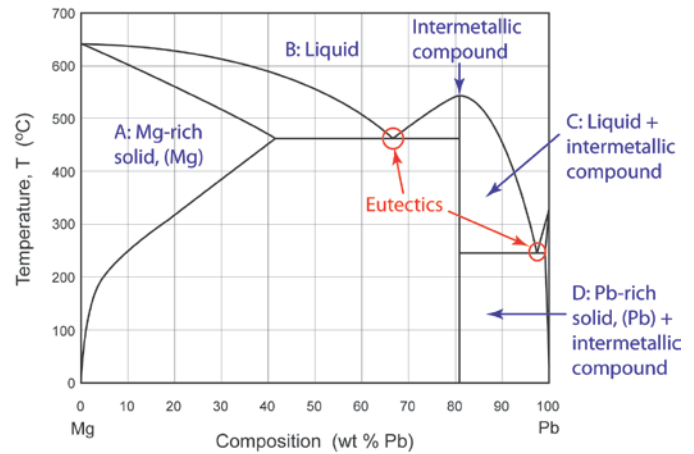1   (a) Intermetallic composition: 81 wt% Pb.

Atomic masses (from Materials Databook):
Mg, 24.312; Pb, 207.19

Ratio of numbers of atoms, Pb:Mg =
$(81/207.19) / (19/24.312) \approx 0.5$.

Hence compound is Mg_2Pb.

Melting point $= 540^oC$.

(b) Phases in fields A-D: see figure.

Eutectics:
66 wt % Pb, $460\,^oC$
97.5 wt % Pb, $250\,^oC$

(c) (i) 10wt% Pb:

At 640^oC: nucleation of Mg-rich solid, (Mg), within the liquid
At 600^oC: completion of transformation to grains of Mg-rich solid, (Mg)
At 250^oC: moves into two-phase field, (Mg) + Mg_2Pb, so precipitation of Mg_2Pb starts.
Cooling to 20^oC: with volume fraction of Mg_2Pb increases, with (Mg) becoming purer.

Final phases, proportions (from lever rule), and compositions:
(71/81) Mg-rich (virtually pure) solid (Mg)
(10/81) intermetallic compound, Mg_2Pb (81wt%Pb)

     (ii) 90wt% Pb:

At 460^oC: nucleation of intermetallic compound, Mg_2Pb, within the liquid
At 240^oC: roughly 60:40 liquid + Mg_2Pb, liquid then transforms at this temperature to eutectic
of Pb-rich solid (Pb) + Mg_2Pb (rough proportions 90:10 within the eutectic)
Cooling to 20^oC: (Pb) becomes purer, by increase in proportion of Mg_2Pb in eutectic.

Final phases, proportions (from lever rule), and compositions:
(9/19) Pb-rich (virtually pure) solid (Pb)
(10/19) intermetallic compound, Mg_2Pb (81wt%Pb)

Final microstructures:
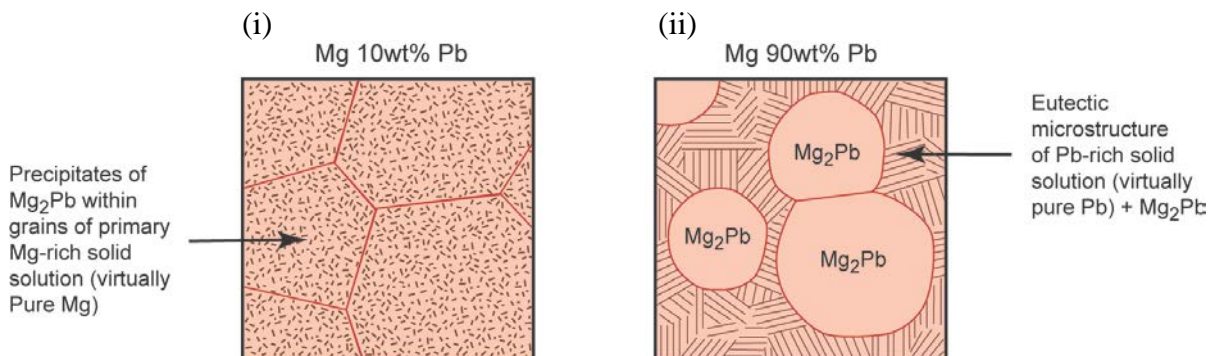
Note that in (ii), the proportion of Mg_2Pb grains to eutectic two-phase microstructure should
reflect the proportions of Mg_2Pb to liquid, just *above* the eutectic temperature (i.e. approx. 60%
liquid, which forms the eutectic microstructure).

2 (a) From the graph:

Stress (MPa)	Strain, ε	Time (minutes)	Strain-rate (s^{-1})
232	0.01	0	3.33×10^{-8}
	0.04	15,000	
190	0.005	0	1.0×10^{-8}
	0.02	25,000	

At constant temperature, $\dfrac{\dot{\varepsilon}_1}{\dot{\varepsilon}_2} = \left(\dfrac{\sigma_1}{\sigma_2}\right)^n$, hence $\dfrac{3.33\times10^{-8}}{1.0\times10^{-8}} = \left(\dfrac{232}{190}\right)^n$

giving $n = 6.02$ (i.e. $n \approx 6$).

Substitute data at one stress level to find B:

$$3.33\times10^{-8} = B\,(232)^6 \text{ giving } B = 2.14 \times 10^{-22} \text{ (MPa}^{-6}.\text{s}^{-1})$$

(b) (i) Ignoring the mass of the rod, the stress is constant: $\sigma = Mg/\pi R^2$

The rate of extension of the rod is given by: $\dfrac{dL}{dt} = L\dot{\varepsilon} = BL\,(Mg/\pi R^2)^n$

(ii) Now including the mass of the rod, consider a distance x from the lower end of the rod, at which point the stress is: $\sigma(x) = \left[Mg/\pi R^2\right] + \rho g x$

The strain-rate at a distance x from the lower end of the rod is: $\dot{\varepsilon}(x) = B\left[\sigma(x)\right]^n$

The extension-rate of an element of length dx is $\dot{\varepsilon}(x)\,dx$, hence integrating along the length of the rod gives the overall extension rate of the rod:

$$\dfrac{dL}{dt} = \int_0^L \dot{\varepsilon}\,dx = B\int_0^L \left(\left[Mg/\pi R^2\right] + \rho g x\right)^n dx$$

$$\dfrac{dL}{dt} = B\left[\dfrac{\left(\left[Mg/\pi R^2\right] + \rho g x\right)^{n+1}}{(n+1)\,\rho g}\right]_0^L = \dfrac{B\left(\left[Mg/\pi R^2\right] + \rho g L\right)^{n+1}}{(n+1)\,\rho g} - \dfrac{B\left(\left[Mg/\pi R^2\right]\right)^{n+1}}{(n+1)\,\rho g}$$

For a rod mass = 1% of the supported mass, M: $0.01\,M = \rho \pi R^2 L$, or $\rho = 0.01\,M/\pi R^2 L$

Eliminating ρ from the expression above:

$$\dfrac{dL}{dt} = \dfrac{B\pi R^2 L}{(n+1)\,0.01\,M\,g}\left\{\left(\left[Mg/\pi R^2\right] + 0.01\,Mg/\pi R^2\right)^{n+1} - \left(\left[Mg/\pi R^2\right]\right)^{n+1}\right\}$$

$$\dfrac{dL}{dt} = \dfrac{100\,B\pi R^2 L}{(n+1)\,M\,g}\left(1.01^{n+1} - 1\right)\left[Mg/\pi R^2\right]^{n+1} = \dfrac{100\,BL}{(n+1)}\left(1.01^{n+1} - 1\right)\left(Mg/\pi R^2\right)^n$$

From (i), the rate of extension ignoring the rod was: $\dfrac{dL}{dt} = L\dot{\varepsilon} = BL\,(Mg/\pi R^2)^n$

Hence, the ratio of the two results is a factor of $\dfrac{100\left(1.01^{n+1}-1\right)}{(n+1)}$, which for $n=6$ is equal to 1.03, i.e. a 3% error.

(iii) The mass of the rod $= \pi R^2 L\rho$. For steel density $\rho = 7850$ kg/m^3 (from Materials Databook), $L = 0.5$m, $R = 3$mm: mass $= 111$g. This is a very small fraction (0.06%) of the supported mass (200kg), so we can ignore it and use the result from part (i).

Applied stress $= Mg/\pi R^2 = \dfrac{200\times 9.81}{\pi(0.003)^2} = 69.4$ MPa

Assumption: the creep regime at this stress is assumed to be the same as that operating at the stress levels in the test data (190 to 232 MPa).

Extension rate: $\dfrac{dL}{dt} = BL\left(Mg/\pi R^2\right)^n = 2.14\times 10^{-22} \times 0.5 \times (69.4)^6 = 1.20\times 10^{-11}$

Hence length change $= \dfrac{dL}{dt}\times t = 1.20\times 10^{-11} \times 10{,}000 \times 3600 = 0.43$mm (i.e. 0.086%)

[Examiner's comments: Part (a) well-answered by almost all students, but few took the time to write down the units of B. This was unfortunate as some students retained unusual units, for instance MPa and kilo-minutes, and hence failed to use it properly in (b)(iii). In part (b)(ii) most students understood that the stress was now non-uniform along the rod, but only a few properly calculated the integral.]

3   (a)   Particle diffusion is due to the random motion of particles caused by thermal fluctuations. Generally speaking, the higher temperature, the faster the diffusion.

In solids, diffusion follows Arrhenius Law: rate $\propto \exp(-Q/RT)$, where Q is the activation energy, R is the gas constant and T is the temperature (in Kelvin).

Physical basis of Arrhenius Law:
Atoms vibrate at high frequency about equilibrium locations (A and B) where their free energy G is minimum (e.g. interstitial atom in a lattice hole). Atomic 'jumps' between location must overcome a free energy barrier, q (J / atom). Average energy per atom: $E = 3kT$ where k is Boltzmann's constant, T is the absolute temperature.
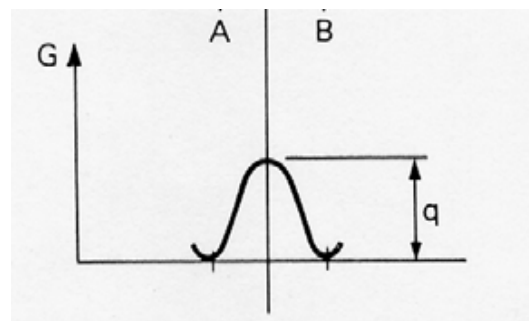
There is a statistical distribution in the energy per atom, such that the probability p of an atom having an energy greater than q is: $p = \exp(-q/kT)$. This temperature-dependence controls the rate of diffusion.

(b) (i) From Maths Databook, square wave Fourier series of wavelength l is:

$$f(x) = \frac{4}{\pi} \sum_{m=1}^{\infty} \frac{\sin(2m-1)(2\pi x/l)}{2m-1}$$

Replacing the index m with n (odd): $f(x) = \frac{4}{\pi} \sum_{n=1,3,5....}^{\infty} \frac{\sin(2n\pi x/l)}{n}$

Comparing this with the solution in the question:

$$C(x, t=0) = C_0 + \sum_{n=1,3,5...} \frac{2C_1}{\pi n} \sin\left(\frac{\pi n x}{h}\right)$$

C_0 is the offset in the mean concentration = 2 at% X

To find C_1: $\dfrac{4}{\pi n} = \dfrac{2C_1}{\pi n}$, hence $C_1 = 2$ at% X

Similarly, $h = l/2 = 2$ μm.

(ii) Fick's 2nd Law: $\dfrac{\partial C}{\partial t} = D \dfrac{\partial^2 C}{\partial x^2}$

Differentiating general solution $C(x, t=0) = C_0 + \sum_{n=1,3,5...} \frac{2C_1}{\pi n} \sin\left(\frac{\pi n x}{h}\right) \exp\left(-\frac{t}{\tau_n}\right)$

$$\frac{\partial C}{\partial t} = \sum_{n=1,3,5...} \frac{2C_1}{\pi n} \sin\left(\frac{\pi n x}{h}\right) \exp\left(-\frac{t}{\tau_n}\right) \times \left(-\frac{1}{\tau_n}\right)$$

$$\frac{\partial^2 C}{\partial x^2} = \sum_{n=1,3,5...} \frac{2C_1}{\pi n} (-1)\left(\frac{\pi n}{h}\right)^2 \sin\left(\frac{\pi n x}{h}\right) \exp\left(-\frac{t}{\tau_n}\right)$$

Substituting into Fick's 2nd Law: $\left(-\dfrac{1}{\tau_n}\right) = D(-1)\left(\dfrac{\pi n}{h}\right)^2$

Hence $\tau_n = \dfrac{h^2}{\pi^2 n^2 D}$, where D is the diffusion coefficient.

(iii) The timescale of decay of the exponential term scales with $1/n^2$, i.e. 1, 1/9, 1/25......, and the amplitude of the corresponding term in the sine wave scales with $1/n$. Hence for timescales greater than τ_1, the terms for $n > 1$ are negligible.

For $t = 0.5\tau_1$, $t = \dfrac{h^2}{2\pi^2 D}$.

At this time:
- peak amplitude of 1st term ($\times 2C_1/\pi$) = $\exp(-1/2) = 0.607$
- peak amplitude of 2nd term ($\times 2C_1/\pi$) = $(1/3) \exp(-9/2) = 0.0037$ (n > 3 negligible)
Error = $0.0037/(0.607+0.0037) = 0.6\%$

(iv)   Diffusion constant $D_o = 2.6 \times 10^{-4}$ m^2/s

Hence diffusion coefficient at 500°C: $D = 2.6 \times 10^{-4} \exp\left(-\dfrac{180000}{8.314 \times 773}\right) = 1.78 \times 10^{-16}$ m^2/s

Time constant for exponential decay: $\tau_1 = \dfrac{h^2}{\pi^2 D} = \dfrac{(2 \times 10^{-6})^2}{\pi^2 \times 1.78 \times 10^{-16}} = 2277\text{s} = 38$ mins.

For t = 1 hour, solution using first term only will be accurate enough:

$$C(x,t) = C_0 + \frac{2C_1}{\pi} \sin\left(\frac{\pi x}{h}\right) \exp\left(-\frac{t}{\tau_1}\right)$$

Maximum and minimum concentrations where sin term = ±1.

Substituting for C_0, C_1 and τ_1: $C = 2 \pm (4/\pi) \exp(-60/38) = 2.26$ at% and 1.74 at%.

[Examiner's comments: Fairly unpopular question. However, the students attempting it usually did well. A typical error was to substitute $h^2 = 4$ in parts (b)(ii,iii), forgetting that h was calculated in microns. This caused many numerical errors in (b)(iv). In part (b)(iii), the factor 1/3 in the n=3 term was often forgotten.]

4   (a)   early stages of artificial ageing of Al-Cu alloy after solutionising and quenching:
- precipitation of fine-scale metastable precipitates (initially GP zones of pure Cu);
- nucleation and growth of clusters by diffusion of Cu from surrounding super-saturated solid solution;
- driving force is change in free energy from solid solution to Al-rich solid plus (metastable) second phase (with some penalty in producing a high surface area of coherent boundary between precipitates and matrix);
- this is a phase transformation.

(b)   annealing of Al-Mg alloy after cold rolling:
- prior deformation produces increase in dislocation density;
- recovery: dislocations of opposite sign are attracted together and annihilate; and dislocations re-arrange into sub-grains;
- recrystallization: statistically larger sub-grains become nuclei of new grains, with the boundaries growing outwards by atomic jumps across the boundary from the old to the new crystals;
- driving force is the line energy of the dislocations (local elastic strain round the dislocation core), with recrystallization leading to a substantial drop in dislocation density;
- this is *not* a phase transformation (remains an Al-Mg solid solution throughout).

(c)   slow cooling of eutectoid steel from 800 °C to 20 °C:
- austenite transforms to 100% pearlite below the eutectoid temperature;
- nucleation and growth of BCC ferrite and iron carbide platelets on prior (FCC) austenite grain boundaries; iron atoms jump across interface to take up new crystal structures; carbon diffuses ahead of plate edges to concentrate the carbon into the iron carbide, leaving the ferrite virtually carbon free; the plate-like structure minimises the carbon diffusion distance required;
- driving force is change in free energy between austenite and (ferrite + iron carbide);
- this is a phase transformation.

(d)   water quenching of eutectoid steel from 800 °C to 20 °C:
- austenite transforms to 100% martensite, between martensite start and finish temperatures (may be some retained austenite at this carbon content);
- displacive transformation without diffusion: shear transformation of bands of martensite nucleating from austenite grain boundaries, leading to needle-like structure of BCC iron heavily super-saturated in carbon;
- driving force is change in free energy between austenite and (metastable) martensite (with some energy penalty due to the elastic strain in the lattice caused by the supersaturation of carbon, such that greater undercooling is needed with increasing C content;
- this is a phase transformation.

(e)   holding annealed sample of pure Cu for a prolonged period close to its melting point:
- only microstructural features in annealed pure metal will be grain boundaries: grain growth occurs when temperature approaches melting point;
- curved boundaries migrate away from centre of curvature, by atomic jumps across the boundary;
- driving force is grain boundary energy (per unit area): grain growth leads to reduction in area of grain boundary;
- this is *not* a phase transformation (solid pure Cu throughout).

[Examiner's comments: marks were mostly lost for lack of detail in describing atomic mechanisms – e.g. it was not sufficient to just say "diffusion" – and for confused statements such as "driving force is the undercooling". In (b), many referred to "strain energy" with no reference to dislocations, and some sketched the area under a stress-strain curve, confusing this with the stored energy of dislocations. In (a) and (d) many thought the lattice strain due to supersaturation on quenching was the main driver for the transformation, rather than being an energy penalty that needs to be overcome by the free energy change. In (e) there were many guessed attempts to invoke recrystallization (though already annealed), creep (but no applied stress), or undercooling below the melting point (though already in the solid state).]

5   (a)   immersion of a gear in molten carbon-rich salt, followed by surface heating with a traversing laser beam:
- diffusion of additional carbon into surface layer (carburising), with the laser treatment giving transformation hardening (thermal cycle converting surface layer to austenite, self-quenching to martensite);
- key property is hardness (for wear resistance): the added carbon leads to the formation of high carbon martensite (helped by hardenability being increased by the added carbon), giving enhanced surface hardness (without making whole component brittle).

(b)   quenching and tempering a cutting tool made of a high carbon steel containing tungsten:
- formation of supersaturated (brittle) martensite on quenching, from which iron carbide and alloy carbides precipitate during tempering, giving high yield strength and hardness, and acceptable toughness;
- high carbon content and tungsten both enhance hardenability, making it easier to form 100% martensite through-thickness without a severe quench (which may cause cracking);
- high carbon content leads to high fraction of fine-scale carbides, for strength;
- tungsten forms tungsten carbide, giving high temperature strength, and also contributes solid solution strength.

(c)   casting of Ni superalloy turbine blades, followed by coating with zirconia:
- controlled solidification to make single crystal blade, to eliminate grain boundary short-circuit diffusion mechanism and creep by diffusional flow;
- superalloy composition also provides resistance to power-law creep (Ni has high melting point, alloying gives precipitation hardened microstructure);
- zirconia coating provides thermal barrier (high melting point, low thermal conductivity), enabling increase in turbine gas temperature.

(d)   cold drawing of polypropylene for fishing lines:
- cold drawing aligns molecules, such that axial loading is carried by the covalent C-C bonds in the polymer;
- significant increase in stiffness and strength.

(e)   stretch blow moulding of PET bottles for carbonated drinks:
- cylindrical "parison" first stretched axially, then inflated to a larger radius against a mould;
- molecules aligned within the cylindrical wall, giving enhanced stiffness and strength, with the greater strain (and thus orientation strengthening) in the circumferential direction (as the hoop stress under inernal pressure is the greater);
- temperature controlled carefully to limit crystallinity to around 20%, to retain transparency of amorphous state.

[Examiner's comments: many good, thorough answers, picking up subtle details. Weak answers stood out as being largely guesswork and having a poor grasp of technical terminology (e.g. invoking Al age hardening for Ni alloys, discussing dislocations and grains in polymers), or using stiff-strong-tough more or less inter-changeably. In (c) a few candidates discussed superalloy wind turbines!]
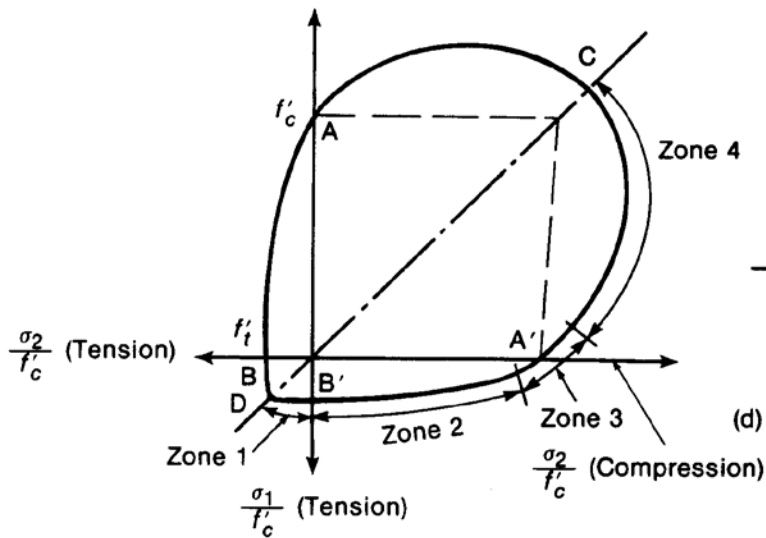
6   (a)   (i) Failure surfaces:

(1,2) Tresca and von Mises criteria for yielding in metals:
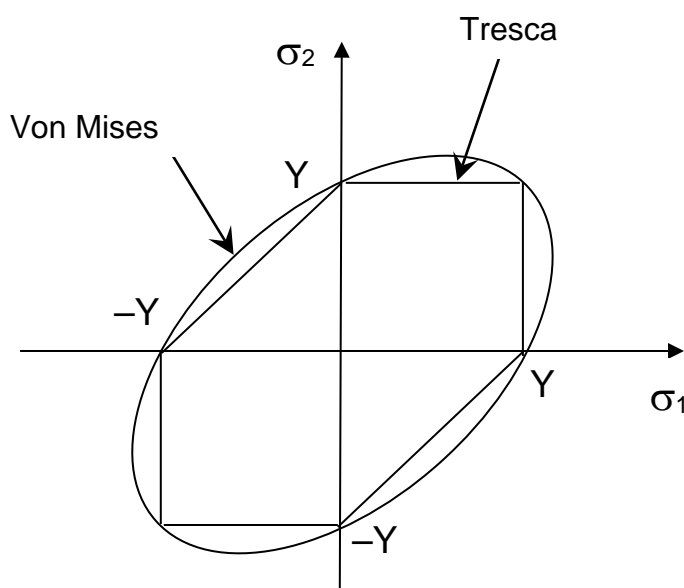
(3) maximum stress criterion in uniaxial fibre composites (σ_1 in fibre direction, i.e. no applied shear parallel to the fibres):
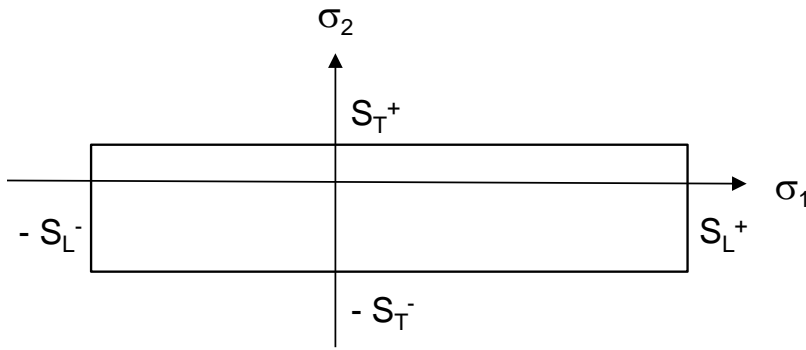
(4) failure of concrete (axes reversed, showing compression positive, tension negative):

(ii) (1) Tresca: $\max.\{\,|\sigma_1 - \sigma_2|,\ |\sigma_2 - \sigma_3|,\ |\sigma_3 - \sigma_1|\,\} = Y$ (Y = uniaxial yield stress).

In 2D: $\max.\{\,|\sigma_1 - \sigma_2|,\ |\sigma_2|,\ |\sigma_1|\,\} = Y$

   (2) von Mises: $(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 = 2Y^2$

In 2D: $(\sigma_1 - \sigma_2)^2 + (\sigma_2)^2 + (\sigma_1)^2 = 2Y^2$

   (3) Uniaxial fibre composite, maximum stress criterion:

Four failure limits (assuming zero shear):

   - normal loading parallel and transverse to the fibres in *tension*
   - normal loading parallel and transverse to the fibres in *compression*

$$- s_L^- < \sigma_1 < s_L^+, \quad - s_T^- < \sigma_2 < s_T^+$$

(iii)   Tresca and von-Mises: same failure stress in tension and compression, whether based on maximum shear or minimum plastic work: failure governed by yield (dislocation motion), and isotropic (equal in all directions).

Fibre composites: tension stronger than compression, parallel to the fibres (due to buckling in compression); much weaker in transverse direction, with greater strength in compression (governed by matrix strength), whereas in tension the weaker fibre-matrix interface influences failure.

Concrete: much stronger in compression than in tension: largest flaw governs tensile fracture, whereas compression leads initially to stable crack growth and material crushing.

(iv)   Limitations to maximum stress criterion in fibre composites: when principal stresses are not aligned with fibres, giving other failure mechanisms than axial failure in tension or compression, e.g. shear failures:
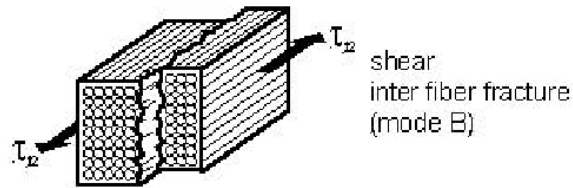
(b)   Open die forging: rectangular or cylindrical billets between parallel flat platens. Typical pressure 1-2 × Y

Closed die forging: enclosed, space between profiled dies. Typical pressure 5-10 × Y

Closed die forging
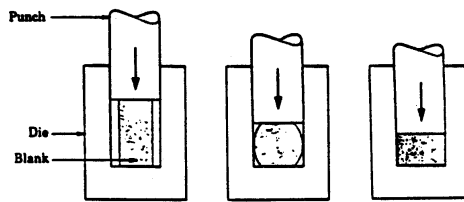
Friction prevents lateral slip across platens or dies, generating transverse compression within the billet, for equilibrium. Yield criteria based on differences in principal stress, hence greater vertical compression needed to cause yield in presence of transverse compression. In open-die forging the pressure can fall to Y at the free edges, where there is no transverse load; but in closed die forging the material presses against the die, giving greater constraint and transverse compression.

[Examiner's comments: unpopular question, though in some cases this was clearly the last question answered under time pressure. Discussion of failure mechanisms was often weak, with all failures described as "yielding".]

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