

Constants/Basics

$k_b = 1.380 \cdot 10^{-23} = \frac{4.1 \cdot 10^{-21}}{25 + 273.15} \frac{J}{K} |eV = 1.602 \cdot 10^{-19} J| R = 8.314 \cdot 10^{23} \frac{J}{K mol}$
SI-Units: micro - E-6, nano - E-9, piko - E-12, femto E-15
Young's Modulus: $E = \sigma/\varepsilon$, where $\sigma = F/A$ and $\varepsilon = (L - L_0)/L_0$, ex. values: Metals-100GPa, Plastics-few GPa, Diamond-1000 GPa, Elastom.-10 MPa
Energy: Densities: most nonfoam solid mat. $\sim 1000 kg/m^3$ (metals/techn. ceramics 3-10x denser)
Thin-Walled Cylindrical/Spherical Vessel: $V = e2\pi R(L + 2R)$

Vertical stress $\sigma_z = \frac{p\pi R^2}{2\pi Re} = \frac{pR}{2e}$ and hoop/wall stress $\sigma_\theta = \frac{pR\delta}{e\delta} = \frac{pR}{e}$ with wall thickness e and δ going along the wall

Buckling: $F \leq \pi^2 EI/L^2$

Annealing: improve machinability, involves heating steel to spec. temp. where recrystallization can occur (any defects caused by deformation of the metal are repaired) and then cooling at very slow and controlled rate.

Makes metal more ductile, larger crack size. **Tempering:** reduce excess hardness, involves heating the metal to a precise temp. below the crit. point, int. stresses in metal are relieved

Hardening: harden the surface of a metal by infusing elements into material's surface, forming a thin layer of harder alloy

Necking: preventing localization of deformation for having a ductile material. Improve ductility with: large strain hardening rate, strong positive dependence on deformation rate, particles preventing the formation of shear bands.

Dielectric const of non conducting materials must be as high as possible if material used for antenna, miniaturization of mobile devices.

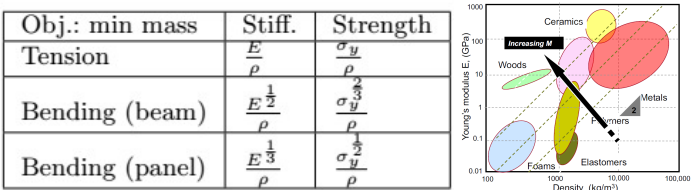
Materials Selection

Material Index:

Valid constraint: lenght, stiffness, max load, min fracture toughness. Component performance is limited by the material index: single material property (therm conductivity), or material property group (modulus / density).

Example: Material index for a stiff, light beam

- 1. Function:** Beam
- 2. Constrain:** Length L and C is specified, must have bending stiffness $> S^*$.
Equation for constraint on area A : $S^* = \frac{CEI}{L^3} = \frac{CEA^2}{12L^3} \rightarrow A = \left(\frac{12L^3 S^*}{CE}\right)^{1/2}$
- 3. Objective:** Minimize mass m : $m = AL\rho$
- 4. Performance metric m :** $m = \left(\frac{12L^5 S^*}{C}\right)^{1/2} \left(\frac{\rho}{E^{1/2}}\right) \rightarrow$ choose material with largest index $M = \left(\frac{E^{1/2}}{\rho}\right)$



To rank the result in charts, often the log is taken: $M = \frac{E^{1/2}}{\rho} \rightarrow E = \rho^2 M^2$
 $\rightarrow \log E = 2 \cdot \log \rho + 2 \cdot \log M$.
This results in a slope of 2 for beams. With increasing M the line is being moved to the top.
For a tie-rod the index is E/ρ with slope 1, for a panel the index is $E^{1/3}/\rho$ with slope 3.

Optimization of Multiple Constraints and Objectives:

Design requirements set constraints on material choice objectives - criteria for optimising

Constraints: The material must be ...

Objectives: Minimize ...

Take, as example, simultaneously minimizing mass m and cost C .

- “Solution”: a viable choice, meeting constraints, but not necessarily optimum by either criterion.
- “Dominated solution”: one that is unambiguously nonoptimal
- “Non-dominated solution”: one that is optimal by one metric (but not usually by both)
- “Trade-off surface”: the surface on which the non-dominated solutions lie (Pareto Front)

Strategy 1:

- Make trade-off (TO) plot
- Sketch TO surface
- Intuition: select sol. on TO surf

Strategy 2:

- Reformulate all but one of the objectives as constraints, setting an upper limit
- Good if budget limit, cost is treated as constraint (not objective)

Strategy 3:

- Change α to define the most important parameter
- Define locally-linear penalty function $Z = \alpha m + C$, (α = cost connect to m)
- Seek solution with smallest Z (Z is lifetime cost)
- Either evaluate Z for each solution and choose materials with the lowest value, or: Make trade-off plot, plot on it contours of Z : $m = -\frac{1}{\alpha}C + \frac{1}{\alpha}Z$ with lines of constant Z and slope $-1/\alpha$, read off solution with lowest Z .

Exchange Constant α :

For the penalty function Z in transport systems: mass m is the fuel, life cost equals to C (initial cost) + fuel cost over life, scaling with mass m .

Shape Efficiency:

If shape is not fixed \rightarrow include S.E
The shape factor φ is dimensionless and characterizes shape. It has an upper limit for each material, set by manufacturing constraints or local buckling.

Bending stiffness:

- Take ratio of bending stiffness S of shaped section to that of a neutral reference section S_0 of same cross-sectional area A
 - Define a standard reference section: a solid square with area $A = b^2$
 - Second moment of area is $I = \int y^2 b(y) dy$; stiffness scales as EI
 - Define shape factor for elastic bending $\varphi_e = \frac{S}{S_0} = \frac{EI}{EI_0} = 12 \frac{I}{A^2}$, $I_0 = \frac{b^4}{12}$
- If the factor were $\varphi_e = 10$, the new shape would 10 times stiffer than the reference shape. Theoretical limit $\varphi_e \approx 2\sqrt{\frac{E}{\sigma_y}}$

Bending strength:

Shape factor for failure $\varphi_f = \frac{F_f}{F_{f0}} = \frac{\sigma_y Z}{\sigma_y Z_0} = 6 \frac{Z}{A^{3/2}}$, $Z_0 = \frac{b^3}{6}$

Example including shape:

The constraint on the area A changes using $\varphi_e = 12 \frac{I}{A^2}$ to $A = \left(\frac{12I}{\varphi_e}\right)^{1/2}$.
Solving equation for S^* after I and inserting into A leads to:

$$m = \left(\frac{12L^5 S^*}{C}\right)^{1/2} \left(\frac{\rho}{\varphi_e E^{1/2}}\right) \rightarrow \text{material with largest } \left(\frac{\varphi_e E^{1/2}}{\rho}\right)$$

Material Stiffness

For alloy calss, yield strength σ_y may change by orders of magnitude!
When a material is stressed, it can increase the enthalpy U (internal energy, stretching bonds) or \downarrow entropy S to compensate (straightening chains).

Enthalpic Response (molecular solids) (Hard materials)

Young's modulus $E \approx \frac{U_b}{r_0^3} [MPa]$, where U_b bond energy [J] (typically $\approx 1eV$) and r_0 bond length [m] (typically $\approx 0.2nm$). The Young's modulus measures the response of a material when a uniaxial stress is applied.

At melting limit: $U_b \approx k_b T$

Bulk modulus $K \approx \frac{U_b}{3r_0(1-2\nu)}$, calculated via the Poisson ratio (compressibility, typical values around $\frac{1}{3}$) $3K(1-2\nu) = E (\rightarrow \nu \approx \frac{1}{3})$. The bulk modulus measures how a material responds to isotropic pressure.

For hard materials $E \approx K$

Entropic Response (polymeric solids) (Soft materials)

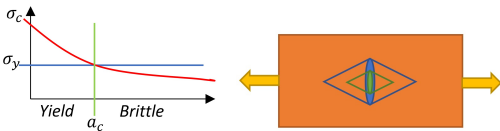
$E \approx \frac{k_b T}{V_c} = \rho_n k_b T$, where V_c =volume of an individual polymer chain and ρ_n =# chains per unit volume of material (crosslinker density). Soft materials have a lot higher K compared to their E , as chains cannot stretch out under pressure (therefore often approximated as incompressible, $K \rightarrow \infty$, $\nu \approx \frac{1}{2}$).
 $V_c \gg r_0^3$, that's the reason why polymers are softer than harb materials (also $k_b T \approx \frac{1}{40} U_b$)

Polymers become glassy at low temperatures!

Average squared polymer end-to-end distance $\langle l^2 \rangle = L_0^2 = \sqrt{Nb^2}$, with L_0 the sample length, N segments of length b per chain.

To increase **UV resistance:** additives, antioxidants, light stabilizers and fluorescent whitening agents

Material Failure



Critical crack size: $\sigma_y = \sigma_c$.

We normally want to avoid unstable crack growth (brittle fracture), which happens when critical stress is reached: $\sigma_c = c \frac{K_{Ic}}{\sqrt{a}}$, where $K_{Ic} [Pa \cdot m^{1/2}]$ the fracture toughness, c being a constant and a the defect size/half the crack length.

By equating σ_c with yield stress σ_y (plastic deformation), we get critical crack size $a_c = (K_{Ic}(\sigma_y)^2)$. When $a \leq a_c$, then **yield**, otherwise **unstable crack growth** will occur first. a_c is submillimetric for brittle and elastomeric materials and can be large for metals.

Relation between K_{Ic} and G_c or E :

The presence of a growing crack da reduces the free energy of the sheet (unloaded sheet region $\approx a^2$) by $at \frac{\sigma_c^2}{E} da$. To create new surface, an energy G_c (Energy for a new crack) per unit area is required (fracture energy, material property). Thus if the crack advances by an amount da , the **energy penalty** (=Energy released) is $G_c t da$. Equation both conditions leads to the condition for crack growth: $\sigma_c \approx \sqrt{\frac{G_c E}{a}}$ or with definition for σ_c : $K_{Ic}^2 \approx G_c E$.
 $G[Pa], \sigma[Pa], E[Pa], a[m]$

(Image: released energy come from the area betw. the green and the blue area)

Fracture energy G_c for Brittle Materials (Low Plastic Deformation)

Does not depend on manufacturing defects!

The energy cost is limited to breaking all bonds along the position of the new crack, resulting in $G_c \approx U_b/r_0^2$.

As temperature decreases: $G_c \downarrow, \sigma_y \uparrow \rightarrow a_c \downarrow$

Higher resistance by: Alloying (carbon blocks dislocations), Precipitation hardening (nanoparticles block dislocations), modified cristal size (boundaries block dislocations), adding dislocations (dislocations make it harder for other dislocations to move)

Lake Thomas Theory $E \propto \frac{1}{n}, G_c \propto n^{1/2}$
We need to give the chain a minimum of $\sim nU_b$ in order to break it, with n monomers. Upon breaking, all stored free energy in the chain is released as heat. We have to supply at least enough energy to break all the bonds in every chain that crosses the fracture surface. On average, this means that we have to effectively break every bond within $\sim r_0\sqrt{n}$ (radius of relaxed monomer chain) from the fracture surface. $G_c \approx \sqrt{n}\frac{U_b}{r_0}$ (\sqrt{n} times more than brittle)

Light Metals

Least number of independent glide systems (and so less ductile): HCP

Aluminium (Al):

Numbering System: at least 99% Al - 1, Copper - 2, Manganese - 3, Silicon - 4, Magnesium - 5, Magnesium+Silicon - 6, Zinc - 7, Other elements - 8. The respective number is then the first of the following sequence (where X also numbers): Al [Number]XXX

Temper Designation System: F - As fabricated (no control employed), O - Annealed, W - Solution treated, T - Thermally Treated, to produce stable tempers other than F, O, or H

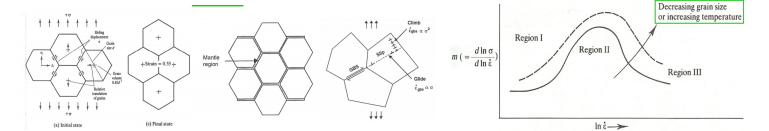
Titanium (Ti):

Alloy Classes:

α : Hexagon Closest Packing (HCP), non-heat treatable, generally very weldable, satisfactory room-temp strength, good toughness, reasonably good ductility, good creep resistance, weldable, bad fabricable. $O, Al(FCC), Ga, N, C_p$
 α/β : 4-6% of β -phase stabilizers, heat treatable, at equilibrium $\alpha + \beta$, \uparrow room-temp strength + \downarrow creep resistance + \downarrow fabricability with $\uparrow \beta$ -stabilization, good toughness, weldable at $\beta V_f < 20\%$, good producibility.

β : Cubic Body Centered (CBC), rich of β -phase, readily heat treatable, at equilibrium $\alpha + \beta$, high room-temp strength, low creep resistance, good toughness, poor weldability, excellent fabricability. Elemen: Mo, V, W, Ta, Si, V

Superplasticity



Prerequisite: Grain size $< 10\mu m$ (and need to be able to rotate and slide relative to each other), High deformation temperature ($0.5 - 0.65T_M$), Low deformation rate/velocity ($10^{-4} - 10^{-3} \frac{1}{s}$) and strain sensitive material $\sigma = K\dot{\epsilon}^m$ with $0.3 < m < 0.8$ ($m = 1$ for Newtonian fluids and $m = 0.001$ for standard deformation in metals) $\rightarrow m = \frac{d \ln(\sigma)}{d \ln(\dot{\epsilon})}$

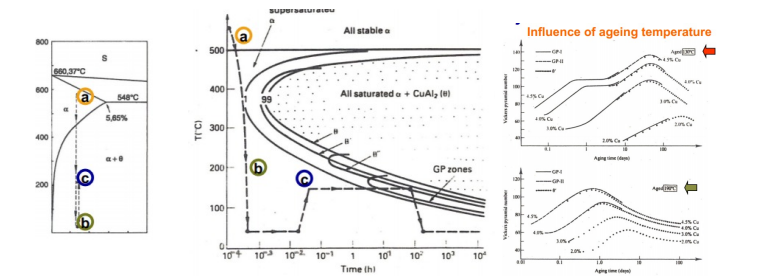
Mechanisms: grain switching (alone would create voids), deformations of the grains (mantle and core, slip and climb). I. flow dominant, II. two mech. and III. dislocation dominant.

Hardening

Low temp.: small grain size and homo. distrib. of precipitate \rightarrow strong alloys.
High temp.: microstructure should NOT include coherent precipitates with a strongly different lattice parameter compared to the matrix.

Lattice Friction (Peierls Stress)	$\Delta\tau = \frac{2G}{1-\nu} \exp\left[-\frac{2\pi w}{b}\right]$	bonding
Solid Solution Hardening	$\Delta\tau = AG_c^{3/2}c^{1/2}$	Rough glide plane
Dispersion hardening	$\Delta\tau = \frac{Gb}{L}$	Interaction \perp / Particle
Cold Working (Taylor-Hardening)	$\Delta\tau = \alpha Gb\sqrt{\rho}$	Interaction \perp / \perp
Grain-Boundary Hardening (Hall-Petch)	$\Delta\tau = k_d c^{-1/2}$	Interaction Dislocation/GB
Creation of threading dislocations At interfaces (Nix-Freund)	$\Delta\tau \approx m \frac{G_{eff} b}{4\pi(1-\nu)h}$	Interfaces

Solid solution hardening: adding alloying elements
Precipitation hardening: adding clusters of elements (size determined by the temperature over time in the forging process)



Dislocation: if particle small (underaged, $\sigma \propto r^{\frac{1}{2}}$) cutting, if cluster big (overaged $\sigma \propto \frac{1}{r}$) Orowan-Mech (encirclement)
Coarse precipitate are bad precipitate.
Work and Dispersion hardening: adding dislocation

High Temperature Materials (Superalloys):

Withstand temperatures above $500^\circ C$, require an oxidation protective coating. Applications: furnace, turbines, rocket nozzles, electr. heating. Requirements: high melting point, strength+creep resistance+microstructure stability (high packing density HCP, $Q_v \uparrow$), fatigue resistance, toughness+ductility, stiffness (E), low density, oxidation+corrosion res., formability, price.

Materials Rh, Ir, Pd, Ag, Pt, Au too expensive; Tc, Ru, Re, Os too dense; Co not bad but less ductile than Ni (FCC); Cr, Mn, Fe BCC; Cu not ideal due to high corrosion. Iron can be added as long as the structure is not changed

Creeping: Slow permanent deformation, occurs under steady loading condition as a function of time, Starts by T over $0.3-0.4 T_m$ (melting point) for metals and $0.4-0.5 T_m$ for ceramics.

$\dot{\gamma} \propto D_{0,v} e^{-\frac{Q_v}{k_B T}}$, where $\dot{\gamma}$ creep shear rate, $D_{0,v}$ diffusion constant for volume diffusion, Q_v activation energy for volume diffusion, Ω atomic volume, D_{T_m}

diffusion constant at melting temperatur. $\bar{\gamma} = \frac{\dot{\gamma} \Omega^{\frac{2}{3}}}{D_{T_m}}$
Measures against creeping: Solid solution hardening, reduction of diffusion (more densely packed lattices HCP or FCC), limits dislocation mobility, increase of E , reduction of the stacking fault energy, coarse grains, γ' -phase at grain boundaries

Fatigue: Loading condition has to be cyclic or varying over time. Measures against fatigue: coarse grain size

Strength: Weakest/longest dislocation starts to glide and causes failure, so finer grain size results in better strength

Cooling: increase operating T (max $300^\circ C$), fast cooling \rightarrow finer grain size

Homologous temperature: rapport at which we can operate the materials
 $T_{hom} = \frac{T_{Operation}[K]}{T_{Melting}[K]}$

Ni Alloys:

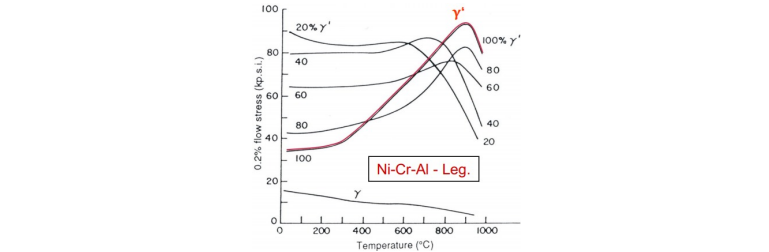
For high T, demanding mech. and corrosive environment
Ni (pure) has γ -phase is FCC

Ni-Al, Ti, Nb, Ta, Fe, Co: ($Ni_3Al = \gamma'$) improves oxidation resistance is ordered, stable, small misfit and homogenous (fine precipitates possible)

Ni-Cr, V, Mo, W, Re, Fe, Co: (Cr_2O_3) improves corrosion resistance (good protection due to few cation vacancies, good adhesion), but reduces T_m , is volatile when $T > 1000^\circ C$ and limits the γ' -phase-fraction. High content \rightarrow risk of σ - phase formation

Ti, Nb, Ta increase $a\gamma'$ (coherency stress), \uparrow antiphase boundary energy

B, C, Hf, Zr: (low solubility in γ due to size difference) Precipitates at grain boundaries **Power-law creep** countermeasures: reduction of diffusion (limits dislocation mobility, increase of Young's modulus & reduction of the stacking fault energy) $\dot{\epsilon} \propto \gamma_F^3$ (γ_F stacking fault energy)



Ideally flow stress should be constant as temperature increases (60, 80 % max)

Optimization of Super Alloys:

$T < 0.3T_m$: Solid solutions, small grain size, Coherent precipitate (high volume fraction, hardening maximum (T6), high APB-energy, große Fehlpassung ϵ) Solid solutions, small grain size

$T > 0.3T_m$: Low diff. const. (FCC!), low stacking fault energy, large grain size, Coherent precipitate (high volume fraction, rather large diameter ($> 0.5 \mu m$), small lattice mismatch (ripening)), Low diffusion constant (fcc!), low stacking fault energy, large grain size

To optimize both \rightarrow dual heat treatment



Ceramics

Ceramic-ceramic joint: + ceramic stiffer than metal, - long term wear shorter, + self polishing effect

Laplace pressure

$$\Delta P = \gamma \left(\frac{1}{r} + \frac{1}{x} \right)$$

Vacancy concentration

$$C_v(\sigma) = C_v(\sigma = 0) \exp\left(\frac{\sigma \Omega}{kT}\right)$$

Flux of atoms

$$J = -D \left(\frac{dC}{dx} \right)$$

Diffusion coefficient:

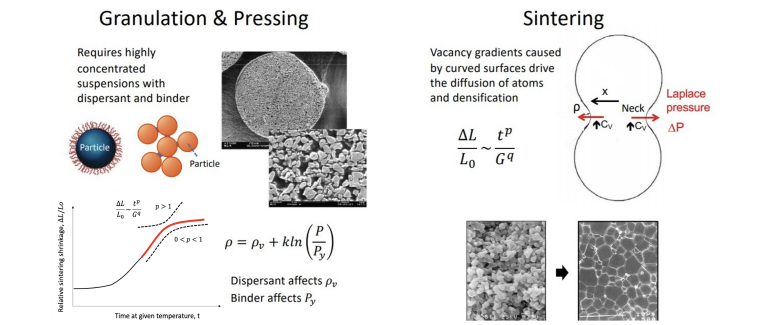
$$D = D_0 \exp\left(-\frac{\Delta G}{kT}\right)$$

Linear shrinkage, $\Delta L/L_0$

$$\frac{\Delta L}{L_0} = \frac{B}{G^q} \left(\frac{\gamma D \Omega t}{RT} \right)^p$$

ΔL : net length reduction
 L_0 : initial length
 G : grain size, m
 B : pre-factor that depends on mechanism
 p, q : empirical scaling exponents
 t : time, s
 γ : surface tension, N/m
 δ : grain boundary width, m
 R : gas constant, J/(mol.K)
 T : absolute temperature, K

Mechanism	p	q	B
Volume diffusion	0.40	1.20	80
Grain boundary diffusion	0.34	1.33	206

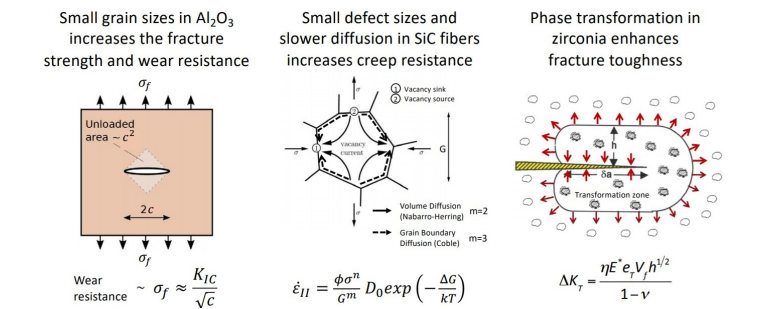


Ceramics are based on covalent and ionic bonds (high E , stronger than metallic bond) and are fabricated through heat. Composition, processing and structure dictate their properties. Their mechanical strength is not a material property and heavily dependent on microstructural defects and manufacturing flaws (defect size a).

Manufacturing:

- $\sigma[MPa] = \gamma[J/m^2]/\rho[\mu m]$
- Powder:** For good powder flowability, g-forces need to be higher than v.d.W. forces, so powder cannot be too fine ground \rightarrow create granulates
 - Granulation:** The particles are dispersed into concentrated suspension and then dry-sprayed (water is removed as the droplet falls in the spray dryer)
 - Concentration: If conc. of particles is too low \rightarrow hollow granules \rightarrow low density. Colloidal particles ($< 1\mu m$) agglomerate in a liquid due to v.d.W. attraction. The agglomerated network of particles increases the viscosity of the liquid which causes low particle conc. in the liquid. Surface electric charge (electrostatic stab.) or a polymer layer (steric stab.) on the colloidal particles can be used to create repulsive forces between particles \rightarrow (to contrast v.d.W.) high particle concentration in the liquid.
 - Granulate Density: The relative density ρ of pressed ceramic compacts depends on the pressure P , packing density ρ_v and yield stress/pressure P_y of granules: $\rho = \rho_v + k \cdot \ln\left(\frac{P}{P_y}\right)$, with k being the pressure coefficient. The dispersant affects ρ_v and the binder affects P_y
 - Binders: improve the mechanical strength of granulates to press without breakage (step 3) PVA (plastized water molecules)
 - Shaping:** For most ceramics, the granulates are then pressed and machined. Other methods: extrusion, injection molding, casting
 - Drying/Debinding:** Binder is removed
 - Sintering:** Occurs through atomic diffusion at high temperatures. Increases density from 50 to almost 100%. Atomic diffusion is thermally-activated and driven by minimization of curved surfaces/surface area (grains grow towards the center of their radius, driven by Laplace pressure) and maximization of entropy (distribution of elements)
 - Shrinkage/Densification: reduce porosity/grain size (=better mechanical strength), $\frac{\Delta L}{L_0} = \frac{B}{G^q} \left(\frac{\gamma D \Omega t}{RT}\right)^p$ with constant T [K], sintering shrinkage ΔL , initial length L_0 , grain size G , pre-factor depending on mechanism B , empirical scaling exponents p, q , time t [s] ($\frac{\Delta L}{L_0} \propto \frac{t^p}{G^q}$), surface tension γ [N/m]
 - Fibers:** small woven fibers increase fracture energy G_c

Zirkonia (ZrO_2):



Toughest ceramic currently known. Has a higher G_c through phase transformation from tetragonal to monoclinic: 4% larger grains lead to compressive stresses that tend to close cracks. The metastable tetragonal phase required for transformation toughening in ZrO_2 (initial phase cubic) can be obtained using specific dopants in different ceramic matrices. Its mechanical strength decays over time due to spontaneous phase transformation back to monoclinic due to cyclic mech. loading. Toughness increase with transformation: $\Delta K_t = \frac{\eta E^* e_T V_f h^{1/2}}{1-\nu}$, with η the factor depending on the zone shape at the crack tip and nature of stress field, E^* the elastic modulus of the matrix around the transformed grains, e_T dilatational strain caused by the transformation, V_f the volume fraction of transformable grains, h the width of the transformation zone from the crack surface and ν the Poisson ratio.

Lifetime:

The mechanical strength of ceramics decay over time due to subcritical crack growth (stress-induced corrosion) due to H_2O molecules or spontaneous phase transformation (in the case of ZrO_2 , see chapter ??).

Griffith's law: $\downarrow \sigma_c = \frac{K_{IC} \downarrow}{Y \sqrt{a \uparrow}}$, with Y a factor which predicts intensity and

distribution of a stress field around a defect caused by an external load.
Paris' law: correlates crack velocity v with stress intensity factor K_I : $v = AK_I^n$, where A, n material dependent constants

Adhesives

- Structural Adhesive:** high-performance adhesives designed for supporting high loads without failure
- Non Structural Adhesive:** lower-performance adhesive for lighter loads
- Sealant:** highly-flexible materials that are designed to fill the gap between 2 surfaces, providing a water/air-tight fitting that will not break as the surfaces flex. Sealants also are designed to be filled into relatively large gaps, without flowing away before they fully cure.
- Pressure-Sensitive Adhesive:** the more pressure is applied, the better the adhesion (ex.: sticky tape)

Materials:

- Liquid monomer can be **polymerized** to form solids (e.g. epoxies and acrylics)
- Liquid polymers can be **crosslinked** to form elastomers (e.g. silicones)
- Glassy polymers can be **melted** by increasing their temperature (e.g. hot melt adhesives)
- Polymers can be dissolved in a suitable **solvent**, which can later be **evaporated** off to leave a glassy polymer (e.g. wallpaper paste)
- Cement and plaster-of-paris are formed by **crystallisation** from wet slurries

Structural Adhesives:

Materials that are strong (shear strength of 10-40 MPa), robust, no degradation after a joint undergoes many loading cycles, high fatigue strength: Polyurethane, epoxies, acrylics, and polyamides

Aerospace adhesives additionally need to be durable, so that they can last for the duration of an aircraft's life. They need to be able to withstand large temperature and humidity changes. Ideally, the adhesives will not expand/shrink too much upon heating/cooling, otherwise the adhesive can expand far more than the parts that it is adhering together, and the large mismatch strains can lead to delamination: Epoxies and acrylic

Sealants:

Stretchable (to allow for flexing of joints), while being resistant to weathering and damage. For example, external sealants need to be UV- and water-resistant, and potentially gas impermeable (depending on their use).

Wetting:

When droplet of liquid is placed on substrate, it can either **totally wet** or **partially wet** surface. In total wetting, droplet will cover up as much area as possible by spreading completely across substrate. Liquid will completely coat surface without leaving tiny air pockets trapped in microscop. rough surface features. In partial wetting, liquid droplet will bead up and sit on the surface.

Air pockets are detrimental to adhesion for 2 reasons:

- reduces the amount of contact area between the adhesive and the substrate, which in turn reduces the bond strength
- when stress is applied to the adhesive joint, the air pockets act as crack nuclei, which can easily grow into a macroscopic crack by joining together - causing the liquid to debond from the substrate

Spreading Parameter:

The spreading parameter S tells how a liquid adhesive will spread across a surface. The surface molecules of a dry surface have a higher energy as they are missing some neighbours. This gives rise to an excess (positive) energy γ_{sa} per unit area (indices s =solid, a =air, l =liquid).

$S = -\frac{\Delta E}{A} = +\gamma_{sa} - \gamma_{la} - \gamma_{sl}$

If $S > 0$ ($\Delta E < 0$), the energy reduces when the surface is covered in liquid. Thus the liquid **will spontaneously spread** (totally wet). Generally, high-surface energy liquids don't spread easily and liquids spread better on high-surface-energy solids.

- γ_{la} : Organic liquids/silicone liquids/epoxy resin $20\text{-}50mJ/m^2$, water $72mJ/m^2$, liquid metals $500mJ/m^2$
- γ_{sa} : Clean metals/oxides/ceramics $>200mJ/m^2$, glass $100mJ/m^2$, plastics/silicones $20\text{-}50mJ/m^2$
- Help adhesion by: cleaning/grinding (remove low energy substrate), chemically treat the surface (increasing the surface energy), plasma treating the surface or by using a primer

Surface Adhesion tests:

To check if the adhesive is making a strong enough bond with the substrate's surface, a peel test can be done. In this test, two substrates are glued together by adhesive in between and then pulled apart. The adhesion fails in 1 of 3 ways:

- Adhesive failure:** A crack will propagate between adhesive and substrate. Afterwards the adhesive will stay on one of the substrates. Generally, this is not wanted. However it can be useful - consider the protective film that comes on the screen of a new phone.
- Cohesive failure:** Crack propagates through the bulk of the adhesive. Adhesive stays on both substrates. This is good, max. potential of adhesive reached.
- Substrate failure:** Crack avoids adhesive layer and goes through substrate. Good, adhesive is not weakest link.

Lap shear test: to measure shear strenght (To plates that are glued together are pulled until the adhesive gives out)

Peel test: The measured force to pull the substrate will typically rise to a plateau value F_p . We get a formula by considering the energy change as we peel a small distance Δx (once we've reached this plateau regime):

- To peel a distance Δx : $Wb\Delta x$, where W the energy per unit area and b the

sample width (top strip of material must be sufficiently stiff that it doesn't significantly stretch)

- The testing machine expends energy $F_p \Delta x$. \rightarrow Equating these two expressions: $W = \frac{F_p}{b}$ (**Peel energy**). For adhesive failure W describes the energy needed to cut bonds in the adhesive zone. For cohesive failure however W describes the energy for plastic deformation of the adhesive layer. $F180/F90 = 1/2$

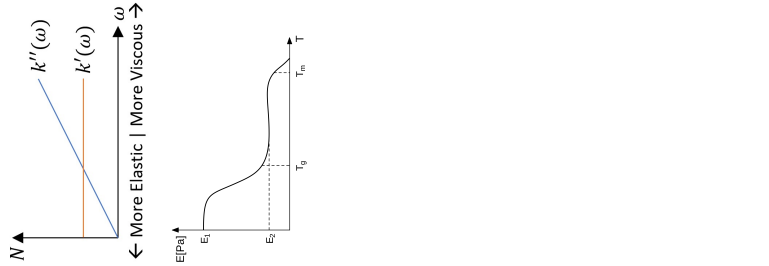
Viscoelasticity/Damping

For vibration damping (e.g. suppressing dangerous resonances, reducing noise from engine vibrations), vibration isolation (e.g. seat cushions, sound isolation) and impact dissipation (e.g. safety-glass).

Viscoelastic Springs: $F(x) = -k'x - c\dot{x}$

If \dot{x} is **small** the body has the same properties as a normal spring

If \dot{x} is **large** the elastic term doesn't matter \rightarrow viscous response



with **oscillatory input** $x = A \sin(\omega t) \rightarrow F(t) = -k'(\omega)A \sin(\omega t) - k''(\omega)A \cos(\omega t)$ (k'/k'' elastic/viscous spring constant)

If ω is small the material has a similar response to an elastic spring, if ω is high it has a viscous spring response

Dissipated Energy per Cycle: energy only from damping, $W_d = \oint F(x)dx = \int_0^{2\pi/\omega} F(t) \frac{dx}{dt} dt$, with $x = A \sin(\omega t)$: $W_d = \pi k''(\omega) A^2$. $k'(\omega)$ is the frequency-dep. el. spring const. and $k''(\omega)$ repr. the visc. behaviour of the mat.+potential for conv. vibr. energy into heat.

Phase Shift due to Damping: Combining the sine double-angle formula ($-kA \sin(\omega t + \delta) = -kA \sin(\omega t) \cos(\delta) - kA \cos(\omega t) \sin(\delta)$) with $F(t)$ from above, we find $k \cos(\delta) = k'$ and $k \sin(\delta) = k''$, so the dissipation factor/loss tangent $\tan(\delta) = \frac{k''}{k'} = \frac{E''}{E'} \approx \frac{W_d}{W_{el}}$, with W_{el} the max. elastic energy during a cycle (for $F(t)$ above it is $W_{el} = k'(\omega) A^2 / 2$). If $\tan(\delta) < 1$ a material is more spring-like, if $\tan(\delta) > 1$ it is more dissipative (spring would stop oscillating quicker).

Stress/Strain with v.e. Moduli: $\sigma = \epsilon_0 E'(\omega) \sin(\omega t) + \epsilon_0 E''(\omega) \cos(\omega t)$, with $\epsilon = \epsilon_0 \sin(\omega t)$ and $E'(\omega)$ the storage/Young's modulus and $E''(\omega)$ the loss modulus.

Total dis. energy per m³ material: $\pi E''(\omega) \epsilon_0^2$

Same principles from can be applied to **viscoelastic shear modulus** G' and G'' .

Free-Layer Damping Model: A thin layer of v.e. material is bonded to beam. When the beam vibrates, alternate stretching and compressing of v.e. layer - effectively applying strain cycles. Then viscous processes inside the layer dissipate energy. The beam will typically have certain resonant frequencies. With beam of thickness $2h_b$ and length L , coated in thin v.e. layer. If beam vibrates with $A = A_0 \sin(\omega t)$, length changes with $\Delta L \approx 8h_b A / L^2$, so osc. strain $\epsilon = \frac{8h_b A}{L^2} \sin(\omega t)$. Dis. energy per unit vol. of v.e. layer $w_d = \pi \left(\frac{8h_b A_0}{L^2} \right)^2 E''(\omega) = \pi \epsilon_0^2 E''$. $\epsilon_0 = \Delta L / L$, $E'' = J / (m^3 \cdot \text{cycle})$

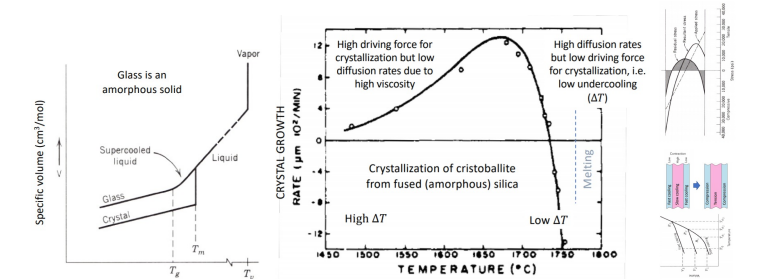
Polymers: Sweet spot between temp and frequency for perfect dissipation

Silica-based Glasses

Glass is an amorphous solid. The phase transformation from liquid to solid occurs at a glass transition temperature ($T_g < T_m$). The T_g and the specific volume (or density) of a glass depend on the cooling rate.

In principle, any material can form glass. One just needs to inhibit crystal growth. (Crystal growth rate: $u = \frac{kT}{3\pi a_0^2 \eta} \left[1 - e^{-\frac{\Delta G_m}{RT}} \right]$, low $\Delta T \rightarrow u = \frac{kT}{3\pi a_0^2 \eta} \left[\frac{\Delta H_m \Delta T}{RT_m} \right]$, High $\Delta T \rightarrow u = \frac{kT}{3\pi a_0^2 \eta}$).

Maximum crystallization rate for easy glass formation is 10^{-4} cm/s



Higher melt viscosity reduces crystallization velocity

Formers: Build a highly viscous tridimensional network that prevents crystallization upon cooling

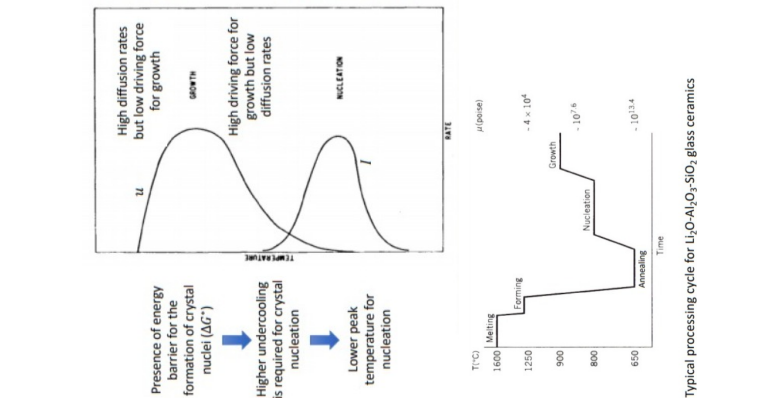
Modifiers: Disrupt the glass network to reduce viscosity and processing temperature. NaO, CaO reduce viscosity to enable process at lower T. B_2O_3 increase viscosity

Intermediates: work as formers or modifiers depending on conc. in glass

Glass production tech: Crown Glass (old, circular, hand made glass), Plate glass (casted glass, then rolled flat, then polished, very costly, high glass wastage), Sheet glass (1914, vertical pulling from molten pool, perfect surface finish but distortion are present), Pilkington float glass process (Glass pulled from furnace at constant rate, cooled in controlled chamber on a molten tin basis, perfect finish and no distortion)

Glass strengthening: Tempering: cooling the top and bottom layer faster than the core induces compressive stress in the surface and tensile stress in the core. When the plate is loaded (transverse loading) the resultant maximum tensile stress is reduced. **Chemical:** change the ions in the surface (from Na+ to K+) to induce the same stresses as in tempering (stress $\sigma = \frac{EB}{1-\nu} (C(x,t) - \bar{C}(t))$, (with C = concentration of K) linear network dilation coefficient $B = \frac{1}{3} \frac{\delta V_{molar}}{V_{molar} \delta C}$, $\bar{C} = \frac{1}{\lambda} \int_0^\lambda C(x) dx$)

Glass ceramics: obtain ceramic from glass (skipping the sintering process, no shrinkage!) increase toughness by crystallizing part of the glass (Typical grain sizes: 1 μm : opaque, $\leq 100 \text{ nm}$: transparent). **Process:** Form glass (melt \rightarrow form \rightarrow anneal) then heat at: nucleation temperature (to prepare nuclei, Nucleation rate: $I = \frac{K}{\eta} e^{-\frac{\Delta G}{kT}}$) \rightarrow Growth temperature (to grow them)



Bioinspiration

Toughening mechanisms in nacre: Crack deflection, Platelet friction, Delamination at platelet-matrix interface, Plastic deformation of matrix

Platelet reinforcement: 2 failure modes fracture and pull out. Maximum load can be carried when $\sigma_{max} A_{section} = \tau_{max, surf} A_{interface} \rightarrow \sigma_{max} \propto \frac{1}{t} \tau_{max}$. **Size of platelets:** $\sigma \propto \frac{1}{\sqrt{c}}$ where c is the size of the largest defect, $c \propto t \rightarrow \sigma_{max} \propto \frac{1}{\sqrt{t}}$ where t is the diameter/thickness of the platelets. **Critical (optimal) aspect ratio** $s \propto \frac{1}{t} \propto \frac{1}{\tau_{max} \sqrt{t}} \propto \frac{\sigma_f}{\tau_{max}}$, $\sigma_f = \sqrt{\frac{\pi G_c E}{t}}$

Making nacre like materials Al_2O_3 platelets in rotating magnetic field (to align) \rightarrow depositing \rightarrow infiltration (with copper/polymers/other ceramics) & hot-pressing \rightarrow material with increasing toughness as crack size increases (with constant stiffness, due to deflection by oriented platelets)

Mineral bridges (form in-situ during hot pressing) increases strength, toughness and elastic modulus (Bridges enhance stress transfer between platelets and thus the composite strength)

Composite strenght $\sigma_{c,f} = \frac{\tau_{m,y} s \phi_r}{2}$ When platelets are connected by mineral bridges, stress transfer happens via mineral bridges rather than the polymer matrix. Therefore, $\tau_{m,y}$ is replaced by γ' (fraction of mineral bridges, variable during the hot press process) in the above equation

