Part 2

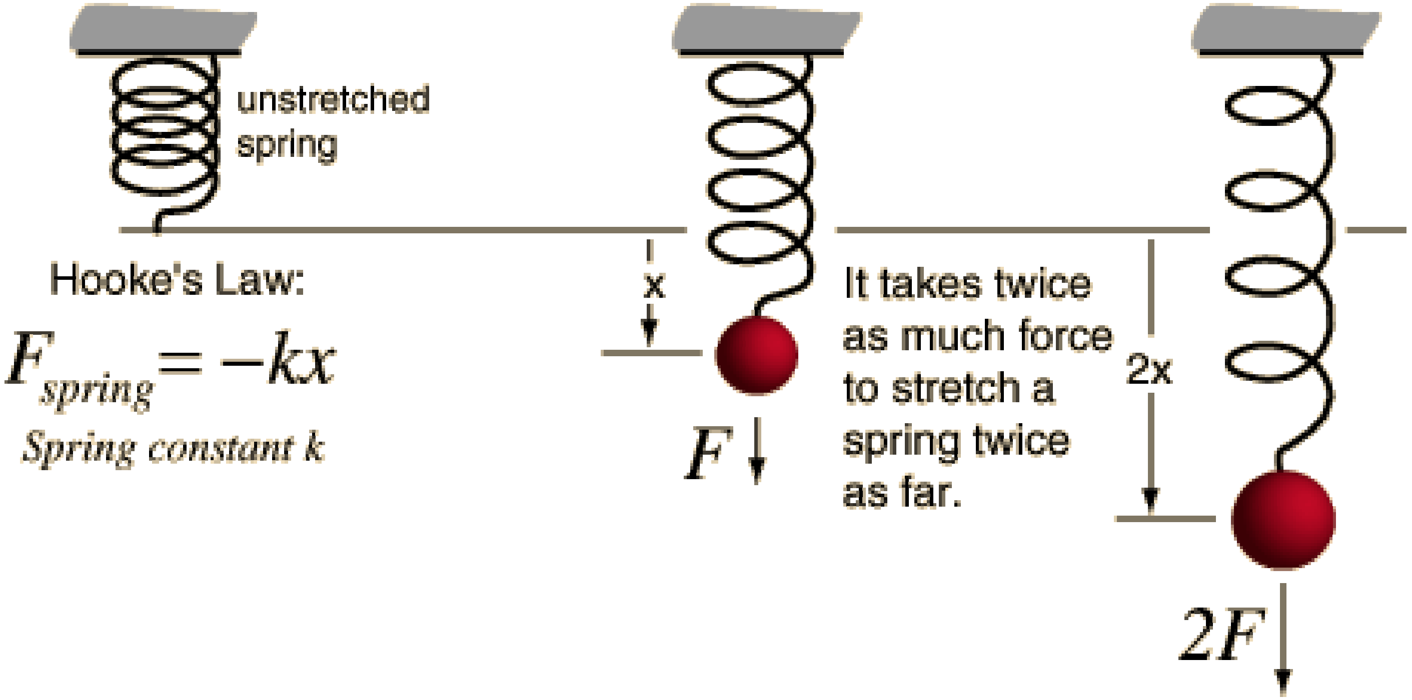
Mechanical Properties of Materials

Elastic deformation – bending of beams

- Why study elastic deformation
  - Essential to predict how materials deform under applied forces
  - In order to choose "best" material for required function

- Examples of beams
  - Hockey sticks
  - Oars
  - AFM lever

Hooke’s Law



Hooke's Law:

$$F_{spring} = -kx$$

Spring constant k

It takes twice as much force to stretch a spring twice as far.

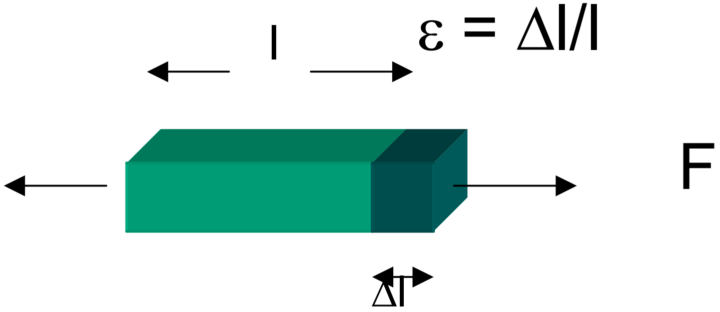
Strain

Definitions

Tensile strain

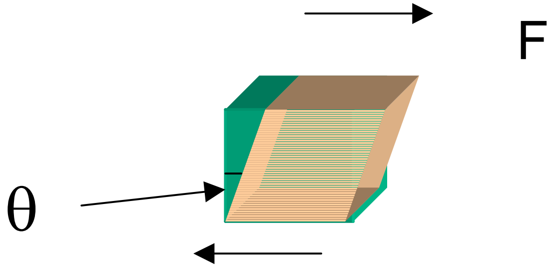
Fractional increase in length

$\varepsilon = \Delta l / l$



Shear strain

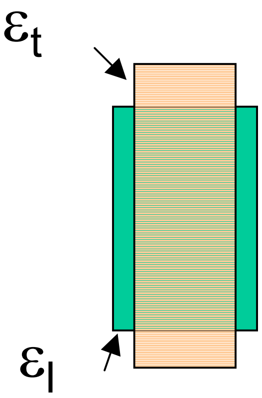
$\gamma = \tan\theta \approx \theta$ (small θ)



Poisson's ratio

$\nu = -$ lateral strain/tensile strain

$= \varepsilon_l / \varepsilon_t$



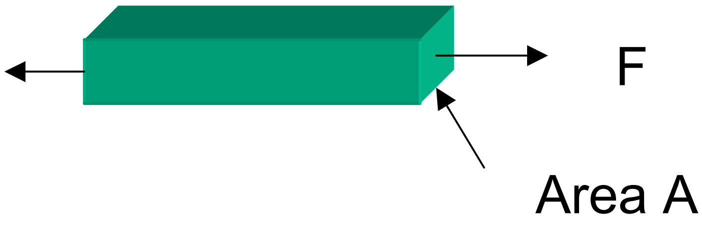
Stress

Definition

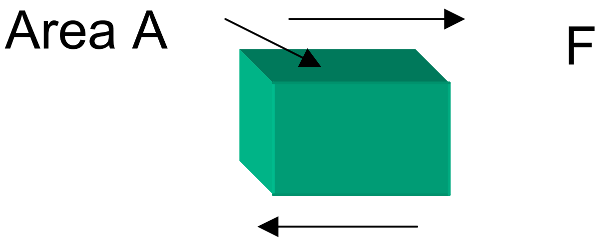
Internal resistance to deformation

$\sigma = F/A$ (units; GPa, 10^9 N m^{-2})

Tensile/ Compressive stress – Force is perpendicular to plane of resistance



Shear stress – Force parallel to plane of resistance (τ)



Elastic deformation

Non-permanent deformation – Material returns to original state when load is removed

Tension / compression

$\sigma = E\,\varepsilon$

E is Young's modulus

Hooke's Law

Shear

$\tau = G\,\gamma$

G is the Shear Modulus

Pressure

$P = -K\,\Delta V/V$

K is the Bulk Modulus

For isotropic materials

$G = E/2(1+\nu)$

$K = E/3(1-2\nu)$

Elastic Energy

Work done in extending a cube of material (side L) by dL

$=\text{Force} \times dL$

$= \frac{1}{2}\,\sigma\, L^2\, (\varepsilon L)$

$= \frac{1}{2}\,\sigma\varepsilon\, V$

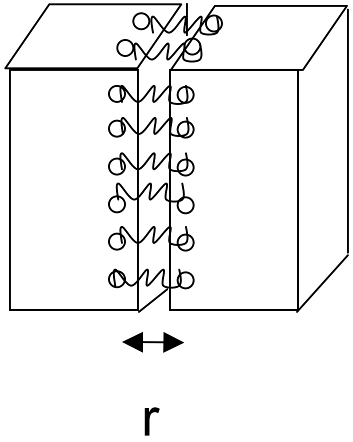
Energy per unit volume = Work per unit volume

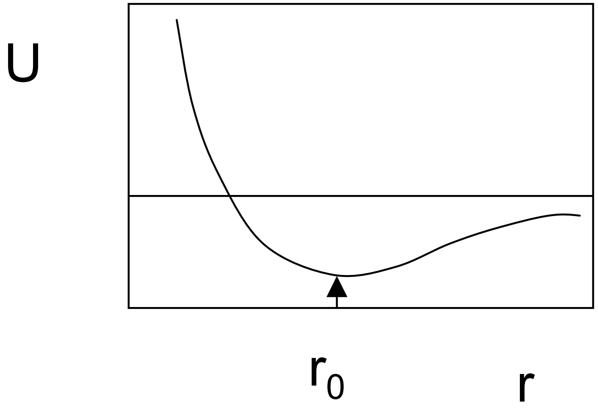
Energy per unit volume = $\frac{1}{2}\,\sigma\varepsilon$

Modulus of Resilience

Amount of elastic energy stored in a material at point of failure

Young’s Modulus and Interatomic forces





$$F = dU/dr$$

Stiffness of bond $S = dF/dr = (d^2U/dr^2)_{r0}$

$\sigma = NS(r - r_0) = E\,(r - r_0)/r_0$

$E = S/r_0$

N is number of bonds

per unit area $= 1/r_0^2$

Young’s modulus – typical values (GPa)

Diamond	1000
Aluminium	69
Tungsten	407
Nylon	2

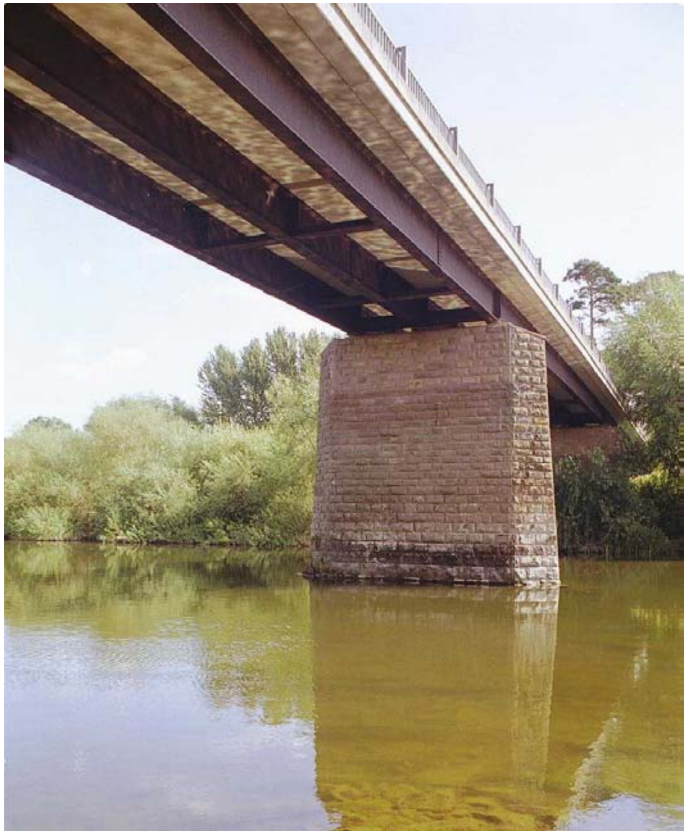
Calculated from interatomic potentials

	S (Nm^{-1})	E(GPa)
Covalent (eg C-C)	50-180	200-1000
Metallic	15-75	60-300
Ionic	8-24	32-96
Van der Waals	0.5- 1	2-4

Beams - Examples

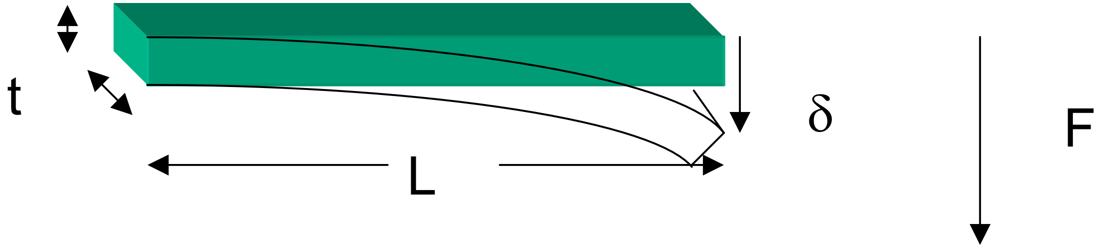
- Roofing beams
- Floor boards
- Bridges
- Diving boards
- Cranes
- Girders
- Aircraft wings
- Oars
- AFM cantilever

Bridges



Bending of beams

Require maximum stiffness and minimum weight



Weight (M) = L t^2 ρ ρ is density

Deflection (δ) = 4 L^3 F/ t^4 E

$M = (4L^5 F/\delta)^{1/2} (\rho^2/E)^{1/2}$

Stiffness = F/ δ

For a given stiffness weight is minimised by minimising $\rho/E^{1/2}$

Performance measure $P = E^{1/2}/\rho$ (Figure of Merit)

Typical values (GPa$^{1/2}$ Mg^{-1}m^{3})

Steel	1.82
Polyurethane foam	2.44
Concrete	2.78
Aluminium	3.13
GFRP	3.23
Wood	5.88
CFRP	11.1

Must also consider cost and ease of manufacture

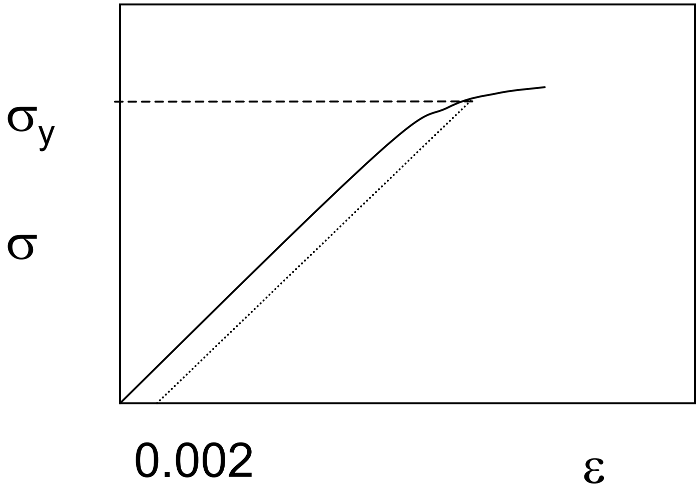
Beyond the elastic limit- Plastic deformation

Why study plastic deformation?

Need to know maximum loads materials can withstand before permanent shape changes occur

Need to know whether materials will fracture or deform

Yield Strength



Typical values (MPa)

Aluminium	35
High strength Steel	1400

Yield stress is stress at which noticeable plastic strain has occurred (eg ε_p = 0.002)

Tensile Strength / Ductility

Tensile Strength

Maximum stress material can

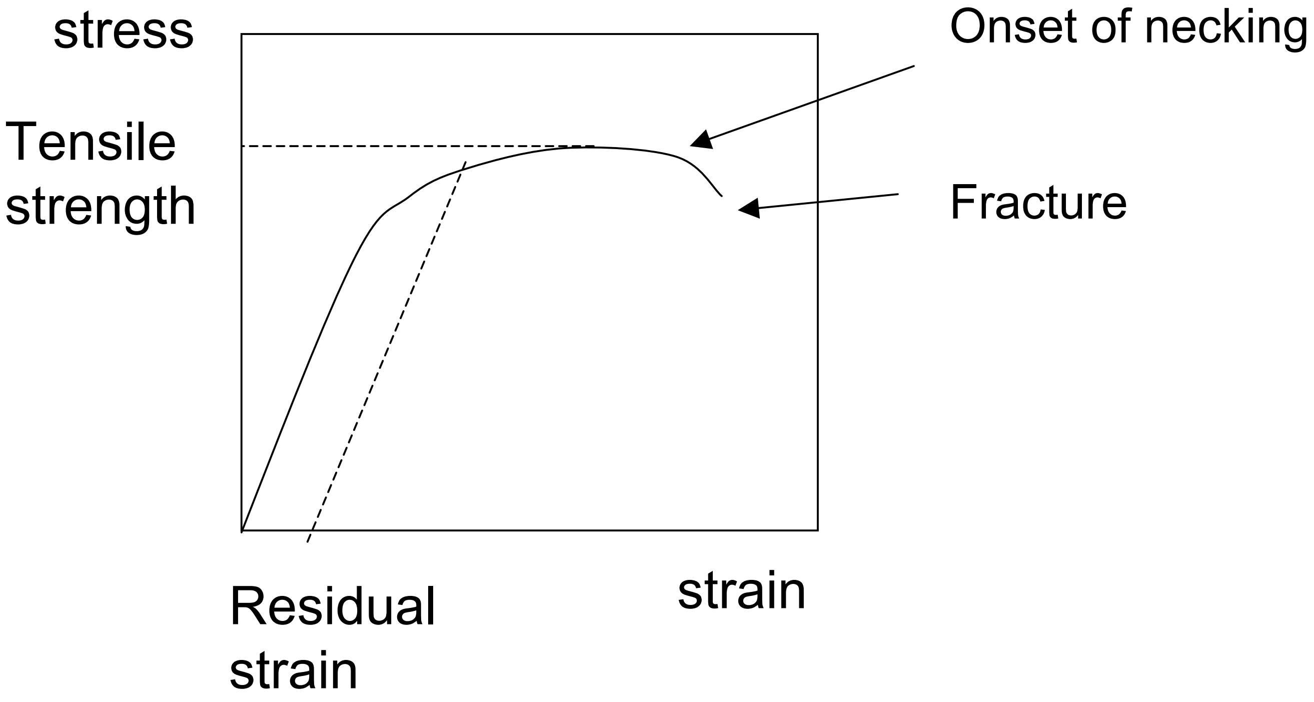
accommodate without fracture

Ductility

Elongation at fracture

Metals ~ 40 %

Ceramics ~ 5%



Toughness

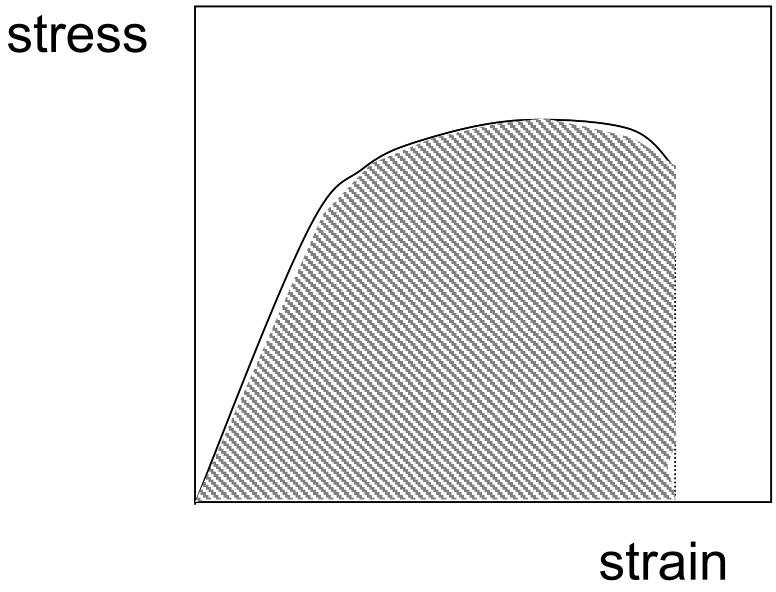
Toughness

Energy required to break a material

Depends on ability of a material to absorb energy up to fracture

Area under $\sigma - \varepsilon$ curve up to fracture

Require high strength and high ductility



Hardness

Resistance to localised plastic deformation (scratching)

<u>Moh's hardness scale</u>

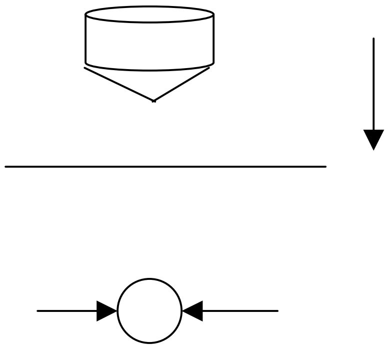
1 Talc

10 Diamond

<u>Hardness test</u>

Small indenter forced into surface and size of indentation measured

Simple, inexpensive and non-destructive



Diamond cone

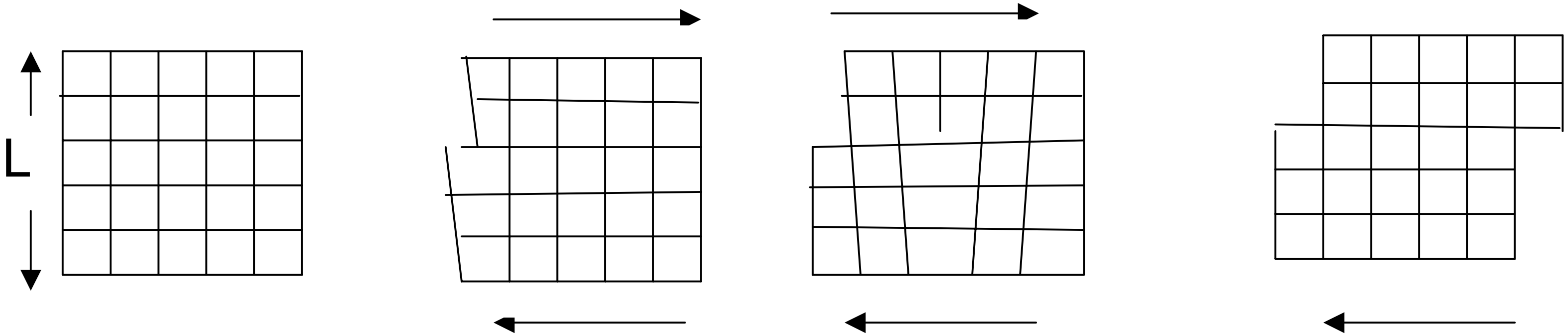
Measure size of indentation

Mechanisms for plastic deformation

Dislocation motion

Edge dislocation

Shear stress

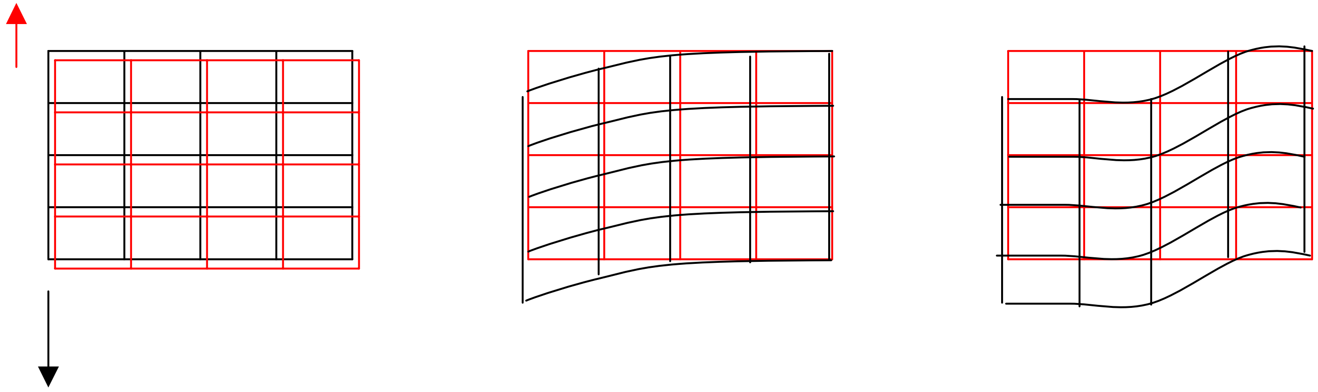


Dislocation glides along easy direction –slip plane

Unit of slip – Burgers vector

Plastic shear strain of b/L per dislocation moved through the crystal

Screw dislocation

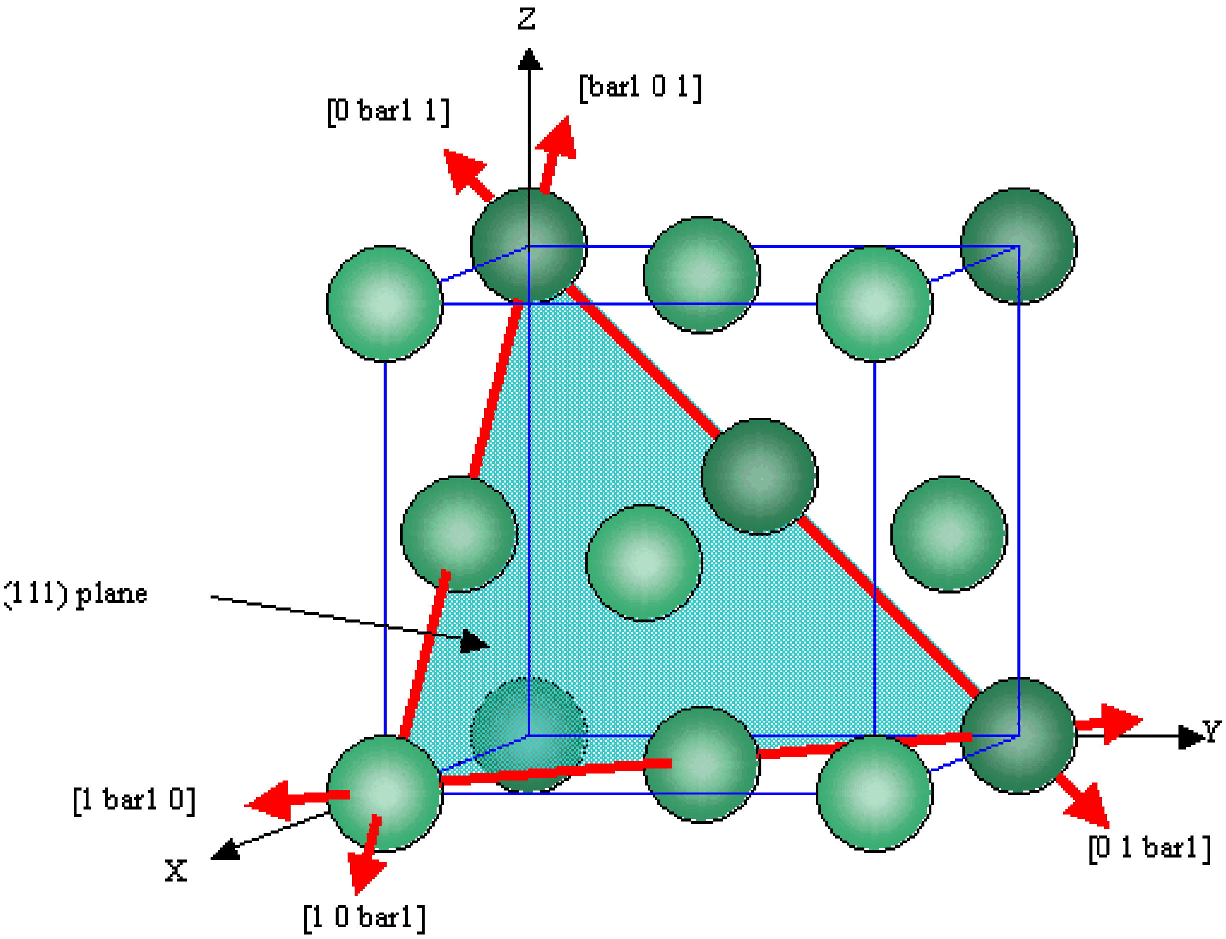


Slip plane between
red an black planes

FCC Slip planes

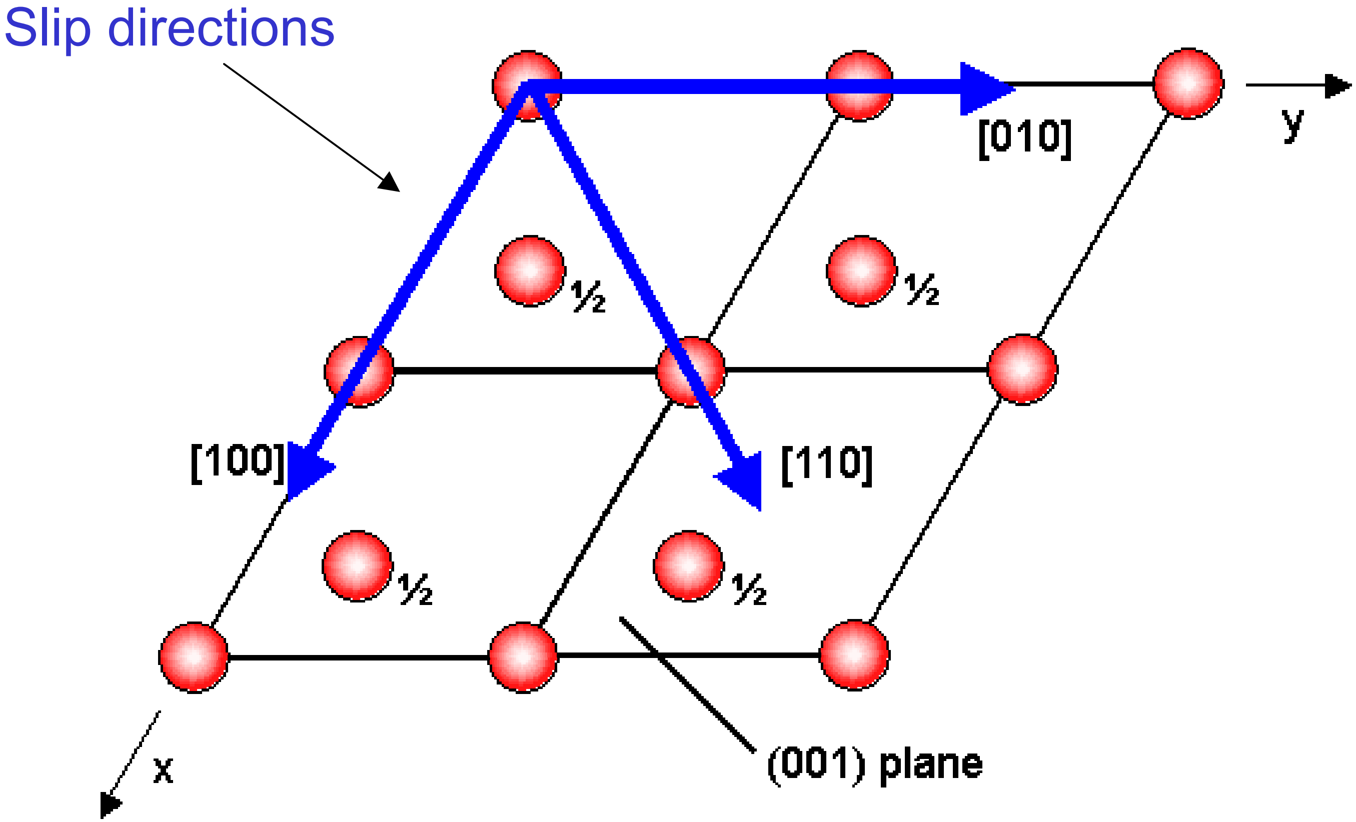
(111) close-packed planes

(0 bar1 1) close packed directions



HCP Slip planes

(001) Plane (close packed)



Slip Systems

Crystal Structure	Slip Planes	Slip Directions	Number of slip systems
FCC (Cu,Al,Ni,Ag,Au)	{111}	<110>	12
BCC (Fe,W,Mo)	{110}	<111>	12
HCP (Cd,Mg,Ti,Be)	{001}	<110>	3

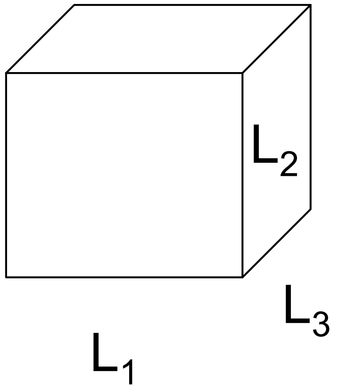
FCC metals soft at all temperatures

BCC metals brittle at low T – slip planes not close packed

HCP metals tend to be brittle – few slip planes

Dislocation motion

- Force per unit length on dislocation line F
- The movement of dislocations allows the applied stress (τ) to do work
- On moving a dislocation through crystal (distance L_1) work done by τ is $\tau b L_1 L_3$



- Work done on dislocation is $F L_1 L_3$
- Equating the work gives $F=\tau b$
- Only component of stress on slip plane does work

Critical Shear Stress

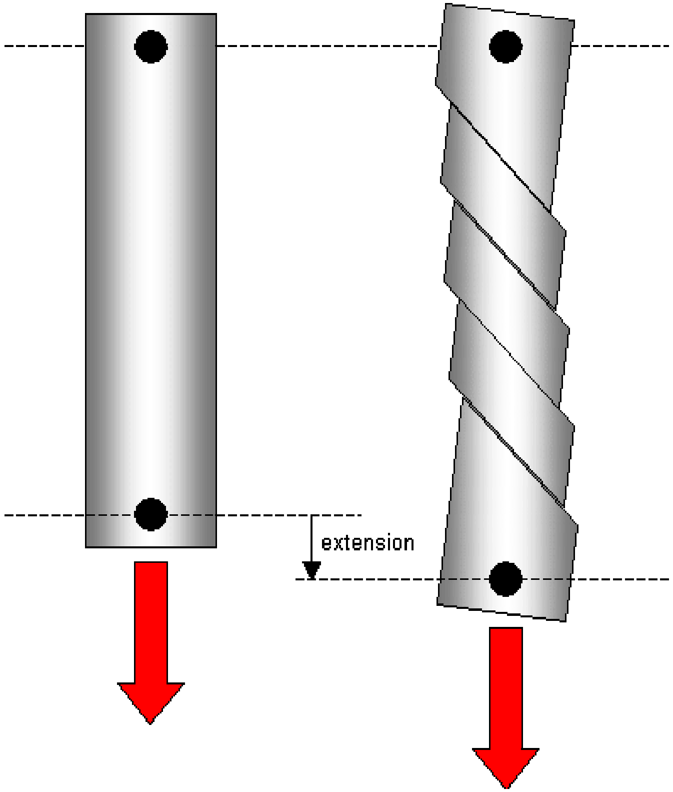
τ_{crit} = G exp –(2πW/b)

W is width dislocation core

Dislocation cores are narrow in covalent materials but can be extended in metals

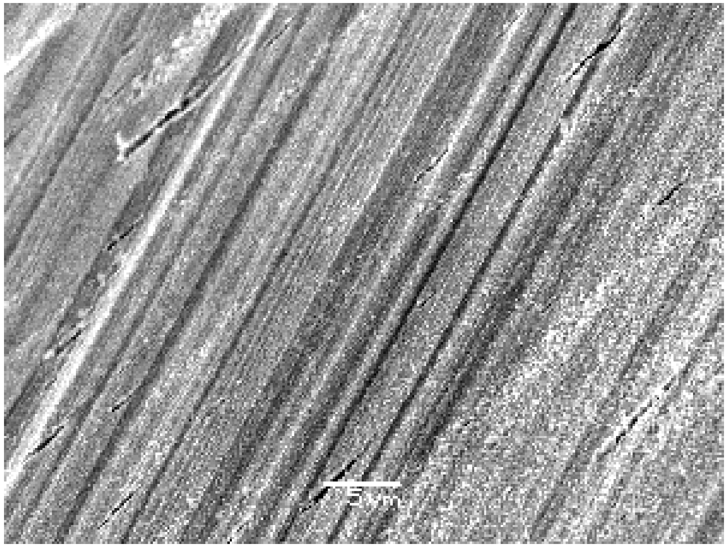
Slip

www.msm.cam.ac.uk/doitpoms/tlplib/index.php



Unslipped single crystal fixed at top end.

Single crystal after plastic deformation by tensile stress in the direction of the arrow. Slip occurs on distinct parallel planes.



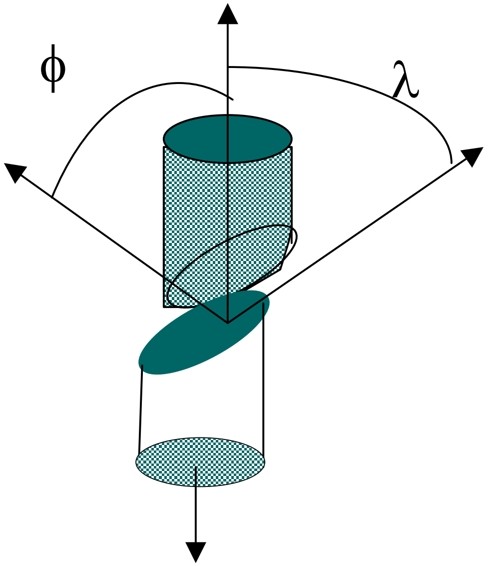
Slip in single crystals

Dislocation motion or slip occurs when the resolved shear stress reaches a critical value

ϕ is angle between normal to slip plane and applied stress

λ is angle between the slip direction and the applied stress

Resolved shear stress $\tau_R = \sigma \cos\phi \cos\lambda$



Slip occurs when maximum τ_R exceeds a critical value τ_{crss} (property of a material)

$\sigma_y = \tau_{crss} /(\cos\phi \cos\lambda)_{max}$

Minimum yield stress when $\phi = \lambda = 45°$

Slip bands formed

Single Crystal Slip

- Slip start on single plane when resolved stress reaches τ_{crit}

- As deformation continues the number of slipped planes increases and the slip per plane increases

- For bcc and fcc metals a second slip system may be initiated

Slip bands

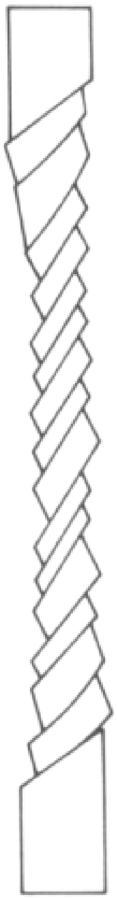
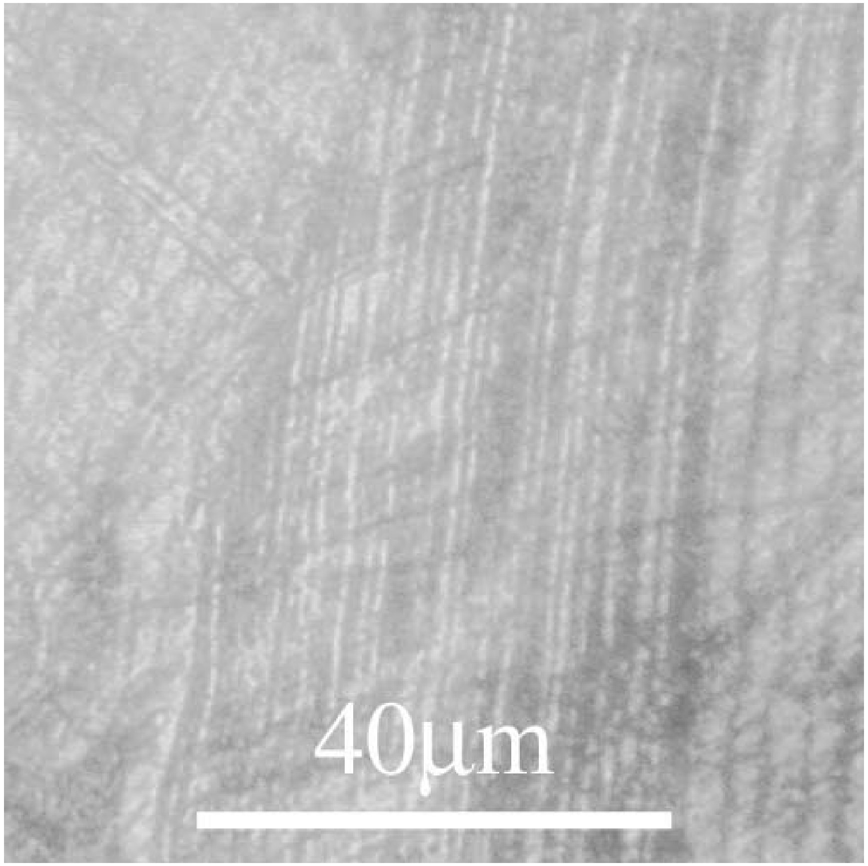


Figure 11 - Graphical
representation of
slip bands. (*from Hertzberg.*^{5})



Slip bands in brass

Deformation in polycrystalline materials

Random orientation of grains means slip planes differ in different grains

Plastic flow occurs first in most favourably oriented grains

Plastic deformation restricted by the need for the crystal to fit to neighbouring grains

After deformation grains elongated along direction of load

Grain boundaries reduce dislocation motion

Polycrystalline materials stronger than single crystals

Strengthening Materials

Why study material strengthening?

To understand the relationship between microstructure and strength

Awareness of available processes for maximising material performance

Increasing the Yield Strength

Dislocations – carriers of deformation

The ability of a metal to plastically deform depends on the ability of dislocations to move

Reducing the mobility of dislocations increases yield strength

Restricting or hindering dislocation motion renders a material harder and stronger

Solid solution strengthening

High purity metals are softer than alloys of the same base metal

Add substitutional and interstitial impurities (add to melt)

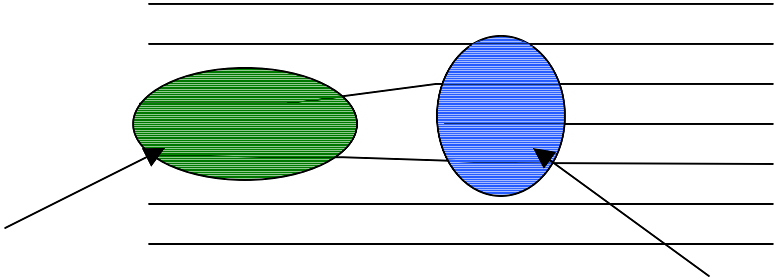
Large and small impurities diffuse to dislocations to reduce strain energy.

Larger stress required to separate dislocation for motion

$\sigma_y \alpha$ concentration, size mismatch, Shear modulus

Most metals have limited solubility in other metals

Interaction between dislocations and impurities



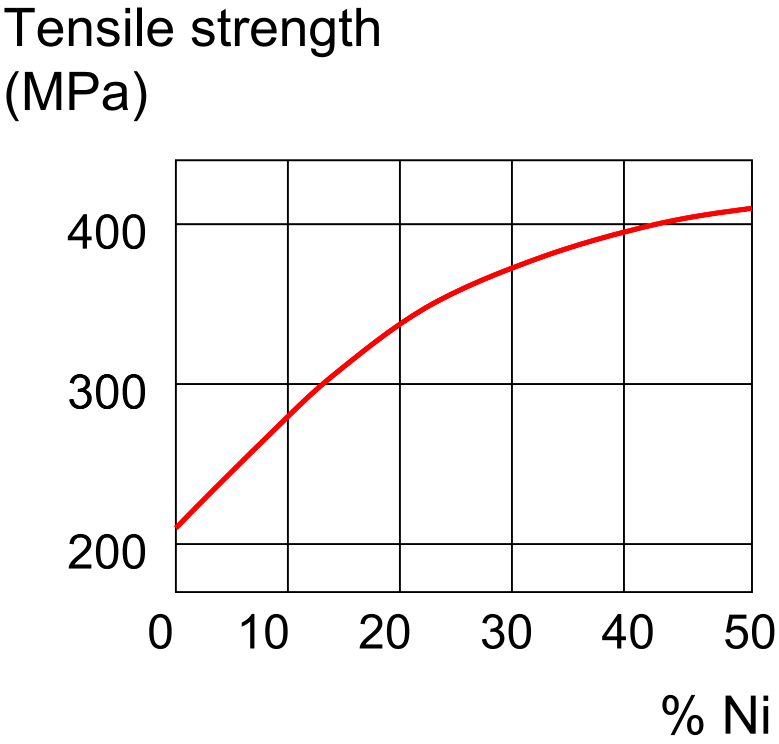
Region of dilation

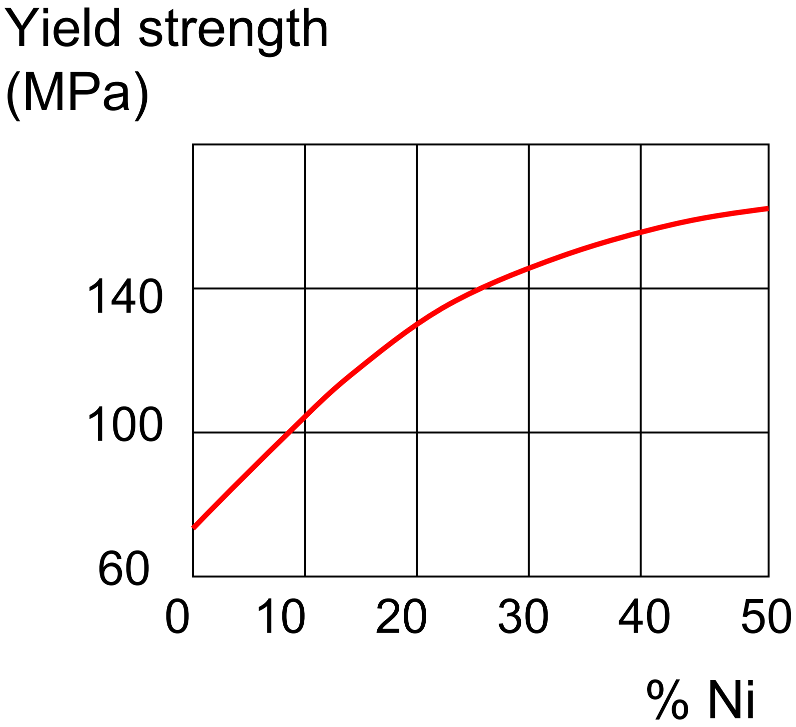
Large impurities diffuse here

Region of Compression

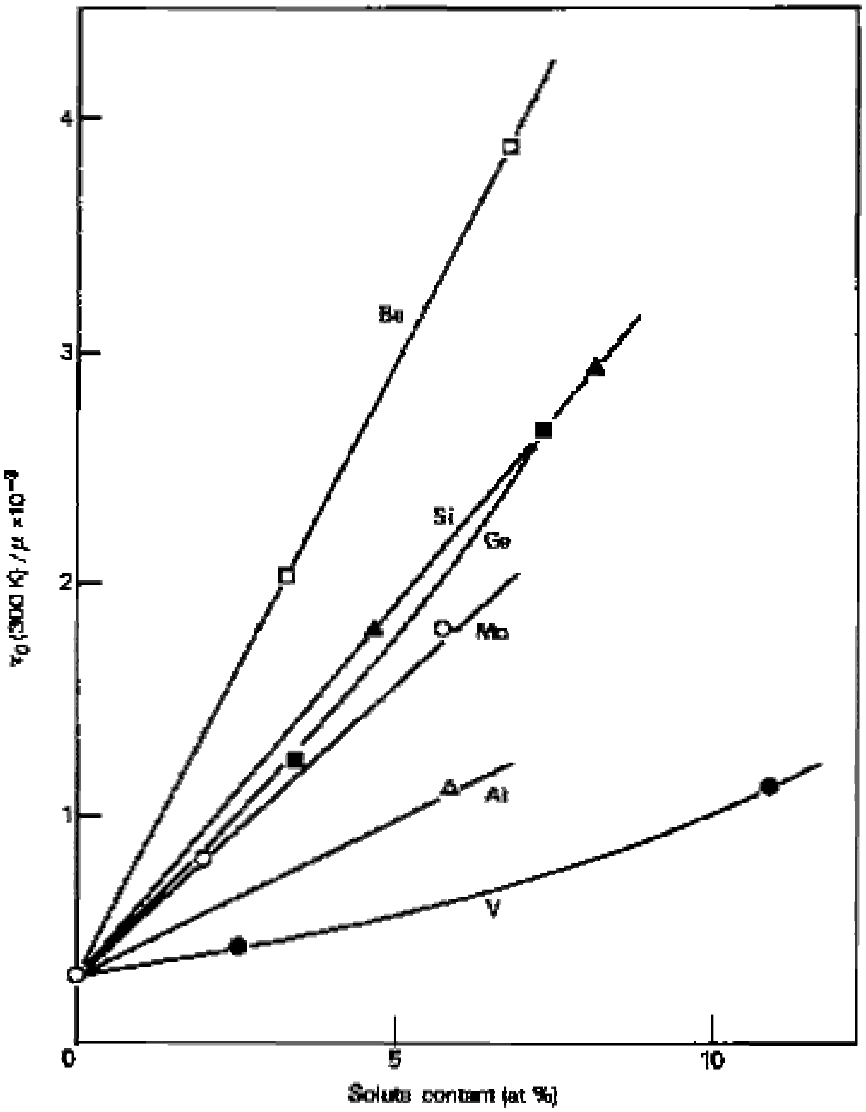
Small impurities diffuse here

Cu/Ni Alloys


Tensile strength
(MPa)
400
300
200
0
10
20
30
40
50
% Ni


Yield strength
(MPa)
140
100
60
0
10
20
30
40
50
% Ni

Steel



Larger size difference gives greater strengthening

Reduce grain size

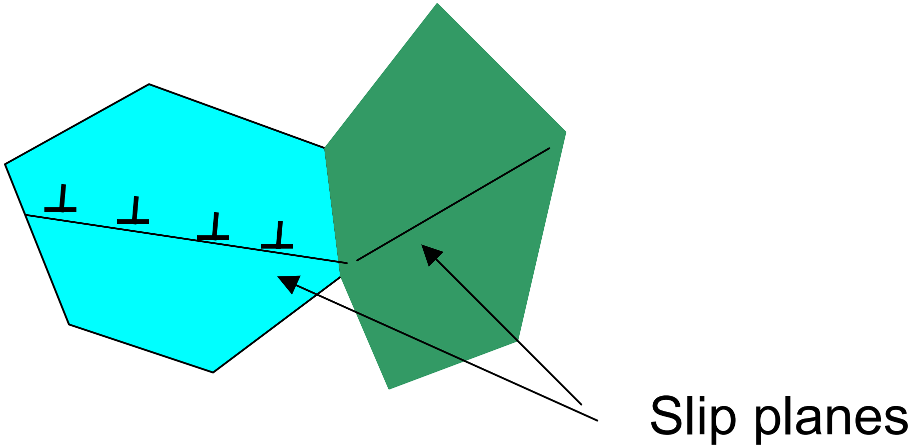
Dislocation must change direction when crossing grain boundary

Dislocations may pile up at boundaries repelling further dislocations

Small angle grain boundaries are not effective in blocking dislocations

Twin boundaries do block dislocations

Phase boundaries block dislocations

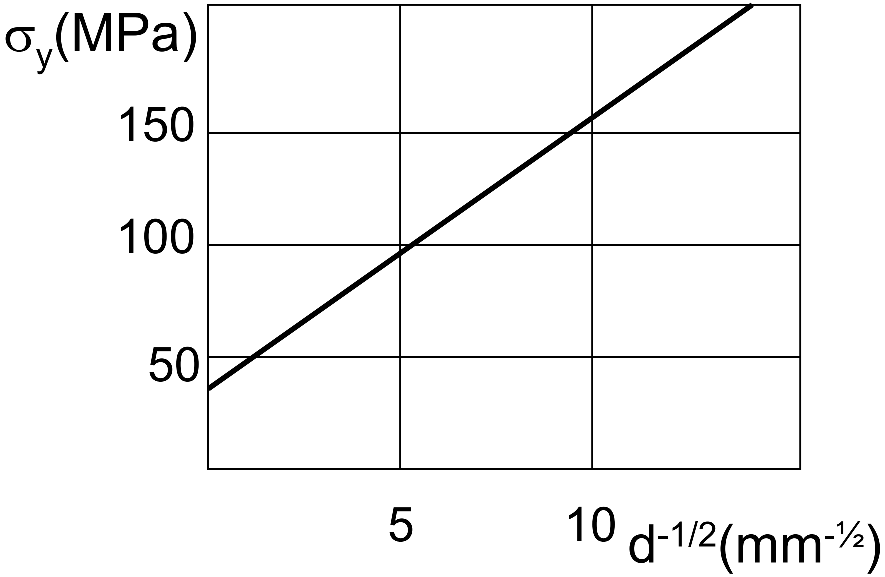


Hall-Petch Relationship

For average grain size d

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

eg Brass (70%Cu 30%Zn)



Grain Size Regulation

- By rate of solidification from the liquid phase
  - Rapid cooling produces small grains
  - Slow cooling produces large grains

- Grain size can be varied by plastic deformation (to increase dislocation density) followed by heat treatment (to rearrange dislocations into grain boundaries)

Precipitation Hardening

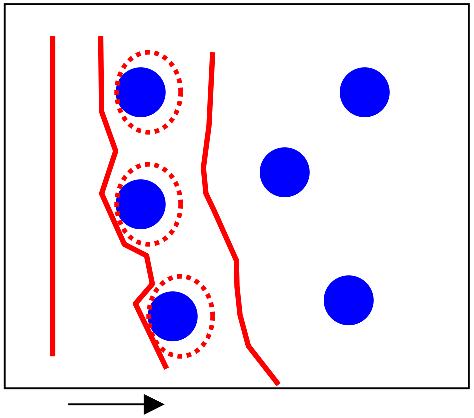
- Weak obstacles
  - Coherent particles
    - Lattice planes continuous
    - Long range stress field
    - Dislocations can cut through – costs energy
  - Partially coherent particles
    - Most lattice planes continuous
    - Long range stress fields from misfit dislocations
    - Dislocations can cut through
- Strong obstacles
  - Hard precipitates
  - Dislocations cannot cut through
  - Critical stress required to bypass particles

Precipitation hardening

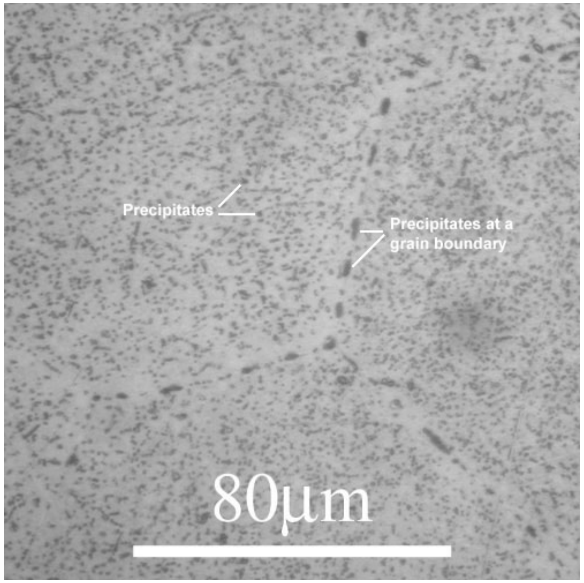
Add small hard precipitates (eg SiC in Fe)

Particles are difficult to shear – pin dislocations

$\sigma_y \propto 1/S$ (spacing between precipitates)



Dislocation motion



Al with 0.04% Cu

Strain hardening (cold working)

The phenomenon whereby a ductile metal becomes harder and stronger as it is plastically deformed

Increase dislocation density by repeated tensile loading

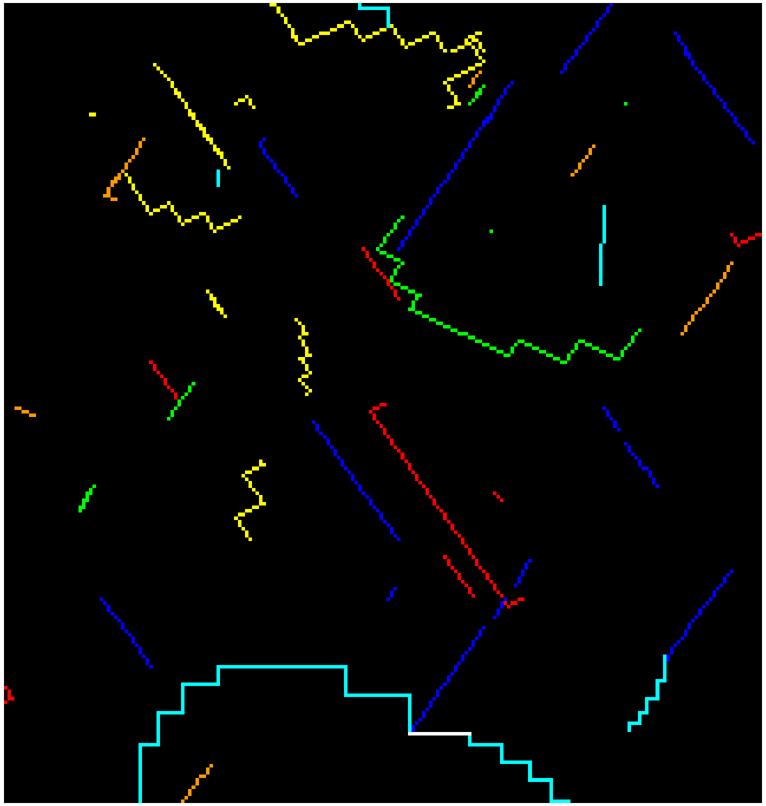
Dislocations repels each other and get entangled

Decrease in dislocation motion.

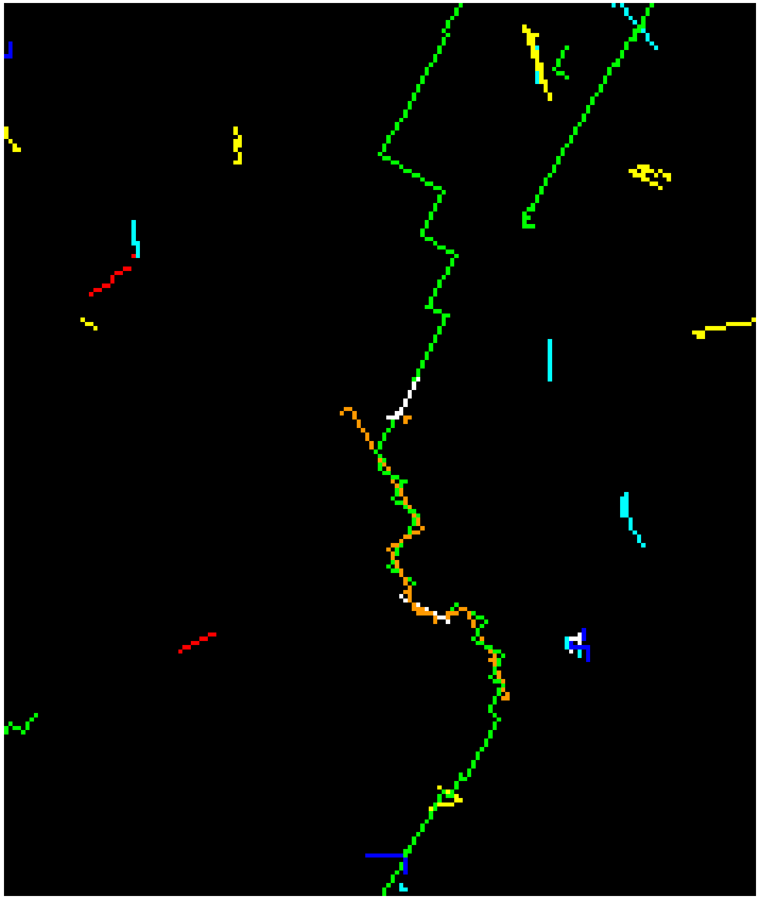
σ_y increases with dislocation density (ρ_d ~10^{10} mm mm^{-3})

Dislocation interactions

//zig.onera.fr/DisGallery/index.html

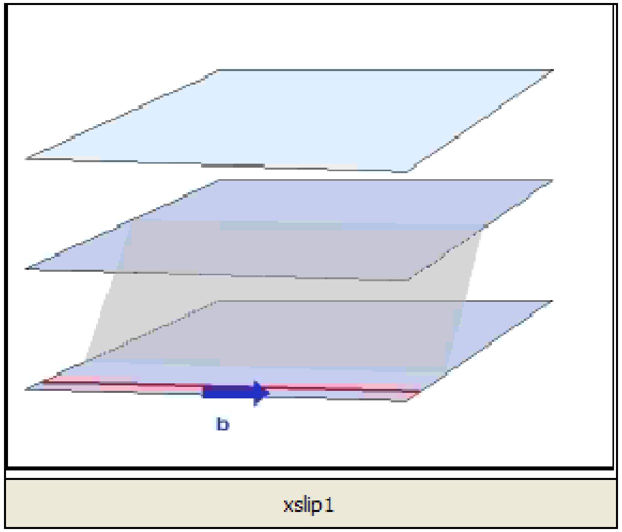


Dislocation debris



Cross-slip

Screw dislocation can glide in any plane containing slip vector

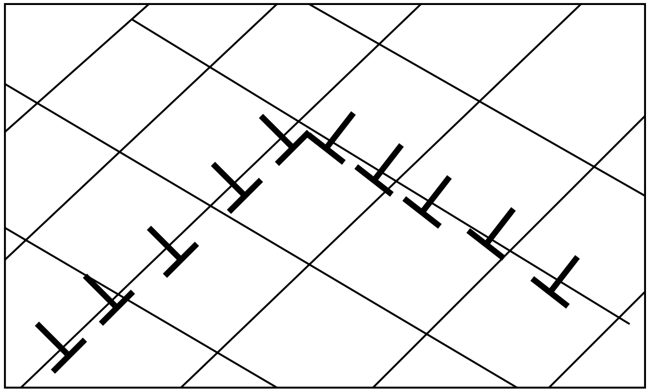


Percentage Cold Work

$$\%CW = (A_0 - A_d)/A_0 \times 100$$

A_0 original area

A_d area after deformation



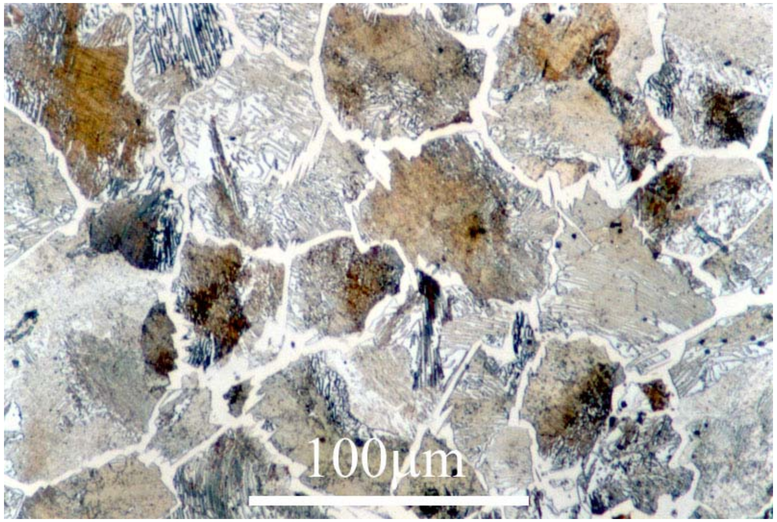
Softening materials - Annealing

○ Exposed to elevated temperature for extended period then slowly cooled

Relieves stress introduced by machining and non-uniform cooling

Increases softness ductility and stiffness

Changes micro structure



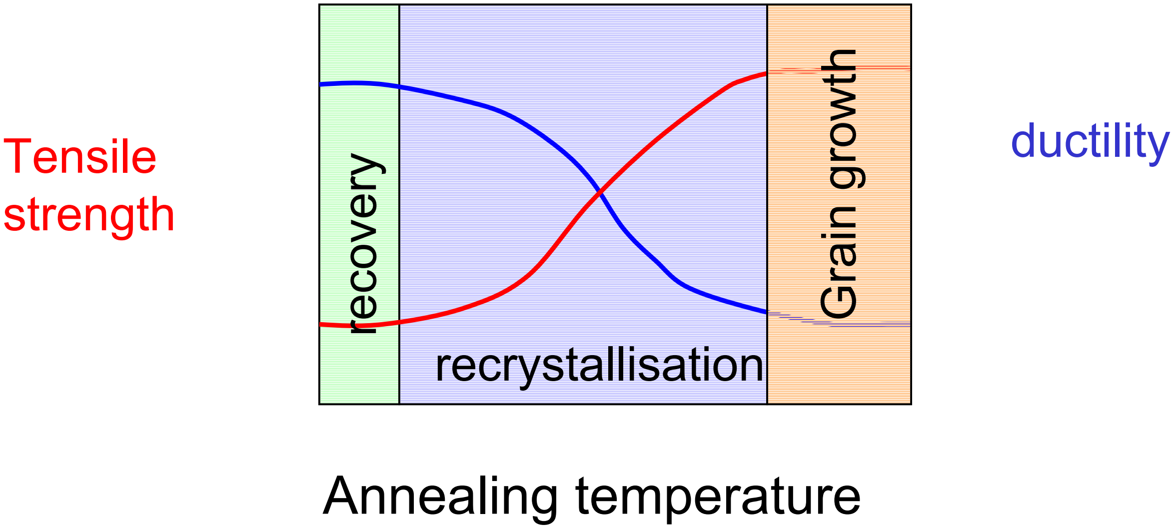
Fe, C 1.3 (wt%) steel, annealed at 1100ºC

Stages of annealing

Recovery – annihilation reduces dislocation density and dislocations rearrange to lower energy conformations

Recrystallisation – new strain-free equiaxed grains with low dislocation density are formed. Nuclei grow until parent material consumed

Grain growth - large grains consume smaller grains



Strengthening - Summary

- Solution strengthening
  - Useful for moderate strength increase (few 100 MPa)
  - Limited solubility for solutes with large misfits

- Decrease grain size
  - Limited strength increase (few 100 MPa)
  - Grains grow at moderate temperatures

- Precipitation hardening
  - Can achieve strength increase of 1000 GPa for fine dispersion of hard particles
  - Particles tend to dissolve at high temperatures

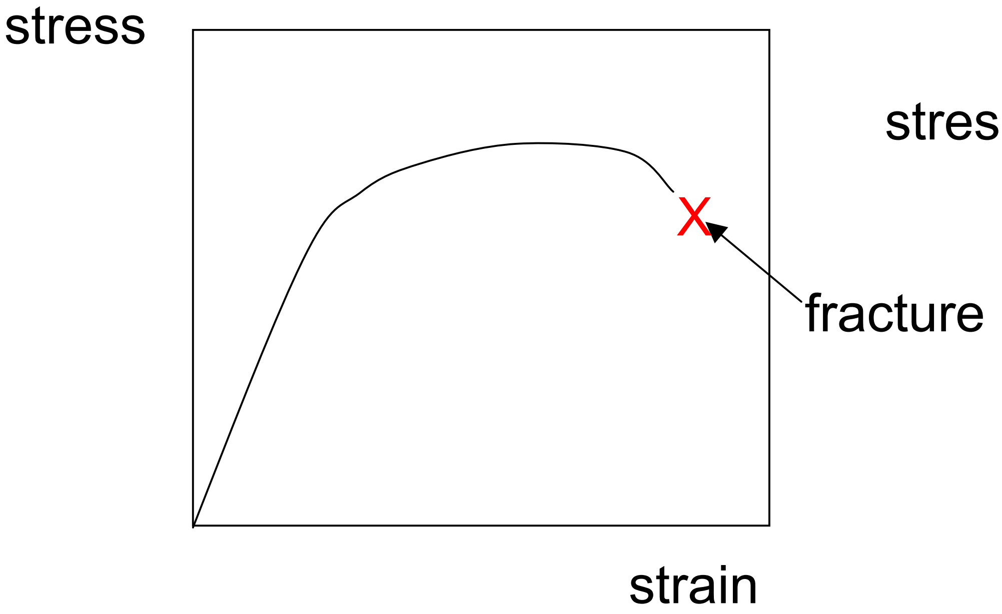
- Cold Working
  - Increases strength but reduces ductility and toughness
  - Anneals out at moderate temperatures

Fracture and fatigue

- Why study failure and fatigue?

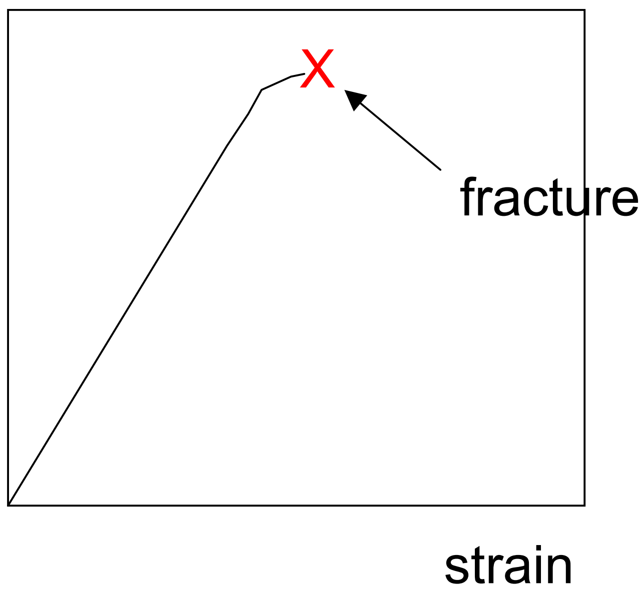
Need to understand the various failure modes in order to minimize the chances of failure in a design

Fracture



Ductile Material

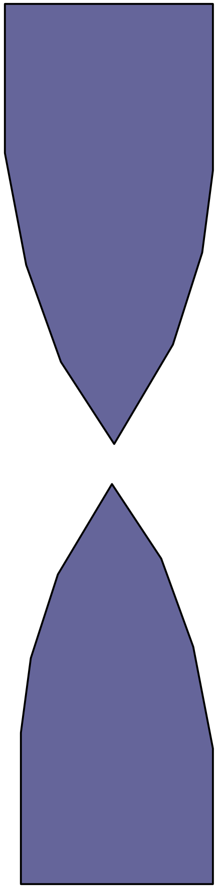
Large energy absorption before fracture



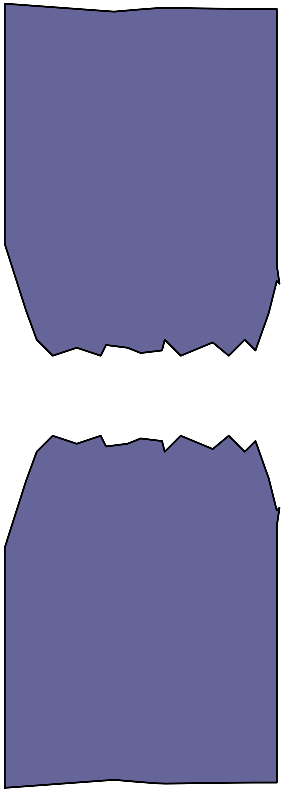
Brittle Material

Low energy absorption before fracture

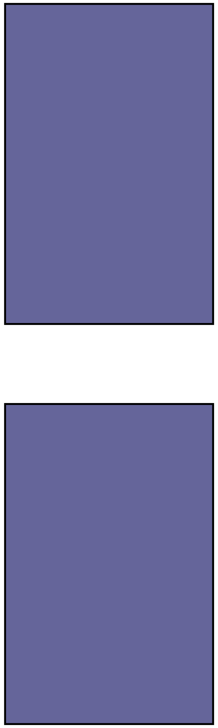
Types of Fracture



Very ductile



Moderately ductile



Brittle

Brittle Fracture

- Some materials break suddenly while still elastic
- Rapid progression of crack perpendicular to direction of applied stress
- Broken surfaces fit together after fracture
- Fracture surfaces have grainy, faceted texture
- Crack propagates by successive breaking of bonds along specific crystallographic directions (cleavage planes)

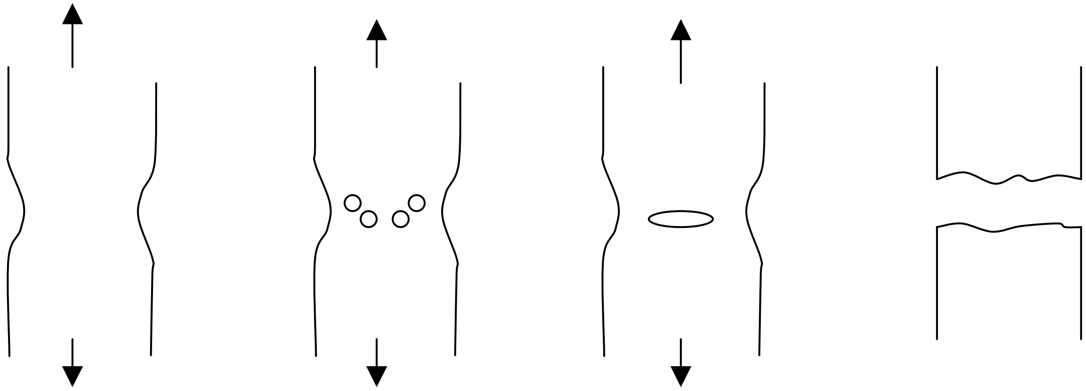
Ductile Fracture

Typical of metals

Failure progresses slowly

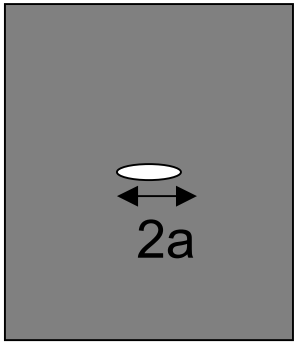
Necking – microvoids-elliptic crack- crack growth – failure

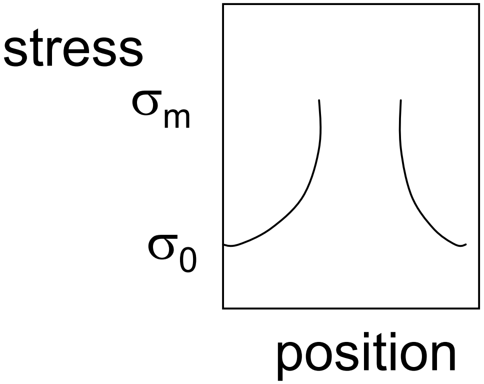
Cup and cone fracture



Fracture Mechanics

- Theoretical strength of materials ~E/10
- Actual strength around 10 to 1000 times lower
- Griffith proposed discrepancy arose because of microscopic flaws in materials
- Applied stress amplified around flaws $\sigma_m=2\sigma_0(a/\rho_t)^{1/2}$





Stress Concentration Factor

$$\sigma_m = 2\sigma_0 (a/\rho_t)^{1/2}$$

$$K_t = \sigma_m/\sigma_0 = 2\,(a/\rho_t)^{1/2}$$

The Stress Concentration Factor K_t is the degree to which the stress is amplified at a flaw or crack

In ductile materials plastic deformation occurs when stress exceeds yield stress – this reduces the stress concentration factor below the theoretical value

Griffith’s criterion

Criterion for rapid crack progression

Stored elastic energy must exceed energy of the crack

cf Inflated balloon

Consider a material with crack length a thickness t

a increases to a + δa

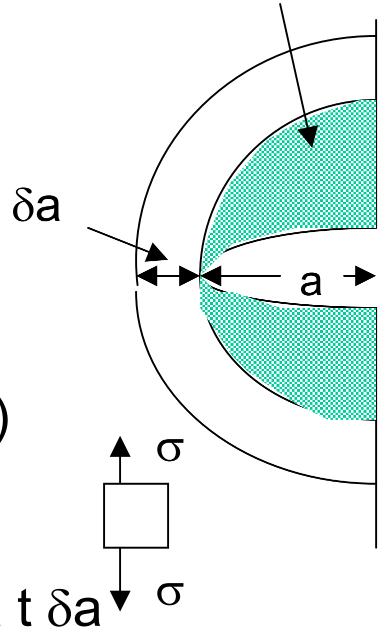
Elastic energy $U_{el} = (\sigma^2/2E)\ (\pi\ a^2 t\ /2)$

Change in Elastic energy $\delta U_{el} = dU_{el}/da\ \delta a$

$= (\sigma^2/2E)\ (2\pi\ at\ \delta a/2)$

Costs $2\gamma_s\ t\ \delta a$ to create new surface

Critical stress when $\delta U_{el} = (\sigma^2/2E)\ (2\pi\ at\ \delta a/2) = 2\gamma_s\ t\ \delta a$



Material relaxes to zero stress

$$\boxed{\sigma_c = 2(E\ \gamma_s/\pi a)^{1/2}}$$

Stress Intensity Factor

General relationship between applied stress and stress at crack tip

Stress Intensity factor K (units MPa $m^{1/2}$)

$$K = Y\sigma\ (\pi a)^{1/2}$$

Y is a dimensionless parameter that depends on crack geometry, specimen size and manner of load application

Fracture Toughness $K_c = Y\sigma_c\ (\pi a)^{1/2}$

Fracture Toughness

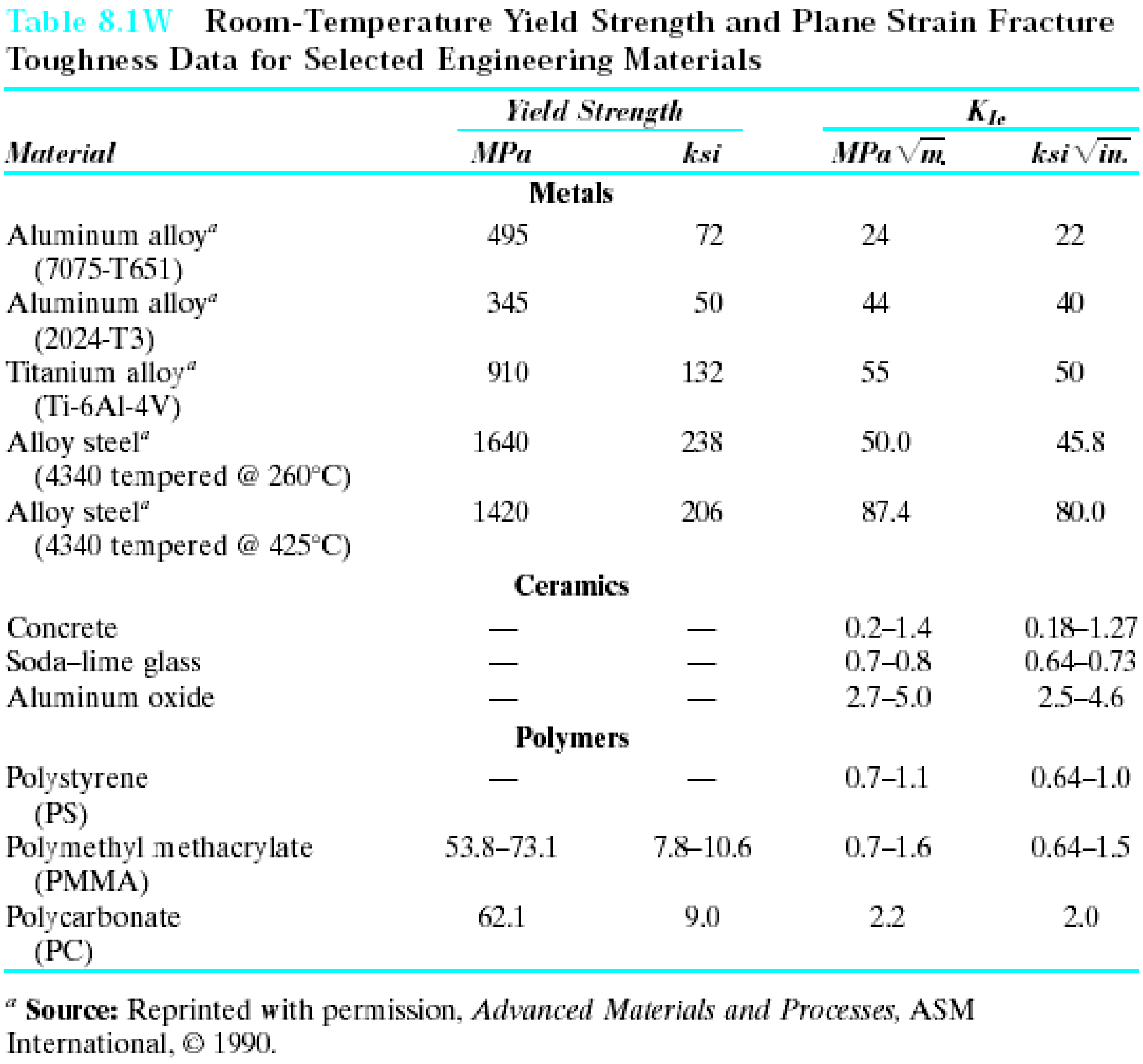


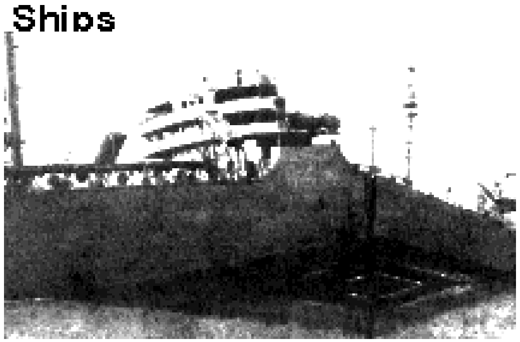
Table 8.1W Room-Temperature Yield Strength and Plane Strain Fracture Toughness Data for Selected Engineering Materials

	Yield Strength		K_{Ic}	
Material	*MPa*	*ksi*	*MPa* $\sqrt{m}$	*ksi* $\sqrt{in.}$
Metals				
Aluminum alloy[a] (7075-T651)	495	72	24	22
Aluminum alloy[a] (2024-T3)	345	50	44	40
Titanium alloy[a] (Ti-6Al-4V)	910	132	55	50
Alloy steel[a] (4340 tempered @ 260°C)	1640	238	50.0	45.8
Alloy steel[a] (4340 tempered @ 425°C)	1420	206	87.4	80.0
Ceramics				
Concrete	—	—	0.2–1.4	0.18–1.27
Soda–lime glass	—	—	0.7–0.8	0.64–0.73
Aluminum oxide	—	—	2.7–5.0	2.5–4.6
Polymers				
Polystyrene (PS)	—	—	0.7–1.1	0.64–1.0
Polymethyl methacrylate (PMMA)	53.8–73.1	7.8–10.6	0.7–1.6	0.64–1.5
Polycarbonate (PC)	62.1	9.0	2.2	2.0

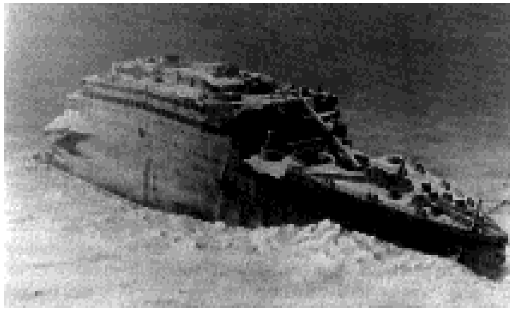
[a] **Source:** Reprinted with permission, *Advanced Materials and Processes*, ASM International, © 1990.

Ductile to brittle transition

- Some metals become brittle below a certain temperature
- Above transition fracture surface is fibrous (shear character)
- Below transition surface is shiny and granular(cleavage character)
- FCC metals do not generally become brittle – dislocation motion not strongly T dependent
- Structures should only be used above transition temperature to avoid brittle failure (transport ships in world war II – weld failure, Titanic)



Hertzberg, Fig. 7.1(a)

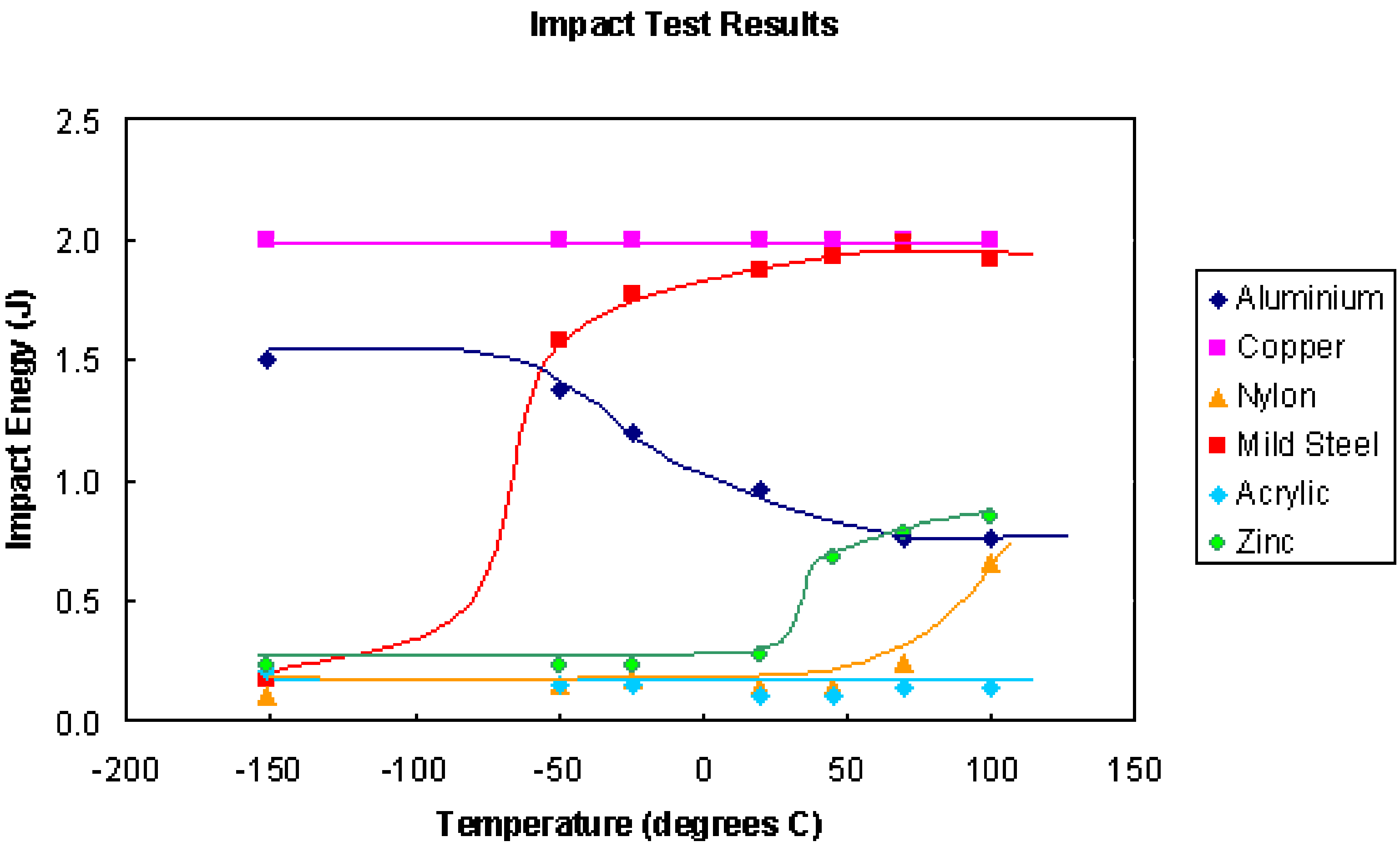


Hertzberg, Fig. 7.1(b)

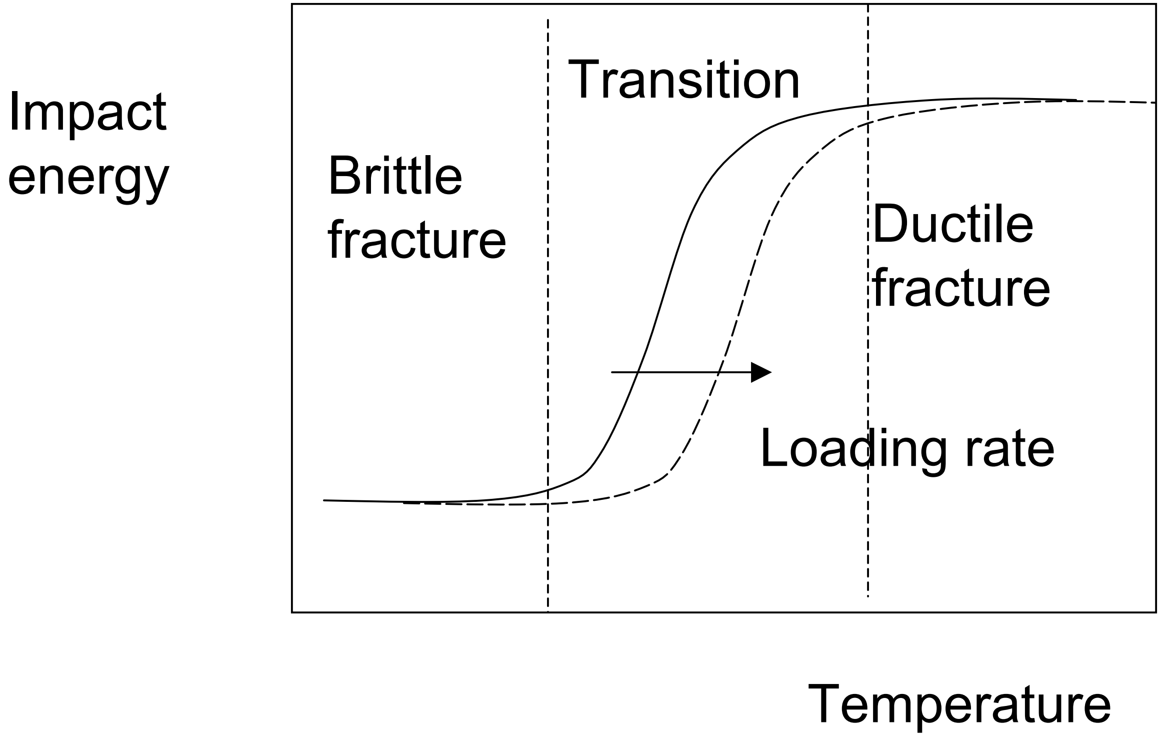
Ductile to brittle transition

- FCC metals do not undergo ductile to brittle transition
- In BCC metals transition temperature is around 0.1 Tm
- For ceramic materials transition temperature is usually greater than 0.5 Tm
- Transition temperature depends on strain rate and pressure

Ductile to brittle transition



Ductile to brittle transition



Impact energy has 3 main components

Elastic strain + plastic work done + energy to create fracture surface

Fatigue

Failure under dynamic fluctuating stress

Largest single cause of failure in metals -

90% engineering failures

Crack propagation at loads well below the critical stress

Definitions

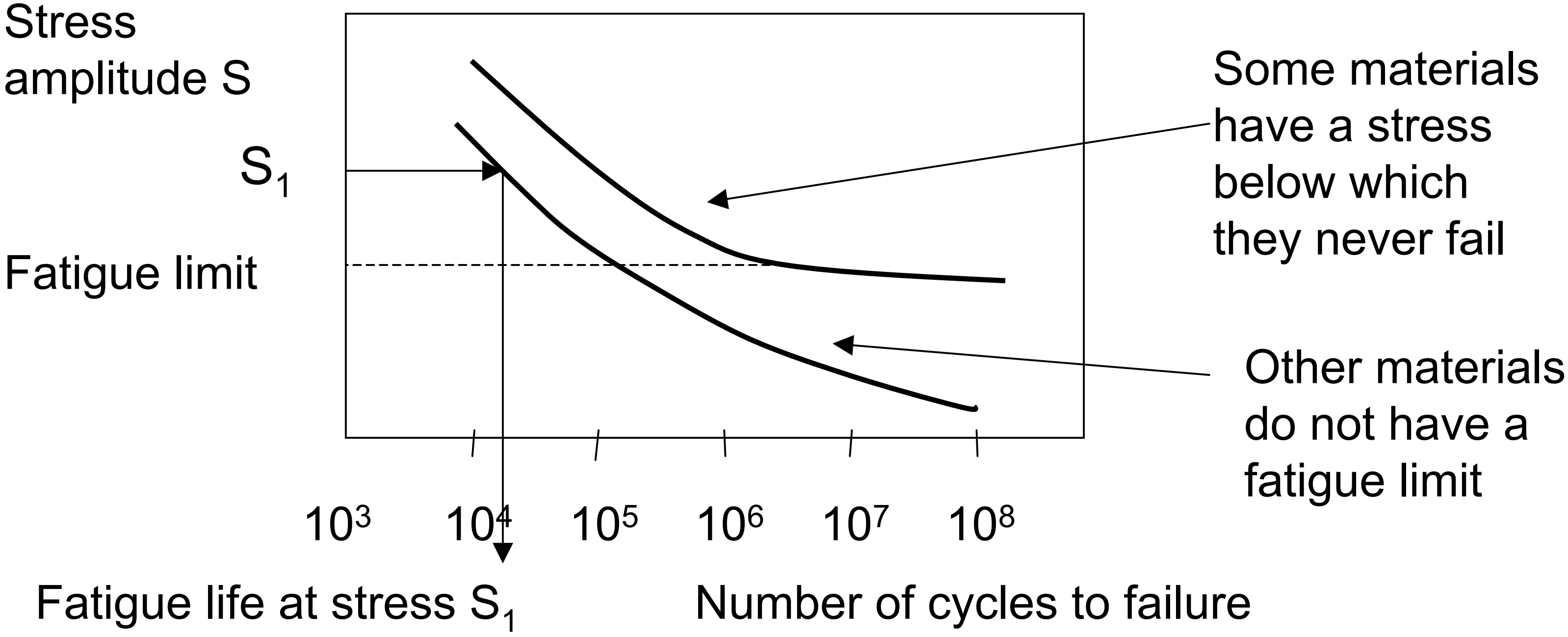
Mean stress $\sigma_m = (\sigma_{max} + \sigma_{min})/2$

Stress range $\sigma_r = (\sigma_{max} - \sigma_{min})$

Stress ratio $R = \sigma_{min} / \sigma_{max}$

Fatigue - S/N Curves

Stress vs Number of cycles to failure



Some materials have a stress below which they never fail

Other materials do not have a fatigue limit

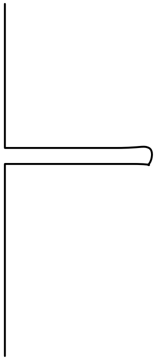
Fatigue Mechanism

- Initiation –
    - formation of micro-crack at surface at point of stress concentration
- Propagation – advances incrementally every cycle
    - Stage I - slow propagation through planes of high shear stress
    - Stage II – faster propagation along direction perpendicular to load

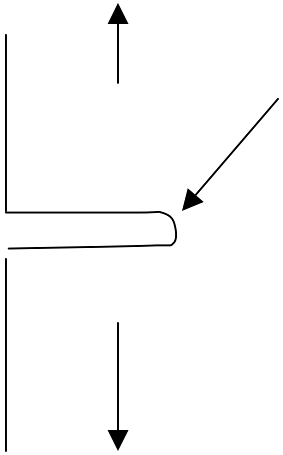
•Final failure – rapid fracture once crack has reached critical size

•At low stress levels large amount of fatigue life utilised in crack initiation

How cracks grow

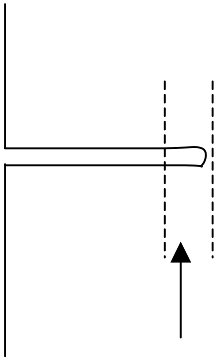


Crack at
zero stress



New surface
$\pi\delta/2$

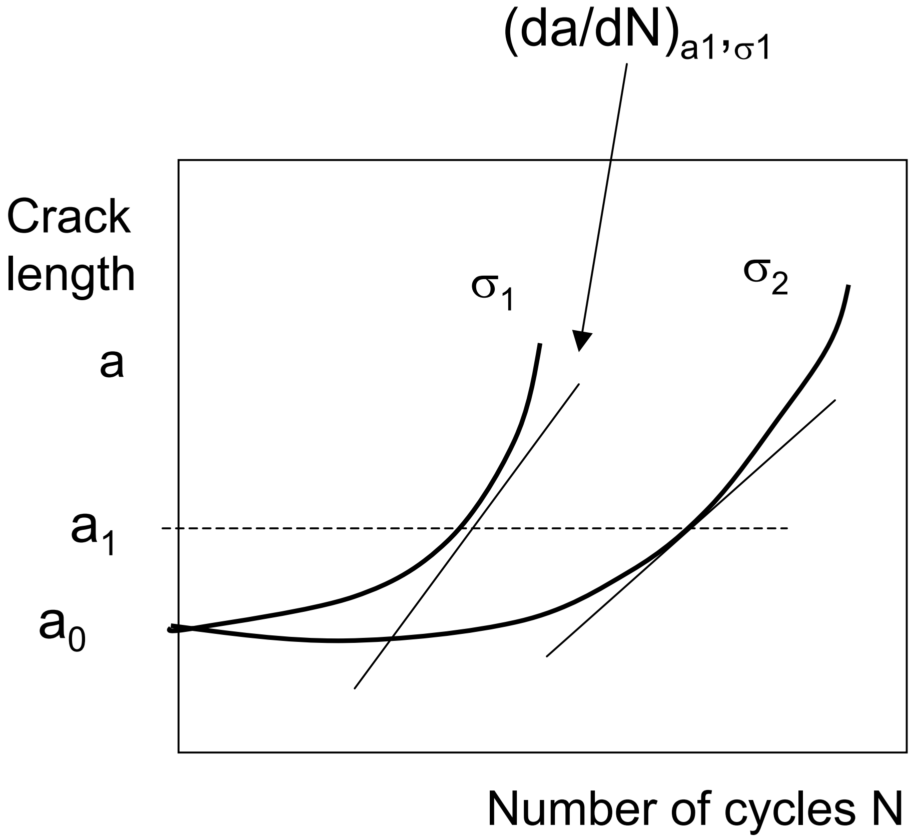
Apply maximum
stress – crack opens



Crack at
zero stress

Crack extended
$\pi\delta/2$

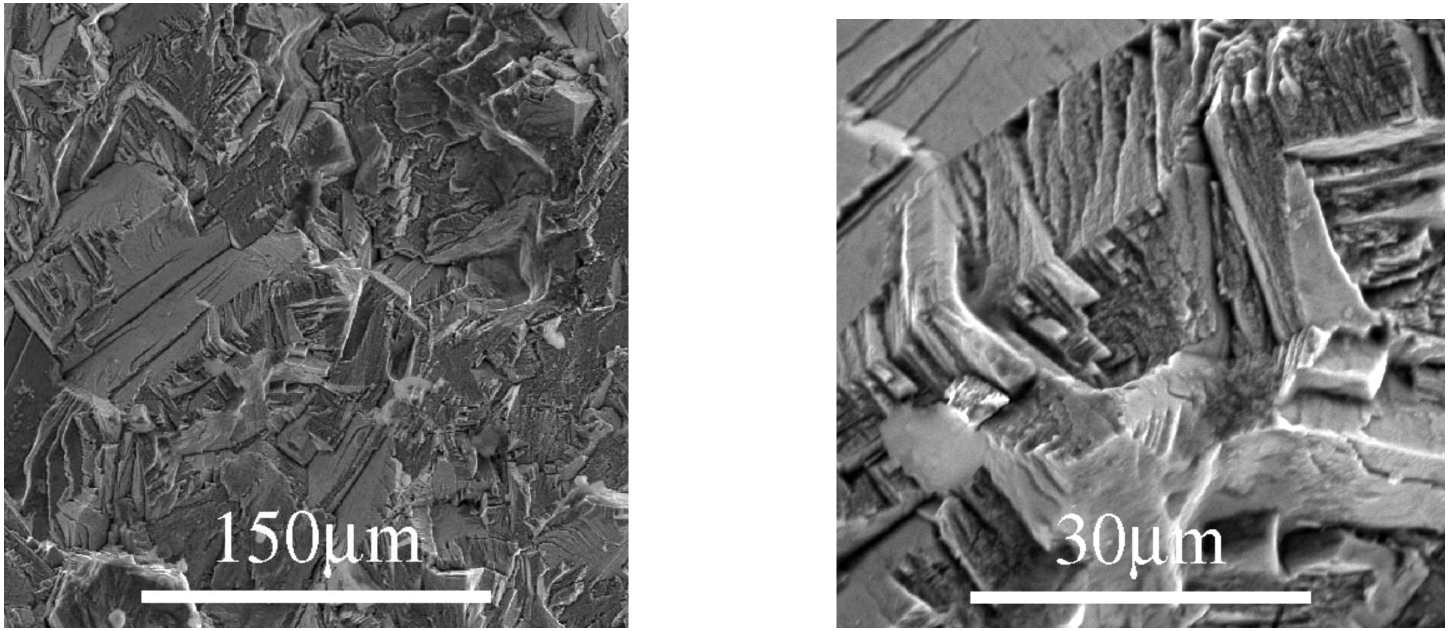
Rate of Crack Growth



$$da/dN = A(\Delta K)^m \quad m=1\text{-}6$$

$$\Delta K = K_{max} - K_{min} = Y(\sigma_{max} - \sigma_{min})(\pi a)^{1/2}$$

Fatigue failure



Fatigue failure in Ni superalloy

Fatigue failure brittle-like in nature – even in normally ductile materials

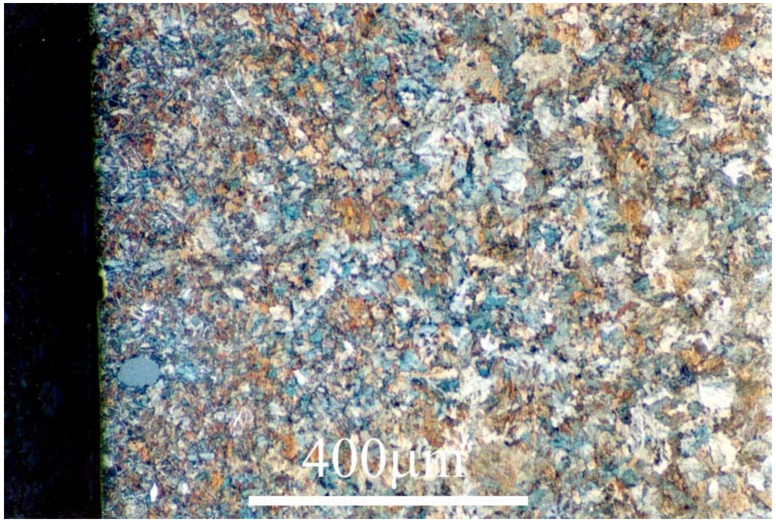
The fracture surface is perpendicular to the direction of applied stress

Strengthening against fatigue

Eliminate sharp corners to reduce stress concentration

Avoid scratches or tears on surface due to manufacture

Reduce residual stresses due to processing



Surface Treatment – impose residual surface stress

Case hardening – surface exposed to carbonaceous or nitrogenous atmosphere at high T

C or N rich outer layer introduced by atomic diffusion

Fe C .07 Mn 2.3%

Carburised at 950 C

Environmental Effects

- Thermal fatigue
  - Fluctuating thermal stresses due to fluctuating temperature under constrained conditions
- Corrosion fatigue
  - Simultaneous action of cyclic stresses and corrosive environments
  - Small pits form as a result of chemical reaction and act as crack nucleation sites
  - Crack propagation enhanced as a result of chemical attack

Creep

Time dependent permanent deformation under a constant stress

Slow replacement of elastic strain by plastic strain

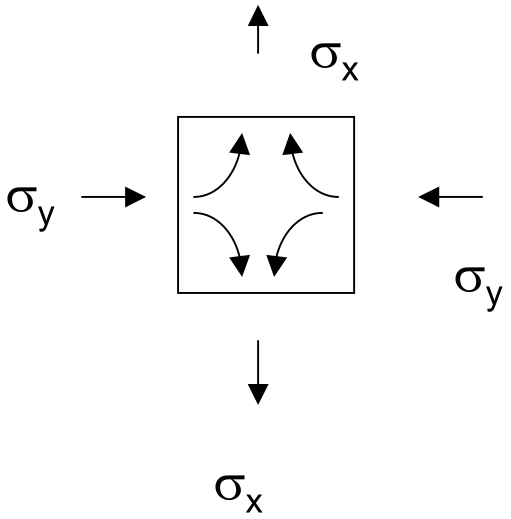
High temperature T > 0.4 Tm for metals

Polymers especially sensitive to creep deformation

Often the limiting factor in the lifetime of a part

Creep Mechanisms

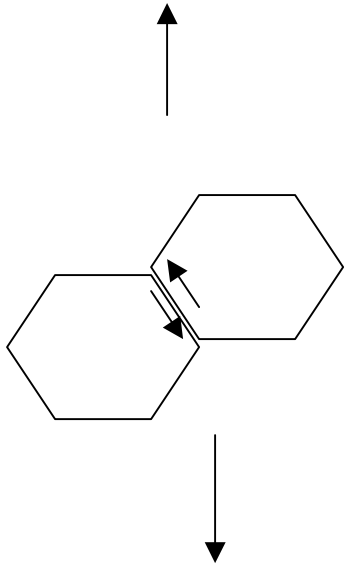
Stress induced vacancy diffusion



Grain boundary diffusion

Dislocation motion (thermally activated)

Grain boundary sliding (displacement of scratch lines during creep testing)

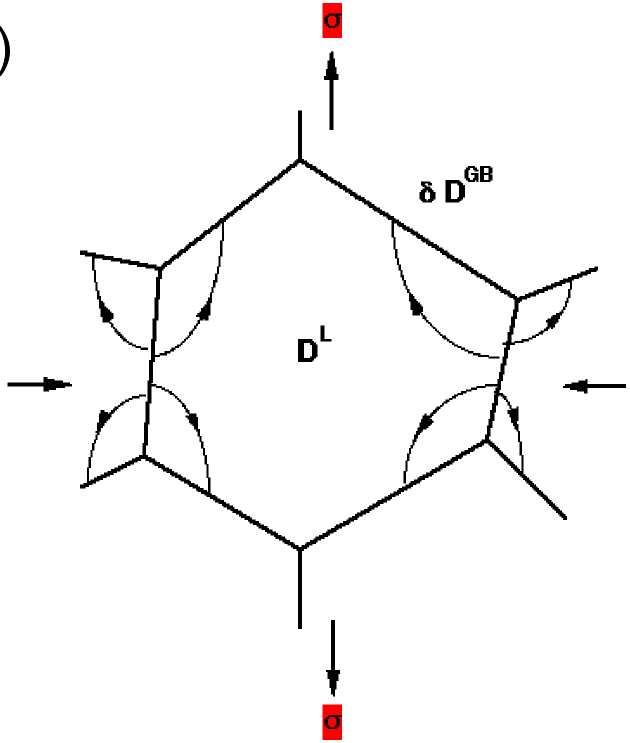


Polymers – viscous flow

Creep Rate for Vacancy Diffusion

Bulk Diffusion (Nabarro-Herring Creep)

$$d\varepsilon/dt \;\alpha\; (D_L/kT)(\sigma)(1/d^2)$$



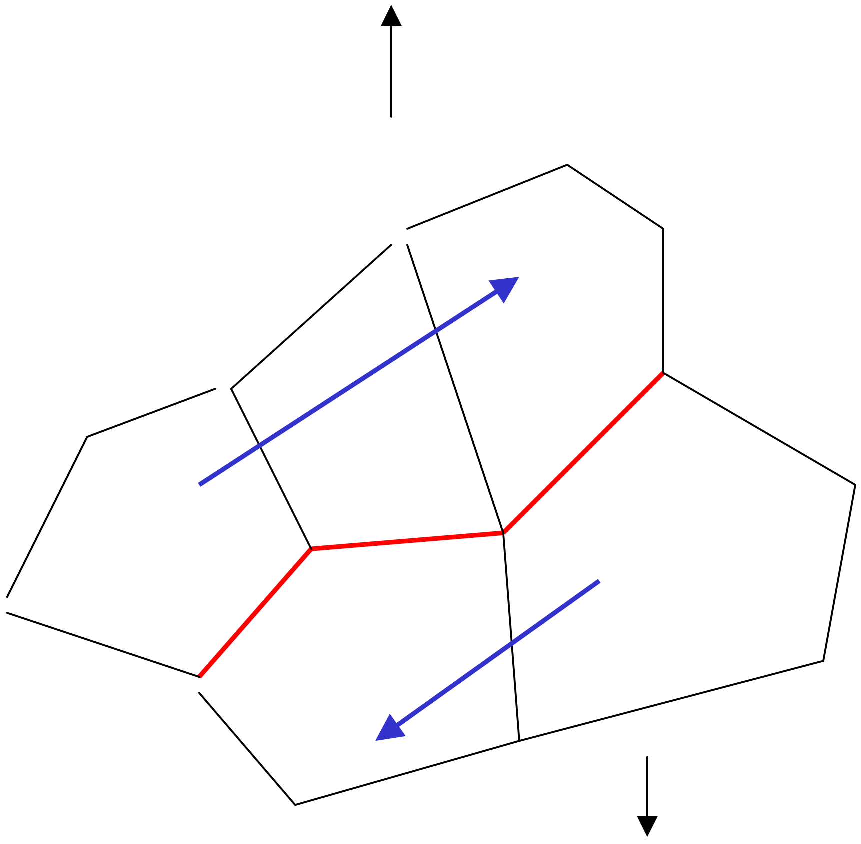
Grain Boundary Diffusion (Coble Creep)

$$d\varepsilon/dt \;\alpha\; (D_{GB}/kT)(\sigma)(\delta/d)(1/d^2)$$

d is grain size

Grain Boundary Sliding

- Flux of matter from zones of compression to zones of dilation leads to smoothing of grain corners
- Leads to the formation of cavities



Dislocation Motion

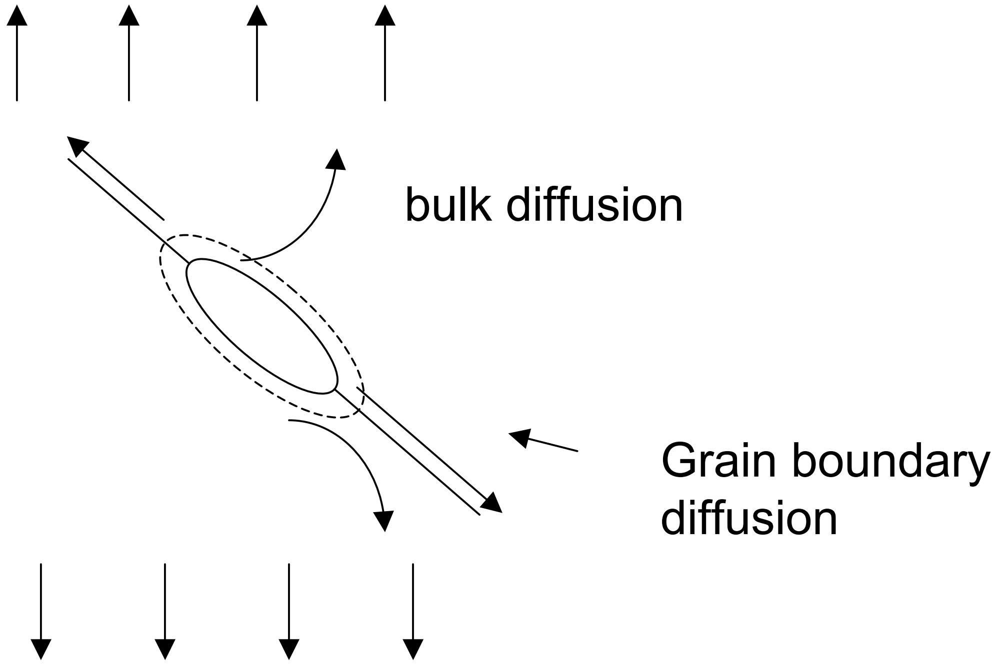
- Dislocation glide as with plastic deformation
  - Stress less than critical shear stress for motion
  - Dislocation motion is thermally activated
- Dislocation climb
  - Vacancies diffuse to core cause movement out of the glide plane
- Work Hardening
  - Dislocations pile up and repel each other
  - Climb results in recovery from work hardening

Creep Failure

Internal cavities accumulate at grain boundaries

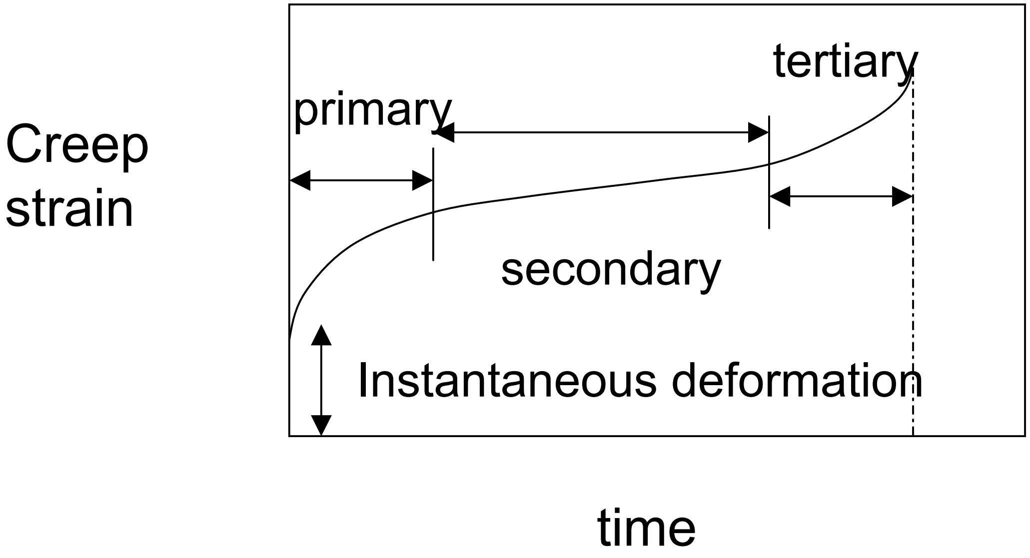
Cavities grow and aggregate

Eventual failure



Growth of voids during creep

Creep Curve



Primary

Decreasing strain rate (work hardening)

Secondary

Constant strain rate

Tertiary

Increasing strain rate

Creep damage accumulates

Steady State Creep Rate

$d\varepsilon/dt = K_1\ \sigma^n$

K_1 and n are material constants

n=1 at low stress

n=3-8 at high stress

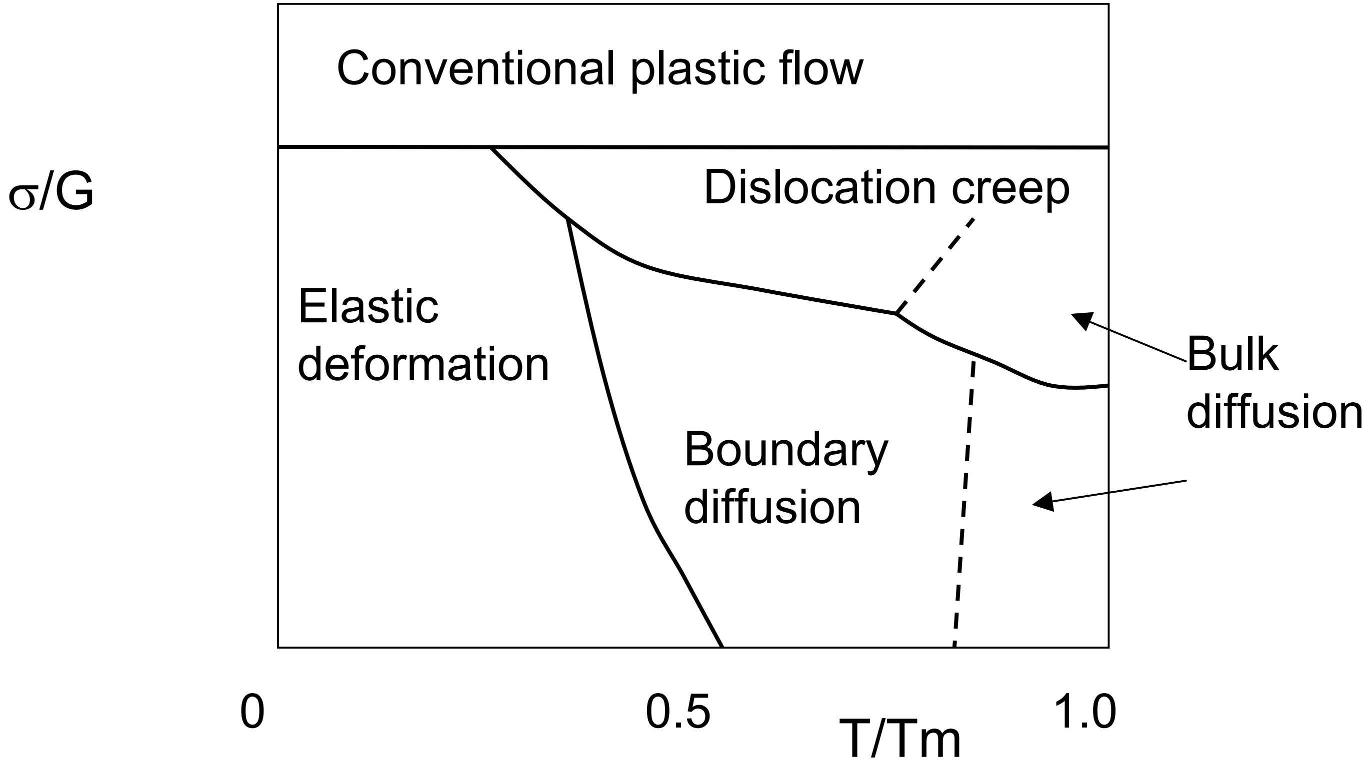
Including temperature

$d\varepsilon/dt = K_2\ \sigma^n\ \exp(-Q_c/kT)$

K_2, Q_c and n are material constants

Q_c is the activation energy for creep

Deformation diagrams



Strengthening against creep

Choose material with high Tm

Choose material with large lattice resistance to dislocation motion

Large grain size to minimize grain boundary diffusion

Precipitates at grain boundaries to prevent sliding

Directional solidification – produced highly elongated grains

Precipitates and impurities restrict dislocation glide

Ni, Al, Re, W, Ta, Cr, Co, Ru (Ni-Superalloy)

The material is in single crystal form for turbine blade application, the operation temperature could easily reach above 1200°C during flight cycles. So, the alloy needs to have good high temperature creep resistance and microstructural stability

Failure - Summary

- Failure under tensile loading
  - Very ductile – necks down to a point
  - Moderately ductile – cup and cone type fracture surface with spherical dimples
  - Brittle – fracture surface shiny and granular perpendicular to applied load. Stress concentration at flaws decrease strength

- Fatigue – failure under cyclic loading
  - S/N curves

- Creep – deformation at high temperature under low stress
  - Eventual failure due to void growth

Corrosion

What is corrosion?

The environmental degradation of materials –examples

- Rusting of an iron pipe
- Patina of a bronze statue
- Pitting of stainless steel

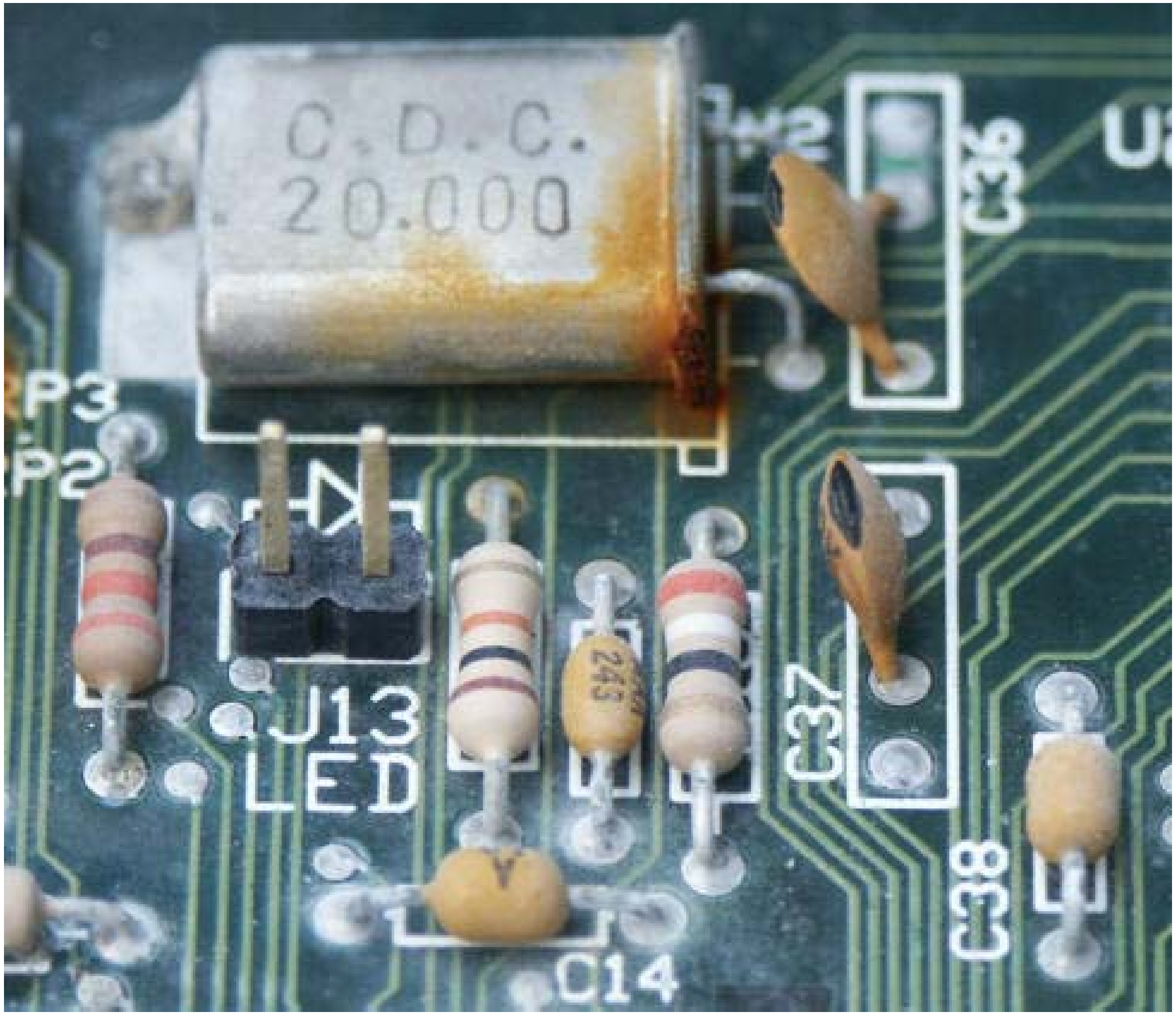
Why should we care about corrosion?

- Cost - around 5% of an industrialized nation's income is spent on corrosion prevention or maintenance
- Safety – airplanes, boilers, bridges, pressure vessels
- Conservation of resources – energy wasted replacing corroded materials

Aloha 737 Accident

www.corrosion-doctors.org

Electronics



Car Corrosion

Dry Corrosion - Oxidation

Mainly concerned with metals

Oxidation reaction: $M + O = MO$

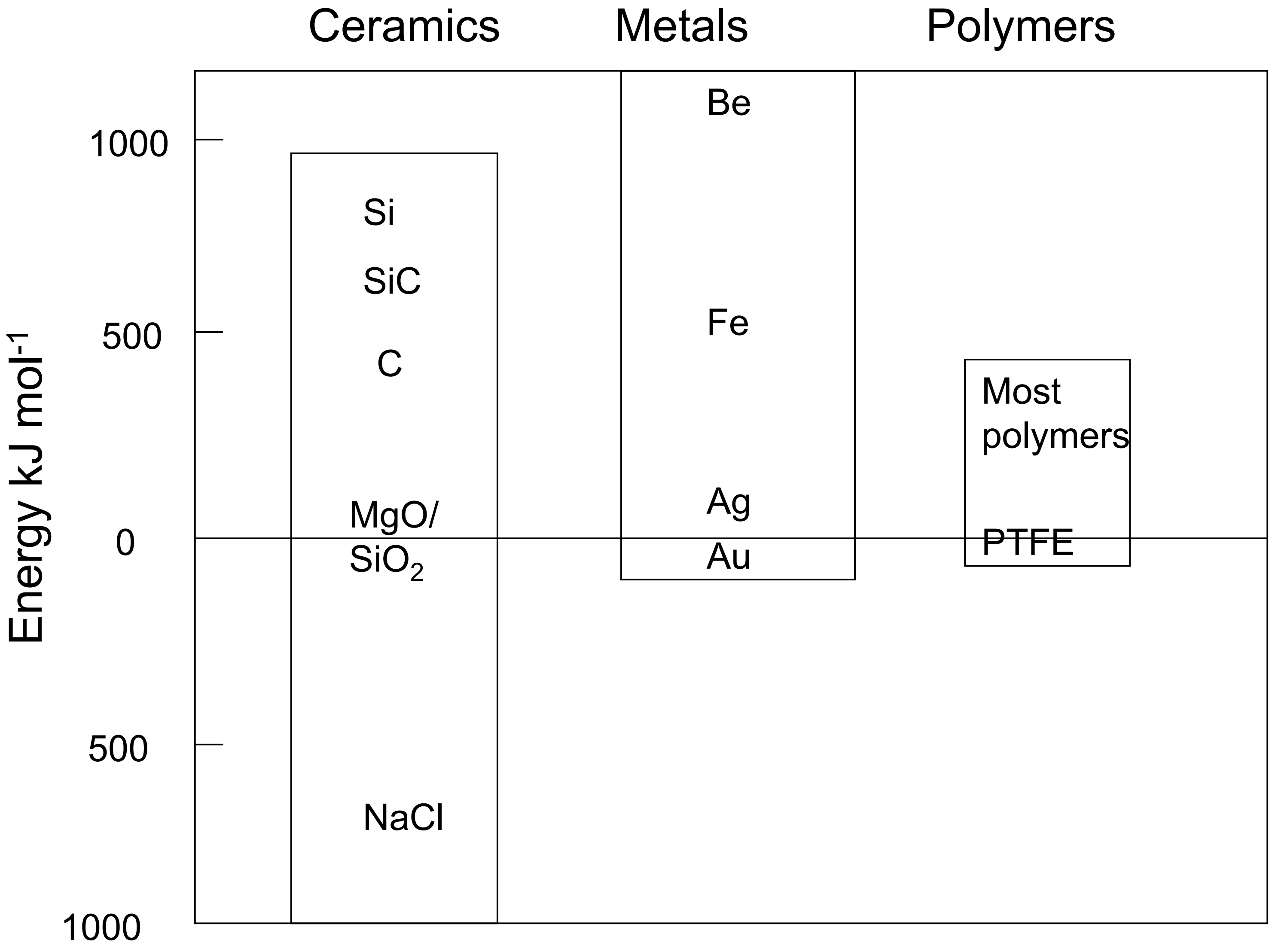
If energy for reaction is positive oxidation will not occur

eg Au, NaCl

If energy is negative oxidation may occur

Eg Zn, Fe Cu

Energies of Oxide Formation



Rate of Oxidation

The rate of oxidation is not correlated with the energy of oxide formation. Why?

Because the oxide often forms a protective scale on the surface which acts as a barrier to oxidation

Experimentally find either linear or parabolic increase in mass (Δm) with time

Linear $\Delta m = k_l t$

Parabolic $(\Delta m)^2 = k_p t$

k_l and k_p follow Arrhenius' law

Rate of oxidation increases exponentially with T

Mechanisms

$$M \rightarrow M^{2+} + 2\,e^{-} \;:\; O + 2e^{-} \rightarrow O^{2-}$$

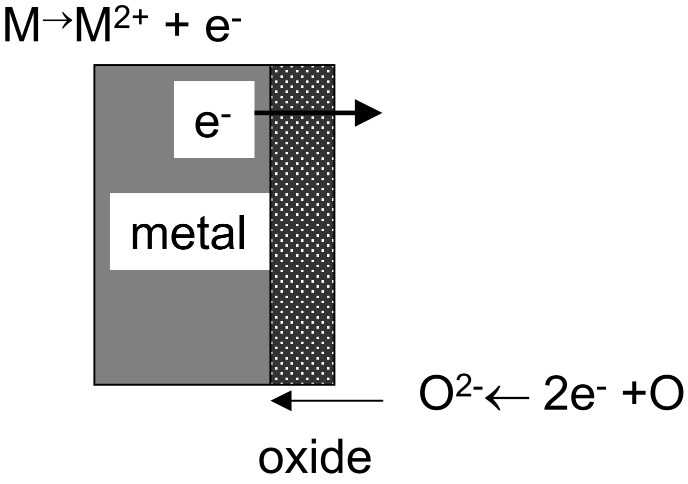
Initial reaction – oxide forms on metal surface

Electrons diffuse through scale to ionise oxygen

O ions diffuse to form scale at metal surface

Electrons and metal ions diffuse through scale

Oxide forms on scale surface



$M \rightarrow M^{2+} + e^{-}$

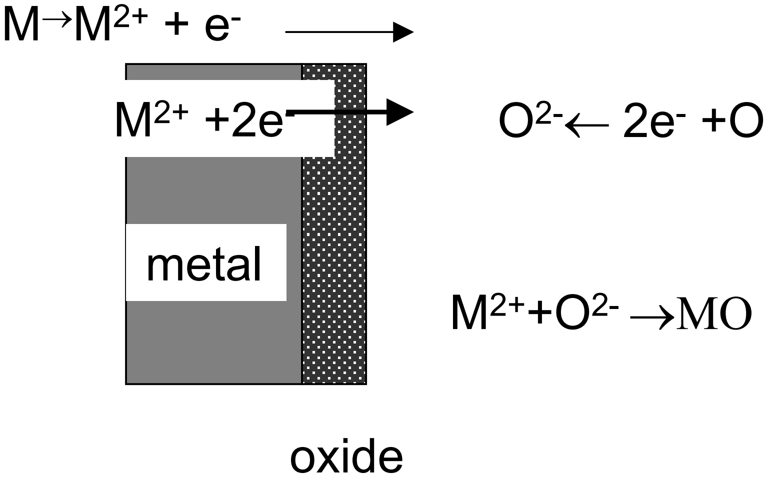
e^{-}

metal

$O^{2-} \leftarrow 2e^{-} + O$

oxide

Case 1



$M \rightarrow M^{2+} + e^{-}$

$M^{2+} + 2e^{-}$

$O^{2-} \leftarrow 2e^{-} + O$

metal

$M^{2+} + O^{2-} \rightarrow MO$

oxide

Case 2

Parabolic Law

Fick's Law

$$j=-D\,dC/dx = -DC/x$$

Integrating

$$x^2 = k_p t$$

$$k_p \propto C D_0 \exp(-Q/kT)$$

Rate of oxidation depends on diffusion coefficient

Electrically insulating scales make very good protective films (eg Al_2O_3)

Linear oxidation

Some scales do not adhere well to metal surface

The oxide may be volatile and evaporate from surface

There may be large volume mismatch between oxide and metal leading to cracking

The absence of a protective scale leads to linear oxidation

Wet Corrosion

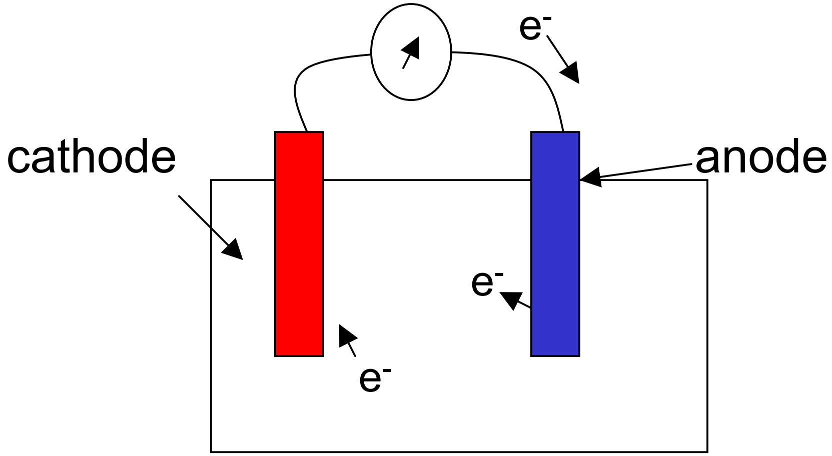
The rate of corrosion increases by several orders of magnitude in the presence of water

Electrochemistry

Electrolyte – solution capable of conducting electricity via ions

Anode – electrode whose atoms lose electrons from the external circuit

Cathode – electrode whose atoms gain electrons from the external circuit



Single metal can have both anodic and cathodic areas

Corrosion – Electrochemistry

Oxidation reaction $M \rightarrow M^{n+} + ne^-$

Eg $Fe \rightarrow Fe^{2+} + 2e^-$

Oxidation takes place at the anode

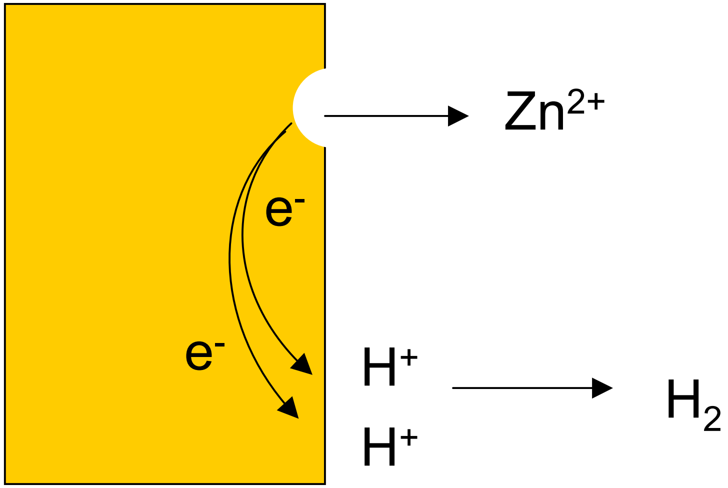
Reduction reaction $X^{n+} + ne^- \longrightarrow X$

Eg $2H^+ + 2e^- \rightarrow H_2$

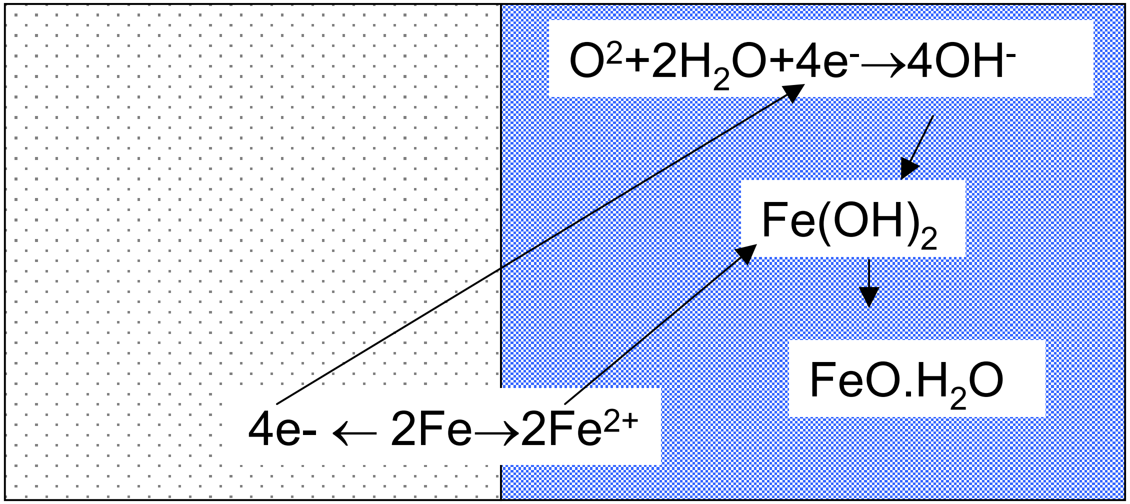
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Reduction takes place at the cathode

Corrosion of Zn in Acid Solution



Rusting of Fe



$O^2+2H_2O+4e^- \rightarrow 4OH^-$

$Fe(OH)_2$

$FeO.H_2O$

$4e- \leftarrow 2Fe \rightarrow 2Fe^{2+}$

Electrochemical potential - EMF Series

Measures tendency for materials to gain or lose electrons (H defined as zero)

Measured in V

$Cu^{2+} + 2e^- = Cu$	+0.34
$Ni^{2+} + 2e^- = Ni$	-0.25
$Fe^{2+} + 2e^- = Fe$	-0.44
$Zn^{2+} + 2e^- = Zn$	-0.76
$Al^{3+} + 3e^- = Al$	-1.66

Lower metal oxidizes (loses electrons)

Higher metal reduces (gains electrons)

Galvanic Series

- EMF series was generated under highly idealised conditions and is of limited utility
- The Galvanic series lists the relative reactivities of metals in sea water
- Metal near the top are unreactive
- Metals near the bottom are the most anodic (tend to oxidize)
- No voltages are given

The Galvanic Series

Gold
Silver
Copper
Nickel
Stainless Steel
Iron
Aluminium Alloys
Cadmium
Zinc
Magnesium

Corrosion Rates

Corrosion Penetration Rate

$$CPR = K W / \rho A t$$

K = constant (depends on units)

W is weight loss in time t

ρ is the density

A is the Area

Forms of Corrosion

- Uniform corrosion
- Stress Corrosion
- Intergranular corrosion
- Pitting
- Galvanic corrosion
- Crevice corrosion

Uniform Corrosion

- Occurs with equivalent intensity over the entire exposed surface

- Examples include general rusting of steel and iron and the tarnishing of silverware

- Easiest form of corrosion to predict and protect against

Stress Corrosion

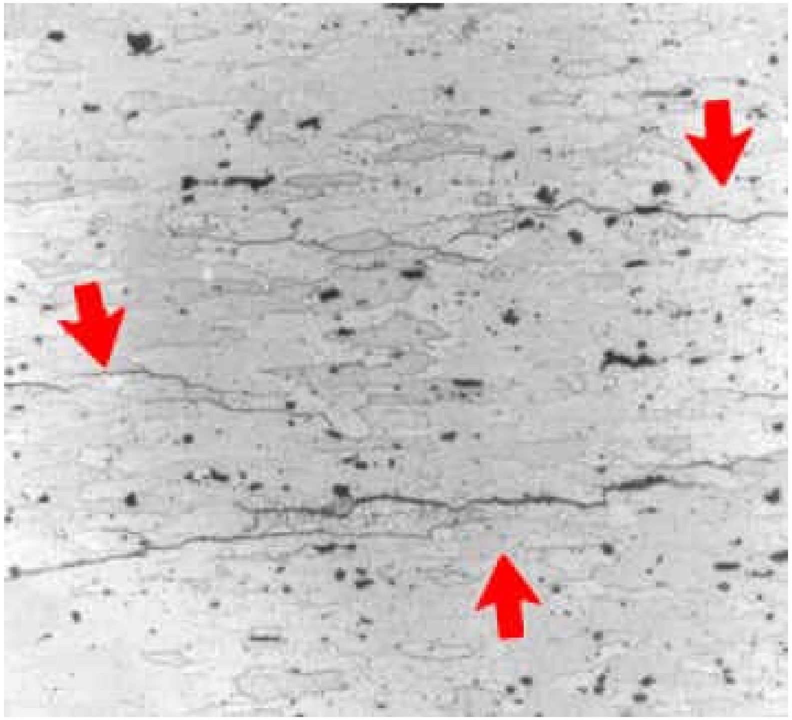
- Results from combined action of stress and corrosion
- Small cracks form and propagate in the direction perpendicular to the stress
- Failure characteristic of brittle material even if metal is ductile
- Stress may be residual (not applied externally)

Intergranular Corrosion

- Occurs preferentially along grain boundaries

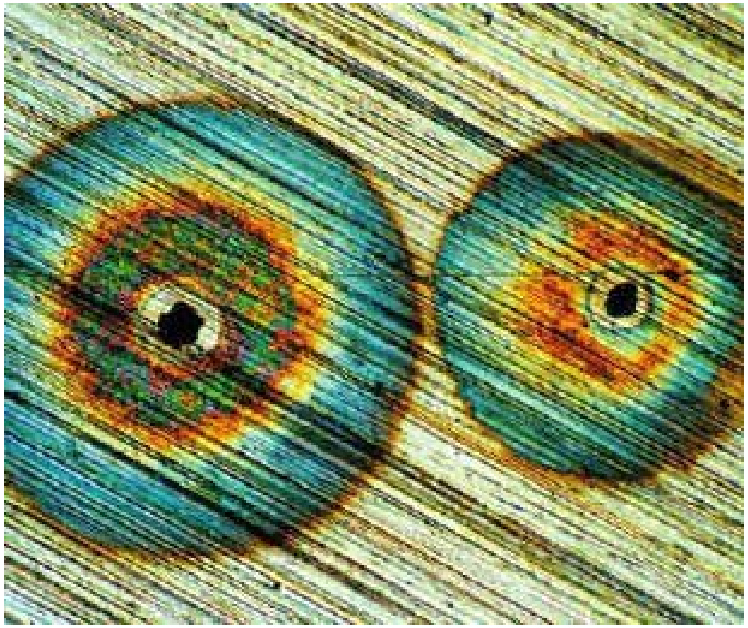
- Macroscopic specimen disintegrates along grain boundaries

- Especially prevalent in stainless steels – Cr depleted region around grain boundaries



Pitting

- Small pits or holes form
- Oxidation occurs in the pit with complementary reduction on surface
- Penetrate from top of a horizontal surface in vertical direction
- Initiated at localised surface defect



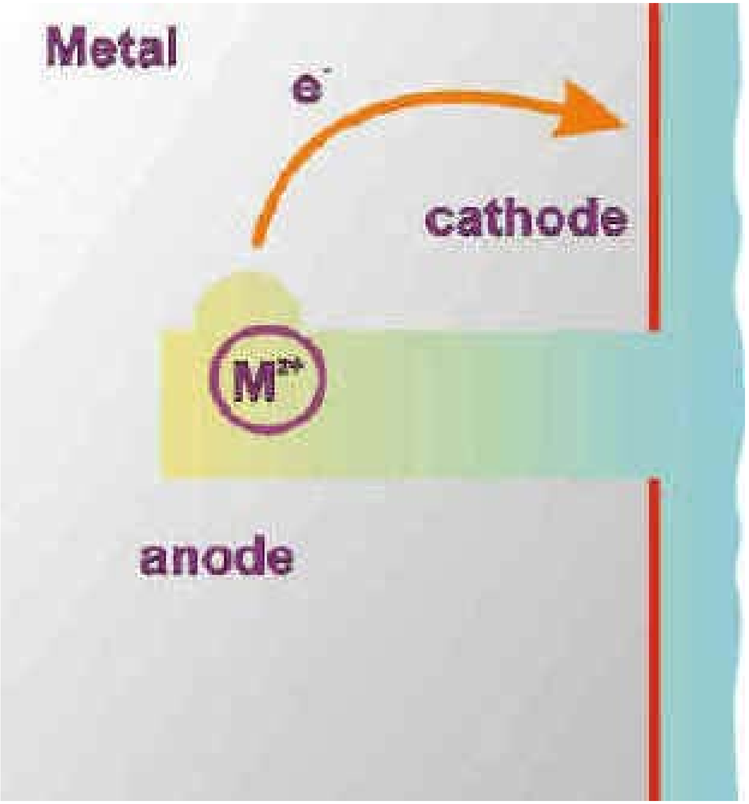
Galvanic corrosion

- 2 different metals electrically connected in an electrolytic solution
- Galvanic series predicts which metal corrodes faster
- eg Steel soldered to Cu – steel corrodes faster

Stainless Steel screw / Cadnium plated washer

Crevice Corrosion

- Electrochemical Corrosion may occur because of concentration differences of dissolved ions between 2 regions of same metal
- Crevices or recesses are examples
- Crevice must be wide enough for solution to penetrate but narrow enough for it to be stagnant



Minimising or preventing corrosion

- Use corrosion resistant material
- Remove aggressive species from environment
- Add chemical to inhibit corrosion
- Separate material from environment – paint
- Remove crevices from design
- Use compatible materials
- Use cathodic or sacrificial protection – galvanized steel

Cathodic Protection

- One of the most effective means of corrosion protection
- Involves supplying electrons from an external source making it the cathode
- The oxidized metal (often Mg or Zn) is called the sacrificial anode
- Common example is galvanizing (coating steel with Zn