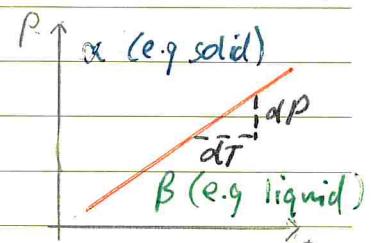
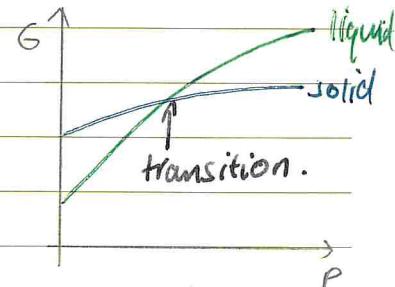


G. Materials in Extreme Conditions

No. 1
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Pressure

- Using the fundamental thermodynamic relation $dU = TdS - PdV$, we define pressure as $P = -\frac{dU}{dV}$ ← i.e positive pressure reduces V at constant U .
- Negative pressures are equivalent to isotropic tensile stresses.
- The Gibbs free energy is critical to phase transformations
 - using $G = H - TS$, $dH = dQ + VdP$ and $dQ = TdS$ for reversible changes at equilibrium, we have $dG = VdP - SdT$
- Changing pressure at constant temp, we have $(\partial G / \partial P)_T = V$, i.e G increases as P increases
 - but gradient of $G-P$ graph is volume
 - as $P \uparrow$, $V \downarrow$ ∴ curves get less steep.
 - i.e the phase of lower volume is preferred by higher pressures
- But $G \downarrow$ as $T \uparrow$: we can plot G against both T and P in 3D. Each phase will have a free energy surface
 - the projection of their intersections forms a $P-T$ phase diagram.



- Consider a small step (dT, dP) on the $P-T$ phase boundary
 - at all points on the phase boundary, $G_\alpha = G_\beta$ because equilibrium.
 - the change in dG along this step is:
$$\Delta(dG) = dG_\alpha - dG_\beta = (V_\alpha - V_\beta)dP - (S_\alpha - S_\beta)dT = 0$$

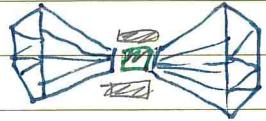
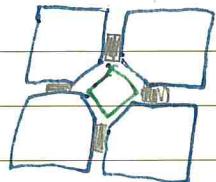
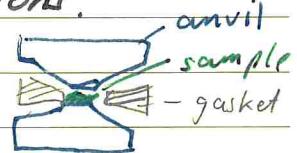
$$\therefore \Delta VdP - \Delta SdT = 0 \Rightarrow \frac{\partial P}{\partial T} = \frac{\Delta S}{\Delta V}$$

- This is the Clausius-Clapeyron equation, which relates the slope of the phase boundary to the relative entropies/volumes of the phases.
 - ↪ requires the approxn that ΔS and ΔV are independent of P, T .

- ↪ in practice, this is reasonable and explains why $P-T$ phase boundaries are almost straight lines.

Determining P-T diagrams

- Ideally, we would hold a sample at a given P-T and observe its phase *in situ*, but this may be impractical.
- Alternatively, we can quench the sample (preserving high P-T structure) then observe phase under ambient conditions.
- Tungsten carbide/diamond anvils can concentrate force onto a small area
 - sample constrained by a tough gasket
 - phase can be observed *in situ* e.g. with XRD.
- Multi-anvil devices can work with larger samples
 - good control over P and T & (with a heater).
 - difficult to observe samples *in situ*.
- To test very high T and P, a diamond-anvil cell can be used
 - temp. controlled by an IR laser or heating the diamond
 - can perform XRD/spectroscopy
 - but sample sizes limited by diamond size.
- Pulsed-laser implosion can replicate P-T similar to the cores of stars for a very short amount of time.



- We only need a few P-T datapoints, from which Clausius-Clapeyron can extrapolate phase boundaries.
- ΔV is easy to measure using XRD at room temp
- ΔS can be measured directly from calorimetry of the latent heat change at equilibrium: $\Delta S = \Delta H / T_{eq}$.
- Or S can be determined directly by heating from 0K to T :

$$C_p = T \frac{dS}{dT} \quad (\text{constant } p) \Rightarrow S(T_i) = \int_0^{T_i} \frac{C_p}{T} dT + \sum_i L_i \approx \text{latent heat.}$$
- In general, we shouldn't use $\Delta G = \Delta H - T\Delta S$. This is only true when we ignore pressure/volume. Thus for equilibrium phase transitions, we can only use $T_{eq} = \frac{\Delta H}{\Delta S}$ at zero pressure.

High pressure

- As $P \uparrow$, lower volumes are achieved by higher packing densities.
- When a **molecular solid** (e.g. ice, dry ice) is under enough pressure, atoms become close enough for molecular identities to be lost
 - electrons can be delocalised locally to form polymers e.g. polymeric CO_2
 - or delocalised completely to form a metal, e.g. orthorhombic molecular I_2 becomes a metallic fcc with 2x packing eff.
- Many useful materials require high pressure;
 - superhard materials e.g. artificial diamond
 - new superconductors/semiconductors
 - new organometallic catalysts

Reconstructive phase transitions

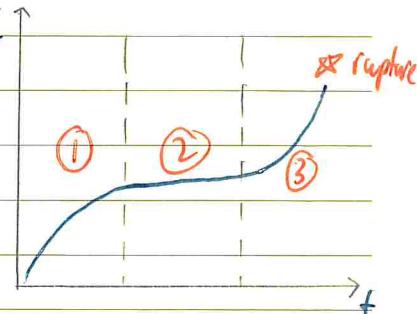
- Phase transitions under pressure are often **reconstructive**: the two structures are not closely related (as opposed to displacive).
 - involves bond breaking, hence there is a high activation energy and metastability is common (e.g. diamond vs graphite)
 - transition is discontinuous (unlike displacive transitions).
 - the new phase must 'precipitate' and grow.
 - e.g. fcc $\text{NaCl} \rightarrow$ cubic P CsCl structure under pressure
- Explains **deep-focus earthquakes** which originate deep in the mantle where rock flows plastically:
 - in upper layers, Mg_2SiO_4 takes the olivine phase
 - as pressure increases, the spinel phase becomes favoured.
 - both polymorphs have SiO_4 tetrahedra and MgO_6 octahedra.
 - olivine exists metastably even at 600km depths. When the phase transition occurs, volume $\downarrow 8\% \Rightarrow$ implosion shock.
- Diamond \leftrightarrow graphite transitions are kinetically unfavourable
 - diamonds are found in nature when deep-Earth materials are rapidly thrust up, before the diamond \rightarrow graphite transition.
 - growing artificial diamonds normally requires diamond seeds to encourage phase growth.

Temperature

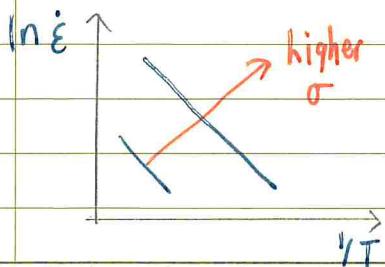
- Supercooling is possible because it is hard to nucleate solids.
- Melting, however, begins to occur even below the melting point.
- The Lindemann theory of melting suggests that melting occurs when vibrations reach a critical fraction of interatomic spacing
 - ↳ cannot explain why the structure breaks down at a specific temp.
- The Born theory suggests that melting occurs when one of the crystal's elastic shear moduli goes to zero. This would involve a 'rigidity catastrophe' that is not observed in reality.
- Actually, melting normally begins on the surface (even below the mp), because it is favourable to have a solid-liquid and liquid-gas interface than solid-gas, i.e. $\gamma_{sv} > \gamma_{ls} + \gamma_{lv}$
 - explains the lack of a nucleation barrier: liquid already there.
 - the layer's thickness increases as T_m is approached on heating.
- This can be modeled as a solid sphere with a liquid layer:
$$r^* = -\frac{2\gamma_{ls}}{\Delta G_v} = -\frac{2\gamma_s}{\Delta S_v \Delta T} \quad \Delta S_v \text{ is entropy of freezing} \quad \Delta T = T_m - T$$
 - if $r < r^*$, the nucleus shrinks i.e. liquid grows in (melting).
 - at low temp, ΔT large $\therefore r > r^*$ and crystal is stable.
 - but as temp T , $r^* \uparrow$ and may exceed r
 - thus particles can melt below their bulk mp, with a 'supercooling' dependent on the particle radius: $\Delta T = -\frac{2\gamma_s}{\Delta S_v r^*}$
- **Superheating** requires the suppression of surface melting, e.g. by coating the crystal or embedding it in a solid matrix
- Alternatively, we can heat very quickly so there is no time to nucleate, e.g. by using laser irradiation.

Creep

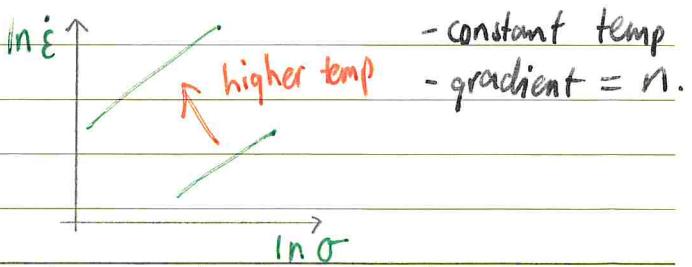
- Creep is the time-dependent plastic deformation of a material under an applied stress which is less than the yield stress
- The creep rate depends heavily on the temperature. Define the homologous temperature as T/T_m (both in Kelvin). Creep becomes obvious at $T/T_m > 0.3$ for pure metals, $T/T_m > 0.4$ for alloys/ceramics
- Creep shows three regimes:
 - ① Primary - $\dot{\epsilon}$ initially high but slows due to work hardening
 - ② Secondary - balance between work hardening and annealing
 - ③ Tertiary - necking and fracture.
- Because ① and ③ are transients, we focus on secondary (steady state) creep. In this case, $\dot{\epsilon} = A\sigma^n$, where n is the stress exponent.



- At high stress, the main creep mechanism is dislocation creep, a.k.a power-law creep, with $n \approx 3-10$.
- Dislocations can climb over obstacles : positive climb absorbs vacancies, negative climb emits vacancies.
- Thus there is diffusion of atoms, leading to gradual deformation even below σ_y . But the exact path depends on temperature :
 - at higher temp, we have bulk diffusion of lattice atoms in/out of the dislocation core
 - at low temp, we have core diffusion i.e only significant diffusion along the dislocation core itself.
- The creep rate is thus closely linked to diffusion i.e $\dot{\epsilon} = A'\sigma^n \exp(-Q/RT)$
 \hookrightarrow thus we can investigate $\dot{\epsilon}$ against σ or T

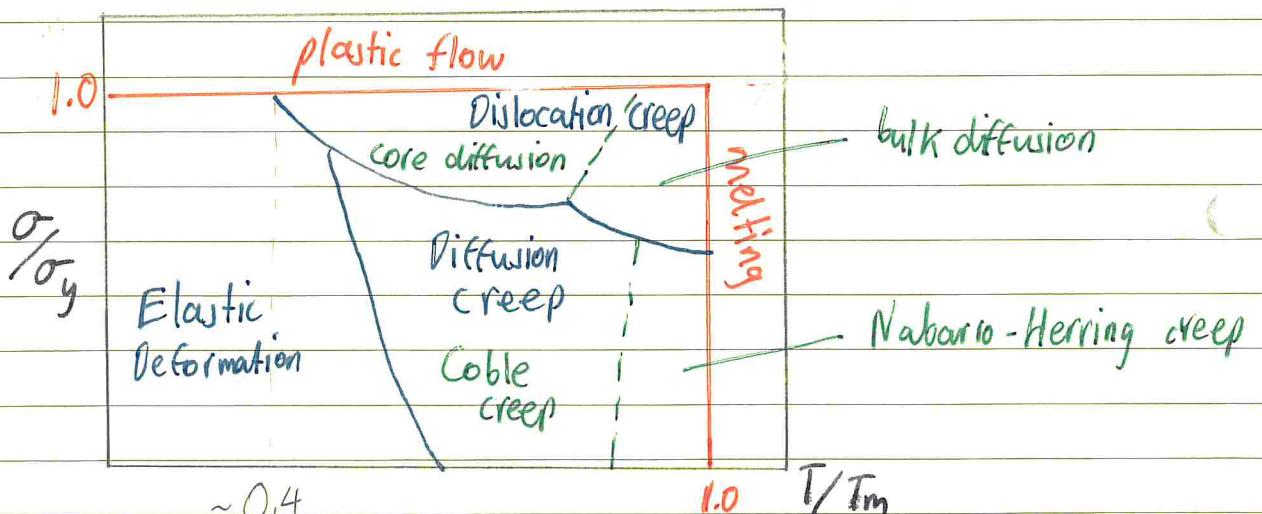
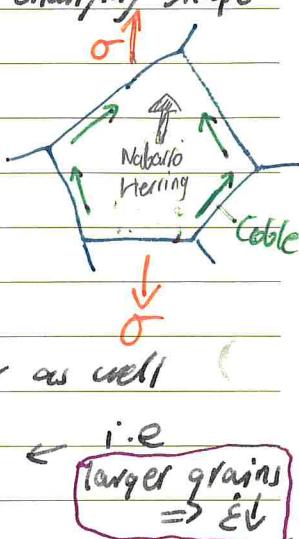


$$\text{constant } \sigma \text{ gradient} = \frac{Q}{R}$$



$$\begin{aligned} &\text{- constant temp} \\ &\text{- gradient} = n. \end{aligned}$$

- However, at low stress, dislocation motion is less important. The main creep mechanism is then **Diffusion creep**, also called **linear creep** because the stress exponent $n \approx 1$.
- Atomic diffusion, biased by stress, may lead to grains changing shape
 - at high temp, diffusion may occur through the bulk lattice - **Nabarro-Herring creep**
 - at low temp, diffusion is mainly along the boundaries (**Coble creep**). This has lower activation energy because grain boundaries are more disordered.
- Overall, diffusion creep depends on the grain diameter as well as the activation energy: $\dot{\epsilon} = \frac{B}{d^2} \sigma \exp\left(-\frac{Q}{RT}\right)$ ← i.e. larger grains $\Rightarrow \dot{\epsilon} \propto d^{-2}$
- ↳ i.e. larger grains have better creep resistance
- ↳ must be a compromise, because smaller grains lead to $\nabla \sigma_y$.
- If grains are oriented, it will be easy for them to slide over each other, hence creep will be easier.

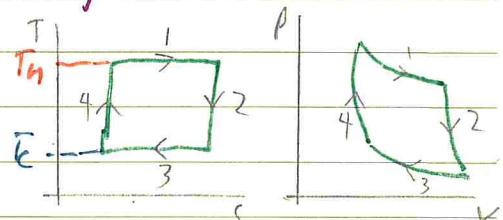


- To design creep resistant alloys:
 - high T_m so T/T_m is low
 - minimal dislocation motion
 - stable precipitates (ie they don't grow)
 - very large grains which should be randomly oriented and pinned to prevent sliding.

Superalloys for jet engines

- The ideal heat engine is modeled by the **Carnot cycle**:

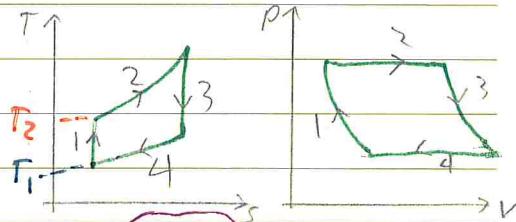
- Isothermal expansion: gas does work
- Adiabatic expansion, cools to T_c
- Isothermal compression, heat released
- Adiabatic compression.



- Work done (useful) is $T_h(S_0 - S_A) - T_c(S_B - S_A)$.
- The **efficiency** is thus $1 - T_c/T_h \Rightarrow$ hotter is more efficient.

- A gas turbine follows the **Brayton cycle**:

- Adiabatic compression of fresh air
- Heating of gas at constant P
- Adiabatic expansion - gas does work
- Hot gas dissipates at constant P .



- The efficiency of a jet engine is then $1 - T_c/T_h$

- This explains the materials challenge: very high temp ($T_c/T_m > 0.25$) and operating stress. Blades can be cooled internally with cold air channels and insulated with a thermal barrier coating, but we still need a good material.

Nickel-based superalloys

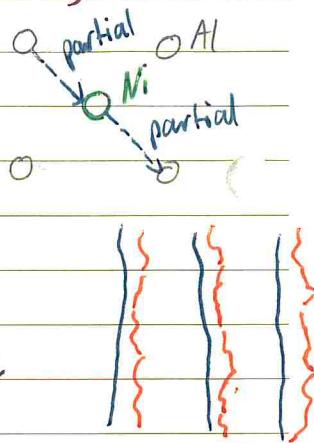
- Ceramics are not tough enough, hence we use metals. T_m is not the only consideration - other problems are:
 - polymorphism**, i.e. phase changes over the temp range, e.g. bcc \leftrightarrow fcc in iron. This is not acceptable because of the volume change.
 - diffusivity**: $ccp < hcp \ll bcc$, $\therefore CCP$ is preferred
 - brittleness**
 - density**, particularly because blades are in a centrifuge
 - oxidation resistance**
- Nickel has a stable CCP structure and has no major issues, hence is the base metal even though it doesn't have the highest T_m .

- Modern Ni alloys are very complex, however they are all based on the γ - γ' microstructure:

- γ is the nickel-based CCP solid solution
- γ' is the precipitating phase, e.g. Ni_3Al
- dense dispersion of γ' ppts (~70%) in the γ matrix.

- γ' is an ordered phase: cubic primitive Al, with Ni on the face-centred sites. This results in order hardening

- $\frac{a}{2} \langle 1\bar{1}0 \rangle$ is not a lattice vector
- but $a \langle 100 \rangle$ is too long
- thus $\frac{a}{2} \langle 1\bar{1}0 \rangle$ does pass, but requires a lot of energy because it creates an antiphase boundary
- these dislocations move in pairs, such that both of them passing through is a perfect dislocation.
- hence there will be a jagged line and a smoother one, because the second partial fixes the structure.

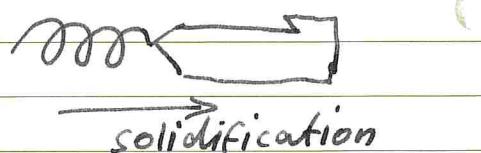


- Order hardening provides significant strengthening and creep resistance.

- The γ and γ' phases are designed to be coherent, such that there is little driving force for precipitates to coarsen.

- We can make single-crystal blades using directional solidification:

↳ growth of the solid starts from the left, growing through the pig-tail grain selector



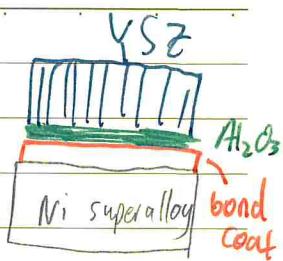
↳ thus only one grain grows into the mould.

Thermal barrier coatings

- Needs low heat conductivity, very high T_m , and adequate strength.
- Technical ceramics have the best strength and max service temp.
- YSZ has a very low thermal conductivity for a ceramic.
- But oxygen easily diffuses through YSZ, so we need a thin dense layer of alumina to prevent oxidation.
- These are attached to the blade with a bond coat (metal alloy 'glue').

- Because YSZ has a lower coeff of thermal expansion, it is grown in a columnar structure.

↳ hence the columns can ~~expand~~ separate very slightly rather than being put under tension.



Ice

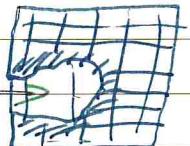
- Ice is special because it remains brittle even near its melting point.
- The most common form is I_h , a stable hexagonal crystal with O atoms in the Zn/rs sites in wurtzite. The orientations are constrained by the ice rules:
 - each O must be covalently bonded to two Hs
 - there is exactly one H atom between each pair of Os.
- Even with these rules, there can be some proton disorder
 - proton disorder disrupts translational symmetry, hence dislocation motion is very difficult \Rightarrow ice is brittle.
 - but because T/T_m is high, ice can undergo creep, which is partially responsible for glacier flow.
- Ice has a thin layer of surface melt ($< 100\text{nm}$ thick)
 - ↳ explains low coeff. of friction and high adhesion

Regelation

- Because ice is less dense than water, when the pressure increases, the melting point reduces, because it prefers to be compact.
- Hence the I_h -liquid phase boundary has a negative slope.
- This leads to **regelation**, in which a material melts under pressure but refreezes when pressure is reduced.
- This allows for **basal sliding**, in which the movement of a glacier is lubricated by a layer of water.

Radiation Damage

- Radiation, i.e. high energy particles, can damage materials.
- In a fission reactor, a uranium fuel releases high energy neutrons, which boils water. Fuel rods are surrounded by cladding, usually austenitic stainless steel.
- High energy neutrons colliding with crystals trigger **displacement cascades**
 - ↳ neutron strikes an atom, ~~and~~ displacing it and creating a **Frenkel pair** (vacancy + interstitial). The interstitial is a **primary knock-on atom (PKA)**.
 - ↳ PKA moves through the lattice ($1\text{nm} \sim 1\mu\text{m}$) creating more knock-ons in a displacement cascade
 - ↳ atoms eventually come to rest.
- This creates a region with high vacancy density surrounded by high interstitial density.
 - ↳ recombination is limited because of the separation
- The accumulated damage in an irradiated material can be quantified as the **displacements per atom (dpa)**, i.e. the number of times a given atom is displaced in a certain time
 - ↳ damage rate depends on neutron flux and the collision cross-section.



Effects of radiation damage

- In an FCC metal (like the austenitic cladding), interstitial atoms can condense into a monolayer disc between $\{111\}$ planes, forming an **interstitial loop**
- However, interstitial atoms tend to be more mobile (and cause more strain), so they tend to be absorbed into dislocations / grain boundaries
- Hence there would typically be an excess of vacancies
 - ↳ these too can condense to form a **vacancy loop**.
- Both of these loops constitute stacking faults, but because $b \perp$ planes, they are **sessile**.

- A constantly-irradiated system will eventually have steady state dislocation density
 - ↳ balance between damage and annealing
 - ↳ i.e. ρ will be higher if neutron flux ↑ or temp ↓
 - ↳ cold-worked materials may actually have $\rho \downarrow$ under irradiation.
- Irradiation at higher temp ($T/T_m > 0.2$) leads to 'precipitation' of vacancies to form **voids** (which are continually produced).
- The formation of voids leads to **swelling**, i.e. volume increases $\sim 1\% / 10^6 \text{ Pa}$.
- At higher temps, there will be fewer voids but they may be larger
 - ↳ less ΔG_f for nucleation but more diffusion for growth.
- Some materials may become **amorphised** by radiation, **partic** as seen in naturally-occurring **metamict** minerals.

Life in Extreme Conditions

- **Extremophiles** are able to survive in extreme conditions. **Polyextremophiles** show resistance to multiple factors, e.g. shrimp near deep ocean vents can survive high temp/pressure/pH.
- Tardigrades can undergo **cryptobiosis**, suspending their metabolism and dehydrating, allowing them to survive almost anything.

Applications

- Thermus brockianus in hydrogen peroxide removal:
 - waste water from fabric/paper bleaching must be treated to remove H₂O₂
 - most catalase enzymes are denatured by temp/pH
 - brockianus is found in geysers, and produces catalase which works in high temp/pH.
 - half life $\sim 10^5$ times more than other catalases.
- **Psychrophiles** (live in low temps) for biological detergents that are effective for washing at room temp.

• Self-healing concrete

- concrete is made by mixing cement, water and gravel.
- it is strong in compression but weak in tension
- this can be improved by reinforcing with steel
- water may infiltrate small cracks, which will grow due to a freeze-thaw cycle
- *Bacillus pasteurii* is an alkaliphile that excretes calcite
- embedded into concrete along with calcium lactate (food source)
- if water gets in, they wake up and eat, excreting calcite and plugging the crack.