Intro to Materials Engineering

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CONTENTS

I. Material Classifications

Microstructure is composed of single atoms → local groups → grains → solid macrostructure.

Metals/Alloys

- Delocalized sea of shared e in non-directional bond
- Moderate/constant E values

Example

Austenitic stainless steel, aluminium, and copper are non-ferromagnetic, so they do not work on an induction stove. Ferritic steel, hot rolled steel, and duplex SS do work.

Ceramics

- Typically higher E values (variable) than metals
- Covalent ceramics have shared valence electrons in directional bond
- Different Pauling's EN (χ) contributed to partially ionic bond:

$$\%ionic = 1 - \exp\left(\frac{(\Delta\chi)^2}{-4}\right) \tag{1}$$

- Ionic ceramics have cation/anions transfer electrons
- Forms non-directional bond

Example

Al_2O_3 can take various forms:

- α Alpha/corundum is high temp applications, highly ordered crystal
- γ is a catalyst for H production, other crystal form
- Amorphous is used for barrier coatings, discrete molecules

Polymers

- Intra-chain bonding is covalent
- Inter-chain is IMF's (e.g. Van der Waals)
- Along with natural materials, have low E

II. Tensile Testing

Stresses: tensile (uniaxial, biaxial), compression (hydrostatic), shear.

Uniaxial Tensile Testing

Testing must be conducted at *room temp* (think Challenger disaster with cold temps causing O-ring flexibility to change). This first requires representative test sample:

- Taken from suitable spot
- Machined according to ASTM (Amer. Soci. for Testing and Mats) standard E8

The sample is measured with l_0 as gauge length, A as area, and:

- t thickness and w width if rectangular
- d_0 diameter if cylindrical

An *extensometer* is used to measure Δl change in gauge length. Load is applied with *low strain rate* (e.g. $\dot{\epsilon} = 5.75 \cdot 10^{-5 \to -6} \frac{1}{s}$ as fractional expansion rate).

$$\dot{\epsilon} = \frac{\Delta l}{l_0 t} \tag{2}$$

Example

High strain rate necessary for impacts.

We measure the load (kg) and l_i (mm) until fracture occurs to create a stress-strain graph.

$$\sigma = \frac{F}{A_0} = \sigma(engg)\left(\frac{N}{mm^2} \equiv MPa\right) \tag{3}$$

Engineering stress is calculated without accounting for change in area.

$$\epsilon = \frac{l_i - l_0}{l_0} \tag{4}$$

Engg strain can be expressed as microstrain (ppm), a fraction, or a percentage. True stress/strain requires a correction as strain changes:

$$\sigma_t = \frac{F}{A_i} = \sigma(1+\epsilon), \epsilon_t = \ln\left(\frac{l_i}{l_0}\right) = \ln(\epsilon + 1) \tag{5}$$

During large strains we must use true strain. While tensile tests are usually a 'pull', ceramics with low tensile strength typically use a 3 or 4 point bend.

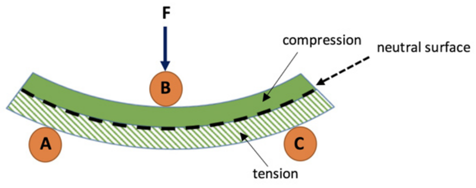


Fig. 1. A 3 point bend on a ceramic

III. Hardness Testing

This measures a material's resistance to localized plastic deformation (NOT a material property!). It is correlated with UTS (used as way to estimate UTS in forensics) and can be measured on various scales: It is also used for quality control to estimate UTS, or assess super tiny samples, or lab research!

Example

A helicopter failed since a pin flew out, and they later found the pin failed hardness testing by a lot ($7.6RC \ll 50RC$)

Testing is accomplished with an indenter forced into the material, leaving an indent which is measured →

calculate an average. Indentations must be separated to avoid *work hardening*. This is when plastic deformation increases the yield stress (pushes it higher up the stress strain curve, or laterally displaces the elastic region!).

Hardness is a distribution due to variations in microstructure.

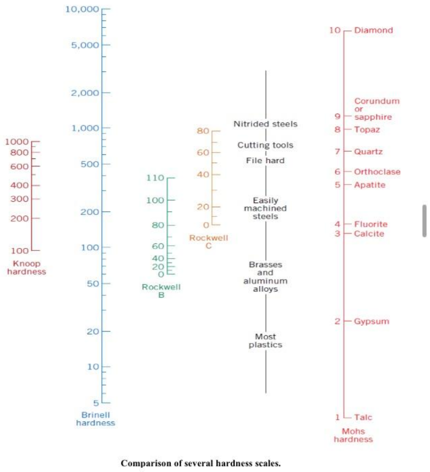


Fig. 2. Comparison of several hardness scales

Rockwell Hardness

- Measure depth of indentation
- Rockwell A is the softest
- Rockwell B (HRB) uses ball indenter for soft mats like Al
- Rockwell C (HRC) uses cone indenter for hard mats (hard steel)

Vickers Micro Vickers

- Dimensions of square indentation are measured
- Good for analysing small regions

Brinell

- Measure diameter of indentation

$$HB = BHN = \frac{2F}{\pi D(D - \sqrt{D^2 - d^2})} \tag{6}$$

- Where D is ball diameter (mm), d is indent diameter (mm), F is load (kg)

Remember – beaver teeth have enamel $1.53x$ stronger than humans.

IV. PROPERTY VARIABILITY

When doing tests, we often get a distribution of results due to unpredictable changes in microstructure, manufacturing, processing, etc. Therefore, express values as range and minimum.

Example

Small changes in Ni dopant to TiO_2 films for semiconductors drastically changes the band gap!

Note

Ceramics are SUPER sensitive to processing and composition, exhibiting a wide range of 3-point bend failure stress.

We describe this with the *Weibull distribution*:

$$\ln\left[\ln\left(\frac{1}{1-F}\right)\right] = m\ln\sigma - m\ln\sigma_0 \tag{7}$$

Where F is the probability of failure, σ_0 is characteristic strength (constant parameter describing rough ‘location’), and m is the Weibull modulus.

If we linearize cumulative failure against stress, we get a slope of m – higher m means tighter failure distribution. Remember how sensitive ceramics are, so they have a low m.

Factor of Safety

This is a design strategy that limits the allowable stresses in a design to stay some safety factor FS under limit stress (the yield stress or the UTS, depending on specs):

$$\sigma_{design} = \frac{\sigma}{SF} \tag{8}$$

V. STRESS STRAIN GRAPH

On a stress strain curve, we have 2 regions:

- Elastic region is non-permanent and linear
- Plastic region is permanent deformation

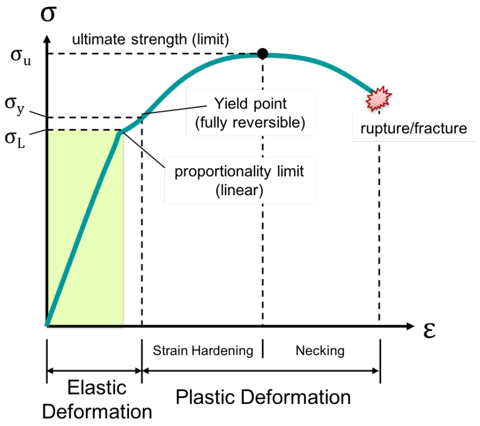


Fig. 3. Stress strain diagram with labels

Elastic We can characterize the *elastic region* with *Young’s Modulus* or the *Modulus of Elasticity*:

$$E = \frac{\sigma}{\epsilon} \tag{9}$$

Where we take the tangent line at the initial linear section. Note that E is defined over an elastic section! Stretching a material past YS will result in plastic deformation, but there will still be an elastic contraction parallel to E. Larger E is stiffer and requires more force to deform.

Example

In implants, mismatched E between Ti alloy implant and bone can result in poor weight allocation on bone, leading to atrophy. Bone has $E = 30GPa$, and we can alter Ti composition to change $E = 100GPa \rightarrow E = 66GPa$. We could also use a diff material, change manufacturing for porosity, or modify modulus with crystallographic orientation.

Poisson's Ratio for **elastic behaviour only** is the ratio of lateral to vertical strain (amount of splodge)

$$\nu = -\frac{\epsilon_x}{\epsilon_z} = -\frac{\frac{\Delta d}{d_0}}{\frac{\Delta l}{l_0}} \tag{10}$$

Increase $||\nu||$ means increased perpendicular strain compared to vertical. A negative ν is rare and means axial compression causes lateral compression.

Stress is always elastic, since there is always a range around a given stress that will result in elastic deformation from that strain point.

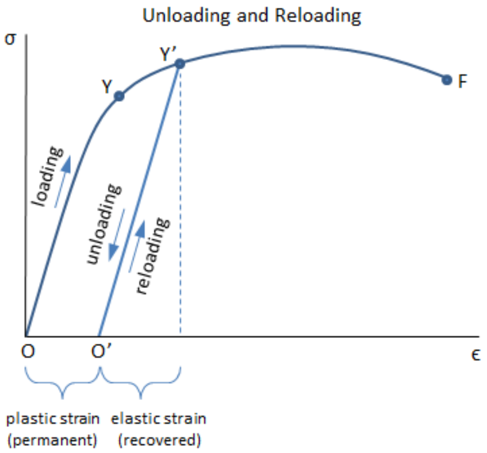


Fig. 4. Elastic strain after plastic deformation

The YS (σ_y) is the stress when plastic deformation starts. This occurs at the Proportional Limit (PL) – idealized! Often, this transition from elastic to plastic (the *yield stress* σ_y) is tough to find. The *0.2% offset method* uses a line parallel to E but offset by 0.2% strain to find yield stress.

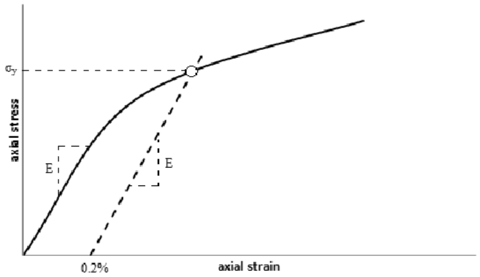


Fig. 5. 0.2% offset method

Note that the peak stress of the curve is the *ultimate tensile strength* – the max tensile stress and the point at which *necking* occurs. Ductility is a measure of the amount of plastic deformation that occurs here, measured as % elongation:

$$\%El = \frac{l_f - l_0}{l_0} \cdot 100\% \tag{11}$$

Where l_f is the length *after* fracture. Note that the length of 'necking' is independent of gauge length l_0 so %El is sensitive to this!

Reduction of area %RA:

$$\%RA = \frac{A_0 - A_f}{A_0} \cdot 100\% \tag{12}$$

is a measure of ductility. Brittle materials have %RA $< 5\%$. Generally, increased yield strength corresponds with decreased ductility.

Note that not all curves are built equal. Ceramics are super steep along little strain, while polymers have really funky shapes and can draw, or strain, a lot.

Example

Arteries, for example, will have a curve that changes shape depending on their elasticity, or health. This can be used in the design of stents and artificial vessels.

Example

TRIP (transformation induced plasticity) steels are used in crumple zones. The area under a $\sigma - \epsilon$ curve is the NRG absorbed. Finding TRIP steels with higher UTS means more energy absorbed during an impact for safer drivers.

VI. BOND ENERGY

The type and strength of atomic bonding affects E, thermal/electrical conductivity.

- Covalent: range of strengths from weak ($Bi = \frac{200kJ}{mol}$) to strong (diamond $= \frac{713kJ}{mol}$)
- Ionic has high strength ($Al_2O_3 = \frac{511kJ}{mol}$)

- Metallic ranges from weak ($Al = \frac{324kJ}{mol}$) to strong $W = \frac{849kJ}{mol}$
- Secondary bonding in polymers is weak ($1-10\frac{kJ}{mol}$)

Interatomic forces are repulsion (like charges) and attraction, which balance at some critical equilibrium length r_0. This is the distance between atom centers at $0K$, and the energy state with balanced forces $F_{net} = 0$. E_0 is the potential well energy at r_0, i.e. the energy required to separate the atoms to ∞. Melting temperature T_m is separating atoms and is proportional to E_0 since the bonds are harder to break.

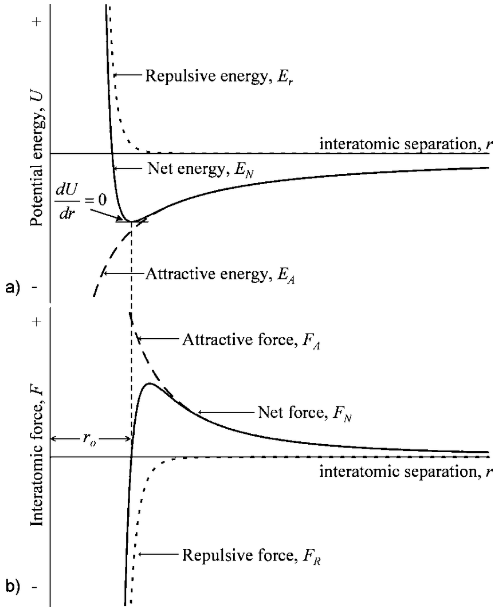


Fig. 6. Atomic forces and potential energy with interatomic separation

E is also proportional to E_0 since stronger bonds have smaller strains with less perm deformation.

$$E = \frac{S_0}{ar_0} \tag{13}$$

α is proportional both to depth E_0 and concavity S_0. Note that bond stiffness S_0 can be found as:

$$S_0 = \frac{\partial F}{\partial r} = \frac{\partial^2 U}{\partial r^2} \tag{14}$$

This means that stiffness, proportional to E, is related to the slope of a $F - r$ graph at r_0 (steeper means more force required to change separation). Also, E is related to concavity of potential well on $E - r$ graph since tighter well requires more NRG to 'climb the walls' and lengthen the bond.

VII. THERMAL EXPANSION

Thermal cycling of materials causes repeated expansion and contraction. The coefficient of thermal expansion, CTE α is the fractional increase in length for a change in temperature.

$$\Delta l_T = \alpha l_0(T_f - T_0) \tag{15}$$

Note that α is determined by the bond-energy curve – a steeper potential well takes more NRG, or change in T, to cause an expansion or contraction. Therefore, as E_0 increases, E increases and α decreases since weaker bonds are easier to change length:

$$\alpha = \frac{\gamma_G \rho C_v}{3E} \tag{16}$$

Thermal Shock

Thermal shock testing is performed to determine ability to withstand sudden ΔT and is very severe. Standards: JEDEC JESD22-A106 and Mil-Std-883 Method 1011.

Thermal shock resistance (TSR) of ceramics (mainly) is a measure of resistance to cracking on sudden temp change.

$$TSR = \frac{\sigma_F k}{E\alpha_l} \tag{17}$$

Where σ_F is the failure stress in tension, k is the thermal conductivity, E is YM, and α_l is CTE. Increasing CTE and YM makes the material more ready to expand and more brittle (resistant to strain). Increasing k will smooth temperature differentials faster, while increasing σ_F obviously just makes the material stronger.

We can avoid these shocks with slow heating and cooling or using ceramics with optimal values from Equation 17.

Thermal Stress

This can be generated in 3 ways:

1. Constraint

Thermal expansion or contraction limited by a constraint causes stress.

$$\sigma = E\alpha(T_0 - T_f) \tag{18}$$

Since $\alpha\Delta T = \epsilon$, this is basically our formula for E rejigged so an 'attempted' strain is limited by some equivalent stress. This ONLY works for the elastic range of stress! Also note that an increase in temperature will result in a *negative* stress (i.e. compression), given by the sign of $T_0 - T_f$.

2. Differing Materials

Multiple materials with diff α will expand at different rates and 'fight' each other.

A bimetallic strip is a simple indicator of this, where two layers of metal cause a curvature under temperature (used as simple thermostat control):

$$R = \frac{\sum t}{(\alpha_1 - \alpha_2)\Delta T} \tag{19}$$

Where R is the radius of curvature of a bimetallic strip.

3. *Differential Temperature*

The same material with a varying temperature will act like two materials with diff CTE and the same temperature. Tempered glass uses this to prevent cracks from spreading too much as seen in Figure 7.

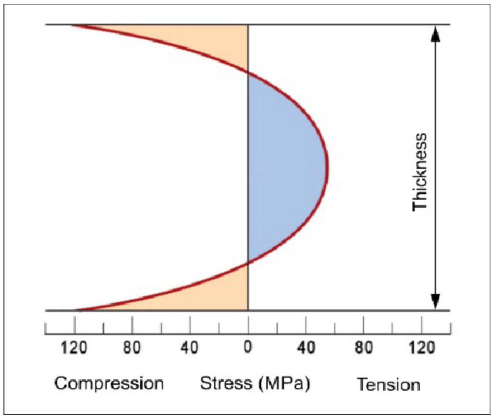


Fig. 7. Tempered glass uses differential temperature when formed to keep the outer layer under tension and reduce crack spreading.

VIII. CONDUCTIVITY

A. *Thermal*

Heat flow due to conduction, q $\left(\frac{W}{m^2}\right)$, on some temperature gradient is

$$q \propto k\frac{dT}{dx} \tag{20}$$

Where k $\left(\frac{W}{mK}\right)$, thermal conductivity, is a measure of a material's heat-conducting ability:

$$k = k_e + k_L \tag{21}$$

Where k_e is the conductivity due to free electrons, and k_L is the heat transport due to lattice waves called *phonons*.

Metals

k_e is dominant due to the sea of free electrons, so $k \propto$ electrical conductivity for metals. This is done as thermal energy is converted to K of electrons. As such, microstructure affecting electron movement also affects heat transfer:

- 2nd phase particles
- Grain boundaries
- Substitutional atoms
- Dislocations

As electrons collide with these features, they lose energy, so purer metals have longer uninterrupted paths and better heat transfer.

Ceramics

Due to lack of free electrons in ionic and covalent compounds, k_L dominates. The energy of lattice vibrations in a rigid crystal lattice is quantized into a *thermal phonon*. We can see that $\frac{1}{k_L} \propto$ number of scattering sites, since increasing scattering sites decreases the ability to transmit phonons effectively. These sites are:

- 2nd phase particles
- Porosity
- Contaminants

These sites decrease the *mean free path (l)* of phonons:

$$k = \frac{1}{3}\rho Cpvl \tag{22}$$

Where v is elastic wave speed.

For a material like diamond with a super pure lattice and no free electrons, k_L dominantes and it's super high ($k = 2000\frac{W}{mK}$). Other single crystal ceramics like SiC, BeO, and AIN.

Polymers

Energy is transported via vibration and rotation of polymer chains, making a mean free path that is super low. Polymers are disordered so they are good insulators.

B. *Electrical*

We know Ohm's law is $V = IR$ and conductivity ($\sigma = \frac{1}{\rho}$ in Mho's), but the resistivity of wires is:

$$\rho = \frac{RA}{L} \tag{23}$$

Where R is the resistance in Ohms and A is the cross-sectional area and L is the length of the wire. Also, conductivity is:

$$\sigma = n\|e\|\mu_e \tag{24}$$

Where n is charge carrier density (number electrons / volume) in the conduction band, $\|e\|$ is the charge of e, and μ_e electron mobility. Increasing scattering sites decreases mobility, conductivity, and therefore increases resistivity. Scattering sites are:

- Impurities
- Vacancies or dislocations
- Interstitial or substitutional atoms
- Thermal lattice vibrations (higher temperature)

We can approximate resistivity as being made up of various resistivity sources:

$$\rho = \rho_t + \rho_i + \rho_d \tag{25}$$

Where t is the thermal contribution, i is the impurity contribution (defects, interstitial/substitutional atoms), and d is the dislocation contribution.

Note: we have various conduction models – electrons (mainly for metals) and Band Theory or *Fermi Sphere* (metal, semiconductor, insulation) where electrons flow in the conduction band. For metals, an E field is enough to promote electrons into this band, while semiconductors, and then insulators, see increasing band gaps.

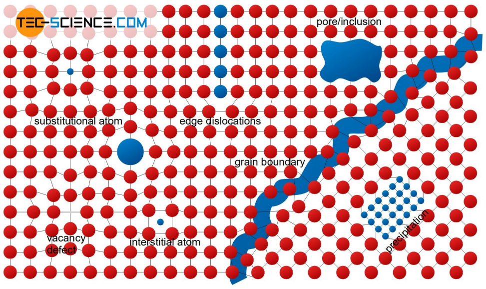


Fig. 8. Types of scattering sites visualized

The magnitude of the band gap is correlated with resistivity.

Metals

Conduction is very high due to free electrons. However, it is still dependent on the electron arrangement and number of electrons that can move.

- Cu, Ag, and Au, the currency group, all have the highest conductivities with 1 valence electron.

Example

While Cu has higher conductivity than Al, we use Al in power cables since it has a higher *specific conductivity*, or conductivity per mass, so we need less weight for the same current.

Semiconductors

Semiconductors have intermediate electrical conductivity with a range of small to medium band gaps.

Intrinsic semiconductors (Si, Ge, GaP, GaAs, InSb) conduct electricity by:

- Valence electrons excited into the conduction band move associated with μ_e
- Excited valence electrons leave behind +holes that electrons can travel through, moving with associated μ_h

$$\sigma = n\|e\|\mu_e + p\|e\|\mu_h \tag{26}$$

Where p is the hole density and μ_h is the hole mobility, or how well electrons move through holes.

Note that increasing the temperature results in more electrons being excited to the conduction band, increasing conductivity of intrinsic semiconductors.

Extrinsic semiconductors (which constitutes most semiconductors) are doped to determine electrical behaviour.

- **n-Type** are doped with P, As, or Sb (5 valence electrons) as *substitutional atoms*

The required concentration of solid solution is $1 : 1{\cdot}10^{12}$ Phosphorus per Silicon, for example, which is insane. These substitutional dopant atoms are introduced via a diffusion process called doping, where high T allows a dopant-containing gas diffuse into non-masked areas of the semiconductor.

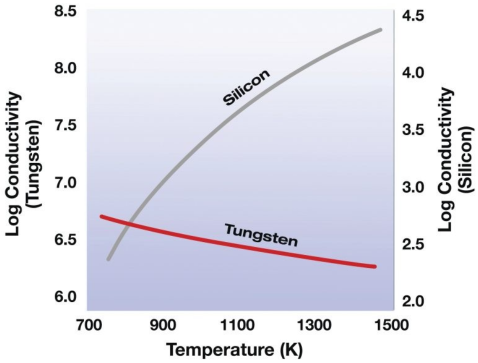


Fig. 9. The effect of temperature on conductivity of intrinsic semiconductors opposes that of metals

The additional electron is not super stable and is easily promoted to the conduction band. As such, more electrons are easily conducting, so we have free electron-based conduction:

$$\sigma \approx n\|e\|\mu_e \tag{27}$$

Where n is the number of electrons and μ_e is the electron mobility.

- **p-Type** are doped with Al, B, or Ga (3 valence electrons) as *substitutional atoms*

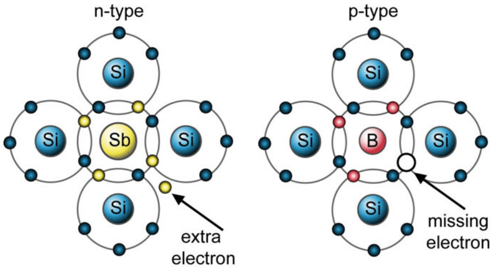


Fig. 10. Electron diagram for p-type vs. n-type semiconductors.

When electrons are excited, they move easily into the *acceptor state* which is just above the valence band. This leave a +hole which other electrons can move through for hole-based conductivity:

$$\sigma \approx p\|e\|\mu_h \tag{28}$$

Where p is the number of holes and μ_h is the hole mobility.

Note that the *carrier concentration* is fixed by the amount of impurity added. Temperature will still affect the electron concentration. For low temperature, the freeze-out region means even the doped electrons are not able to promote, constricting semiconductor function globally. For super high temperatures, the effect

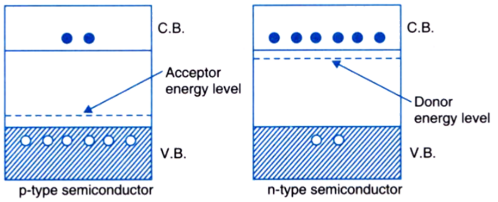


Fig. 11. Band energy for p-type vs. n-type semiconductors.

of dopants is minimized since so many electrons can promote. For mid temperatures, electron concentration is relatively constant for extrinsic semiconductors, reflecting the fixed number of easily-promoted doped electrons.

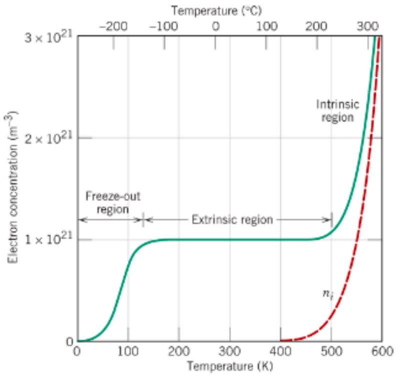


Fig. 12. Effect of temperature on electron concentration for extrinsic semiconductors (green) and intrinsic (red dashed)

Ceramics

Ceramics have a large band gap. Conduction is mainly the diffusion of cations or anions through the lattice:

$$\sigma = q\|e\|\mu_i \tag{29}$$

Where q is the ionic carrier concentration and μ_i is the ionic mobility, which is super low! This depends on

$$\mu_i = \frac{ZqD}{k_B T} \tag{30}$$

Where Z is the valence of the ion, q is the charge, k_B is the Boltzmann constant and T is the temperature. D is the diffusion coefficient, which can be manipulated by:

- Increasing the number of impurity atoms
- Increasing the vacancies
- Increasing the temperature (seems contradictory, but it increases D)

Example

Aluminium wiring is dangerous since:

- Higher thermal expansion coefficient vs Cu (23.8 vs $17 \cdot 10^{-}6$) causes thermal cycling
- Creep causes loosening of connections
- Al_2O_3, alumina, is a ceramic oxide which has high resistivity, so it heats up!

Note that increasing the porosity of a ceramic typically decreases thermal and electrical conductivity due to a lower mean-free path idea.

Polymers

Most polymers are super poor conductors since there are few free electrons due to a large band gap. However, we can synthesize conducting polymers by changing the molecular weight, oxidation level, crystallinity, and doping level. For example, polyaniline is a common conductive polymer that is very 'tunable' by adjusting the doping level. Others, like polymer electrolyte membrane (PEM) is used in fuel cells to conduct H+.

Superconductors

At low temperatures, SCs have zero (or unmeasurable) resistance, where thermal vibrations are minimal. *High Temperature SCs*, or HTSCs are defined as materials that behave as SCs with a critical temperature, T_c, above $-200C$, or $73K$ (reachable with liquid nitrogen). This leads to the Meissner effect.

Most HTSCs are ceramics, the first of which was Yttrium Barium Copper Oxide (YBCO), which has $T_c = 92K$. It has an orthorhombic structure.

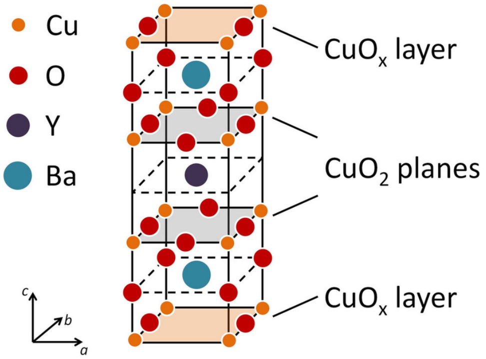


Fig. 13. The orthorhombic unit cell of YBCO.

They can be used in MAGLEV trains, MRIs.

IX. FRACTURE

Failure on the macro level is one piece turning into many. On the micro level, it's the breaking of bonds between atoms. A *fracture*, or crack, propagates through a material. That being said, higher E_0 does NOT make a material more resistant to failure!

- Catastrophic Failure – occurs instantly
- Fatigue – Occurs over a period of time
- Creep – damage or failure at high temperatures

Brittle materials have $\%RA < 5\%$, i.e. the change in area after failure in a tensile test is less than 5% of the original area (little necking). This is common in most ceramics, where all bonds break suddenly. Under an SEM, a brittle fracture is perpendicular to the stress, breaking along flat crystallographic planes. Note that things like cement, grey cast iron, SiO_2 or Si semiconductors have no elongation.

Ductile materials have $\%RA > 5\%$, i.e. they neck a lot during plastic deformation. This occurs when the material is overloaded, undergoing a lot of plastic deformation like most metals and polymers (high $\%EL$). The fracture surface leaves a cup and cone structure, and under an SEM will show microvoids, or dimples.

Fig. 14. The difference between a flat, brittle fracture perpendicular to applied force, versus the cup and cone relic of a ductile fracture.

A. *Griffith's Theory*

Griffith Theory helps us understand the atomic fracture process of brittle materials. This applies to glasses, ceramics, Si, and some super strong metals. These materials are super sensitive to preexisting cracks and flaws, contributing to a very wide property variability.

A crack will propagate when input energy is equal to energy required to form 2 new surfaces. This applied stress can be found as:

$$\sigma_c = \left(\frac{2E\gamma_s}{\pi a}\right)^{\frac{1}{2}} \tag{31}$$

Where σ_c is the critical stress for fracture, E is the modulus in *GPa*, γ_s is the surface energy $\frac{J}{m^2}$, a is $\frac{1}{2}*$ the length of the ideal sharp crack or critical flaw in *mm*. Note the units are pretty weird! Also, we use a as one half the length so we treat internal cracks the same as external ones. Note that as the crack lengthens, the required stress decreases.

Stress Concentrations

Stress concentration is the magnification of applied stress due to flaws. It can be found as:

$$\sigma_m = \sigma_o + 2\sigma_o\sqrt{\frac{a}{\rho_t}} \tag{32}$$

Where σ_o is the applied stress, σ_m is the max stress at the *crack tip*, ρ_t is the radius of the crack tip (the sharpness of the tip, going to 0 for a perfect point), and a is $\frac{1}{2}$ the crack length. a and ρ need the same units.

Fracture Stress for Metals with Plastic Deformation

An idealized equation is:

$$\sigma_f = \left(\frac{2E(\gamma_s + \gamma_p)}{\pi a}\right)^{\frac{1}{2}} \tag{33}$$

Where a is 1/2 the length of an internal crack (full depth of external), E is the Young's Modulus, σ_f is the critical failure stress, γ_s is surface energy and γ_p captures the process (energy absorbed) when we apply energy to create a new surface. Note that plastic deformation blunts the crack tip.

This idea can be used to cut glass by making a weakness, or analyze thin glass fibres with super small flaw sizes.

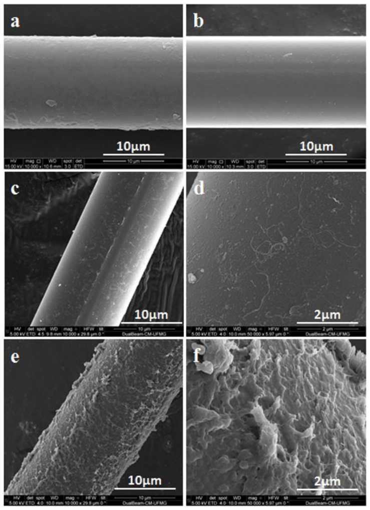


Fig. 15. SEM magnification (to μm level) of fibreglass, with super small flaws

B. *Toughness*

Toughness is a material's resistance to fracture, or perhaps the energy absorbed by a material as it fractures. It can be a mechanical property or material characteristic. We can find *tensile toughness* as the area under the stress-strain curve. Increasing UTS or $\%EL$ increases this area, and therefore toughness, although these properties are a bit contradictory.

Fracture Toughness

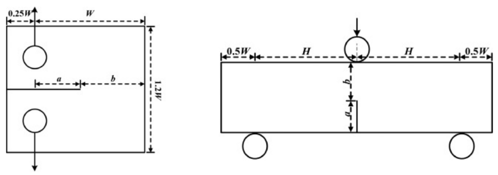
K_c is the resistance of a material to brittle fracture with an existing crack/flaw. This can be tested with compact tension or single edge bend. K_{IC} is the *plain strain fracture toughness*. As yield strength increases, K_{IC}

often decreases due to less $\%EL$. As such, ceramics tend to have low K_{IC} and a low fracture stress when cracks are present.

We can use this to assess how much flaw size affects fracture strength σ_f with:

$$K_{IC} = Y\sigma_f\sqrt{\pi a} \tag{34}$$

Where Y is a geometrical property.



(a) CT (b) SEB

Fig. 16. Examples of a Mode I CT and a single edge notched bend.

C. Impact Testing

We use this to assess a resistance to brittle failure, typically with the *Charpy Impact Testing Procedure* for bulk metals. A small notch is machined into the sample (standardized) causing a stress concentration at the crack tip, and tested under triaxial loading. Temperature is varied from -90 to 100 Celsius.

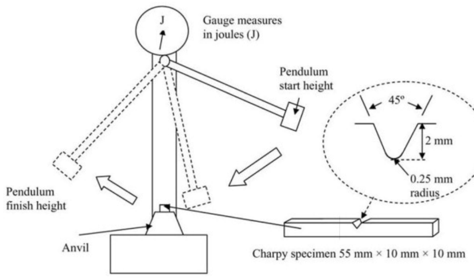


Fig. 17. Image showing the charpy impact test and setup, with the sample + machined notch

The sample is loaded at a super high strain rate, and the total energy absorbed by the sample during fracture is plotted against temperature.

An alternate version of Charpy impact testing is the Drop Weight Tear Test (DWTT), which is the same thing but for larger samples. Sometimes machining a small sample is not feasible, or not representative.

Strain Rate

Strain rate effects the shape of a stress-strain curve. Higher strain rate increases YS and UTS, but decreases $\%EL$.

Temperature

Decreasing temperature typically reduces plastic deformation, but its effect on YS, UTS, and $\%EL$ is material dependent (although E should stay the same)!

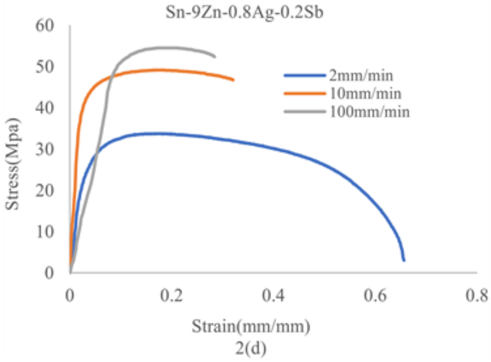


Fig. 18. Higher strain rates cause taller stress strain curves with less elongation

Presence of a Notch

The notch causes plane strain which is complex.

Charpy Energy vs. Temperature

When we plot our Charpy curves, we can see that it differs between materials, and between processing. The main feature we are interested in is the *Ductile to Brittle Transition Temperature (DBTT)*. This temperature indicates when a material changes from brittle fracture (no deformation) to ductile (microvoid coalescence). The idea is that the fracture is $\%50$ brittle and $\%50$ ductile. NOTE: DBTT is NOT a material property (cannot be used for design!) but is instead used to compare materials. We define it in two ways:

- The temperature when the sample absorbs $20J$ of energy.
- The temperature at the average between the max and min impact energies, i.e. the upper and lower shelf.

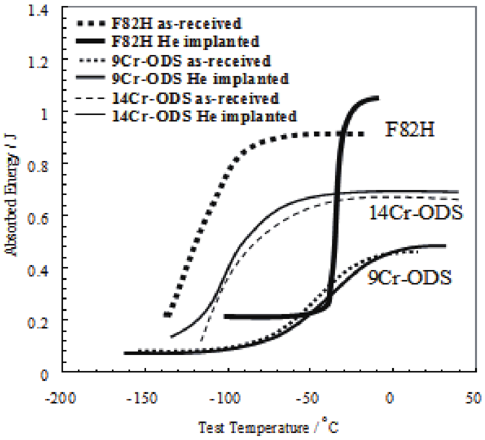


Fig. 19. Multiple Charpy plots showing the change of absorbed energy against temperature of test.

We use DBTT for things like:

- Ensure materials are used at appropriate temperatures
- Lower DBTT means greater resistance to brittle failure (shift to ductile at lower temps)
- FCC metals DO NOT exhibit DBTT

X. FATIGUE

Fatigue results from cyclic load, and therefore occurs for a range of stresses over a range of cycles. This is responsible for about 90% of service failures. This occurs in three stages:

1) Crack initiation
   The crack initiation (typically at the surface) occurs where stresses are the highest (e.g. bending). This often occurs at surface defects due to stress amplification and localized plastic deformation. The beach marks will be centered around the initial crack.
2) Propagation of crack with loading cycle
   Crack propagation presents with 3 distinct features:
   - Beach marks, which are macro-level rings showing the advancement of a crack over a period of time (a set of loading cycles)
   - Striations, which are micro-level rings (require SEM) showing the advancement of a crack over a single loading cycle (occur due to local crack tip plastic deformation)
   - Fracture, which shows signs of either ductile (porous) or brittle fracture (no striations) due to overloading.
3) Fracture due to overloading
   Catastrophic failure after sufficient crack advancement! Due to crack creating stress concentration.

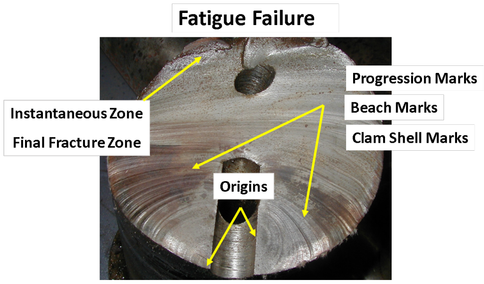


Fig. 20. Distinct visual indicators of fatigue progression

A. *Fatigue Testing*

Note: This is only for evaluating materials, NOT structures!

Fatigue testing is applying a constant load cycle repeatedly over time until the sample fails. Characteristic values of fatigue test:

- **Stress Range:** $\sigma_r = \sigma_{max} - \sigma_{min}$
- **Stress Amplitude:** $\sigma_a = \frac{\sigma_{max} - \sigma_{min}}{2}$
- **Mean Stress:** $\sigma_m = \frac{\sigma_{max} + \sigma_{min}}{x}$
- **Stress Ratio:** $R = \frac{\sigma_{min}}{\sigma_{max}}$

We present this data as an *SN curve*, plotting the stress amplitude against the number of cycles to failure.

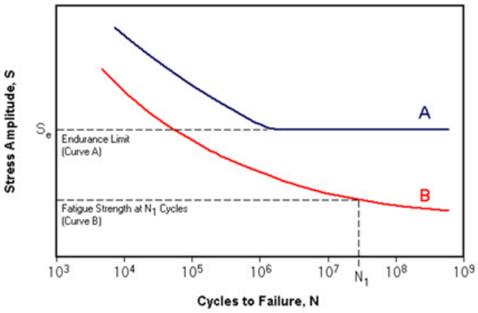


Fig. 21. An SN curve showing the differences between BCC (steel) and FCC (aluminium) behaviour

A higher mean stress, but same stress amplitude will result in a material being less resistant to fatigue, i.e. require less cycles before failure for the same stress amplitude.

The fatigue limit is the stress below which a material will NEVER fail (horizontal asymptote). This only exists for BCC structures for ferrous alloys like steel, not FCC structures like that of Al.

Fatigue Control

- Compressive Residual Stress
  We can improve a material's resistance to fatigue using shot peening. This fires a bunch of small balls at a material, dimpling the surface and causing a compressive stress along the surface layer. This holds cracks together, similar to tempered glass.
- Surface condition
  Surface roughness or mechanical damage affects fatigue. Polished or cold worked materials are more resistant to failure.
- Corrosion
  Corrosion affects surface condition and degrades fatigue performance – it may dip below the fatigue limit of a material that would otherwise hold steady.
- Design
  Avoid sharp corners or even welds, which can degrade fatigue performance.
- Microstructure
  Difference processing and microstructure of materials can affect fatigue performance.

XI. CREEP

Creep is time dependent plastic deformation (and possibly failure) that occurs at "elevated" (relative) temperatures. This may occur for stresses below yield stress due to the effect of temperature.

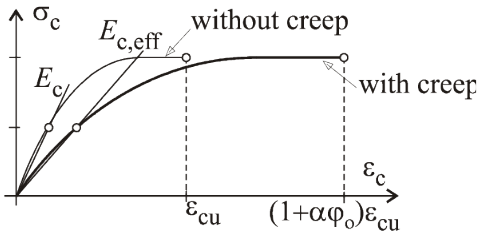


Fig. 22. Holding constant stress can cause plastic deformation over time, shown on a stress-strain curve.

The amount of creep that occurs depends on:

- Temperature
  Temperatures that are elevated (relative to another) can cause significant creep, or accelerate it. For pure metals, creep can become significant at $T \approx \frac{1}{3}T_m$ for metals, where T_m is the melting temperature. Note that for alloys, this fraction is larger, e.g. $\frac{1}{2}$
- Stress magnitude
- Time
- Microstructure

Example

Powerlines can creep when the ambient temperature is high (less heat dissipation to air) and when currents are high (heat up due to resistivity). This can be mitigated by combining different alloys with a strong, creep-resistant core.

Ceramics typically have good resistance to creep since they are resistant to plastic deformation.

Polymers however have low creep resistance.

Creep Test

In a creep test, a constant load is applied and the strain is measured over time until failure. This can be repeated at different temperatures. We measure the strain as a function of time, as well as the time to rupture, or failure (t_f or t_r).

Note that increasing the temperature increases the strain rate, making a steeper curve causes the material to stretch longer (more $\%EL$ but fail sooner). Below some temperatures, creep will not occur (flat line at $\epsilon = C$ for $t \to \infty$).

A creep curve has some distinct regions:

- Initial strain
  This is the initial elastic strain occurring for the material.
- Primary creep
  The material begins to strain at a decelerating rate as *strain hardening* occurs.

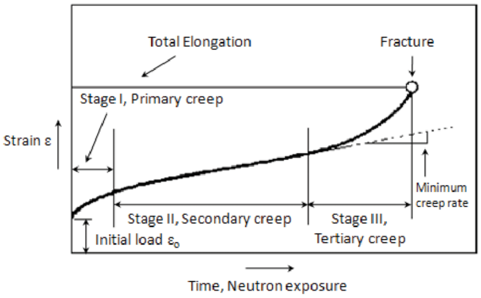


Fig. 23. A characteristic creep test plot showing the different strain patterns through time.

- Secondary creep
  This is *steady state creep* where the strain rate is constant
- Tertiary creep
  The creep rate accelerates towards final rupture and the rupture lifetime t_r

Creep Equations

We can mathematically describe creep.

For *steady state creep*, we can describe the *constant* strain rate $\dot{\epsilon}$ using:

$$\dot{\epsilon} = K_2 \sigma^n \exp\left(\frac{-Q_c}{RT}\right) \tag{35}$$

Where $T(K)$ is the temperature, n and K_2 are material parameters describing creep rate, $Q_c(\frac{J}{mol}$ is the "activation energy" for creep and is related to method of plastic deformation.

This equation only studies the steady state, or linear, portion of the creep graph!

We can semi-quantitatively represent the time to failure for a given material using the *Larson Miller Parameter* (LMP):

$$LMP = T \cdot (\log(t_f) + C) \tag{36}$$

Where $T(K)$ is the temperature, t_f is the time to fracture in a creep test, and C is some material constant (≈ 20 for steel).

We can then use the LMP to predict t_f, or compare different materials. Plotting stress against LMP for different materials, things that are up and right are more creep failure resistant.

XII. STRUCTURE

The *microstructure* of a material can be seen as a hierarchy of grains, made of groups of atoms in particular arrangements.

Short Range Order (SRO) is the grouping of atoms based on nearest neighbours, i.e. unit cells. *Long Range Order* (LRO) is the grouping of unit cells into periodic arrays called *grains* over large atomic distances.

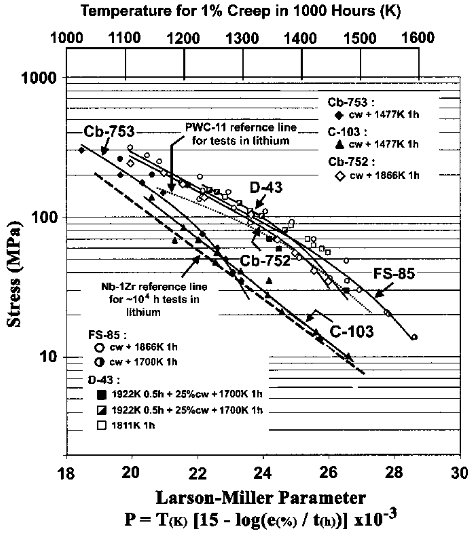


Fig. 24. Comparing the LMP at different stresses for different materials. More up and to the right means a stronger material (larger t_f for same stress)

Materials with only SRO are *amorphous*, while materials with SRO & LRO are *crystalline*. These have random packing of atoms at lower densities. Note that crystalline materials and amorphous materials can fracture differently due to things like dislocations and slip planes in crystals.

Example

Glass is amorphous SiO_2, while quartz is crystalline. Glass is weaker ($E = 37GPa < 76GPa$), less dense ($\rho = 2.20\frac{g}{cm^3} < 2.64\frac{g}{cm^3}$), and transparent.

A given element (e.g. Carbon) has *allotropes* (diff forms of the same element) that are amorphous, like coal, or crystalline, like graphite, graphene, and diamond.

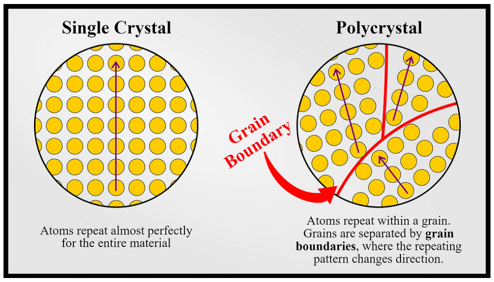


Fig. 25. The grain and grain boundaries of a polycrystalline material compared with the ideal purity of a single-crystal material.

A. *Single/Polycrystalline*

Single Crystals

Single crystals are a crystalline solid with only 1 grain, no interruptions. This requires super specialized processing ($$$) and is used primarily in semiconductors and creep-resistant turbine blades. Single crystal silicon wafers are cut from a silicon meat-stick grown using the Czochralski method. Turbine blades are grown in moulds using a pigtail element to ‘filter’ for a single crystal orientation during the casting process. This results in super creep and fatigue resistant blades.

Polycrystalline

Most materials are made up of many grains which meet at a grain boundary. A given grain is often at a different crystallographic orientation to its adjacent grains. Decreasing grain size can increase electrical resistivity and increase creep rate due to a more disjoint structure. Paradoxically, these grain boundaries can strengthen metals at low temperatures.

Nanocrystalline materials have super small grains on the scale of $< 100nm$, i.e. requiring a TEM to see. The materials sit in the liminal space between amorphous and crystalline, and can greatly change properties like the parameters on their stress-strain curve. For example, nanocrystalline silver burn dressing can improve resistance to infection and promote healing.

Polycrystalline materials are typically *isotropic* materials, which have properties independent of testing direction. Single crystal materials are typically *anisotropic*, where their properties depend on testing direction. For example, in Ni turbine blades, the $< 001 >$ direction offers best creep and fatigue resistance due to its low E.

B. *Unit Cells*

Crystalline materials are made of *unit cells*, repeatable groupings of atoms in a particular orientation and packing. This can influence:

- Density
- Yield strength
- Plastic deformation
- Toughness

The 14 independent *Bravais lattices* are distinguished by lattice parameter, atom placement, and lattice angles are shown in Table I.

The *lattice parameter* a is the size of the cubic structure, which can be related to the radii of atoms contained. Crystalline metals use some of these, including:

- **FCC** - copper, nickel, *aluminium*, platinum
- **BCC** - *iron/steel*, molybdenum
- **HCP** - titanium, magnesium

In FCC, atoms are positioned at each of the 8 corners ($\frac{1}{8}^{\text{th}}$ inside), and at the center of each face ($\frac{1}{2}$ inside) for 4 atoms. The lattice parameter $a = 2\sqrt{2}R$ since the atoms touch along the face diagonal.

TABLE I
THE 14 BRAVAIS LATTICES

Cubic	**Orthorhombic**
Simple cubic	Simple orthorhombic
Face-centered cubic	Face-centered orthorhombic
Body-centered cubic	Body-centered orthorhombic
	Base-centered orthorhombic
Clinic	**Other**
Simple monoclinic	Simple tetragonal
Triclinic	Body-centered tetragonal
Body-centered monoclinic	Hexagonal
	Rhobohedral

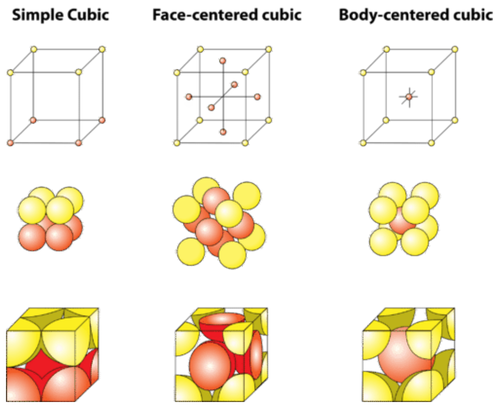


Fig. 26. Visual of most common unit cells.

In BCC atoms are positioned at each of the 8 corners ($\frac{1}{8}^{\text{th}}$ inside), and one at the center of the cube (1 inside) for 2 atoms. The lattice parameter $a = \frac{4R}{\sqrt{3}}$ since the atoms touch along the cube diagonal.

In HCP, the top and bottom surfaces form regular hexagons with 6 atoms per cell: $\frac{1}{6}^{\text{th}}$ of 12 top and bottom atoms, $\frac{1}{2}$ of each center and all 3 interior midplane atoms. The $\frac{c}{a}$ ratio, i.e. height divided by hexagon side length, is about 1.633 but can deviate. The lattice parameter $a = 2R$ since atoms touch along one side length of the 2D hexagon.

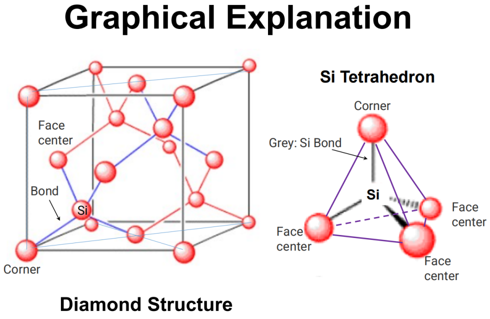


Fig. 27. The unit cell seen in Si, Ge, and the diamond C allotrope, among others.

Something like Silicon and Germanium is weird - they form local tetrahedral structures, which leads to two, slightly shifted and interpenetrating FCC lattices.

Packing

These crystalline structures, which are the physical manifestation of the mathematical arrangement called a *lattice*, can be described by certain parameters.

The *lattice parameter* can be used to find the *Atomic Packing Factor* (APF) for a given unit cell. This is the ratio of solid material to total volume (shown generally and simplified):

$$\text{APF} = \frac{\text{volume of atoms}}{\text{volume of unit cell}} = \frac{\text{No. atoms} \cdot \frac{4}{3}\pi r^3}{a^3} \quad (37)$$

Where $a = cR$ is dictated by the unit cell.

This can be used to find *density*, which is honestly easiest to understand through unit cancellation.

The *linear packing factor* (LPF) is the length of a given directional vector that is covered by atoms centered on the direction vector.

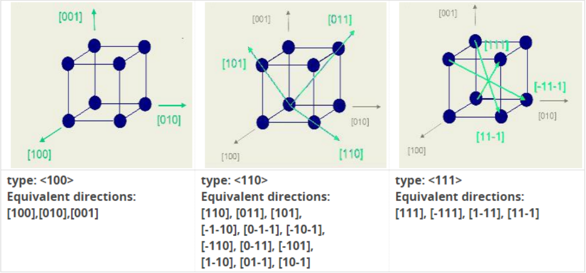
The *planar packing factor* (PPF) is the area of atoms centered on a plane over the total area of that plane.

Directions and Planes

Both types of crystalline behaviour can be described by the directions and planes, which can influence:

- Plastic deformation and weaknesses
- Young's modulus
- Catalytic behaviour
- Etching rates of Si single crystals
  - <100>: fastest rate due to loose arrangement
  - <110>: fast-ish rate
  - <111>: slowest rate due to tight packing
- Growth and dopant diffusion rate of crystals

A *crystallographic direction* is a set of directional indices used to label a vector in a unit cell. Specific directions use square brackets with no commas, with the form $[dxdydz]$ where each dx, dy, dz are the simplest set of integers. Any negative signs are written as overlines. A family of equivalent directions is placed in angle brackets: $< 100 >= [100], [\bar{1}00], [010], [0\bar{1}0], [001], [00\bar{1}]$.



type: <100> **Equivalent directions:** **[100],[010],[001]**	**type: <110>** **Equivalent directions:** **[110], [011], [101], [-1-10], [0-1-1], [-10-1], [-110], [0-11], [-101], [1-10], [01-1], [10-1]**	**type: <111>** **Equivalent directions:** **[111], [-111], [1-11], [11-1]**

Fig. 28. Example of directions and their families in a unit cell.

A *crystallographic plane* is a 2D area in a unit cell defined using *Miller indices*. These are (xyz)coordinates in the form of integer reciprocals of the intersections of each plane with a given axis. They are written using round brackets with no commas, using overlines for negatives, with families of planes written using curly braces.

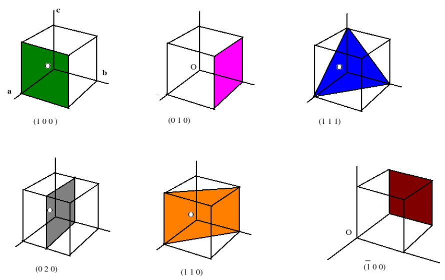


Fig. 29. Example of crystallographic planes. Note that if a plane crosses the origin, its Miller indices are undefined, so we must move our origin. Also note that the plane is described using a normal vector whose components are the reciprocals of the axis intersection coords.

The plane orientation of a single crystal changes electronic properties. These plane directions can be marked by flats on a wafer. This, as well as weakness planes in diamond, is an example of how crystal structure can create anisotropy in materials. Another is that in steel, the predominant fracture plane, or cleavage plane, is the 100 family.

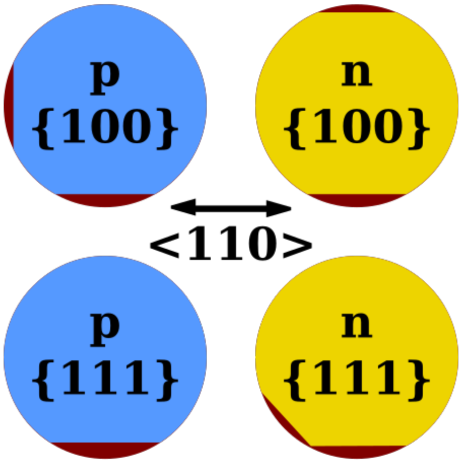


Fig. 30. Classifying semiconductor plane orientation with flats.

This anisotropy is seen again in rolled metals with texture, the dominance of one plane type in a specific orientation. Anisotropy emerges in amorphous material due to the plastic deformation during rolling. This affects properties such as DBTT, and is easily seen with samples tested along the longitudinal (rolling direction) or transverse (perpendicular to rolling) directions.

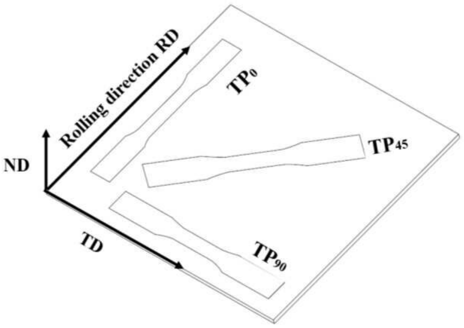


Fig. 31. Sample direction for metals that are rolled can change properties - anisotropy.

C. Finding Structure

Polymorphism

A metal or non-metal may exhibit more than one type of unit cell structure in different forms - *allotropy* in elemental solids. This idea can drastically change the property of materials derived from the same set of elements.

For example, Partially Stabilized Zirconia (PSZ) exhibits cubic, tetragonal, and monoclinic structures. The thermodynamically stable structure depends on the temperature. Additionally, the addition of Y_2O_3 can stabilize small regions of either monoclinic, tetragonal, or cubic at room temperature, depending on the mole%. Due to this polymorphism, PSZ is relatively tough (compared to other ceramics).

A tensile stress near a PSZ tetragonal phase will convert to monoclinic, which has lower APF and expands on transformation. This expansion is typically caused by a localized stress from a crack tip, and creates a compressive stress that resists cracking. It does this by preventing further propagation of the crack tip, a similar idea to that used in tempered glass or shot peening. This is used in thermal barrier coatings and dental crowns. Note that this transformation toughening mechanism can also be induced by dropping the temperature, causing a similar expansion.

Polytypes

These are crystal structures made of one unit cell, but with different stacking sequences and number of layers. For example SiC is made of more than 100 polytypes, like $6H$, $15R$, $4H$, $3C$ (rhombohedral, hexagonal, and cubic). This changes structure, and can make processing SiC for applications tricky to 'select' a polytype.

X-Ray Diffraction

XRD is used to analyze crystal structures using the diffraction of x-rays off of the specific geometry of a given crystal structure. A crystalline material will scatter an x-ray in specific directions due to constructive and destructive interference.

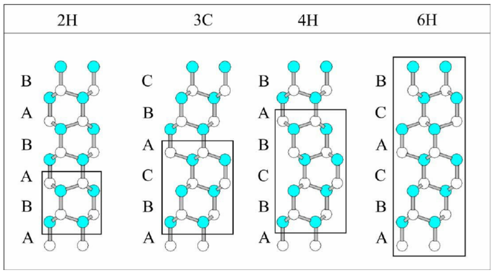


Fig. 32. Visualization of polytypes.

Bragg's law is used to find the double angle 2θ of diffraction, given the distance d between two layers of a crystal.

$$n\lambda = 2d\sin\theta \tag{38}$$

A diffractometer varies the value of θ and measures the response.

Note that specific planes in a material correspond with diffracted x-rays at specific θ values.

One of the applications of XRD is for thin films, however a modified procedure is used as traditional XRD 'bypasses' the thin film altogether. Instead, *glancing angle XRD* is used.

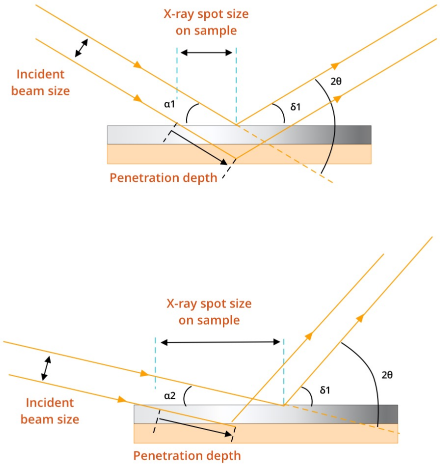


Fig. 33. A visual of glancing angle XRD, noting that the 2θ angle is contained in the interference reflection.

D. Defects

Point Defects

A *vacancy* is a missing atom in the unit cell, occurring in all crystalline materials to varying degrees. The equilibrium number of vacancies N_v is:

$$N_v = N \cdot \exp\left(-\frac{Q_v}{RT}\right) \tag{39}$$

Where $Q_v(\frac{eV}{atom})$ is the activation energy, R is the ideal gas constant, and T is the temperature. N is the total atomic sites per unit volume, found as:

$$N = \frac{N_A\rho}{M} \tag{40}$$

Where M is the atomic mass, $N_A = 6.022 \cdot 10^{23}$ is Avogadros, and ρ is the density in matching units of M.

A *substitutional*, or *solid solution* defect is when one type of atom replaces a base unit cell atom. Note that the replacing atom must be similar size ($< 15\%$ difference in radii), and the amount is dependent on:

- Crystal structure
- Electronegativity
- Valence number

An *interstitial* or *solid solution* defect is when a small atom ($> 80\%$ difference in radii) like N or C occupies an empty space in the unit cell. It fits between the host, or solvent, atoms.

We can calculate the weight and atomic percent of interstitial and substitutional defects:

$$\text{Weight } \% = \frac{\text{mass defect}}{\text{total mass}} \cdot 100\%$$
$$\text{Atomic } \% = \frac{\text{No. atoms defect}}{\text{total No. atoms}} \cdot 100\%.$$

Line Defects

Dislocations are a linear defect in which atoms are misaligned. Basically all crystalline materials have some dislocations, which often arise during processing (PD, thermal stresses, etc.). The motion of dislocations both cause AND result from plastic deformation. The *slip plane* is perpendicular to the 'missing line'.

Dislocations can affect semi-conductor efficiency by 'trapping' electrons in a low energy state – this changes the band gap! This can be seen as decreased LED efficiency, for example.

Area Defects

A *grain boundary* is an example of an area defect. They can reduce conductivity (electron scattering sites), so lower grain sizes and more grain boundaries correspond with lower conductivity.

Volume Defects

Porosity, i.e. voids, often results from processing (e.g. gas bubbles in metal) and can affect thermal conductivity.

XIII. DIFFUSION

Diffusion is atomic motion in solids. It is a thermally activated process, as material is transported through the unit cell. This is important in doping, fuel cells, and other applications.

Interstitial diffusion occurs as an atom moves from one interstitial site to another. This is limited to small

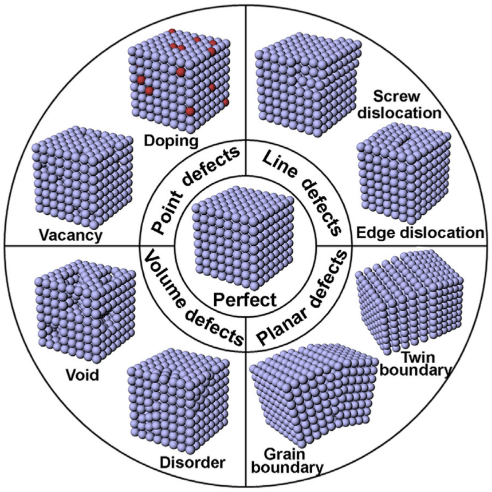


Fig. 34. Visualization of various types of defects.

atoms, like H, C, and N, which can fit into these sites. Smaller atoms typically diffuse faster than larger atoms. Note that there are more interstitial sites than vacancies.

Vacancy diffusion occurs for atoms moving through empty lattice sites from vacancy to vacancy. The diffusing *solute* atoms diffuse through the host *solvent* atoms. Note that the activation energy is much higher for substitutional diffusion than interstitial.

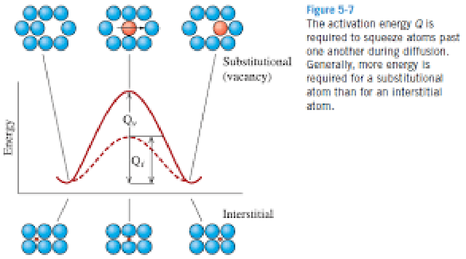


Figure 5-7

The activation energy *Q* is required to squeeze atoms past one another during diffusion. Generally, more energy is required for a substitutional atom than for an interstitial atom.

Fig. 35. Diffusion activation energy for atoms moving from one site to another, noting difference from substitutional to interstitial.

In our hydrogen purification example, H_2 is a small molecule and can diffuse easily through a lattice, isolating it from impure atoms.

A. *Fick's First Law*

Fick's first law describes the diffusion of atoms through a lattice using a simplified, constant model. Atoms move down a concentration gradient, $\frac{dc}{dx}\left(\frac{kg}{m^4}\right)$ which acts as a driving force. The flux of atoms, $J(\frac{kg}{m^2 \cdot s})$ is described by:

$$J = -D\frac{dc}{dx} \tag{41}$$

Where D is the diffusion coefficient. $\frac{dc}{dx}$ is the *driving force*, estimated to be linear as:

$$\frac{dc}{dx} = \frac{\Delta C}{\Delta x} = \frac{C_A - C_B}{x_A - x_B} \tag{42}$$

This assumes that atoms move down a concentration gradient, which in general is not always true. Hydrogen in steel moves *up* a concentration gradient, resulting in fracture by decohesion, or *hydrogen embrittlement*.

Note that we can find the diffusion coefficient $D\left(\frac{m^2}{s}\right)$ (time and temp dependent!) using an Arrhenius-like equation:

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right) \tag{43}$$

Where $Q_d(J)$ is the activation energy and is *system dependent*, $R = 8.314\frac{J}{mol\cdot K}$ is the ideal gas constant, $T(K)$ is the temperature in Kelvin, and D_0 is a constant that depends on the diffusion atom and solvent type. This equation, and idea, is also used in Fick's Second Law.

Note that our D_0 value will follow logically from our knowledge of crystal structures! Fe diffusing in Fe FCC ($APF = 0.74$) will have lower D_0 than for Fe BCC ($APF = 0.68$). However, C diffusing in Fe FCC will have a larger diffusion coefficient than C in Fe BCC in spite of FCC's larger APF because of FCC's additional interstitial sites (C is a small atom). Of course this is still tied to the flux increasing with D_0 $J \propto D$.

Semiconductor Diffusion

For diffusion in semiconductors, the activation energy is sometimes presented in eV, so we use $k = 8.62 \cdot 10^{-5}\frac{eV}{atom\cdot K}$ instead of R. *Intrinsic diffusion* is when the diffusion coefficient is independent of dopant concentration. This assumes no dopant-dopant interactions. *Extrinsic diffusion* is when the diffusion coefficient is *dependent* on dopant concentration.

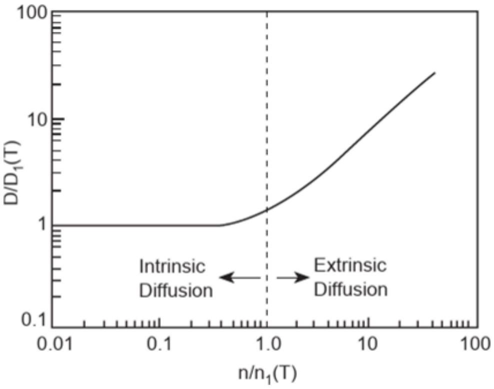


Fig. 36. Intrinsic diffusion is characterized by lower dopant concentration, i.e. the ratio $\frac{n}{n_1} < 1$ where n_1 is a sort of 'critical' concentration. Beyond this point extrinsic diffusion occurs, where the diffusion constant is dependent on, and increases with, external dopant concentration.

The diffusion of P ($r = 0.109nm$) in Si ($r = 0.118nm$) can lead to weird behaviour since the size of P allows it to diffuse via vacancies and interstitial sites. The interstitial diffusion called self-diffusion is due to random motion of atoms (no gradient). Vacancy diffusion is more significant at higher dopant concentrations (it is dependent on gradient), while at low dopant concentrations, interstitial diffusion dominates.

B. *Fick's Second Law*

If the diffusion gradient changes with time, it obeys the DE:

$$\frac{dc}{dx}t = D\frac{d^2c}{dx^2} \tag{44}$$

Which has an analytical solution:

$$\frac{C_x - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) \tag{45}$$

Where C_x is the concentration at any depth x below the surface, C_s is the surface concentration, and C_0 is the initial concentration. erf is the error function, D is the diffusion coefficient (calculated using Arrhenius-like Equation 43), and t is time.

Carburizing is the diffusion of C into steel to change surface properties. The *case depth* is the distance x at which the hardness is $HRC = 50$. This results in super hard surface (high YS/UTS), resistant to surface wear, without a loss of ductility (i.e. toughness). It also increases fatigue resistance. We can characterize the wear using:

$$W = k\frac{FS}{H} \tag{46}$$

Where W is the metal loss, F is the load, S is the sliding distance, k is a constant, and H is the hardness.

Drive-in diffusion, or *2nd diffusion heat treatment* is used to even out the concentration of dopant. It can transport P further into Si, carried out at higher temperatures ($1200C$) in the presence of an oxidizing atmosphere. This forms SiO_2 at the surface to prevent the loss of doping atoms out of the system. The approximate solution is:

$$C(x,t) = \frac{Q_0}{\sqrt{\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right) \tag{47}$$

Where Q_0 is the total dopant introduced during the first diffusion event, *predeposition*:

$$Q_0 = 2C_{sp}\sqrt{\frac{D_p t_p}{\pi}} \tag{48}$$

Where t_p is the time for predeposition and D_p is the predeposition diffusion coefficient.

XIV. PLASTIC DEFORMATION

Elastic deformation is the stretching of bonds, while plastic deformation is the permanent motion of dislocations. This is called *slip*, when bonds are broken and reformed. For this to occur, materials need dislocations (always present), a plane of atoms called a *slip plane*, a crystallographic direction for dislocations to move, and a shear stress parallel to the slip plane.

The slip plane is a plane of high PPF. The slip direction occurs along the slip plane where there is high LPF. Together, these form the slip system. Higher PPF and LPF results in shorter distances for atoms to move before bonding to another atom, which is favourable for PD. Increasing both the number and the quality of slip systems makes PD easier. For example, PD on a close-packed plane (HCP, $PPF > 0.90$) requires *no thermal activation*, while thermal activation is required for non-close packed planes.

> Example
>
> FCC has a close-packed plane while BCC does not. As such, FCC does not require thermal activation for PD. This contributes to FCC having no fatigue limit and no DBTT, as it has high quality slip systems ($PPF > 0.90$, $LPF = 1$).

FCC Metal

- Close packed plane family $\{111\}$, 4 per unit cell
- Close packed direction family $< 1\bar{1}0 >$, 3 per plane
- 12 high quality slip systems

HCP

- Close packed plane family $\{0001\}$, 1 per unit cell
- Close packed direction family $< 11\bar{2}0 >$, 3 per plane
- 3 high quality slip systems

BCC

- Primary slip plane family (not close packed) $\{110\}$, 6 per unit cell
- Close packed direction family $< \bar{1}10 >$, 2 per plane
- 12 low quality slip systems which require thermal activation
- There are other 36 other low quality slip systems (total 48 low quality girlfriends D:)

Dislocation occurs on the plane where the resolved shear stress reaches a critical value, the *critical resolved shear stress* τ_{CRSS}. It is a function of the applied load and orientation of the stress with respect to the slip plane.

$$\tau_{CR} = \sigma\cos\lambda\cos\phi \tag{49}$$

The Schmidt factor $\cos\lambda\cos\phi$ is maximized when both angles are 45.

XV. STRENGTHENING

We can view the yield strength of a material as having various contributions:

$$\sigma_y = \sigma_o + \sigma_s + \sigma_d + \sigma_{ppt} + \sigma_{tex} + \sigma_g \tag{50}$$

Where σ_y is the yield strength, and the subscripts correspond to:

- σ_o: intrinsic strength, analogous to critical resolved shear stress
- σ_s: solid solution strengthening (lattice stress/strain)
- σ_d: dislocation strengthening
- σ_{ppt}: precipitation strengthening
- σ_{tex}: preferred orientation of grains
- σ_g: grain size strengthening

Microalloyed steels are a critical application example of this, which use thermomechanical processing (TMCP) to be super strong.

Grain Size

The Hall-Petch equation describes the effect of effective grain size, d, and strengthening coefficient, k_y, on the grain size contribution:

$$\sigma_g = \frac{k_y}{d^{\frac{1}{2}}} \tag{51}$$

Where the units of d and k_y must match!

Grain boundaries are barriers to the motions of dislocations, and they interrupt motion and resolve shear stress along a slip plane. Atomic disorder along this boundary creates a discontinuity and higher resistance to dislocation motion. As such, smaller grain size has higher yield stress. Somewhat surprisingly, decreasing grain size also increases toughness, despite higher yield stress typically inversely correlated with $\%EL$ and therefore causing lower toughness. This is because it *decreases the DBTT*, leading to more ductile behaviour at more temperatures.

We can estimate grain size using the circle grid method: choose a center and measure the number of grain boundary intersections each radial line crosses - get 'average grain size'. A second option is *electron backscattered diffraction* EBSD.

Solid Solution Strengthening

The presence of substitutional and interstitial solute atoms can impose strains on lattices.

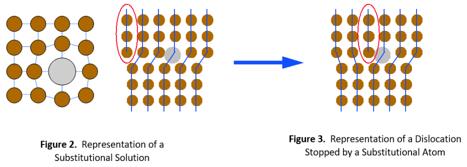


Fig. 37. A graphic of how solute atoms can stop the motion of dislocations by putting strains on lattices.

These strains increase the resistance to dislocation motion since they 'flow worse' through the strained lattice, and struggle to get around the solutes atoms. Solute atoms tend to localize inside dislocation cores. We can calculate the strengthening contribution with:

$$\Delta\sigma_i = k_i c_i \tag{52}$$

Where k_i is the strengthening coefficient for the ith solute and c_i is its $wt\%$ in the solid.

Example

This is particularly important in aluminium cans, where a 5XXX alloy Mg-rich lid is solid-solution strengthened, as well as a 3XXX alloy Mn-rich body.

Strain hardening

Strain hardening, or *cold working*, or dislocation hardening, is when there is a local increase in material strength due to plastic deformation. Dislocations are generated during PD, and the greater the number of dislocations, the greater resistance to further dislocation motion. Dislocations moving along the same plane 'repulse' each other due to the internal stresses generated by them. This contribution is found as:

$$\sigma_d = \alpha G b \rho_{dis}^{\frac{1}{2}} \tag{53}$$

Where G is the shear modulus, α is a constant, $b(m)$ is Burgers vector, and $\rho_{dis}\left(\frac{m}{m^3}\right)$ is the dislocation density.

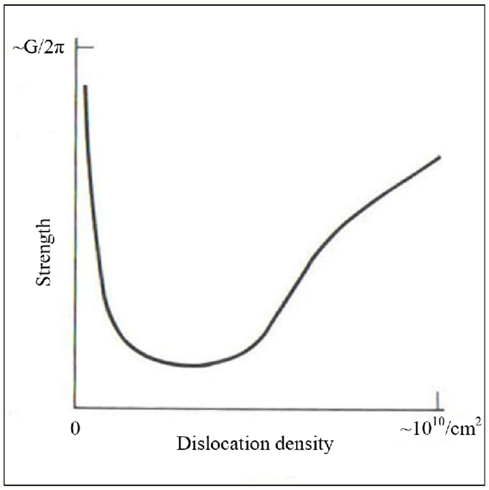


Fig. 38. A few dislocations is a very pure material that doesn't PD much. An example of this is 'whiskers', which are super small with few dislocations and are super duper strong. Many dislocations 'hardens' the material as well.

This can be pictured as 'pushing' the yield stress further up the stress-strain curve, also reducing ductility.

Example

When drawing copper wire, the PD causes strain hardening, increasing strength and decreasing ductility.

When growing crystals, thermal stresses can be generated causing plastic deformation. If PD occurs and the *von mises stress* is sufficiently high, dislocations can be generated. These generated dislocations ($3000/cm^2$) can trap e in lower energy states, influencing the electrical behaviour.

Cold Working

Cold working is plastic deformation (approximately occurs at $\approx T < 0.4T_{melt}$). CW is defined, for a rolling operation, as:

$$\%CW = \frac{A_0 - A_f}{A_0} \cdot 100\% \tag{54}$$

This increases strength and decreases ductility, and therefore toughness. This is the same formula as $\%RA$ for a tensile test.

Precipitation Strengthening

Dislocation motion can be interrupted by the presence of 2nd phase particles. Depending on their size, dislocations either have to move around them (*looping bypass*) or 'cut' through them (*cut/shear*). For shearing:

$$\tau_y = \tau_0 + \Omega G \left(\frac{Rf}{b}\right)^{\frac{1}{2}} \tag{55}$$

And for looping:

$$\tau_y = \tau_0 + \frac{Gb}{R}\left(\frac{f}{\pi}\right)^{\frac{1}{2}} \tag{56}$$

Where R is the precipitate radius and f is the volume fraction of the 2nd phase particles.

Another equation is:

$$\sigma_{ppt} = \left(\frac{10.8 f^{\frac{1}{2}}}{X}\right) \ln\left(\frac{X}{6.125 \cdot 10^{-4}}\right) \tag{57}$$

Where the contribution $\sigma_{ppt}(MPa)$ has units of MegaPascals and $X(\mu m)$ is the *diameter* of the spherical particles (WATCH UNITS), and f is the volume fraction of the 2nd phase particles. Note that smaller second phase particles and higher volume fraction impede more!

Precipitation strengthening depends on the size of the particles, which can be controlled by heat treatment, and the volume fraction, controlled by composition. In general, we treat precipitation strengthening as *decreasing* with increasing particle size.

A. *Annealing*

We've seen that decreasing grain size increases toughness and reduces YS, and cold working decreases $\%EL$ and again increases YS. Often we cold work a material into shape but reset properties using *annealing*: heat treating material to 'reset' microstructure to pre-deformation conditions.

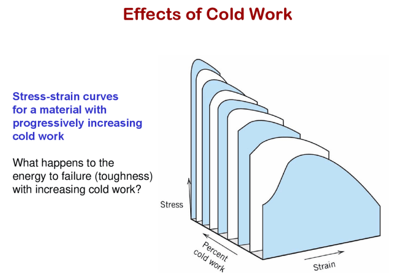


Fig. 39. Cold work 'shifts' the start point of the stress strain curve, increasing YS while decreasing %EL and toughness. Annealing reverses this process

This occurs in 3 steps:

Recovery

Recovery is the rearrangement of dislocations, leading to a slight reduction in dislocation density. Must happen before REX

Recrystallization or REX

Highly strained grains reform into new, (basically) *strain-free equiaxed* grains. These REXed grains are often finer than the predeformed grain size and the dislocation density *decreases*. The driving force of REX is the energy associated with a high number of dislocations, and therefore requires a minimum amount of cold work $\approx 5\%$ to even occur. Increasing the amount of cold work makes REX happen faster.

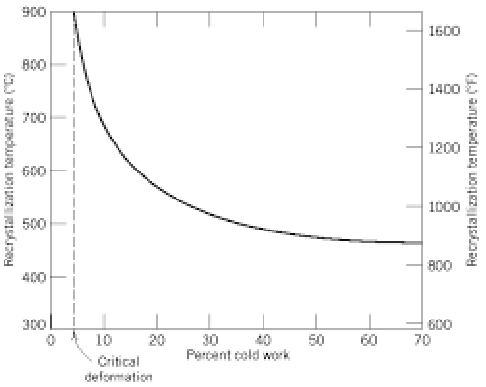


Fig. 40. Past the critical deformation amount, increasing the amount of cold work decreases overall REX time.

Note that FULL recrystallization only happens past the recrystallization temperature – for pure metals its roughly $T > \frac{1}{3}T_m$ and $T > 0.7T_m$ for alloys, similar to creep thresholds (below this temp only recovery happens). Increasing T beyond this point increases the rate of transformation, just like increasing the amount of cold work does (faster kinetics). Below this temperature, work on the metal will remain cold work (see hot work below for a combination).

Grain Growth

It happens.

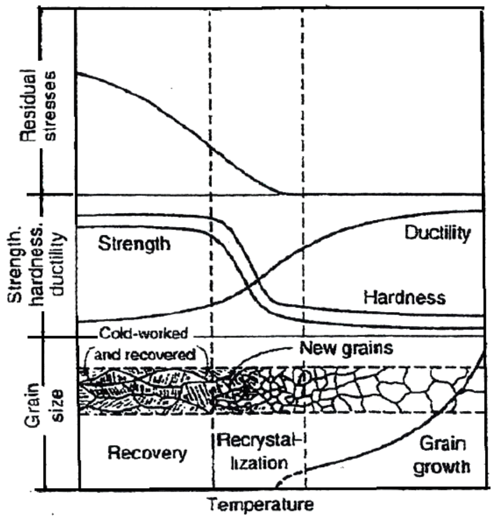


Fig. 41. Stages of REX visualized.

One application of REX is in annealing polycrystal Si solar cells to reduce dislocation density and make them more efficient.

Hot Working

An alternative to cold work + annealing is *hot working*, when deformation is done *above* the recrystallization temperature. This allows REX to occur during the shaping, as it occurs quite quickly.

XVI. Phase Diagrams

A *phase* is a homogenous portion of a system with uniform physical and chemical properties. Two phases could be liquid vs. solid, but could also be two different crystal forms of the same material. Phase diagrams illustrate the relationship between temperature and composition of a material and its transitions, at *equilibrium*!

For all phase diagrams, we use the lever rule to determine the wt% or at% of each phase in a 2+ phase region. First we draw the *tie line* at the correct temperature. The ends of the tie line give us bounds for the $wt\%$ of each component, and we use the 'current' $wt\%$ of the composition as a whole to choose the horizontal position along the tie line. To find the weight fraction of a given phase, take the ratio of the 'farther' side of the tie line over the entire length of the tie line.

Isomorphous Phase Diagram

Two components that are fully soluble in each other (e.g. substitutional solid solution) form a special, simple binary phase diagram.

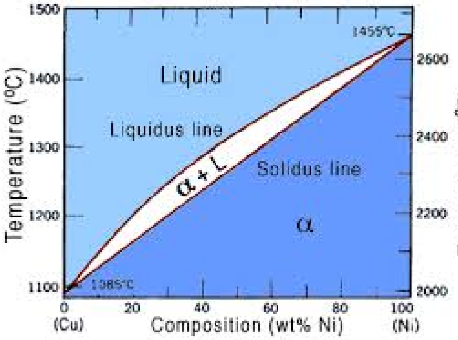


Fig. 42. An Ni-Cu isomorphous phase diagram.

The liquidus and solidus are the respective lines separating the liquid/solid mix from the solid and the liquid. The solvent is the component in major concentration, while the solute is in minor concentration.

General Binary Phase Diagram

These curves also have liquidus and solidus lines. A new line is the solvus line, which represents the limit of solid solubility. The solids are divided into three sections:

- α, which is (in this case) a Copper-rich phase with Ag in solid solution
- β, which is (in this case) a Silver-rich phase with Cu in solid solution
- $\alpha + \beta$, which is (in this case) a two phase region of both solids

A *eutectic point* is a point where there is an equilibrium between 2 solid phases and a liquid. *Hypoeutectic* is the nominal composition (of a given element) less than that of the eutectic point, and *hypereutectic* is the opposite. Cooling a eutectic composition liquid will result in a *lamellar*, or layered structure - $L_e = \alpha_e + \beta_e$. Cooling a hypoeutectic composition liquid will result first in the formation of a *primary phase* (α for hypo, β for hyper) in sections, and then eventually the remaining liquid portion will finally cool into a lamellar structure.

A. FeC PhaseD

Steel is given a grade (roughly proportional to tensile strength and C content) and is labelled with a four digit number $ABXY$, where the last two digits XY indicate a $0.XY\%wtC$ content.

- Ferrite α

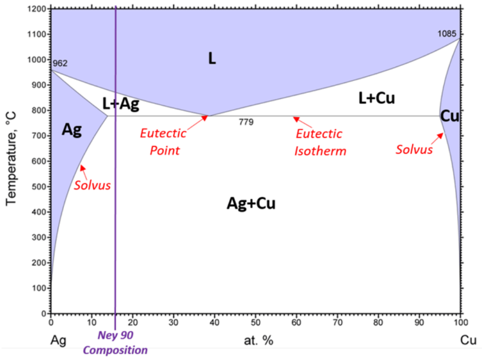


Fig. 43. A binary phase diagram for Ag-Cu.

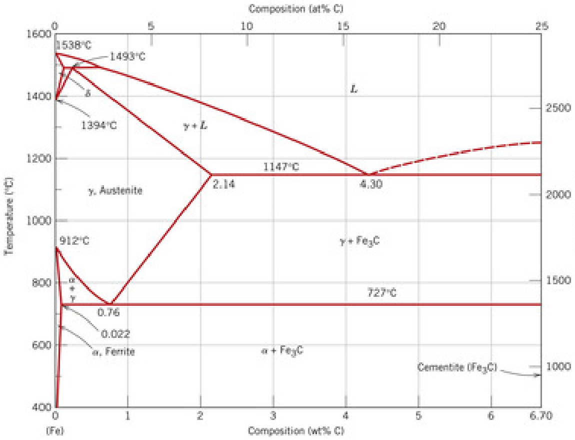


Fig. 44. FeC phase diagram

Ferrite is a low temperature BCC structure of iron, with a maximum C solubility of $0.022\%wtC$. It is moderately strong and ductile.

- austenite γ

austenite is a high temperature FCC structure of iron. It is very ductile (useful when forming stuff) and has a high C solubility (mostly in interstitial solid solution).

- Cementite Fe_3C

Cementite is a metastable orthorhombic crystal structure. It is very hard and brittle (ceramic-esque), sitting at about $6.7wt\%C$.

Eutectoid is when a single solid phase transforms into two new solid phases, occurring for FeC when cooling austenite at $0.76wt\%C$ and $727C$. This forms *pearlite*, a two phase lamellar microstructure consisting of fine layers of ferrite α and cementite Fe_3C. Pearlite is stronger and less ductile than ferrite, since the repeating phase boundaries impede dislocation motion. For hypoeutectoid plain Carbon steels, increasing $wt\%C$ increases strength, decreases ductility, and increases the DBTT (bad) due to increased Fe_3C in the pearlite.

Non-equilibrium Phase Transformations

While manipulating $wt\%C$ can help dictate steel properties, processing in non-equilibrium conditions also lets us affect the phases through the temperature/duration of phase transformation. Phases like coarse pearlite, fine pearlite, bainite, and martensite allow us to get high strength and reasonable ductility steels.

Phase transformation from austenite to α and Fe_3C is diffusion of C from ferrite regions to cementite regions.

First, the *nucleation* event occurs, requiring *undercooling* to form 'starter crystals'. When the temperature is below the equilibrium transformation temperature by some ΔT, this creates a driving force for the transformation. Increasing undercooling $\Delta T = T_e - T$ increases the rate of nucleation.

$$\frac{dN}{dt} = N_0 Z \beta \exp\left(-\frac{\Delta G}{kT}\right) \tag{58}$$

Where $\frac{dN}{dt}$ is the speed of nucleation, and T is the temperature.

The *growth* of these phases relies on atomic diffusion. Since decreasing T decreases the diffusion coefficient, increasing undercooling decreases the rate of growth.

As such, the overall rate of transformation is maximized for some intermediate amount of undercooling. Therefore, for a lot of undercooling, nucleation occurs quickly but growth propagates the thickness of these layers slowly, leading to many layers.

B. Isothermal Transformation Curves (TTT)

TTT curves for *a given composition* of steel predict the phase of steel formed when *austenite* (always the starting phase!) is quenched (cooled infinitely fast) to a temperature below the eutectoid temperature, and held for some time. Note that for temperatures close to

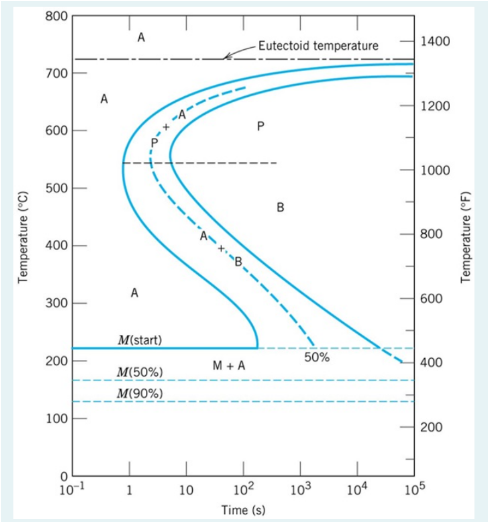


Fig. 45. A TTT curve for a given composition of steel.

T_e, nucleation is the limiting factor, while for large undercooling, growth is the limiting factor. The ‘peak’ is that magic temperature when transformation quickly occurs. The phases that form from austenite are plotted on temperature vs. time. P is for Pearlite - fine pearlite is harder (more boundaries or lower interlamellar spacing) while coarse pearlite is more ductile. Fine pearlite forms at lower temperatures, due to an increased number of layers when growth is slow. B is for Bainite, which is ferrite and a fine dispersion of cementite. M is for Martensite, which is a diffusionless, or athermal transformation (line shows when $XX\%$ of austenite has converted to Martensite). Note that following grain size rules, hardness decreases from $M > B > P$

If a steel is quenched to a certain temperature and held there, draw a horizontal isothermal line until the given time. If the material is then ‘requenched’, make note of the amount of austenite remaining – this is the only part of the steel that can still transform! Then, requench to this isothermal line, restarting at $t = 0$, noting that only the austenite weight fraction of the still will further transform following this TTT behaviour.

Note that we can also take a specimen with cementite and hold it at a high-ish temperature (a bit below critical temperature) for *spheroidization* to occur, where the cementite plates break down and form spheres. This increases ductility and toughness and lowers hardness.

XVII. CORROSION

Corrosion causes an estimated more than $2 trillion in damages annually (majority due to corrosion of steel), which can lead to safety hazards, industrial damage (pipes, machinery, electronics), and damage to the environment.

Corrosion is a RedOx (Red Cat An Ox reaction pair) reaction in which a metal is oxidized to form a positive ion and electrons. Oxidation occurs at the anode, while reduction occurs at the cathode. A common set of reactions is:

$$\text{Cathode/Reduction} = O_2 + 2H_2O + 4e^- \to 4OH^-$$
$$\text{Anode/Oxidation} = Fe \to 2e^- + Fe^{2+}.$$

In an acidic environment with dissolved oxygen, a stronger reduction reaction is:

$$\text{Cathode/Reduction} = O_2 + 4H^+ + 4e^- \to 2H_2O.$$

We can measure the electromotive force involved in a reaction using a standard half cell (1M at 25 C against a reference electrode of 1M H+ with an inert Pt electrode). More reactive metals have more negative standard electrode potentials (they oxidize easily), while metals with large positive EMFs are resistant to corrosion. For a reaction to occur spontaneously, the difference in the reduction potentials $V_{r,cathode} - V_{r,anode} > 0$. Note that the negative corresponds with the anode reaction being an oxidation reaction, akin to ‘flipping’ the reduction potential into an oxidation potential. The magnitude of this difference indicates the strength of the driving force of this reaction, not the kinetics.

We use the *galvanic series* to rank the reactivity, or susceptibility to corrosion, of metals under real conditions (exposed to seawater, i.e. Chlorine). Metals on one end, like Pt, Au, or passive stainless steel, are unreactive, while metals on the other end, like cast iron, aluminium, and active stainless steel, are very reactive.

GALVANIC SERIES CHART
METALS AND ALLOYS

+ CORRODED END
ANODIC, LEAST
NOBLE

Galvanic Series Chart
Metals and Alloys
Magnesium
Magnesium alloys
Zinc
Aluminum 1100
Cadmium
Aluminum 2024-T4
Steel or iron
Cast iron
Chromium-iron (active)
Ni-Resist Cast Iron
Type 410 Stainless steel (active)
Type 304 Stainless steel (active)
Type 316 Stainless steel (active)
Lead tin soldiers
Lead
Tin
Nickel (active)
Inconel nickel-chromium alloy (active)
Hastelloy Alloy C (active)
Brasses
Copper
Bronzes
Copper-nickel alloys
Type 410 Stainless (passive)
Monel nickel-copper alloys
Silver solder
Nickel (passive)
Inconel nickel-chromium alloy (passive)
Chromium-iron (passive)
Type 304 Stainless steel (passive)
Type 316 Stainless steel (passive)
Hastelloy Alloy C (passive)
Silver
Titanium and titanium alloys
Graphite
Gold
Platinum

− PROTECTED END
CATHODIC, MOST
NOBLE

Table 1

Fig. 46. The galvanic series.

These unreactive metals are known as noble metals, and do not like to lose electrons (i.e. get reduced) due to their electron configuration.

Types of Corrosion

- General Corrosion

General corrosion is the rusting of steel in oxygenated water. Various oxides or hydroxides can form, e.g. $Fe\left(OH\right)_2$, which may affect subsequent corrosion.

- Galvanic corrosion

When two metals are in contact, the more reactive metal will corrode (act as the anode), while the less reactive metal will act as the cathode (reduction reaction is often $H+ \to H_2$ or $O_2 \to OH^-$). In this way, the less reactive metal is protected from corrosion by the *sacrificial anode* metal. Note that the cathode reaction is the rate limiting step, so the rate of corrosion at the anode depends on the ratio of cathode area to anode area. Increasing the cathode area means more reaction sites, and faster corrosion.

- Crevice Corrosion

Oxygen cannot get into a crevice, and it is depleted by corrosion. As such, this O-depleted region becomes anodic, while the O-rich area outside the crevice becomes cathodic (and therefore protected). As this occurs, Cl^- builds up inside the crevice, forming an acidic and aggressive region of corrosion. This idea of one metal and two separated environments is different from galvanic corrosion's two metals and one single environment.

- Pitting Corrosion (and active vs. passive SS)

Over 80% of stainless steels are type 304, which is very resistant to various atmospheric, chemical, or petroleum environments. The reason for this is the formation of a nm-scale Chromium oxide layer, which reforms on itself when damaged (*repassivation*). Note that a minimum of $10.5\%wtCr$ is required to form this layer. This constitutes *passive stainless steel*.

When pinholes extend into a material, pitting corrosion can occur on the surface of the *active stainless steel*. Pores can form in which a low pH, high Cl^- environment creates an anode below the cathodic surface layer of the passive SS. This is a form of crevice corrosion, in which O is depleted from the anodic pit and therefore prevents repassivation from occurring.

Controlling Corrosion

We can prevent corrosion by examining how we can remove factors necessary for corrosion.

- The flow of electrons (and ions to maintain a complete circuit.)

We can use coatings or barrier layers to prevent electrical conductivity between cathode and anode.

Another idea is *cathodic protection*, when we apply a DC current and force the oxidation reaction to go in reverse.

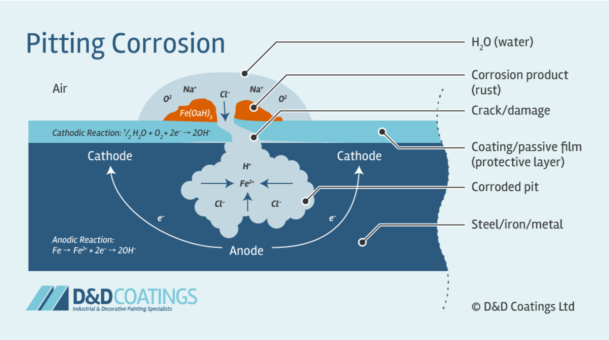


Fig. 47. A diagram showing how a crevice corrosion system results in localized, severe corrosion of stainless steel. This can happen, for example, when salt is added to boiling water early, outside in general, and less so when Mo is added (type 316 SS)

We can also use a *sacrificial anode*, in which we use a more reactive metal in contact with our metal of importance. The amount of the more reactive metal dictates how long the protection lasts (e.g. Zn or Aluminized steel).

- H_2O is required for a common cathode reaction

Polymer coatings can form a barrier against water contact, used for pipelines and rebar. However, coatings are never perfect – we can only achieve high $\%$ coverage for reasonable cost. However, these defects can be sites for accelerated corrosion. To address this, we can apply corrosion-conscious design practice, for example design to avoid the build-up of water.

- O_2 is required for neutral or basic solutions

We can remove oxygen from systems, for example in boiler systems, using special machinery.

- Metals can be anodic to other metals

We can try to mitigate galvanic coupling by using metals close to each other on the galvanic series We can also minimize cathode-to-anode surface area ratio to reduce the importance of galvanic corrosion. We can also try to insulate metals from one another with polymer fittings, or better combine all 3 practices.

- Material resistance

Some materials are more resistant to corrosion than others, although this is typically a cost-to-benefit tradeoff. For example, prosthetics are made with titanium (low cost compared to high-cost operation). A lower-cost alternative is weathering steels (add $0.20\%wtCu$) which are more protected than plain carbon steel.

XVIII. PLASTICS

Polymers are used in electrical insulation (ABS, PVC), but can also be used as conductive layers (polyanilines). They are used as coatings and sealants (epoxy). We define engineering plastics as the set of polymers used for engineering applications. For example, thermoplastics are plastics that soften on heating and harden on cooling. We also have thermosets, which after curing, don't soften on heating, and elastomers, which are polymers that can undergo large elastic strains. Note that plastics are not very reusable! They degrade over time (microplastics)

Structure

Plastics have low E/strength, high ductility. They are made up of many chains, composed of multiple monomers (smallest repeating units) linked together. Note that these chains can also have branching.

Example

HDPE has less branching than LDPE, as the chains can pack better and are therefore higher density.

The *molecular weight* is the sum of atomic weights in a chain – for polymers this exists as a distribution.

$$\overline{M}_n = \sum x_i M_i \tag{59}$$

Where M_n is the number averaged molecular weight, x_i is the number fraction of each M_i mean molecular weight of size range i. It's equivalent to finding the mean of a histogram, where the bin sizes represent the x_i's. The weight averaged molecular weight is found similarly as

$$\overline{M}_w = \sum w_i M_i \tag{60}$$

Where we use the weight fractions w_i as weightings for each sample molecular weight. This differs from the number average (which is just a normal unweighted average) as it weights molecules with higher masses more and is therefore 'sensitive' to the presence large molecules.

The *degree of polymerization* n_n is the number of monomers in the chain, and can be found as:

$$n_n = \frac{\overline{M}_n}{m} \tag{61}$$

Where n_n is the number-average DoP and m is the monomer weight. This is just a typical average approach. Similarly, the weight average DoP n_w is:

$$n_w = \frac{\overline{M}_w}{m} \tag{62}$$

This also finds the rough number of monomers in the chain, but again is derived from a weighted average of masses, not an unweighted one.

Increasing DoP results in increasing strength and increasing softening temperatures. Note that when we recycle plastics, the $\overline{M}_w$ decreases, resulting in lower DP and weaker plastics.

Properties

Thermoplastics have low E, since plastic deformation is primarily contained in the 'untangling' and sliding of polymer chains. In theory, this E value would be as low as $E \approx 0.003GPa$ if plastic deformation was impeded solely by secondary bonding. This occurs in elastomers.

Polymers exhibit some crystallinity, which shifts some load onto the $C - C$ bonds, increasing the actual E. Additionally, large polymer side groups increase E via crosslinking (thermosets are fully crosslinked polymers), where these side groups interact with other polymers.

Polymers behave similar to other materials in tension:

- Elastic zone up to yield point
- Viscous region where chains slide past each other

One difference is that there is no work hardening, since there are no dislocations. At large strains, the chains become aligned and the $C - C$ bond bears more of the tensile load, increasing their strength significantly near failure. Polymers like Kevlar take advantage of this by using aligned chains. Elastomers take very large strains until failure, while fully cross-linked plastics have greater strength but little viscous flow.

Similar to metals, increasing the strain rate increases strength and decreases ductility as chains are less able to slide past each other.

Glass Transition Temperature

The *glass transition temperature* T_g is the temperature at which a non-crystalline polymer transforms from a solid to a very viscous liquid. On a specific volume vs temperature curve, we can see that 100% amorphous materials have an increase in the slope $\frac{dV}{dT}$ at T_g and little increase at T_m, while 100% crystalline solids only have a large jump at T_m. Most polymers are a mix of these, and have an intermediate set of properties. This also changes the stress-strain curve, as below T_g we see higher strength and lower ductility while above T_g, the curve is much flatter and the elastic modulus much lower. Note that E will continue to decrease with increasing temperature, and is very brittle below T_g.

T_g increases with increasing molecular weight, crystallinity, and crosslinking (more intermolecular forces between chains make it harder to become liquid).

Degradation

Polymers degrade due to heat, UV, oxygen, chemicals, and other biological factors. Chains are either scissioned or cross-linked. We can protect against this using stabilizers (e.g. $1\%wt$ hindered amine light stabilizers/HALS) or UV absorbers (e.g. TiO_2 composite particles or carbon black).

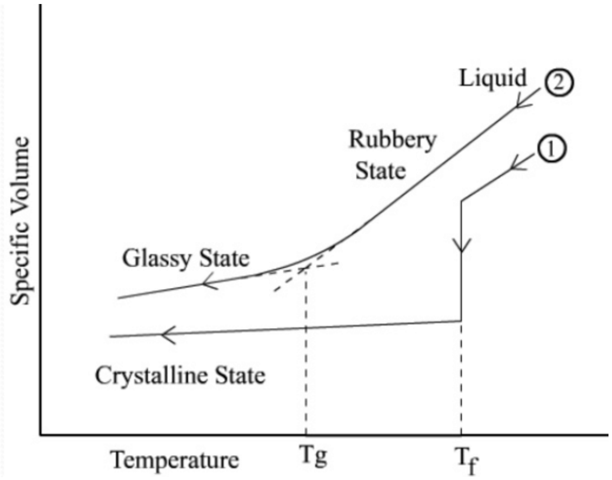


Fig. 48. Specific volume against temperature for an amorphous versus a crystalline plastic. Note the difference in behaviour around the glass transition and melting temperatures.