

# G. Materials in Extreme Conditions

No. 1

Date 14 . 5 . 17

## 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.

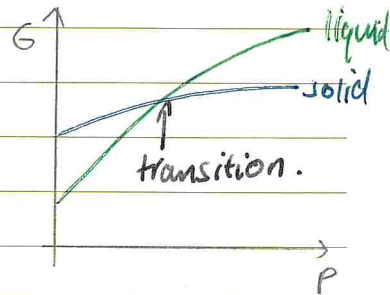
• The Gibbs free energy is critical to phase transformations  
↳ using  $G = H - TS$ ,  $dH = \int q + VdP$  and  $\int q = Tds$  for reversible changes at equilibrium, we have  $dG = VdP - SdT$

• 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

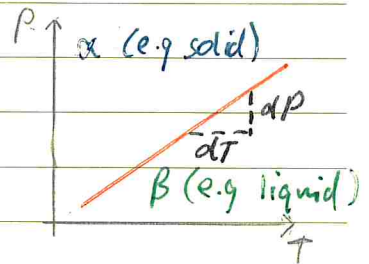
- as  $P \uparrow$ ,  $V \downarrow$  ∴ curves get less steep.

- 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 intersection 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:

$$\Delta(dG) = dG_\alpha - dG_\beta = (V_\alpha - V_\beta)dP - (S_\alpha - S_\beta)dT = 0$$

$$\therefore \Delta V dP - \Delta S dT = 0 \Rightarrow \frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

• This is the Clausius-Clapeyron equation, which relates the slope of the phase boundary to the relative entropies/volumes of the phases.

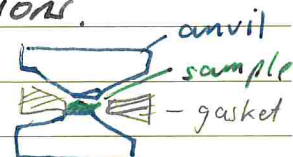
↳ requires the approx that  $\Delta S$  and  $\Delta V$  are independent of  $P, T$ .

↳ 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.

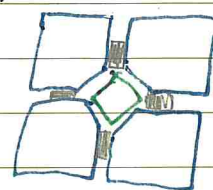
- Tungsten carbide / diamond anvils can concentrate force onto a small area



- sample constrained by a tough gasket
- phase can be observed in situ e.g. with XRD.

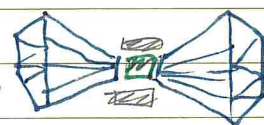
- Multi-anvil devices can work with larger samples

- 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.

- $\Delta V$  is easy to measure using XRD at room temp

- $\Delta S$  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:

$$C_p = T \frac{dS}{dT} \quad (\text{constant } p) \Rightarrow S(T_1) = \int_0^{T_1} \frac{C_p}{T} dT + \sum_i L_i \quad \text{latent heat.}$$

- 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 PT, 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  $\text{CO}_2$
  - or delocalised completely to form a metal, e.g. orthorhombic molecular  $\text{I}_2$  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

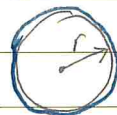
- Phase transitions under pressure are often **reconstructive**: the two structures are not closely related (as opposed to displacive).
  - involves bond breaking, hence there is a high activation energy and metastability is common (e.g. diamond vs graphite)
  - transition is discontinuous (unlike displacive transitions).
  - the new phase must 'precipitate' and grow.
  - e.g. fcc 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,  $\text{Mg}_2\text{SiO}_4$  takes the olivine phase
  - as pressure increases, the spinel phase becomes favoured.
  - both **polymorphs** have  $\text{SiO}_4$  tetrahedra and  $\text{MgO}_6$  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:

$$r^* = -\frac{2\gamma_{ls}}{\Delta G_v} = -\frac{2\gamma_{lv}}{\Delta S_v \Delta T} \quad \begin{array}{l} \Delta S_v \text{ is entropy of freezing} \\ \Delta T = T_m - T \end{array}$$

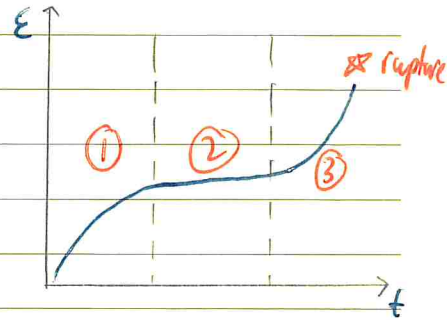


- if  $r < r^*$ , the nucleus shrinks i.e. liquid grows in (melting).
- at low temp,  $\Delta T$  large  $\therefore r > r^*$  and crystal is stable.
- but as temp  $\uparrow$ ,  $r^* \uparrow$  and may exceed  $r$
- thus particles can melt below their bulk mp, with a 'supercooling' dependent on the particle radius:  $\Delta T = \frac{-2\gamma_{lv}}{\Delta S_v r^*}$
- **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.

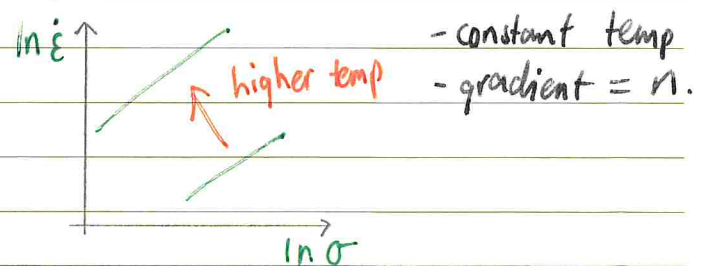
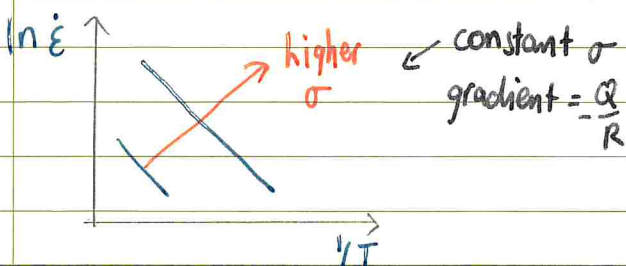


## Creep

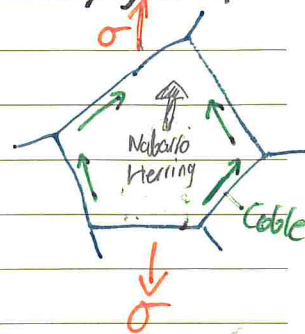
- Creep is the time-dependent plastic deformation of a material under an applied stress which is less than the yield stress
- The **creep rate** depends heavily on the temperature. Define the **homologous temperature** as  $T/T_m$  (both in Kelvin). Creep becomes obvious at  $T/T_m > 0.3$  for pure metals,  $T/T_m > 0.4$  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  $\sigma_y$ . 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.  $\dot{\epsilon} = A'\sigma^n \exp(-Q/RT)$   
 $\rightarrow$  thus we can investigate  $\dot{\epsilon}$  against  $\sigma$  or  $T$



- 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  $n \times 1$ .
- 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.



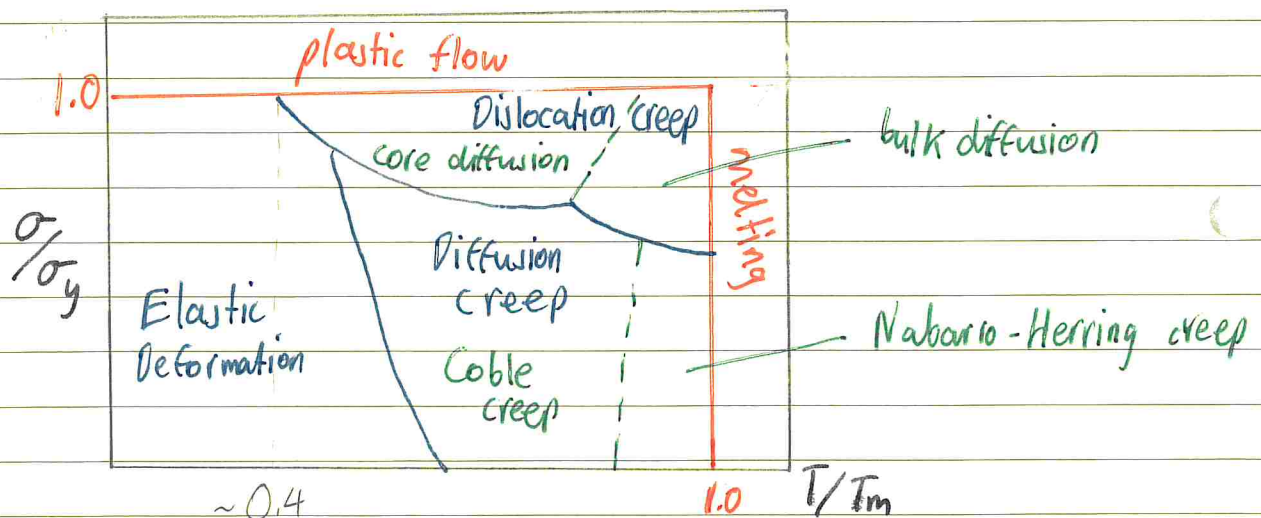
- Overall, diffusion creep depends on the grain diameter as well as the activation energy:

$$\dot{\epsilon} = \frac{B\sigma}{d^2} \exp\left(\frac{-Q}{RT}\right) \leftarrow \text{i.e. } \boxed{\text{larger grains} \Rightarrow \dot{\epsilon} \downarrow}$$

↳ i.e. larger grains have better creep resistance

↳ must be a compromise, because smaller grains lead to  $\sigma_y$ .

- 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:

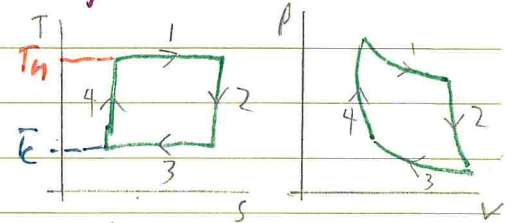
- high  $T_m$  so  $T/T_m$  is low
- minimal dislocation motion
- stable precipitates (ie they don't grow)
- very large grains which should be randomly oriented and pinned to prevent sliding.



## Superalloys for jet engines

• The ideal heat engine is modelled by the **Carnot cycle**:

1. Isothermal expansion: gas does work
2. Adiabatic expansion, cools to  $T_c$
3. Isothermal compression, heat released
4. Adiabatic compression.

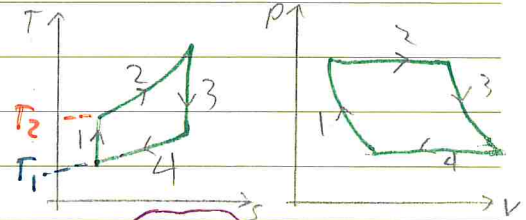


• Work done (useful) is  $T_H(S_B - S_A) - T_C(S_B - S_A)$ .

• The **efficiency** is thus  $1 - T_C/T_H \Rightarrow$  hotter is more efficient.

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

1. Adiabatic compression of fresh air
2. Heating of gas at constant  $P$
3. Adiabatic expansion - gas does work
4. Hot gas dissipates at constant  $P$ .



• The efficiency of a jet engine is then  $1 - T_1/T_2$

• This explains the materials challenge: very high temp ( $T/T_m > 0.25$ ) 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.

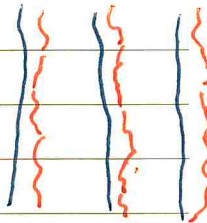
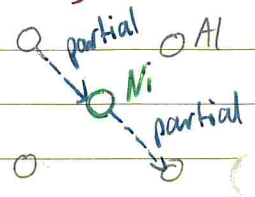
## Nickel-based superalloys

• 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**:  $ccp < hcp < bcc$ ,  $\therefore$  ccp is preferred
- **brittleness**
- **density**, particularly because blades are in a centrifuge
- **oxidation resistance**

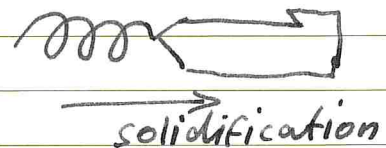
• Nickel has a stable ccp structure and has no major issues, hence is the base metal even though it doesn't have the highest  $T_m$ .

- Modern Ni alloys are very complex, however they are all based on the  $\gamma$ - $\gamma'$  microstructure:
  - $\gamma$  is the nickel-based ccp solid solution
  - $\gamma'$  is the precipitating phase, e.g.  $Ni_3Al$
  - dense dispersion of  $\gamma'$  ppts (~70%) in the  $\gamma$  matrix.
- $\gamma'$  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  $\gamma$  and  $\gamma'$  phases are designed to be coherent, such that there is little driving force for precipitates to coarsen.



↓ motion

- 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.

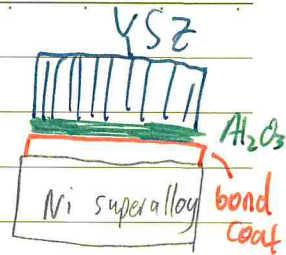


## Thermal barrier coatings

- 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.



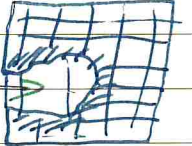
## Ice

- 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  $2n/5$  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, displacing it and creating a Frenkel pair (vacancy + interstitial). The interstitial is a primary knock-on atom (PKA).
  - ↳ PKA moves through the lattice (1nm ~ 1µm) 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  $b \perp L$  planes, they are sessile.



- A constantly irradiated system will eventually have steady state dislocation density
  - ↳ balance between damage and annealing
  - ↳ i.e.  $\rho$  will be higher if neutron flux  $\uparrow$  or temp  $\downarrow$
  - ↳ 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  $\sim 1\%/dpa$ .
- At higher temps, there will be fewer voids but they may be larger
  - ↳ less  $\Delta G_v$  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  $H_2O_2$ .
  - 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.