tending to get tangled over areas and use of the molar masses.]

Question 5

(a)(i)

When temperature decreases, there will be bigger chill and equiaxed zones, while the columnar zone will be smaller. The size of grains in all zones will reduce.



(a) (ii) Segregation occurs on two main length scales:

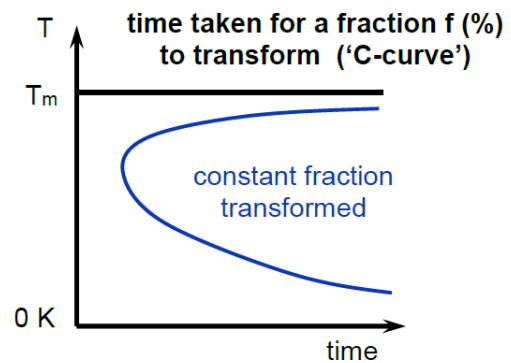
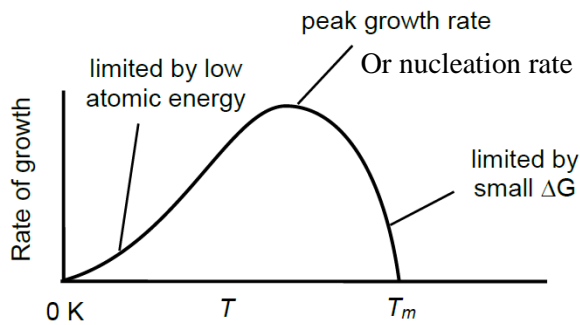
- Grain-to-grain: micro-segregation
- Whole casting (mould-to-centre): macro-segregation

Consequences of segregation on mechanical properties include:

- Non-uniform distribution of main solute alloying elements, which leads to variations in yield strength (by solid solution or precipitation hardening).
- Concentration of impurities on grain boundaries, which may form solid phase (a problem if these are brittle) or they may form trapped bubbles of gas (giving porosity). Toughness is mostly affected by such segregation processes.

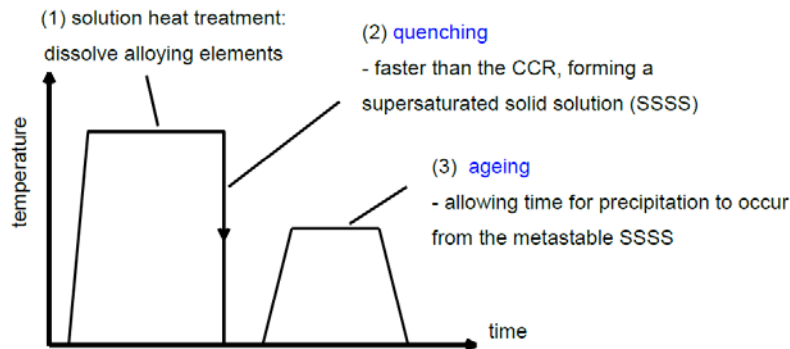
(b) The overall rate of transformation depends on both the nucleation rate and the growth rate of the new phase. These two processes have similar temperature dependence as shown in the figure below. The origin of the shape of the curve is because of two dominating factors:

- (1) Thermodynamic factor from the free energy difference: since the total free energy for transformation is directly proportional to the undercooling: $\Delta G \propto (T_m - T)$, the larger the undercooling, the greater the 'bias' in free energy barrier. Hence, the net atomic flux from liquid to solid will increase.
- (2) Kinetic factor from the thermal energy: the thermal energy will also affect the rate of atomic motion, and hence the net flux from liquid to solid. Thermal energy will reduce as temperature falls.

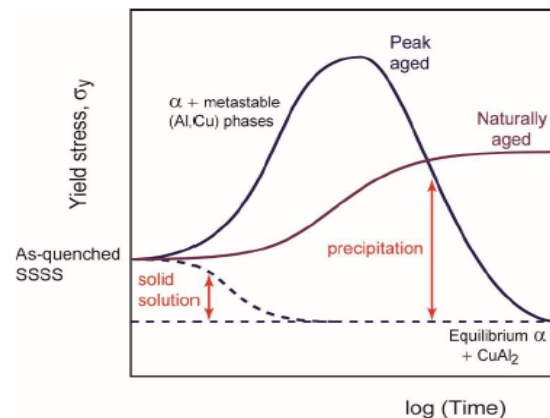


For practical applications, it is convenient to invert the rate axis, and express it instead in terms of the time taken for a certain fraction to transform. The resulting '**C-curve**' is exhibited by a wide range of phase transformations that experience a competition between a thermodynamic driving force and the kinetics of atomic motion as the temperature changes.

5 (c) (i) Aircraft components made of age-hardened copper-aluminium alloys. These alloy components need to have good yield strength. The copper-aluminium alloy composition should produce an equilibrium phase diagram, with a single solid solution phase at high temperature (high solubility of alloy additions), and two-phase region at low temperature (low solubility of alloy additions). During processing, if the Cu-Al alloy is quenched faster than the CCR, at room temperature, it remains as a single phase solid solution. This is a metastable state, with super saturated solid solution. Precipitation hardening can be achieved through age hardening of the alloy. This involves either through artificial aging: re-heat for a few hours at a slightly higher temperature in the two-phase region to allow for precipitation; or natural aging, leave for several days at room temperature.



During aging, the yield stress of the material varies with time as shown below:



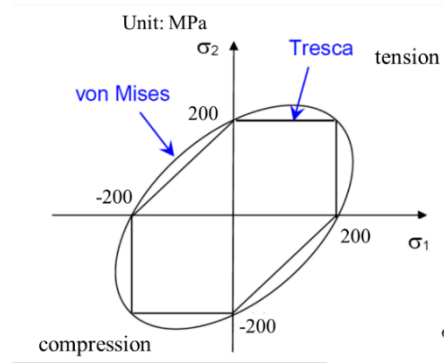
(c)(ii) Cutting tools made of high alloy steels. Cutting tools need to have good hardness. They also often operate at high temperatures (due to the heat generated by plastic deformation). In plain C steel, the Fe_3C precipitates may coarsen (or re-dissolve) – unavoidable softening takes place. To prevent this, high alloy steels are used (containing Mo, W and V – up to 20wt% in total). These elements perform multiple functions, including: (1) increasing the hardenability; (2) the quench and temper treatment leads to the formation of alloy carbides (Mo_2C , W_2C , and VC) – these are stable at high temperatures, retaining precipitation hardening in service; (3) the alloy addition also contributes to high temperature solid solution hardening.

[Examiner's comments: A popular question. Lost marks tended to be associated with incomplete descriptions of the relevant processes, rather than any general lack of knowledge or understanding. In the final part many people failed to remark on the presence of alloying components such as tungsten and vanadium in providing hardenability, precipitation and solid solution strengthening, focussing instead on the role of carbon.]

Question 6

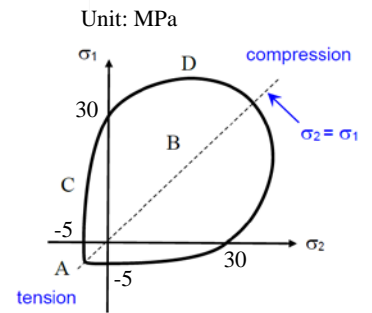
(a) (i)

The tensile and compressive strength are the same. The von Mises criterion better captures the true failure surface.



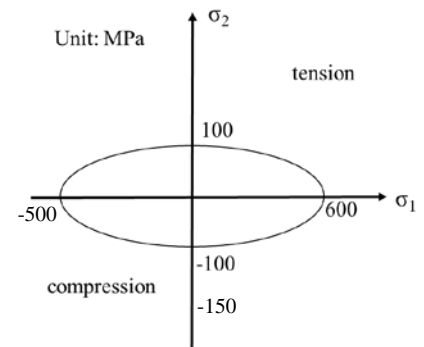
(a) (ii)

Note that biaxial compression tends to lead to a higher failure stress than uniaxial compression.



(a) (iii)

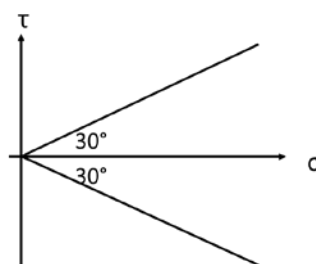
Based on maximum stress criteria, assuming the matrix is much weaker than the fibre. Approximate transverse strengths estimated as a factor of the epoxy failure strength, which can be found from the data book. Include a factor of two reduction in tensile strength in the estimate of the tensile strength as the fibres constitute only half of the load-carrying area. In compression the strength may be a bit lower than the tensile value, depending on the microbuckling compression failure mechanism.



Transverse compressive strength tends to be a bit higher than tensile strength as this is a matrix failure, which is more brittle in tension.

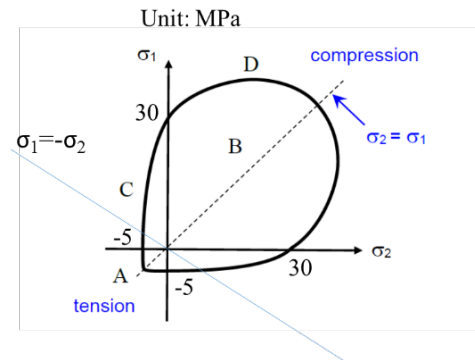
(a) (iv)

No strength in tension.



(b)

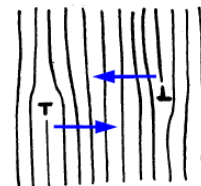
From a Mohr's circle, the in-plane principal stresses are $\sigma_1 = k$ (shear stress) = $-\sigma_2 = 8$ MPa. Thus failure will occur as the loading lies outside the failure surface.



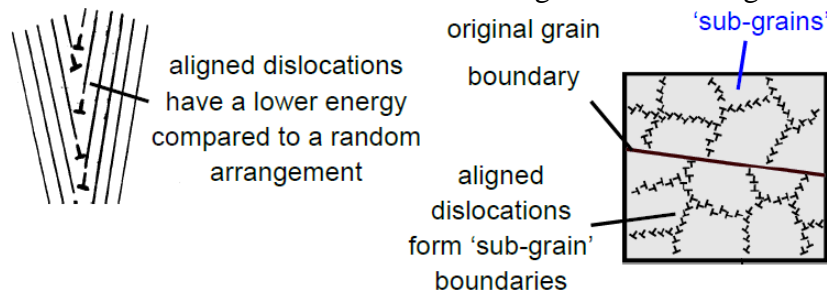
(c) In both cases there is no phase change, and the driving force comes from the reduction in stored dislocation energy.

Recovery: rearrangement of dislocations into lower energy configurations, such as subgrains, and the annihilation of dislocations of opposite sign. There is a modest reduction in stored dislocation energy. These processes occur by both glide of dislocations and local rearrangements of the crystal structure by diffusion of atoms, where rate is temperature dependent. During recovery, a minimum annealing temperature of $\sim 0.1T_m$ is required for recovery to occur. The process only involves a small drop in dislocation density, then a small drop in the yield stress, with increased ductility.

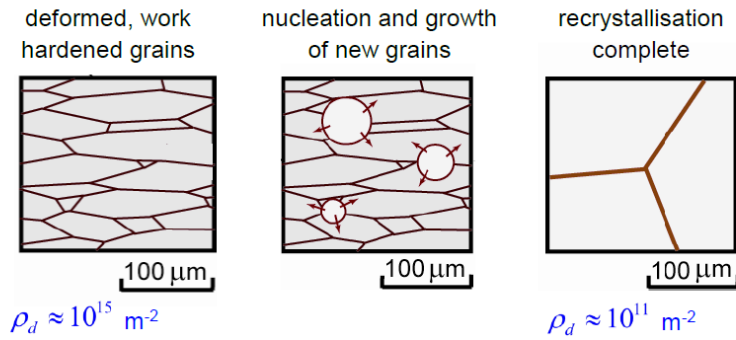
(1) Dislocations of opposite orientation can annihilate each other



(2) Dislocations of similar orientations can align and form subgrains.



Recrystallization: nucleation and growth of new grains of low dislocation density, replacing the deformed microstructure. Usually a subgrain located on a grain boundary acts as a nucleus. The driving force again comes from the (large) reduction in stored dislocation energy. The recrystallised grain size depends on the number of nuclei formed, which depends on the stored energy. The higher the strain, the more nuclei form and the smaller the final grain size. Hence the grain size can be controlled by changes in deformation conditions. Recrystallization results in fresh grains, thus leading to much lower dislocation densities, and a large drop in yield stress, but much improved toughness. The larger microstructural change than for recovery gives larger changes in mechanical properties. Recrystallization requires a minimum annealing temperature of $0.3 T_m$, higher than for recovery on account of the increased energy needed for the larger microstructural changes to occur.



[Examiner's comments: This was generally well done, with marks lost by failing to justify choices for values not quoted. In part (b) many people failed to use their (generally correct) sketches of the failure surface to justify the effect of equal biaxial tension and compression on failure. In part (c), the knowledge of these processes was generally good, but again candidates failed to answer the question, which asked for these processes to be compared and contrasted.]