# Part 3

## Phase Diagrams and Alloys

# Phase Diagrams

## What are Phase diagrams?

Maps showing the equilibrium phase of a material at a given temperature and composition

## Why study Phase diagrams?

Phase diagrams enable us to –

select a phase

select a processing route

select a microstructure

# Definitions - 1

- Component – Pure metal of which the alloy is composed

- Solute – Component of solid solution present in minor concentration

- Solvent – Component present in greatest amount

- Solubility limit – Maximum concentration of solute that can dissolve in solvent

- Phase – A homogenous portion of a system with uniform physical and chemical characteristics

# Definitions -2

- Equilibrium – system whose thermodynamic free energy is a minimum
- Phase equilibrium – State achieved with minimum free energy in systems with more than one phase
- Metastable State – A state which has not reached equilibrium
- Equilibrium Phase Diagram – The relationship between the temperature and compositions of phases present at equilibrium

# More Definitions

- Constitution
  - The constitution of an alloy is described by
    - the phases present
    - the weight fraction of each phase
    - the composition of each phase

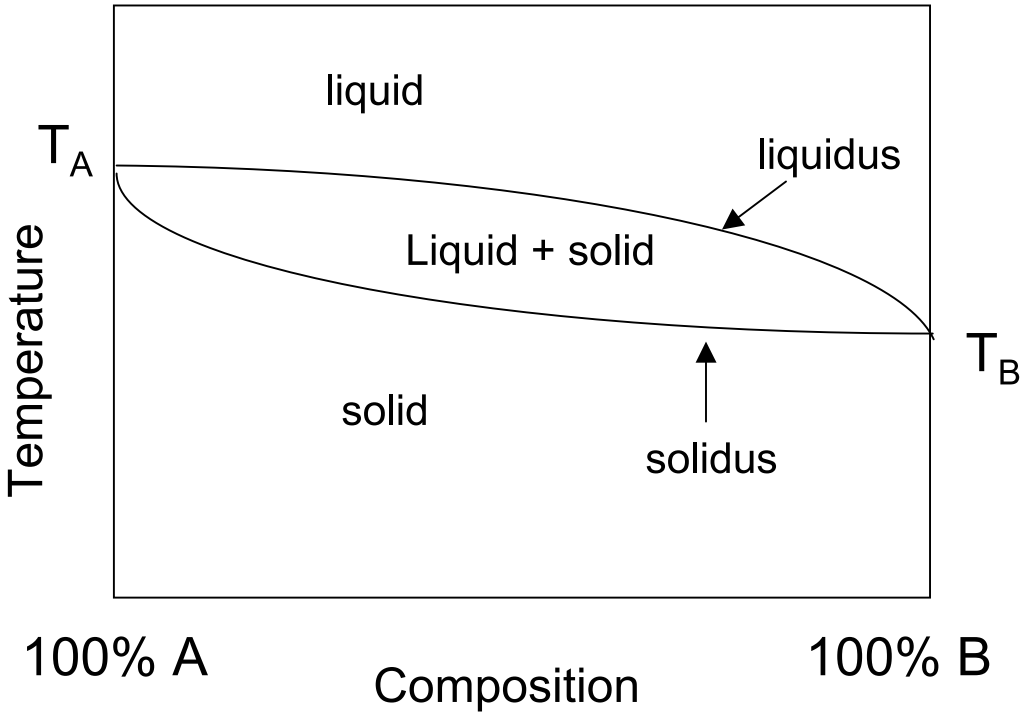
- The equilibrium constitution is when the alloy has no further tendency to change at a given temperature and pressure

# A simple binary phase diagram

Consider a mixture of 2 metals A and B

Solid exists as a solution at all temperature (isomorphous)

A solidifies at $T_A$ : B solidifies at $T_B$



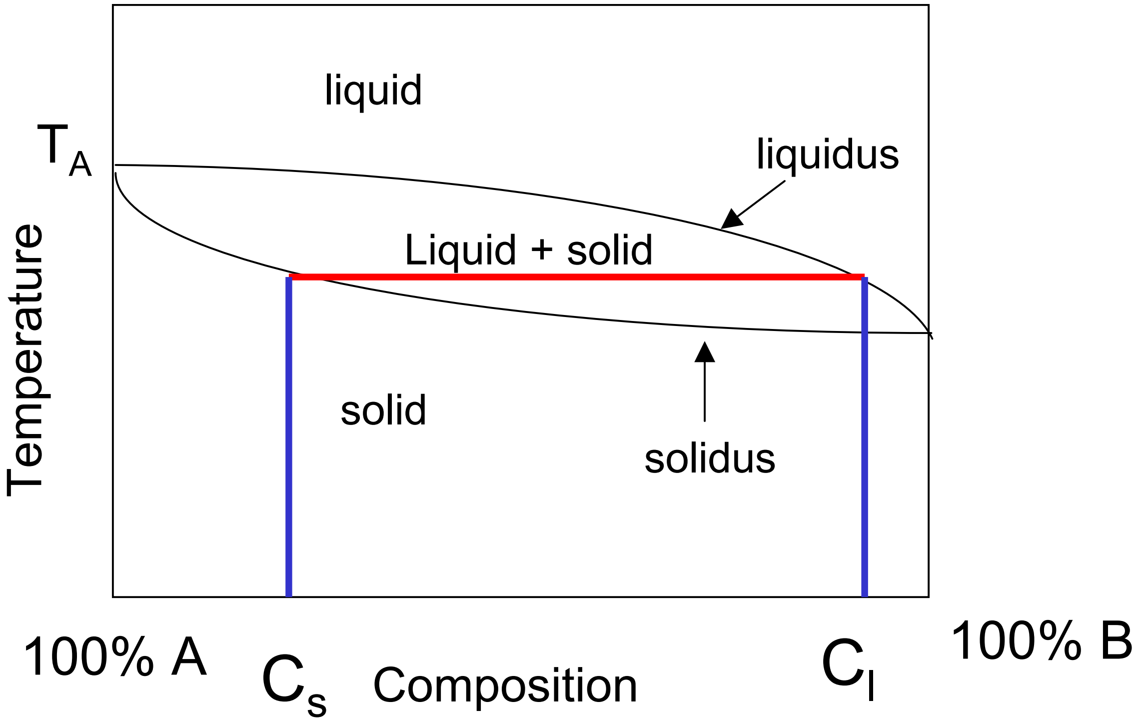
Liquidus – line at which solidification begins

Solidus – line at which solidification is completed

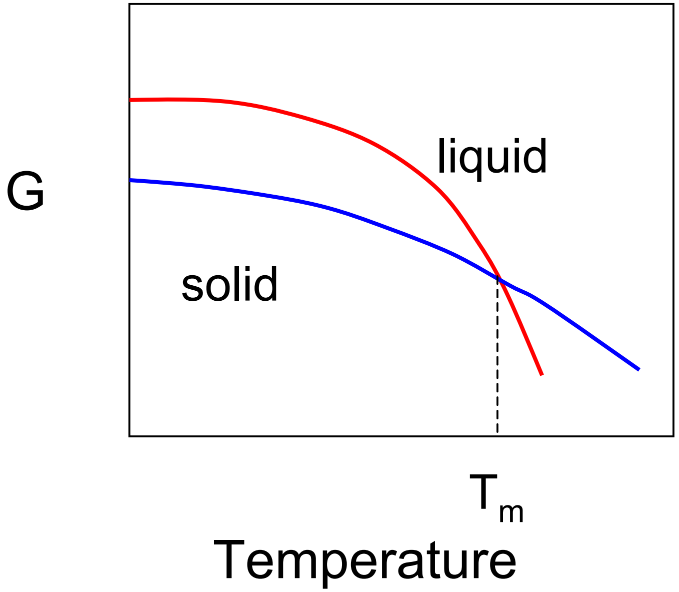
# Tie Lines

Horizontal Isotherm at a given temperature

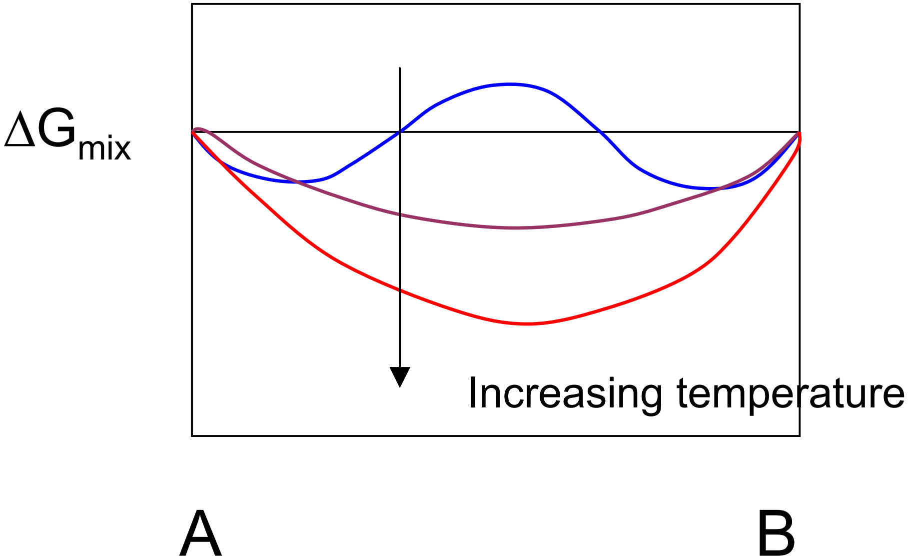
Determines compositions of the 2 phases (liquid and solid)



# Free energy considerations



Pure substance

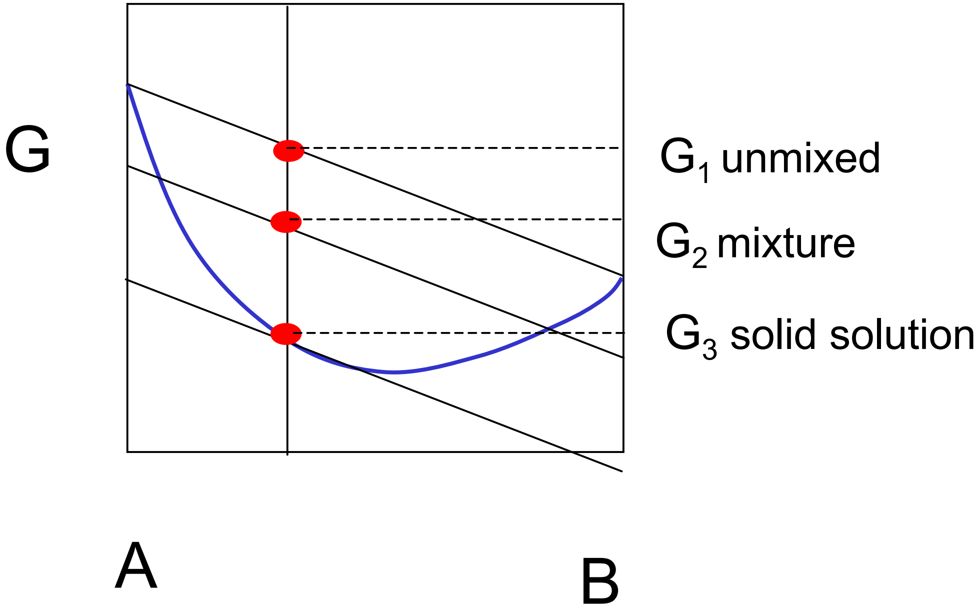


Solutions

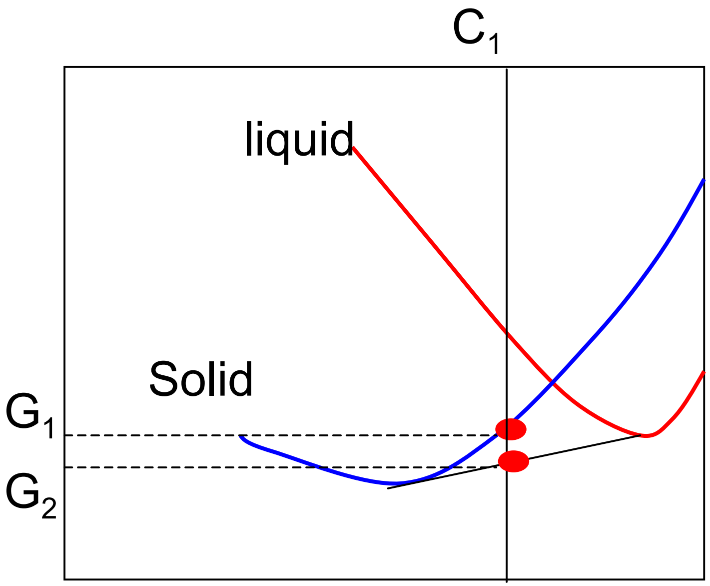
At high T there is complete solution and a single minimum in the free energy curve

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = x_A x_B \Omega + RT\,(x_A \ln x_A + x_B \ln x_B)$$

# Free energy and phase diagrams



Single phase



When more than 1 phase present system can reduce the free energy separating into 2 phases

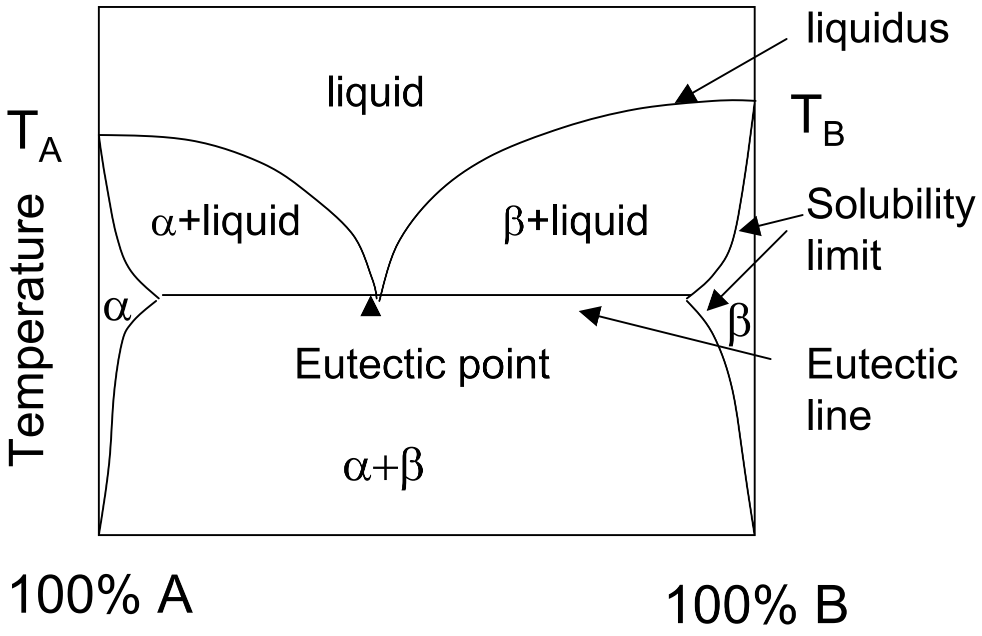
When temperature is altered the compositions of solids and liquids in equilibrium change and build up the solidus and liquidus lines

# A Binary Phase Diagram

## Limited solubility of A in B and B in A

Consider a mixture of 2 metals A and B

A solidifies at $T_A$ : B solidifies at $T_B$



Liquidus – line at which solidification begins

Eutectic line - solidification occurs

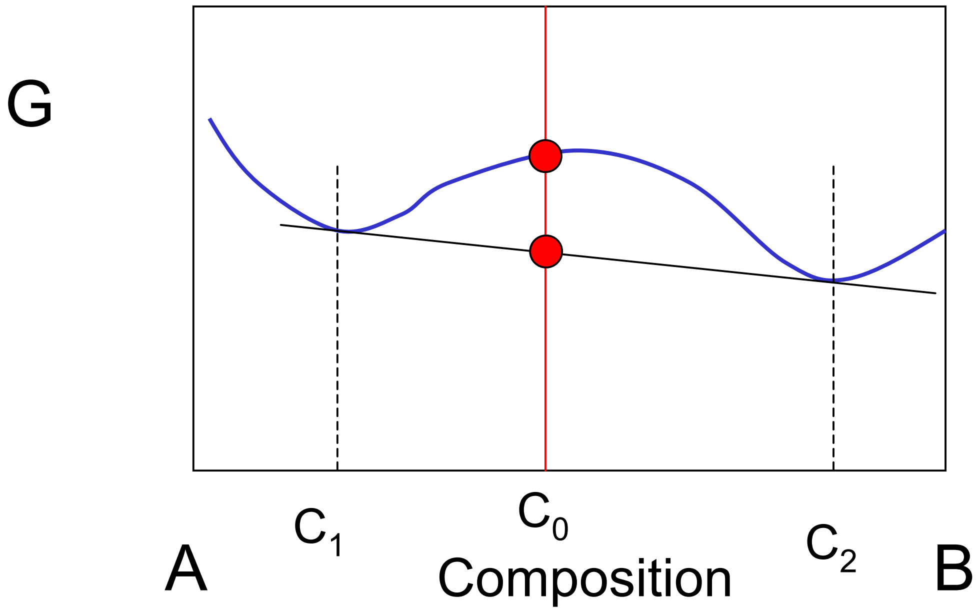
Eutectic point – lowest melting point

α – A rich solid solution

β – B rich solid solution

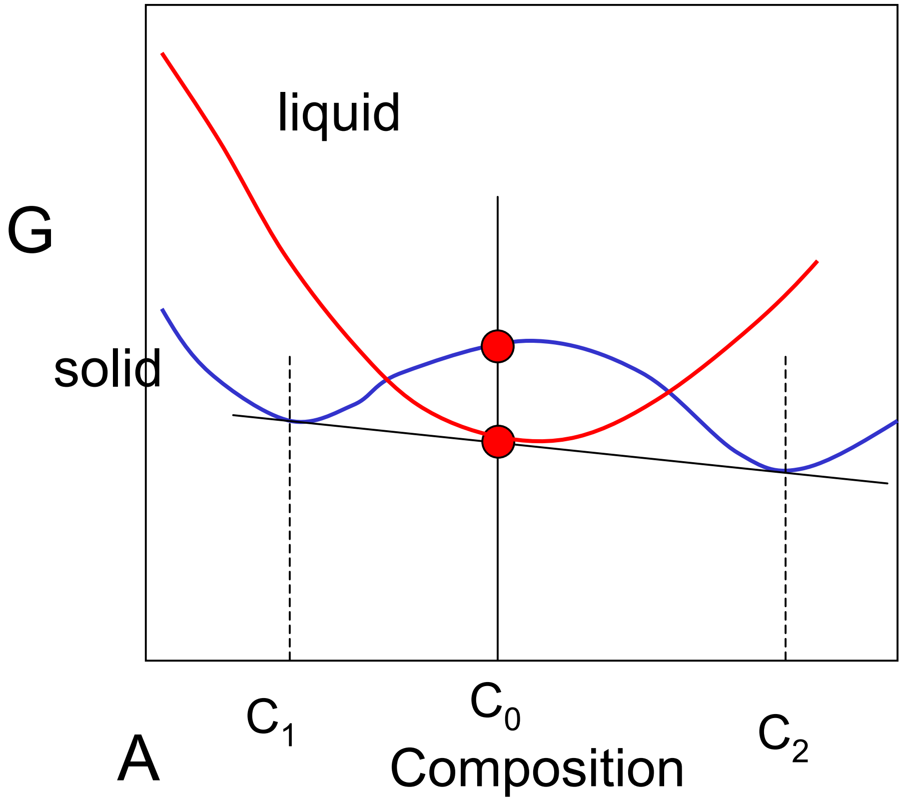
# Free energy – binary phase diagrams

System can lower free energy by separating into 2 solid phases



Liquid may solidify as single phase but separates into 2 phases on further cooling

# Eutectic systems

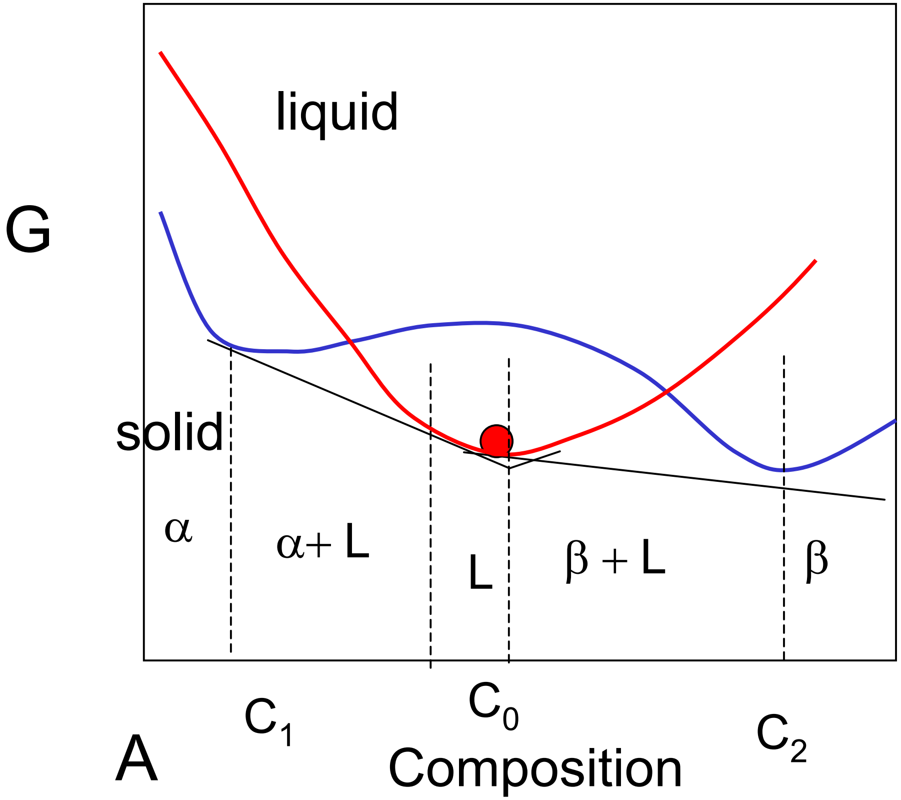


For a particular temperature the free energy curve of the liquid has a common tangent to the line joining the minima

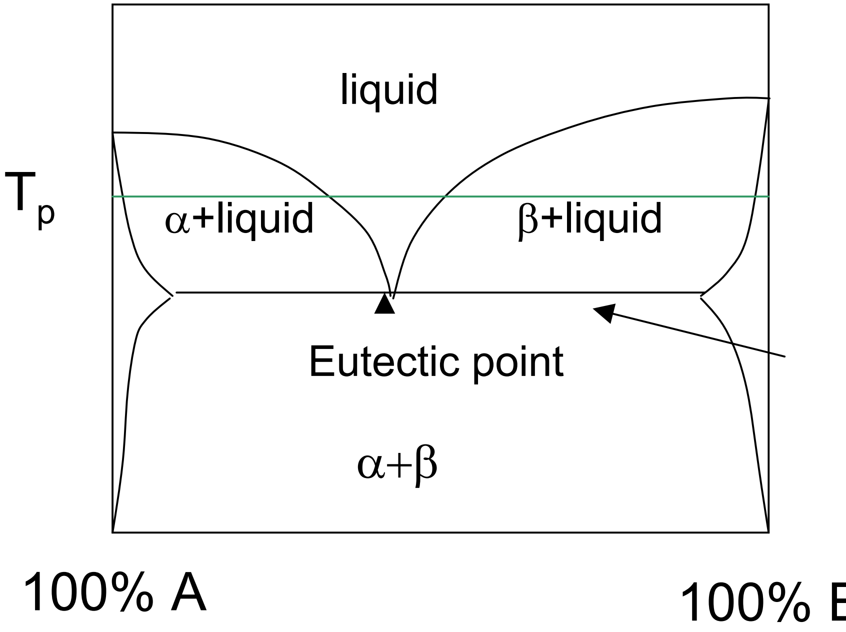
All 3 phases exist in equilibrium at the eutectic temperature

Liquid solidifies directly into 2 phases α and β

# Free energy at general temperature



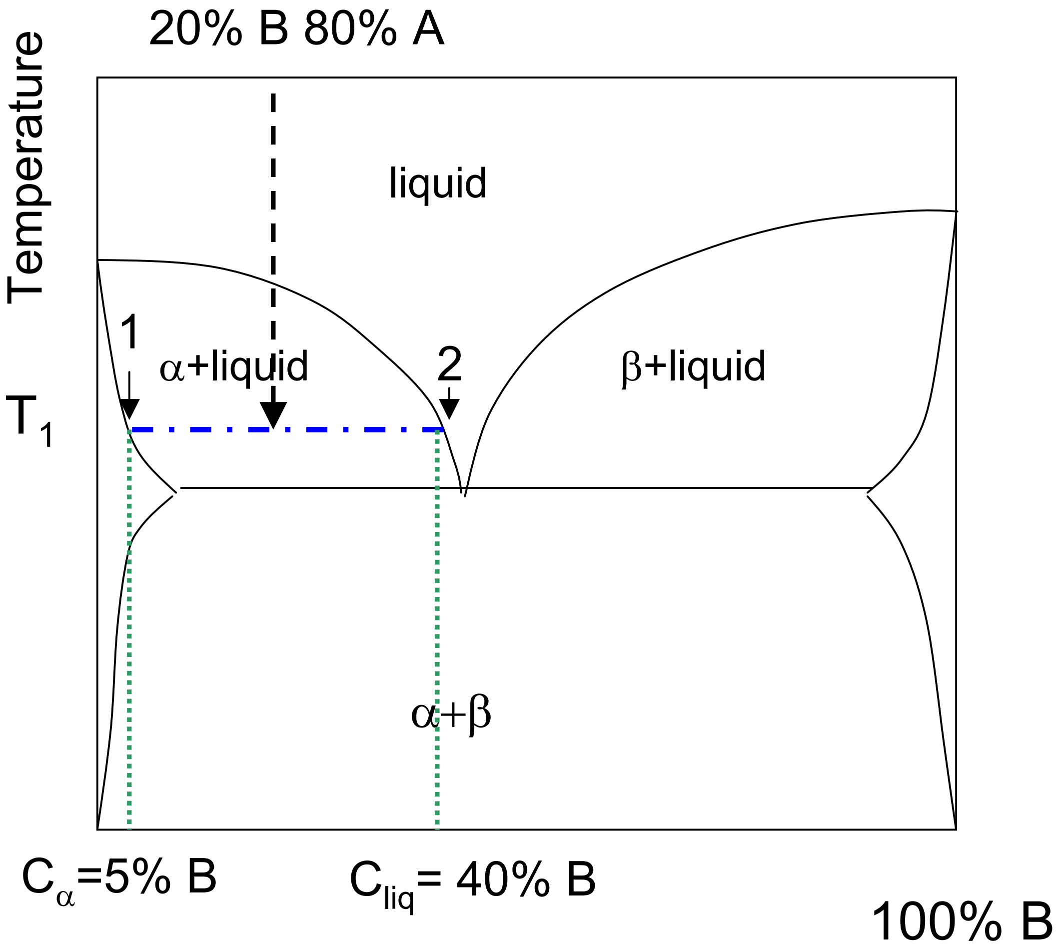
At a general temperature $T_p$ 2 minima have different tangents to the liquid curve



# Eutectic

- Eutectic – means easily melted (Greek)
- Eutectic point – the bottom point of the V formed by 2 liquidus lines
- Eutectic line – the horizontal line running through the eutectic point
- The Eutectic reaction – a 3 phase reaction in which , on cooling, a liquid transforms into 2 solids
  - $L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})$

# Phase Diagrams – Tie Lines



Cool liquid mixture

20% B 80% B to a temperature $T_1$

Draw horizontal line at this temperature

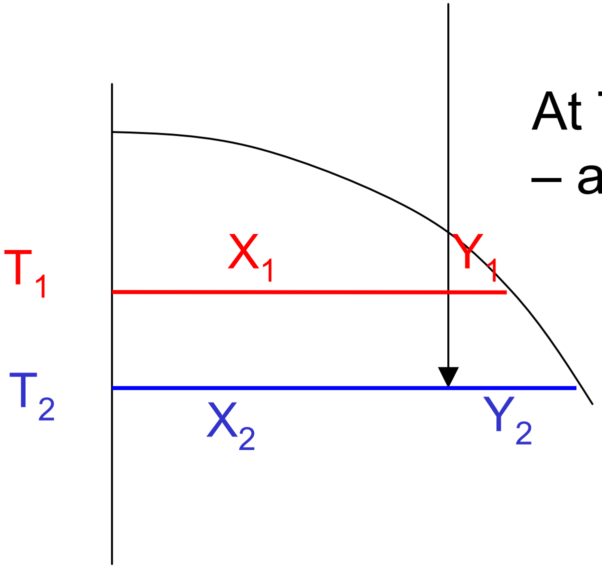
Line meets liquidus at 1 and solubility limit line at 2

At $T_1$ the composition of α is that corresponding to point 1 and the composition of the liquid corresponds to point 2

# The Lever Rule

The relative amounts of each phase at a given temperature and composition is given by the relative lengths of the tie lines

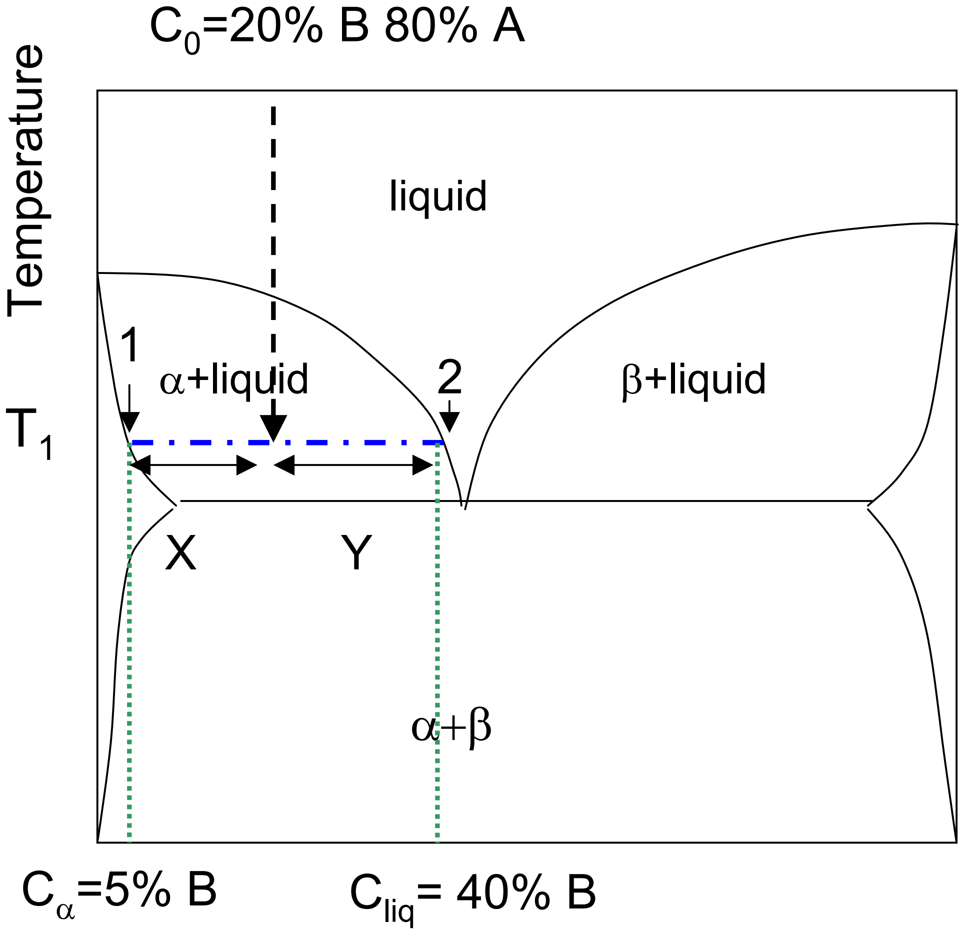
For each phase use the line furthest from that phase



At $T_1$ line is close to liquidus – almost all liquid

At $T_2$ line is further from the liquidus – less liquid

# The Lever Rule - Proof



Conservation of mass

$C_0 = f_\alpha C_\alpha + (1\text{-}f_\alpha)\ C_{liq}$

Rearranging

$f_\alpha = (C_{liq} - C_0)/(C_{liq} - C_\alpha)$

$(C_{liq} - C_0)=Y$

$(C_{liq} - C_\alpha) = X + Y$

So $f_\alpha = Y/X+Y$

And $1\text{-}f_\alpha = X/X+Y$

Here X=15;Y=20

$f_\alpha = 20/35$

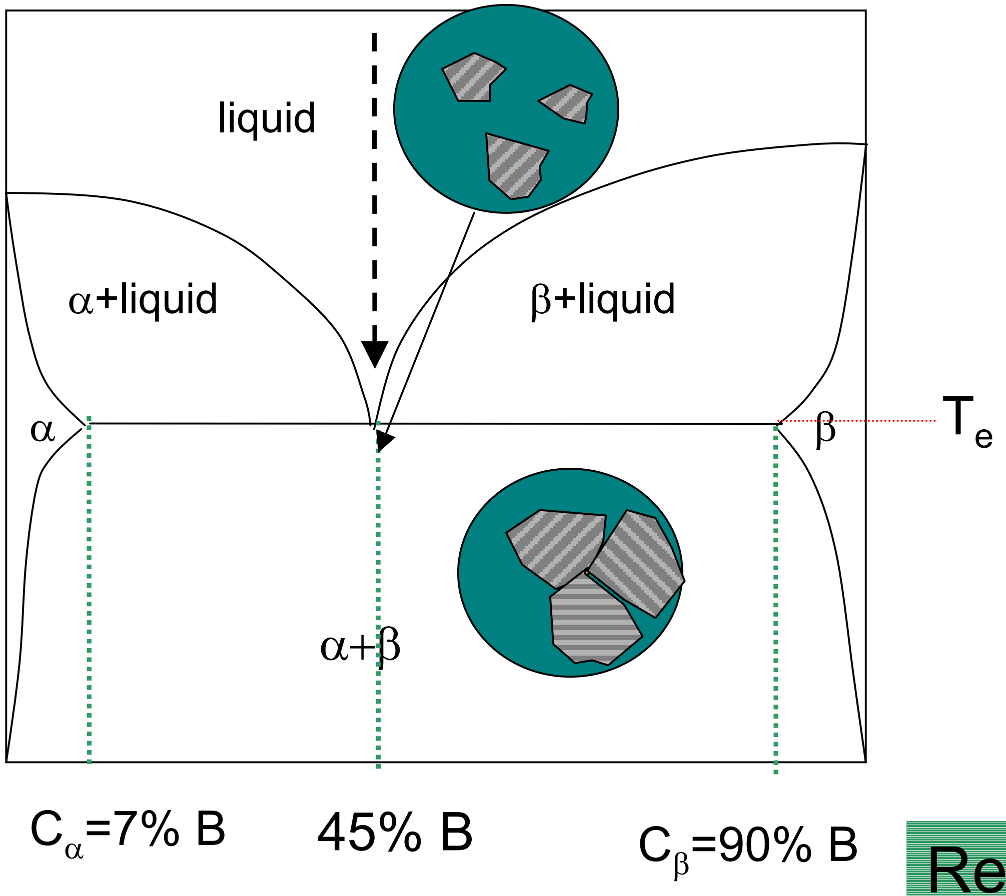
$1\text{-}f_\alpha = 15/35$

# Case Study – Solder (Ashby)

| Type | Composition | Melting Range | Uses |
|---|---|---|---|
| Soft eutectic (free flowing) | 62 Sn 38 Pb | 183 | Electronic assemblies |
| Soft general purpose (moderately pasty) | 50 Sn 50Pb | 183-212 | Plumbing joints sheet metal work |
| Soft Plumbers (pasty) | 35 Sn 65 Pb | 183-244 | Wiped Joints car body filling |
| Soft High melting (free flowing) | 5Sn 93.5 Pb 1.5 Ag | 296-301 | Higher temperatures |

# Eutectic Alloy

Cool liquid with eutectic composition ($C_e$= 45% B)



At $T_e$ liquid starts to solidify at favourable nucleation sites

Alloy forms stripes of α and β phases – stripes often of the order of 1 micron thick

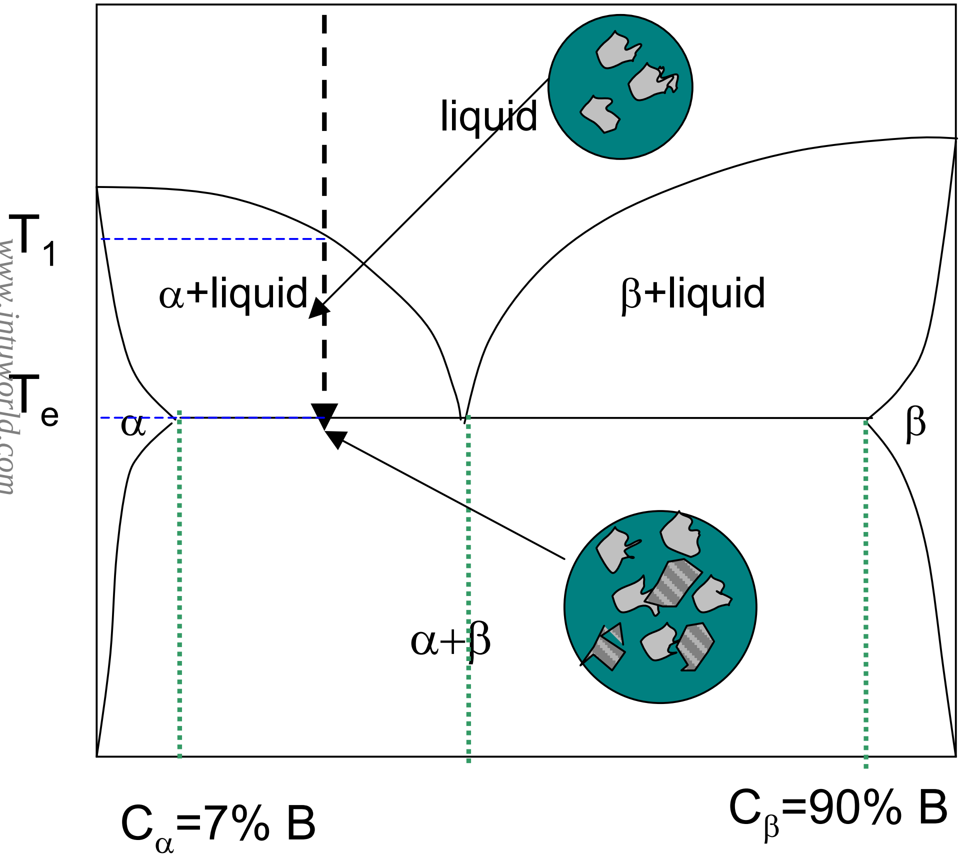
On further cooling nuclei grow adding α to α and β to β

Crystals eventually coalesce and form grain boundaries

Result polycrystalline metal with uniform composition

# Hypo-eutectic Alloy

Cool liquid with composition to the left of the eutectic



At $T_1$ α phase nucleates

On further cooling a grains grow and liquid becomes rich in B

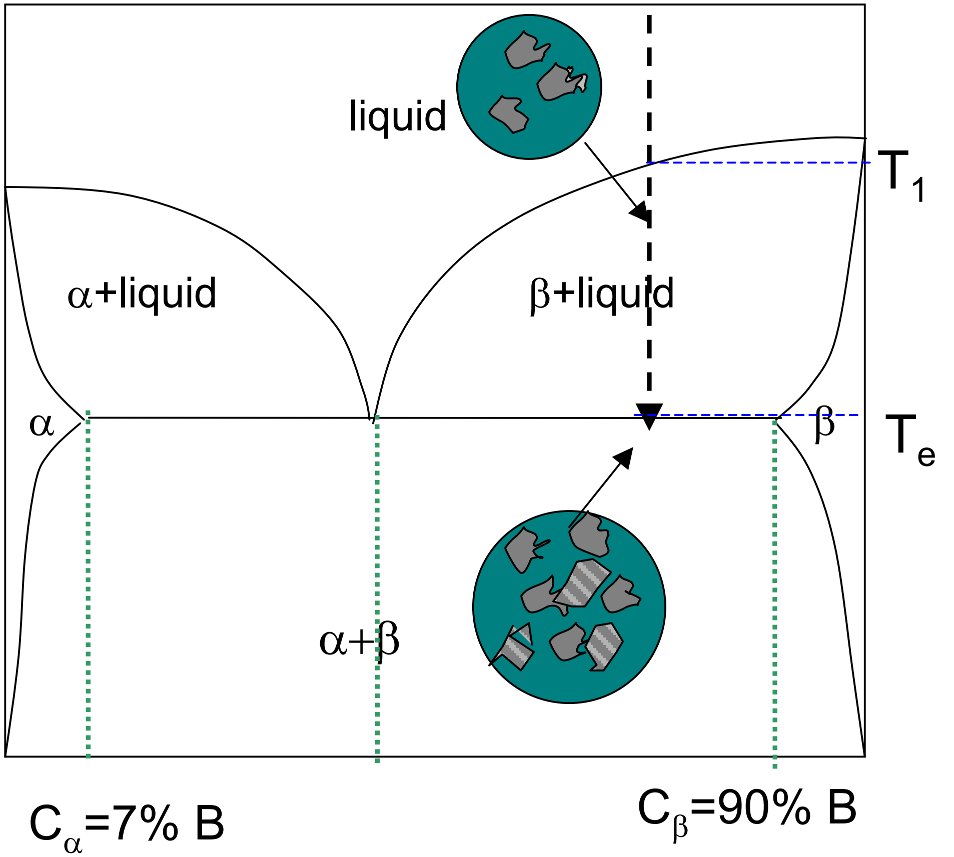
At $T_e$ Remaining liquid has reached the eutectic composition

2nd phase grows – lamellar phase of α and β

**Result polycrystalline metal with grains of α and grains of lamellar α and β**

# Hyper-eutectic Alloy

Cool liquid with composition to the right of the eutectic



At $T_1$ β phase nucleates

On further cooling a grins grow and liquid becomes rich in A

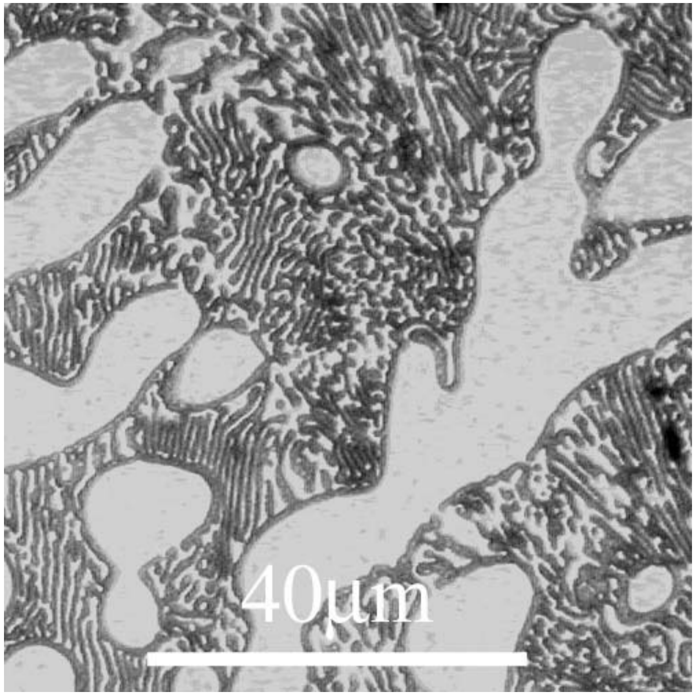
At $T_e$ Remaining liquid has reached the eutectic composition

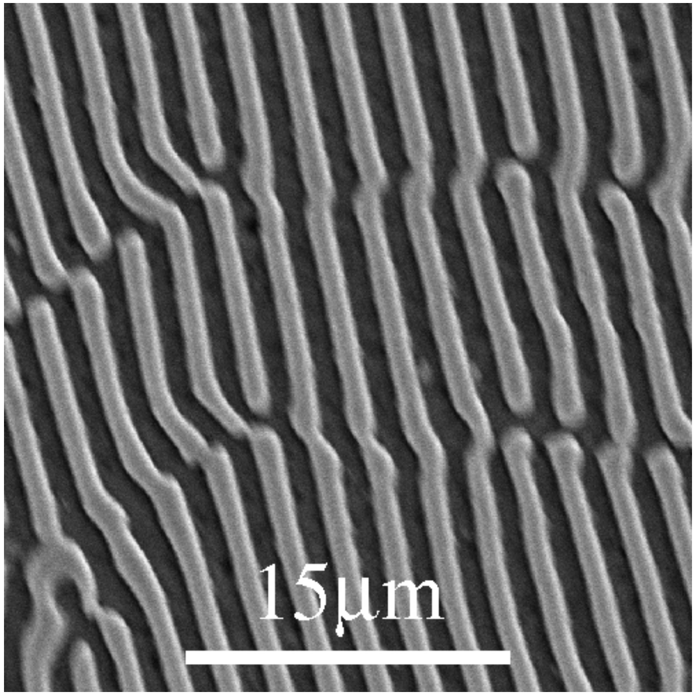
2nd phase grows – lamellar phase of α and β

Result polycrystalline metal with grains of β and grains of lamellar α and β

# Examples of Al Cu Microstructures

From www.msm.cam.ac.uk/doitpoms





Al$_{.75}$Cu$_{.25}$ hypoeutectic

Reflected light microscope

Al$_{.67}$Cu$_{.33}$ eutectic alloy

SEM

# Complex Binary Phase Diagrams

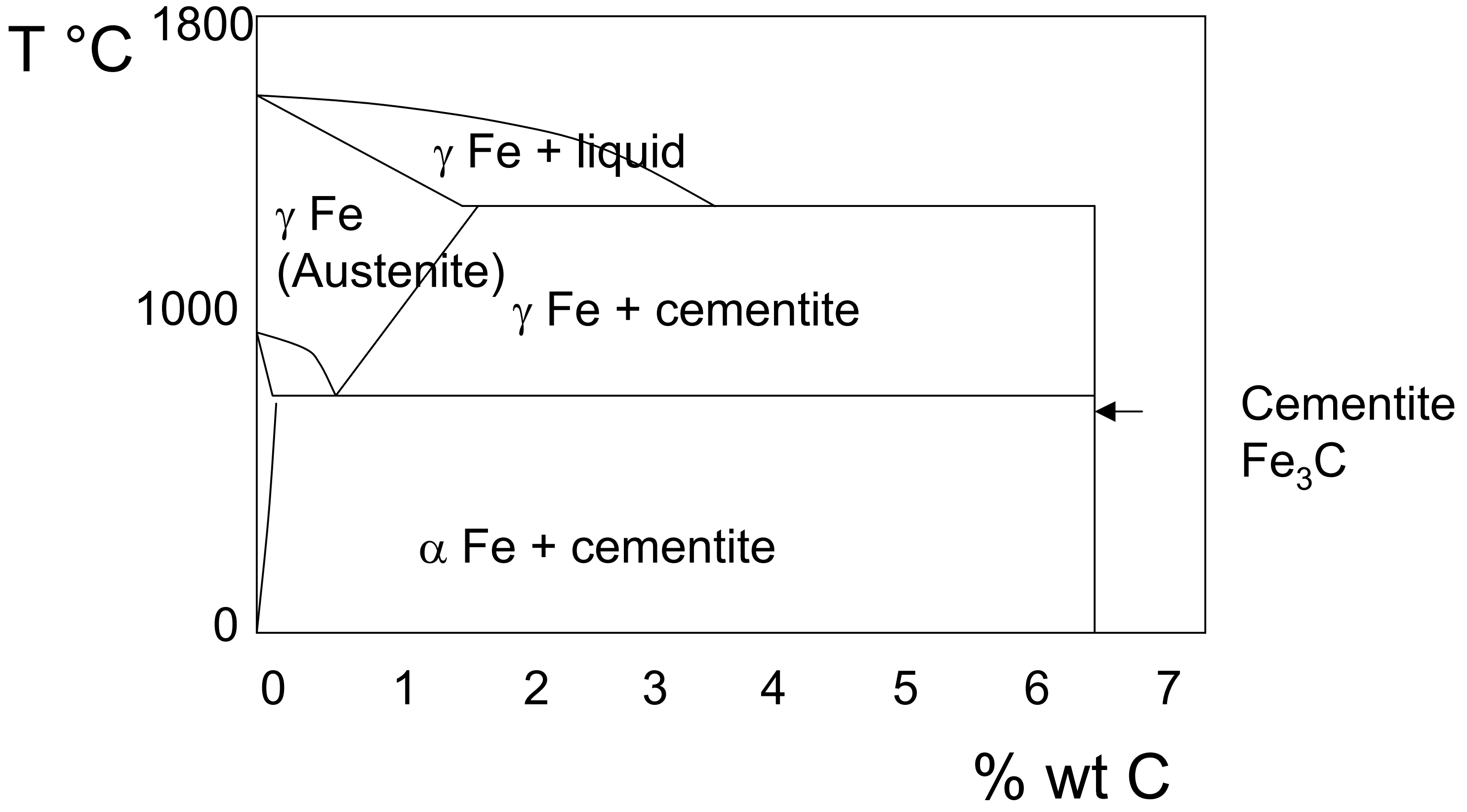
- In some systems intermediate phases exist in which A and B form ordered structures (eg Brass CuZn)
- Intermetallic compounds between A and B are also possible
- Intermetallic compounds have distinct structures and chemical compositions (eg $Mg_2Pb$)
- Solid solutions between ordered and intermetallic compounds and other phases can exist, leading to complex phase diagrams

# Invariant Points

- Invariant points involve 3 phases in equilibrium
  - Eutectic – 1 liquid and 2 solid
  - Eutectoid – 3 solid
    - Horizontal line known as eutectoid line or isotherm
    - Eutectoid reaction $\delta \rightarrow \gamma + \varepsilon$
    - Eutectoid structure is similar to eutectic but on a much finer scale
  - Peritectic – Solid + liquid transforms to solid
    - Peritectic reaction $\delta + L \rightarrow \varepsilon$

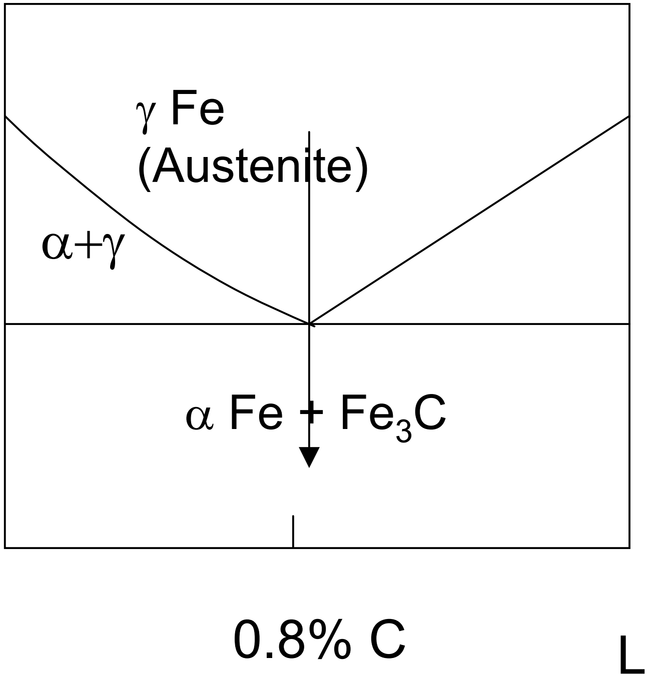
# Fe / C System (Steel)

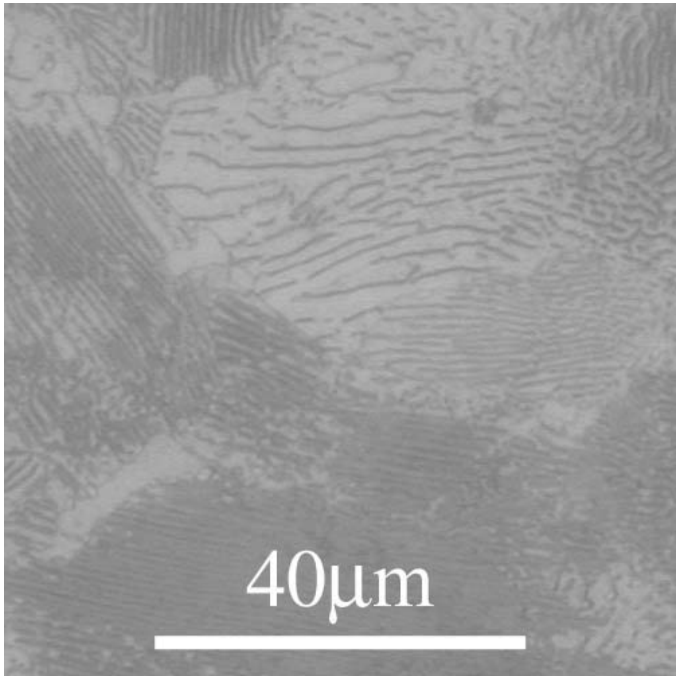
| | | | | |
|---|---|---|---|---|
| Pure Fe | Room T | BCC | α iron | ferrite |
| | > 912 C | FCC | γ iron | Austenite |
| | > 1394 C | BCC | δ ferrite | |



# 0.8% C Steel - eutectoid

## Pearlite





Lamellar structure – tough microstructure controlled by cooling rate

# Phase Transformations - Kinetics

- Development of microstructure involves phase transformations – an alteration of the number and/or character of the phases

- Three types of transformation
  - Diffusion dependant with no change in number or composition of phases (eg solidification of pure metal)
  - Diffusion dependant with a change in number and/or composition of phases (eg eutectoid)
  - Diffusionless – metastable state produced (eg Martensite)

# Avrami Equation

The fraction of transformation (y) at time t is given by

$$y = 1 - \exp(-kt^n)$$

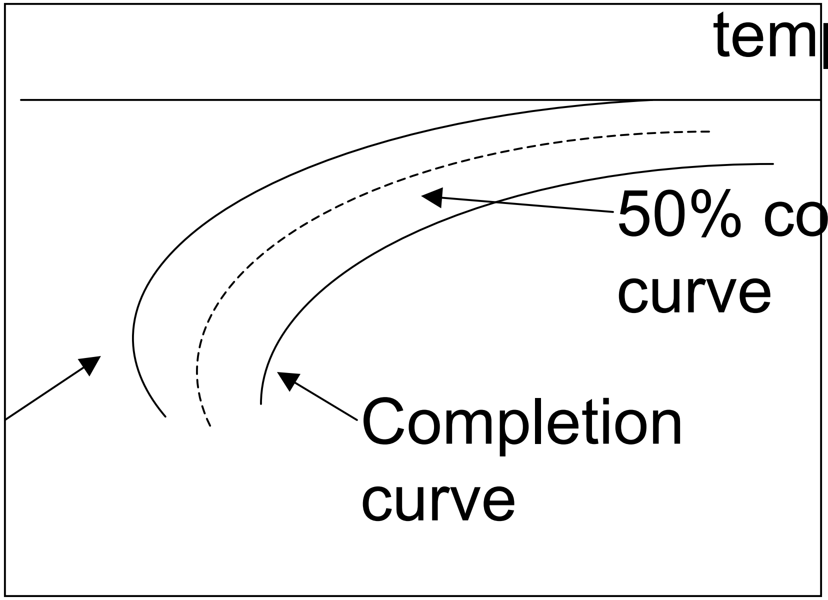
The rate of a transformation (r) is taken as the reciprocal of the time for the transformation to proceed half-way to completion

$$r = 1/t_{0.5}$$

For thermally activated reactions

$$r = A \exp(-Q/kT)$$

# TTT Plots



Transformation temperature

Temperature

50% completion curve

Completion curve

Begin curve

time

# Steel

- Probably the most important engineering material
  - Structures – buildings, bridges
  - Transport – trains, cars, ships
  - Tools – screw drivers, cutting tools, knives
  - Architecture

- Very versatile - properties controlled by heat treatment and alloying

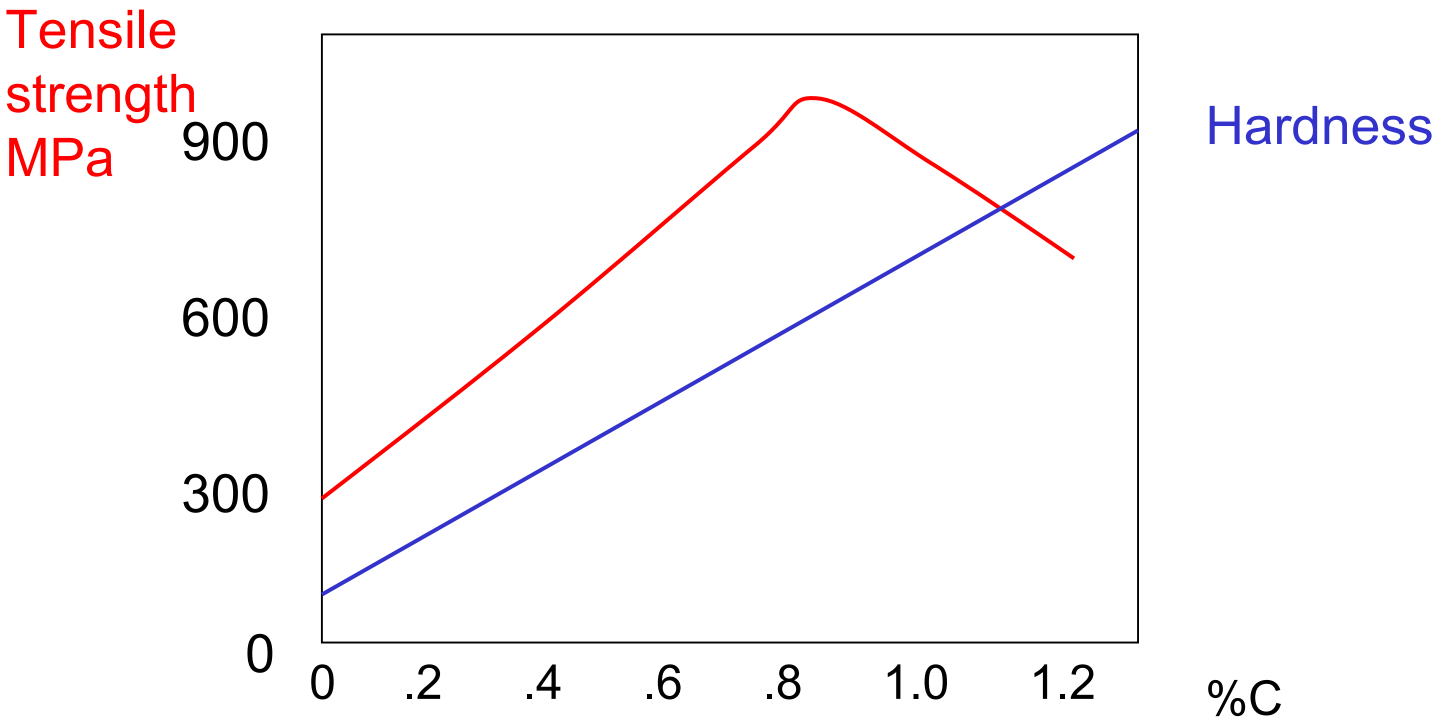
# Types of Steel

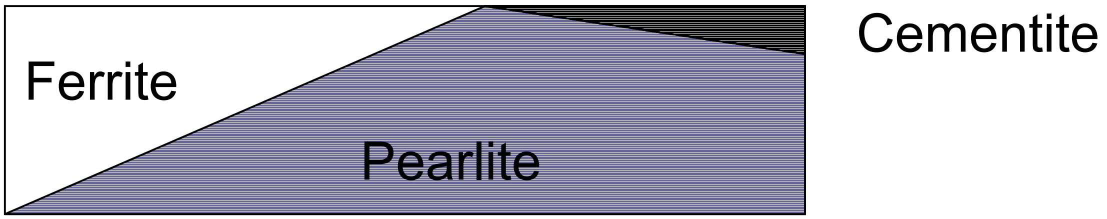
- Carbon steel
  - Low carbon < 0.1% C
  - Medium carbon < 0.25% C
  - High carbon
- Alloy steels
  - Co, Ni, Mo, Ti, V, Nb, Al in varying amounts
- Stainless steels
  - Cr gives good corrosion resistance

# Phases

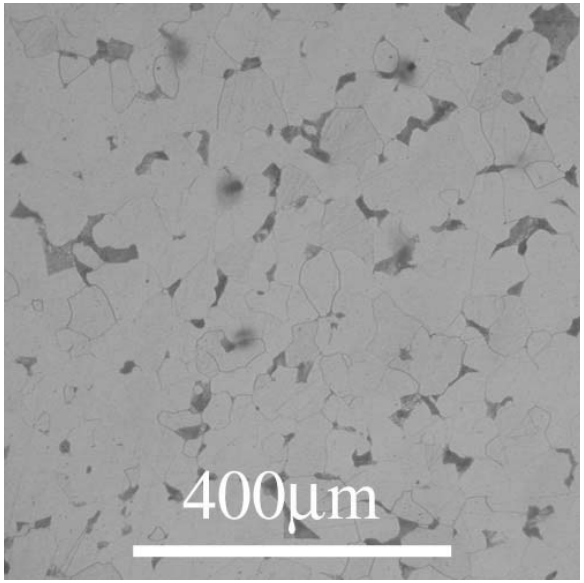
- Ferrite ($\alpha$ steel) bcc – limited solubility of C
- Ferrite ($\delta$ steel) bcc – only relevant at very high T
- Austenite ($\gamma$ steel) fcc – high solubility of C
- Cementite $Fe_3C$ – orthorhombic (6.67% wt C)
- Pearlite – eutectoid intergrowth of ferrite and cementite

# Carbon Steels - Properties



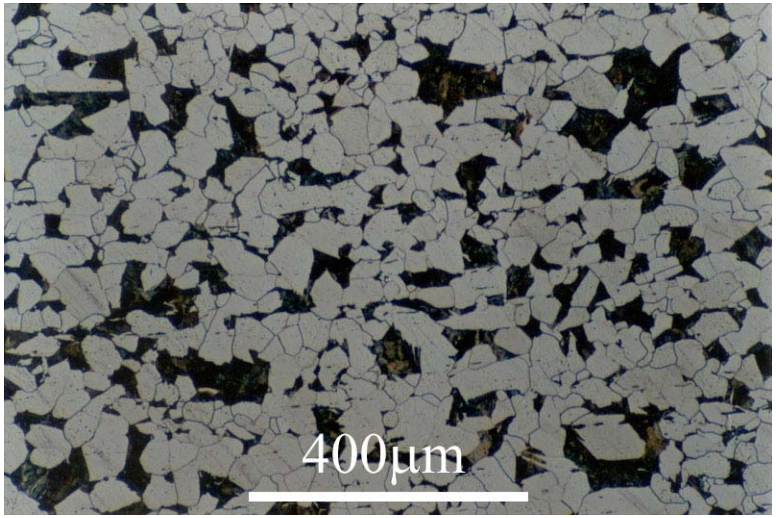


# Micrographs

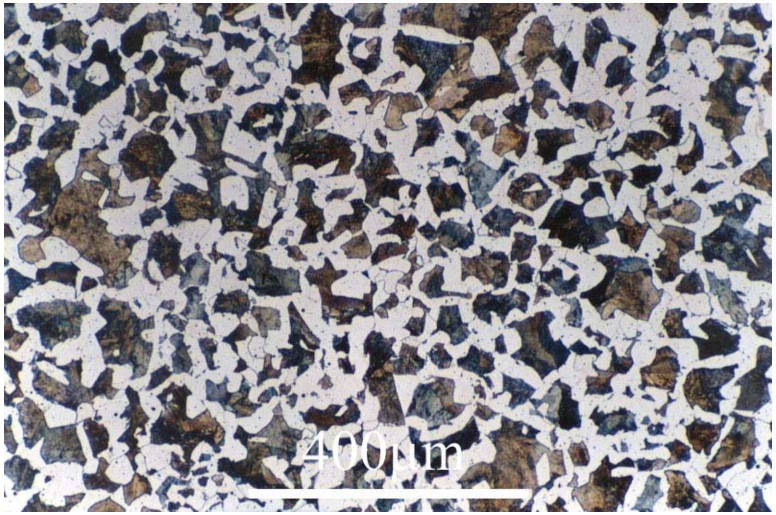


0.1% C

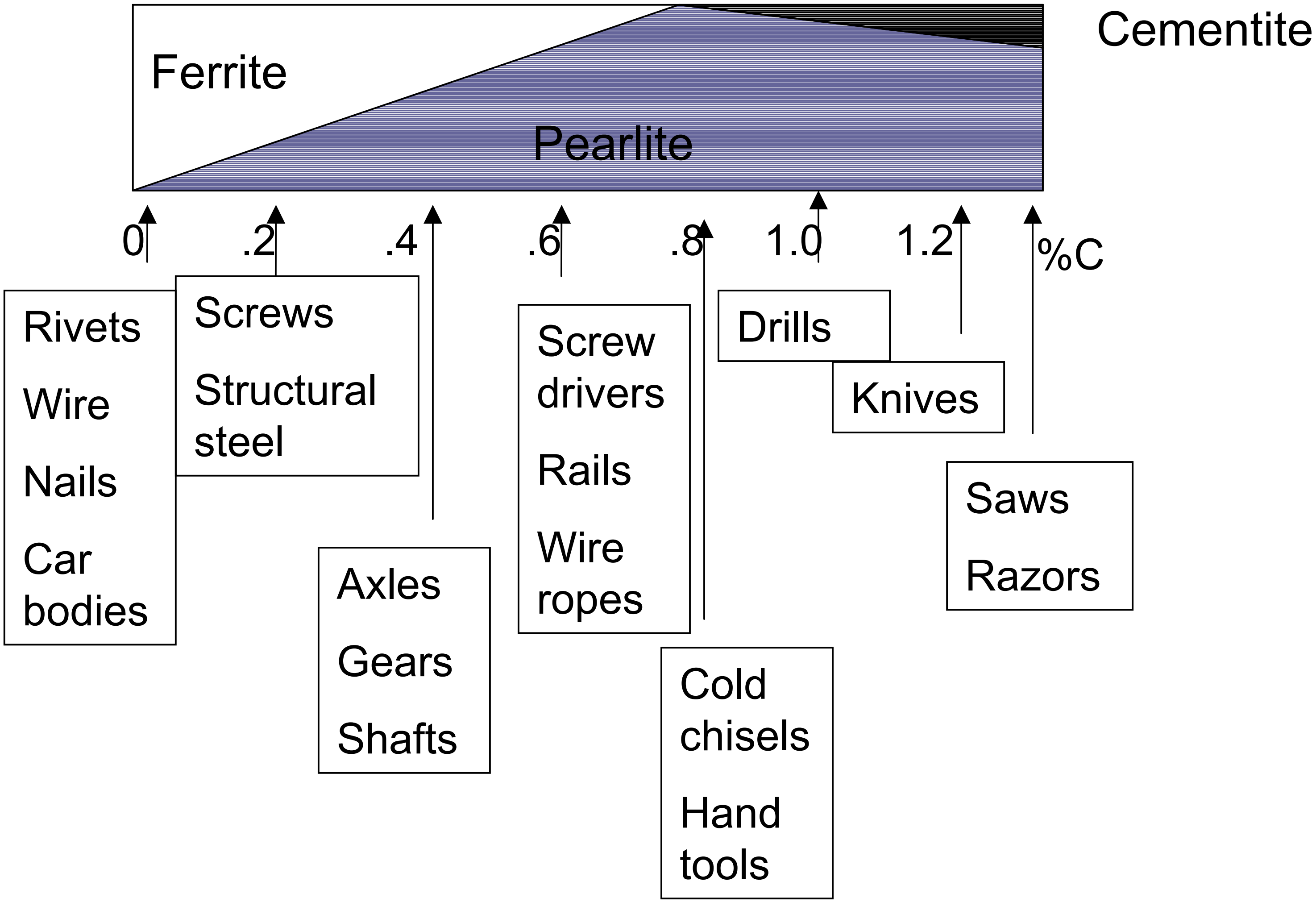
0.2% C



0.4% C



# Carbon Steels - Uses


Ferrite

Pearlite

Cementite

0 .2 .4 .6 .8 1.0 1.2 %C

Rivets

Wire

Nails

Car bodies

Screws

Structural steel

Axles

Gears

Shafts

Screw drivers

Rails

Wire ropes

Cold chisels

Hand tools

Drills

Knives

Saws

Razors

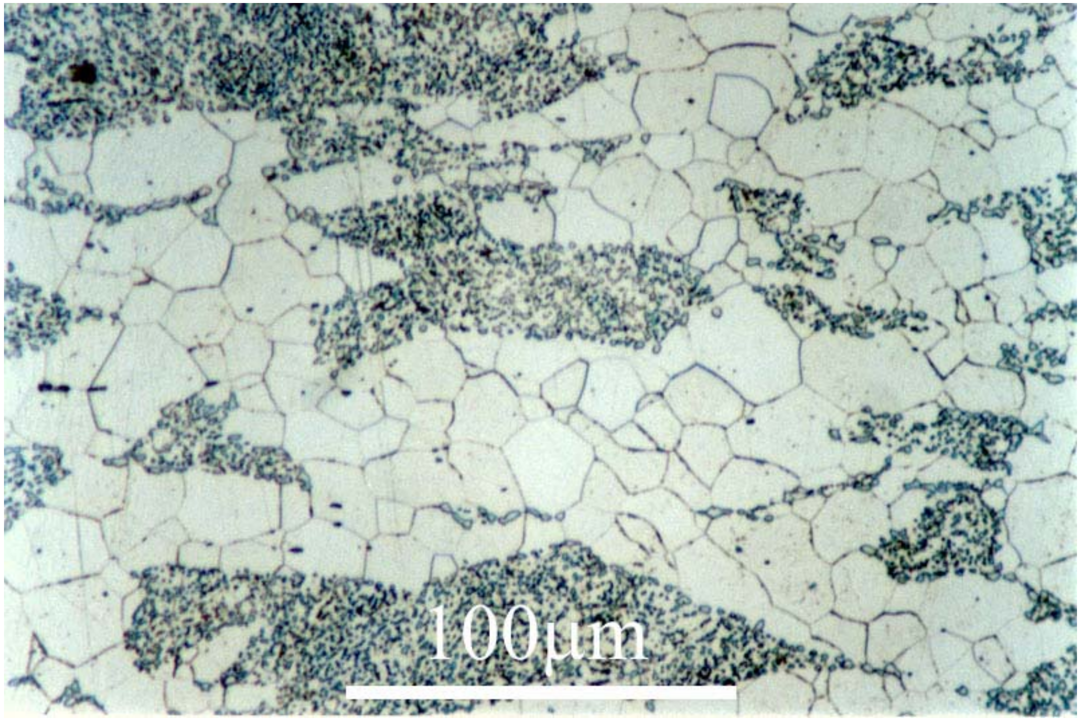
# Carbon Steels

- Spheroidite
  - Formed by holding pearlite at 700 C for 18 – 24 hours
  - $Fe_3C$ particles form spheres in ferrite matrix
  - Reduces high energy phase boundaries

- Bainite
  - Formed by cooling austenite between 200 C and 500C
  - Thin needles of ferrite separated by elongated particles of cementite

- Martensite
  - Non-equilibrium single phase (bcc) resulting from quenching from austenite (fcc)
  - High residual stress

# Spheroidised Steel

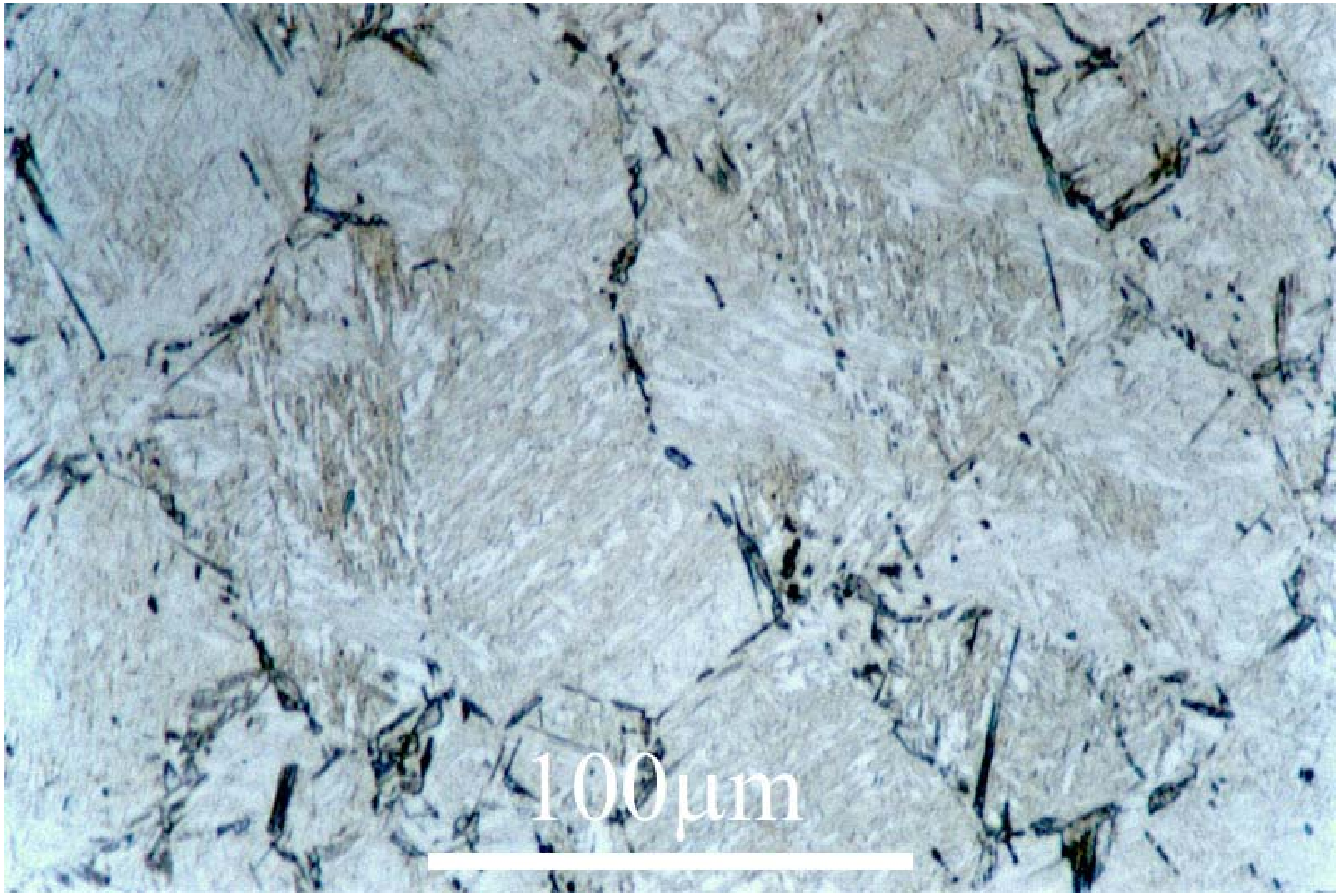


0.3% C annealed just below the transformation temperature.

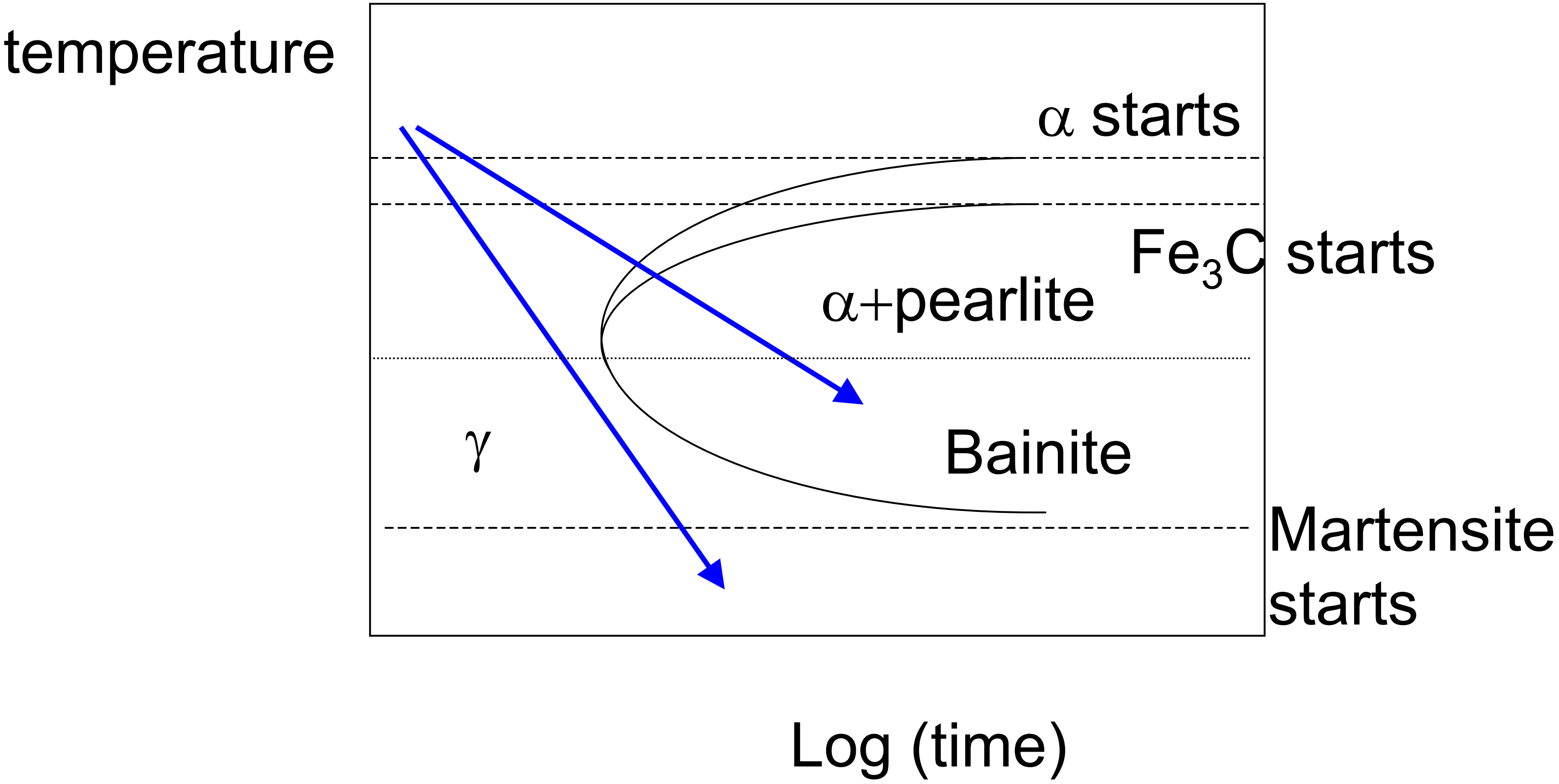
Cementite forms spherical particles

Softer and more ductile than pearlite

# Bainite - Microstructure



# TTT Plot


temperature
α starts
Fe$_3$C starts
α+pearlite
γ
Bainite
Martensite starts
Log (time)

# Quenched Steels - Martensite

$\gamma$ is supercooled too fast for $\alpha$ to nucleate

$\gamma$ is well below transformation T but diffusion is slow. C is stuck in supersaturated solution

At Martensite temperature driving force is large enough to nucleate $\alpha$ – but with trapped C atoms

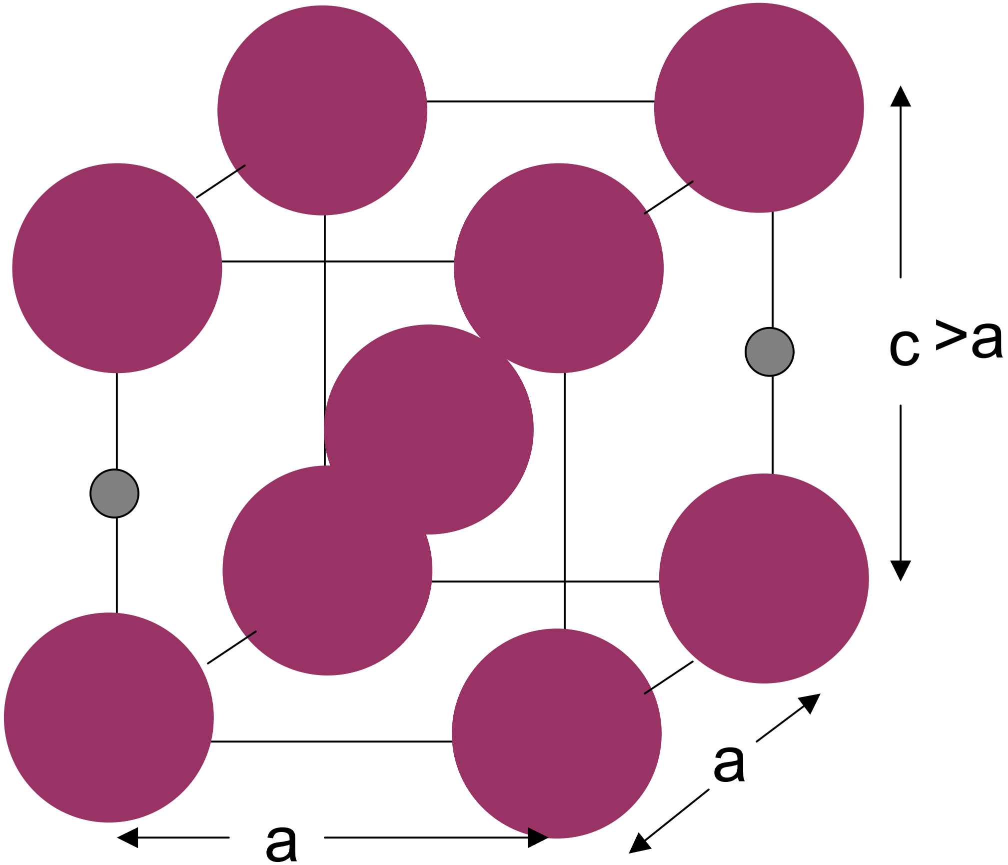
The trapped C atoms distort the bcc unit cell of the a phase in 3 possible directions

The distorted cells lock in large stresses

# Displacive vs Diffusive Transformations

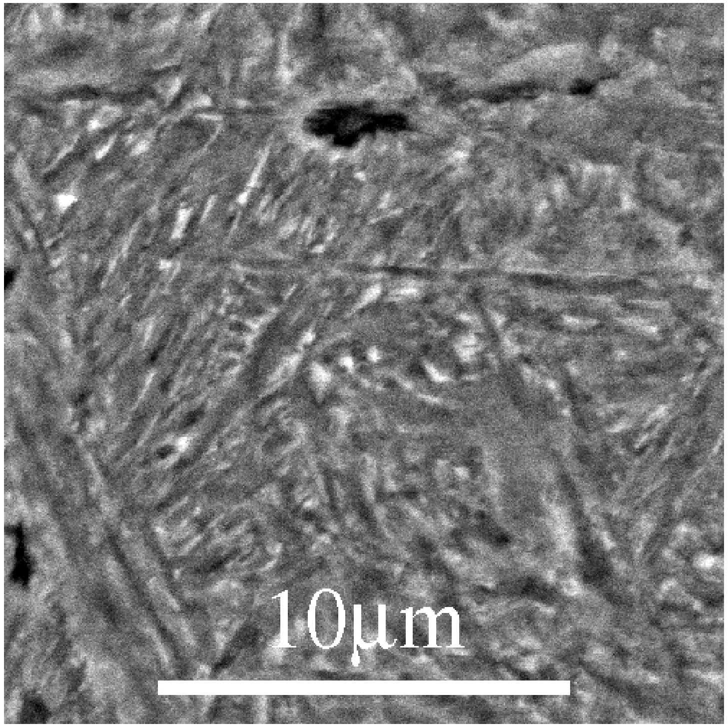
| Displacive | Diffusive |
|---|---|
| Atoms move < interatomic distance | Atoms move 1-$10^6$ interatomic distances |
| Atoms move in precise sequence | Atoms move randomly by hopping from site to site |
| Speed ~ velocity of sound | Speed of transformation depends on temperature |
| Extent of transformation depends on T (not time) | Extent of transformation depends on time and T |
| Composition cannot change | Composition of phases can change |

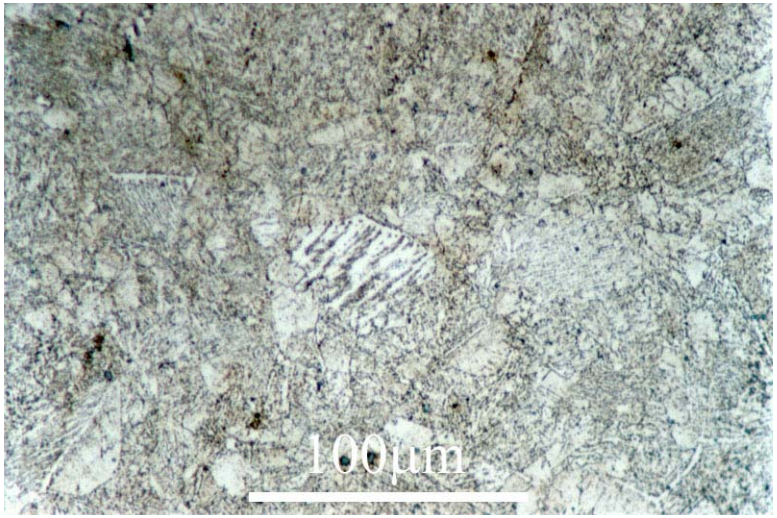
# Martensite - Structure



Distorted BCC

# Martensite - microstructures





Fe, C 0.9 (wt%) steel,
Water quenched from 800 °C

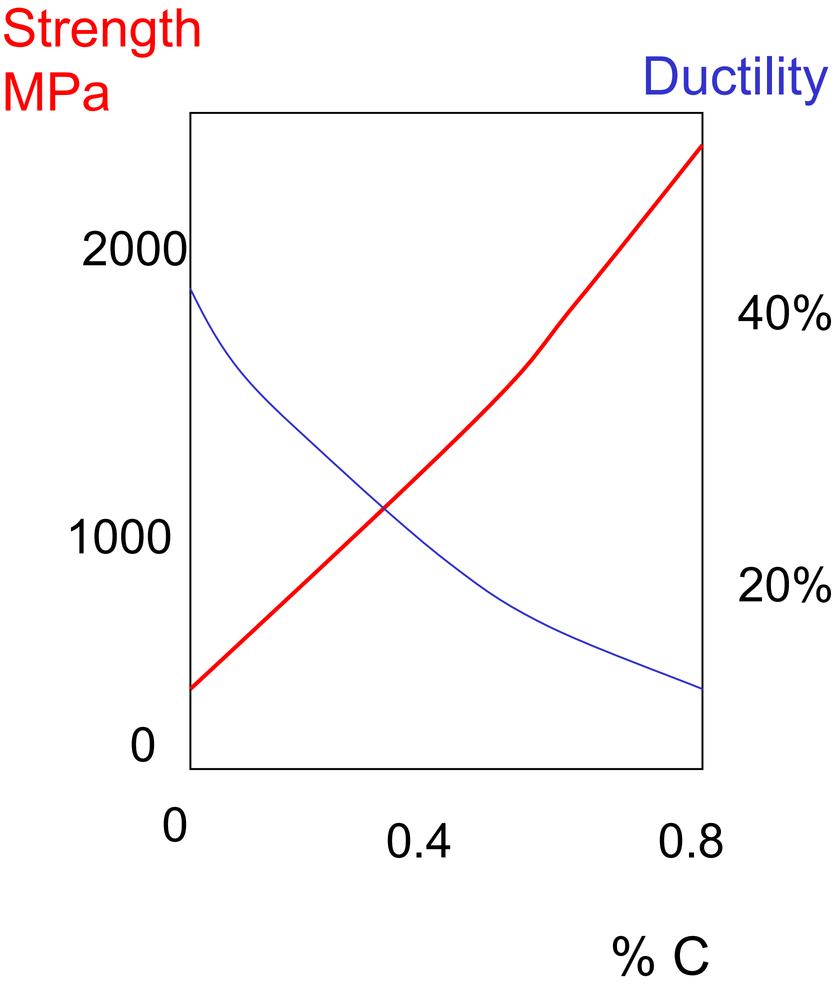
Fe, C 0.75 (wt%) steel,
quenched and tempered

# Martensite - properties

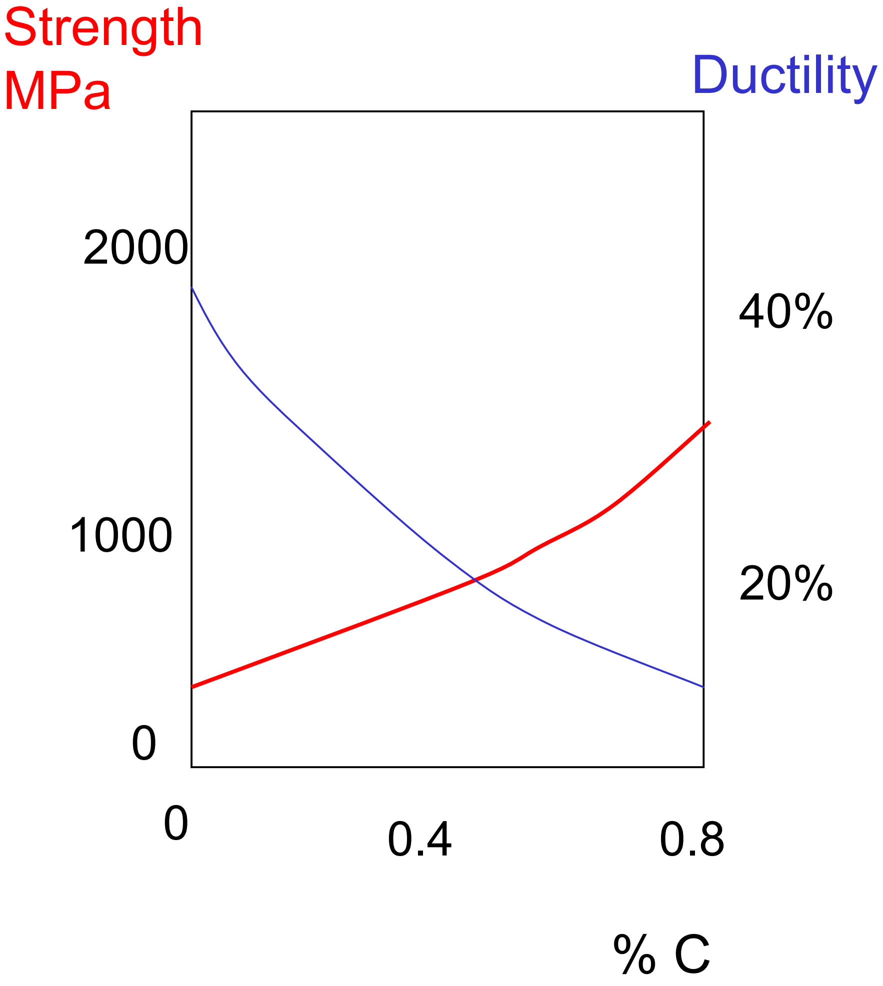
- As quenched martensite is very hard and brittle
  - Many interfaces and strongly varying local stresses
  - Very high resistance to dislocation motion

- Tempering increases ductility and toughness
  - Low temperature < 350 °C - C precipitates as $Fe_3C$ and internal stresses disappear
  - Moderate temperatures 350°C<T<500 °C – C precipitates at $Fe_3C$
  - High temperature T>500 °C $Fe_3C$ particles coarsen and become more widely spaced

# Mechanical Properties



Quenched and tempered steel



Normalized steel

# Alloy Steels

- Alloying elements added to steel to
  - Improve hardenability
    - Alloying increases the CCR permitting the formation of martensite with slower cooling
  - Give solution strengthening and precipitation hardening (Si, Mn)
  - Give corrosion resistance (Cr)
  - Stabilize austenite (Ni)

# Stainless steels

- Based on Fe-Cr-Ni system
- 12% Cr forms tenacious oxide film
- Ni stabilises fcc $\gamma$ phase
- Cr stabilises bcc $\alpha$ phase less strongly
- Types
  - Ferritic
  - Martensitic
  - Austenitic

# Types of Stainless Steel

- Ferritic
  - 13% Cr 0.45% Mn <0.05% C
  - Poor mans stainless steel
  - UTS~500 MPa $\sigma_y$ ~ 350 MPa $\varepsilon_F$ ~ 30%
  - Cutlery, sinks
- Martensitic
  - 13% Cr 0.5% Mn 0.3% C
  - Quench from 1000 C, temper at 150-400 C
  - UTS~1500 MPa $\sigma$y ~ 1100 Mpa
  - Sharp edged tools and springs
- Austenitic
  - 18% Cr 8% Ni <0.1% C
  - ☐ $\gamma$ phase stabilised at room T by Ni
  - ☐ $\sigma_y$ ~ 550 MPa $\varepsilon_F$ ~ 40% ductile, good creep resistant
  - Chemical industries (vats, pipes) Structural parts, decorative work

# Steel - Summary

- Steel is the most common engineering material
- A wide variety of properties can be obtained by additives and processing
- Adding carbon to Fe increases toughness
- Adding Cr to Fe increases corrosion resistance

# Light alloys

- Light alloys are those with a density < 4.5 Mg $m^{-3}$
- 14 pure metals fall into this category but most are not widely used because they are
  - Too chemically active
  - Melting point is too low
- 3 important light metals
  - Aluminium – use exceeds all other metals apart from Fe
  - Magnesium
  - Titanium
- Stiffness to weight ratio and strength/weight ratio of all 3 are superior to steel
- Original usage confined to the aerospace industry – now their use is widespread and growing at 7% per annum

# Properties of Light metals

| Metal | Density (Mg $m^{-3}$) | $T_m$(°C) | Comments |
|---|---|---|---|
| Titanium | 4.50 | 1667 | Excellent creep resistance |
| Yttrium | 4.47 | 1510 | Good strength+ ductility, scarce |
| Scandium | 2.99 | 1538 | Scarce |
| Aluminium | 2.70 | 660 | |
| Strontium | 2.60 | 770 | Reactive in air/water |
| Beryllium | 1.85 | 1287 | Difficult to process, very toxic |
| Calcium | 1.54 | 839 | Reactive in air/water |
| Sodium | 0.97 | 98 | Very reactive in air/water |
| Potassium | 0.86 | 63 | Very reactive in air/water |
| Lithium | 0.53 | 181 | Very reactive in air/water |

# Mechanical Properties of Light Alloys

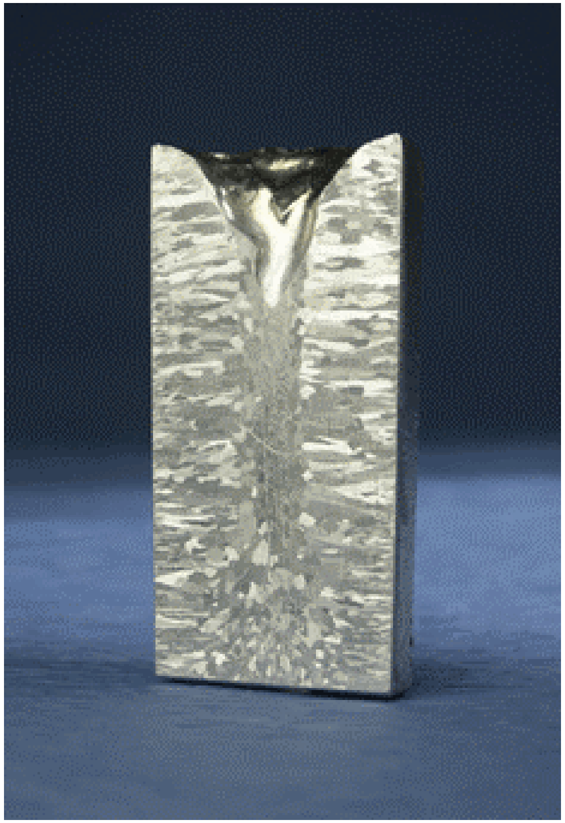
| Alloy | Density $\rho$(Mg m$^{-3}$) | Young's Modulus E(GPa) | Yield $\sigma_y$(Mpa) | $E/\rho$ | $E^{1/2}/\rho$ | $E^{1/3}/\rho$ | $\sigma_y/\rho$ | Creep Temperature (°C) |
|---|---|---|---|---|---|---|---|---|
| Al alloys | 2.7 | 71 | 25-600 | 26 | 3.1 | 1.5 | 9-220 | 150-250 |
| Mg alloys | 1.7 | 45 | 70-270 | 25 | 4.0 | 2.1 | 41-160 | 150-250 |
| Ti alloys | 4.5 | 120 | 170-1280 | 27 | 2.4 | 1.1 | 38-280 | 400-600 |
| (steel) | 7.9 | 210 | 220-1600 | 27 | 1.8 | 0.75 | 28-200 | 400-600 |

# Aluminium Alloys - Uses

- Construction
  - Window frames
  - Doors
- Packaging
  - Drinks cans
  - Al foil
- Transport – weight saving leads to fuel efficiency
  - Cars – from components to complete chassis
  - Boats (QE 2)
  - Aircraft
- Electrical
  - Power lines – reduced weight compensates for lower conductivity (60% of Cu)

# Aluminium Alloys - Properties

- Light $\rho$=2.702 Mg m$^{-3}$
- Low modulus/ high specific modulus E= 71 GPa
- Low strength –improved by alloying
- Low fatigue strength
- Excellent corrosion resistance
  - Forms a thin protective (insulating) coating on exposure to air
- Good thermal and electrical conductor
- Good machining properties
- Ductile at low T (fcc)

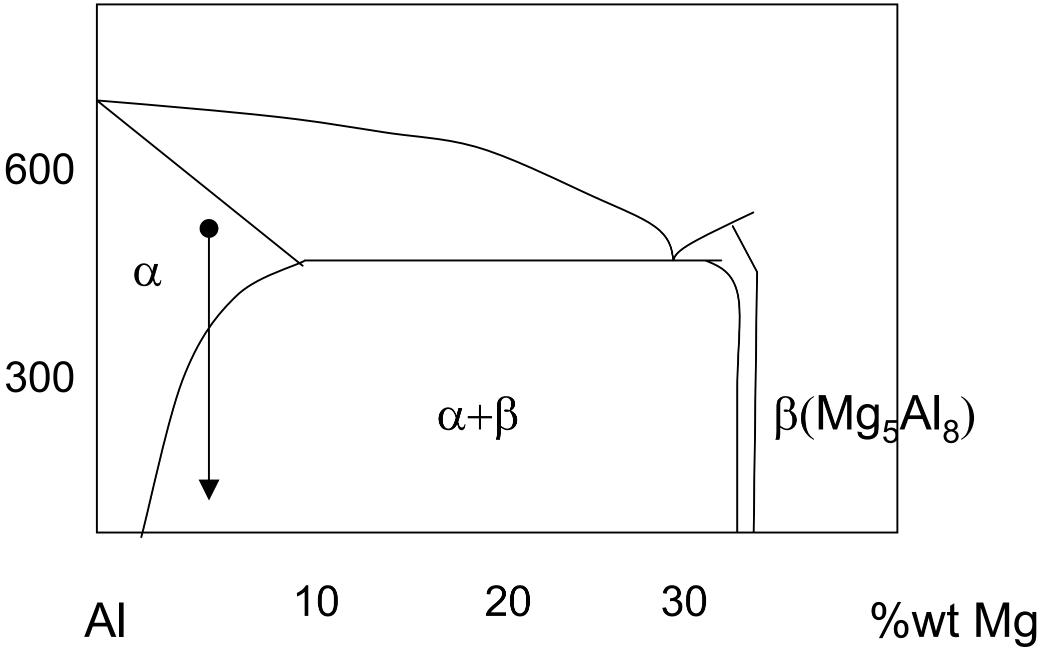


Pure Al forged – grain growth in direction of cooling front

# Aluminium Alloys

| Main Additions | Strengthening | Main Applications |
|---|---|---|
| None | None | Foil, Electrical |
| Cu | $CuAl_2$ | Aircraft wings |
| Mn | Work hardened | General purpose, cookware |
| Si | Si needles | Casting alloy |
| Mg | Work hardened | Common, structural and boats |
| Zn Mg | $ZnMg_2$ | High strength alloy |
| Li | $Li_3Al$ | Low density - aircraft |

# Al/Mg Alloys



High solubility of Mg in Al

Hold at 450 C to dissolve 5.5% Mg

Cool rapidly to room temperature

Miss nose of TTT curve – all Mg remains in supersaturated solution

Solution strengthening

# Al Drinks Cans

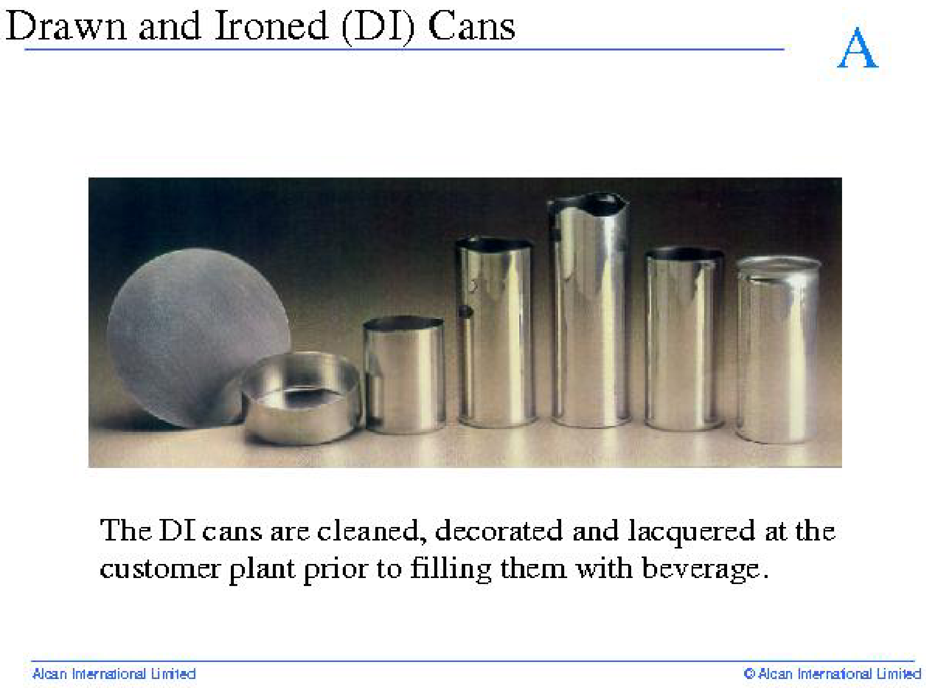
- 8.5 Billion drinks cans manufactured in the UK each year
- 12% global Al output used for drinks cans
- Al suitable because it is
  - Light
  - Corrosion resistant
  - Ductile
- Alloy Al 1%Mg,1%Mn,0.4%Fe,0.2%Si
- More Mg less Mn in cap

# Design Requirements

- Minimise weight (transport costs)
- Minimise material
- Minimise joints
- Strength – must withstand
  - Manufacturing
  - Customers
  - 90 psi (3x car tyres pressure)
- Recycling can save 95% energy costs

# Manufacturing method

- Circle cut from Al sheet
- Formed into shallow cup
- Ironed and punched to form final shape (0.25 mm thick)



Drawn and Ironed (DI) Cans

A

The DI cans are cleaned, decorated and lacquered at the customer plant prior to filling them with beverage.

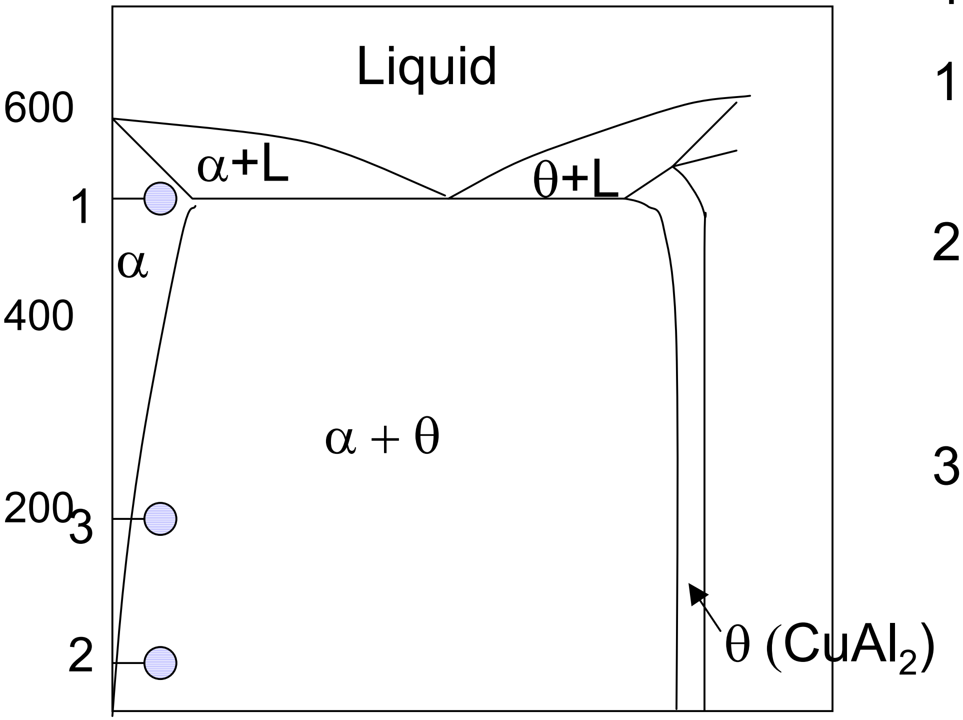
Alcan International Limited

© Alcan International Limited

# Steel cans

- Steel cans 50% heavier than Al
- Dominate for cooked food
  - High pressure
  - High temperatures
- Corrosion can be a problem
  - Polymer coated steel
- Some have Al tops – recycling problem

# Al – Cu Alloys (Duralumin)



4% Cu

1 Hold at 550 C until all Cu is in solution

2 Quench to room T – supersaturated solution

3 Age at 200 C – $CuAl_2$ forms precipitates

[Quenching directly to aging temperature would cause precipitates to form at grain boundaries]

# Age Hardening in Duralumin

- After quenching Cu dispersed randomly in supersaturated solution

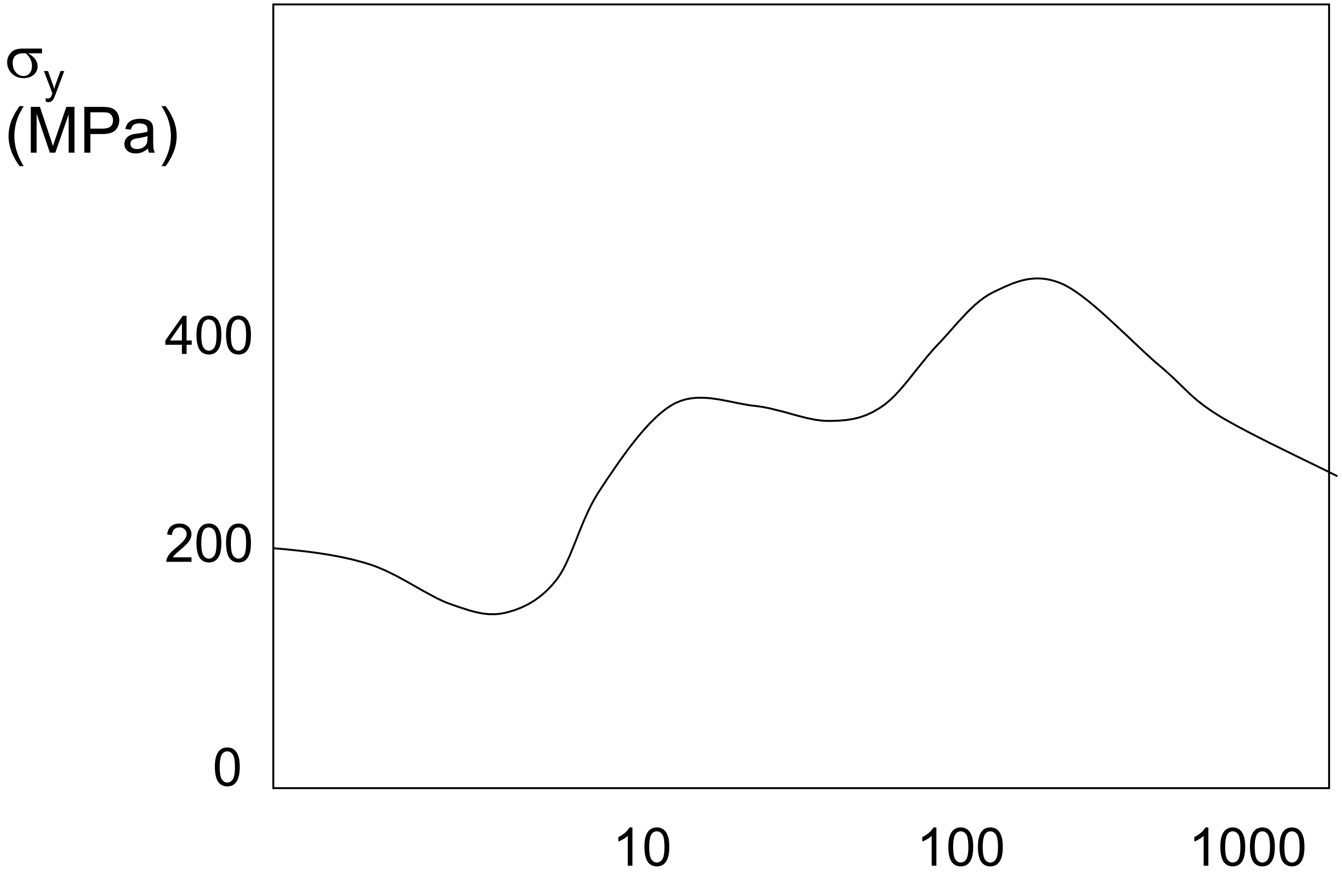
- Initial stages of annealing leads to formation of single layer discs of Cu ~ 10 nm wide
  - Disc faces and edges coherent
  - Disc edges have coherency strain

- Further annealing leads to formation of θ'' phase 10 nm by 100 nm
  - Disc faces and edges coherent
  - Disc edges have coherency strain

- Further annealing leads to formation of θ' phase 100 nm by 10 μm
  - Disc faces and edges coherent
  - Disc edges incoherent

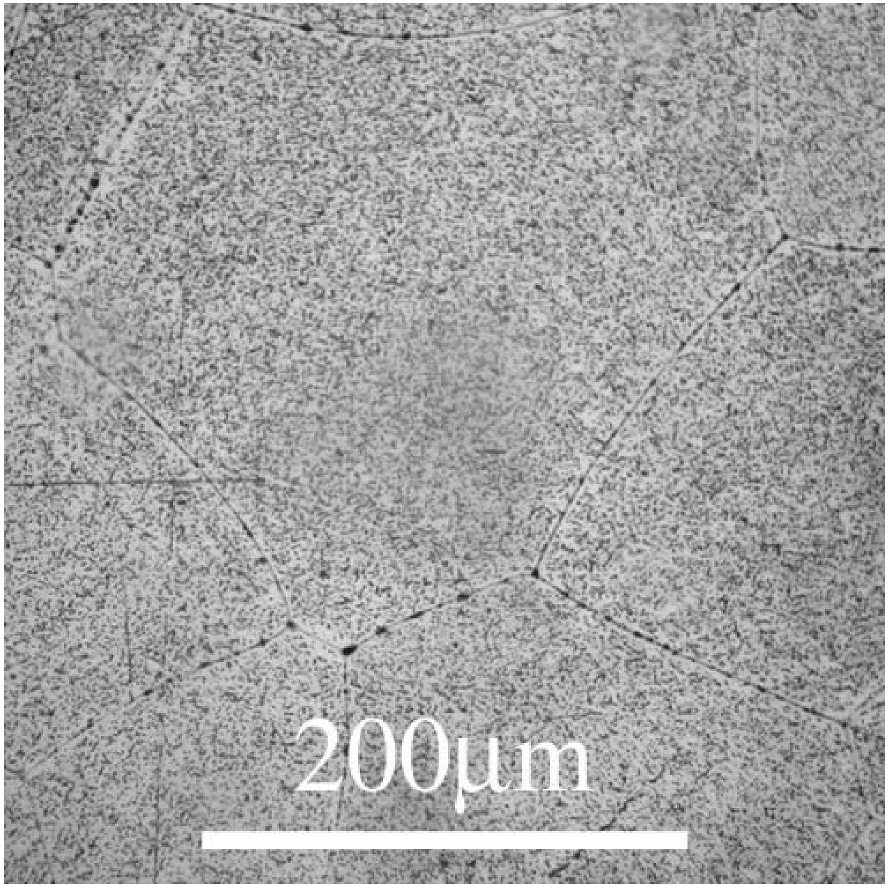
- $AlCu_2$ precipitates form – no coherency strain

# Yield Strength vs Ageing Time



Ageing time (hrs) at 150 C

# Al – Cu Alloys (Duralumin)



Al 96, Cu 4 (wt%), solution treated and overaged - precipitation hardening

# Magnesium Alloys - properties

- Lightest useable metal $\rho$= 1.7Mg m$^{-3}$
- Mg is 33% lighter but more expensive than Al
- Easier to cast and machine than Al
- Impact strength low
- Corrosion resistance very poor
  - anodise, chromate or coat with epoxy resin

# Mg Alloys

- Al, Zn Th –precipitation hardening
- Mn – Corrosion resistance
- Zr – grain refinement

# Ti Alloys

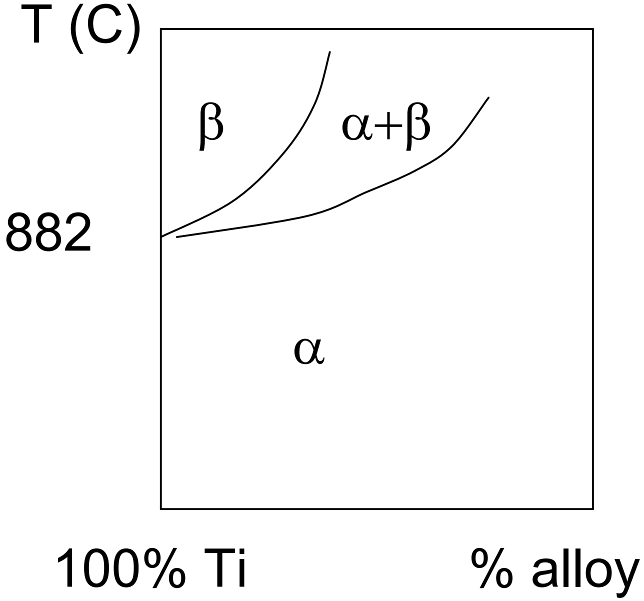
- 80% Ti produced used in aerospace industries
- Production – several hundred thousand tonnes per year (cf 750 million tonnes per year)
- Price would need to decrease by ~ 30% before used in mass-market cars

# Titanium Alloys - Properties

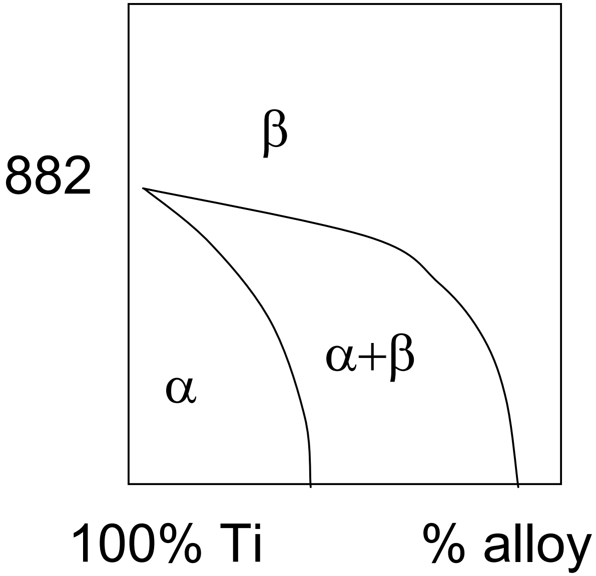
- Outstanding resistance to corrosion in oxidising chloride environments
- High melting temperature (1667 C) therefore good creep resistance
- Susceptable to catching fire – limited to temperatures of 400 C in aero engines
- Density 4.5 Mg $m^{-3}$
- HCP ($\alpha$) at low T – transforms to BCC ($\beta$) at 882 °C

# Alloying Elements

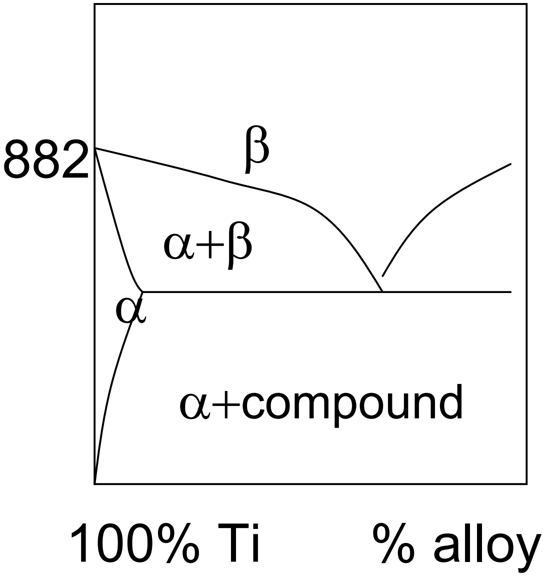
α phase stabilisers
Al O C N



β phase isomorphic stabilisers
Mo, V, Nb, Ta



β phase eutectic stabilisers
Fe Cr Mn



# Alloys

- Near α alloys
  - Al main alloying element
  - Zr, Sn added for solution strengthening
  - Mo added to give some β phase (ductility)

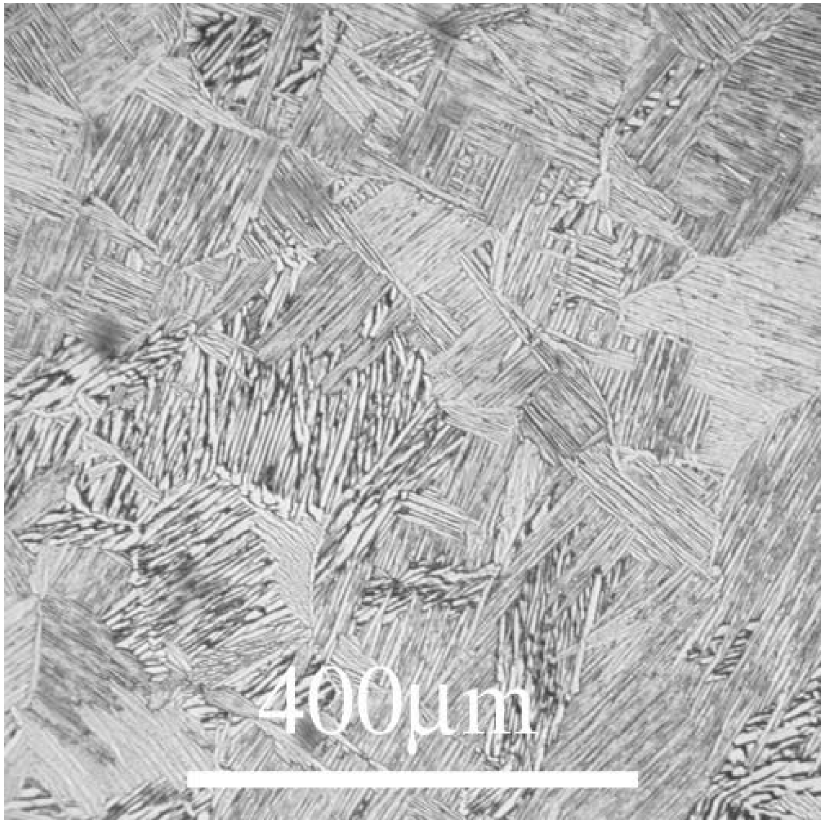
- α + β alloys - Ti 6%Al 4%V
  - Al provides strength and reduces weight. V increases β phase giving good ductility
  - 50% all Ti produced
  - Good strength (1100 MPa), creep resistance and fatigue resistance
  - Ductile to brittle transition (bcc). Brittle fracture at room T
  - Heat treatable – controlled transformation from β to α to improve strength

# Ti alloys

- □ β phase – Ti 35%V 15% Cr
  - Burn resistant alloy, increases operating temperature to 510 C

- Titanium Alumides
  - Laminar structure made up from layers of hexagonal $Ti_3Al$ and tetragonal TiAl
  - High strength, low density, good creep resistance
  - Used extensively for aerospace turbochargers

# Ti - Microstructure



The α hcp phase (light) precipitates out as plates from the high T β bcc phase (dark)

Ti 6% Al 4% V

# Ti - uses

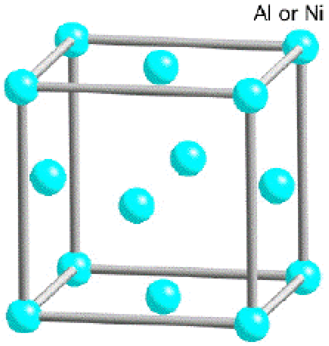
- Jet engines
- Ships propellers
- Chemical plants
- Artificial hips
- Sports equipment
  - Golf clubs and balls
  - Baseball bats
  - Tennis rackets
  - Bicycle frames
- Glasses frames
- Jewellery
- Architecture (Guggenheim museum in Bilbao)

# Ni Based Superalloys

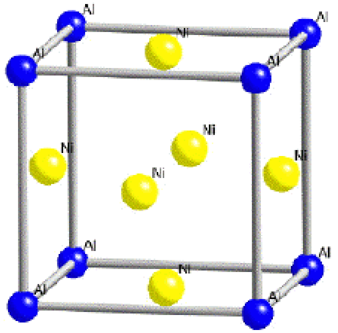
- A superalloy is one that can be used at high T – up to 0.7 $T_m$
- Creep and oxidation resistance are the main design criteria
- Superalloys are based on Fe, Co or Ni
- Ni generally must suitable for aero engine applications

# Alloys

- Alloying metal is either Al or Ti
- 2 phases – very similar lattice parameters



$\gamma$– solid solution with fcc structure



$\gamma$’ – intermetallic compound $Ni_3Al$ with cubic structure. Al on cube edges and Ni in face centres

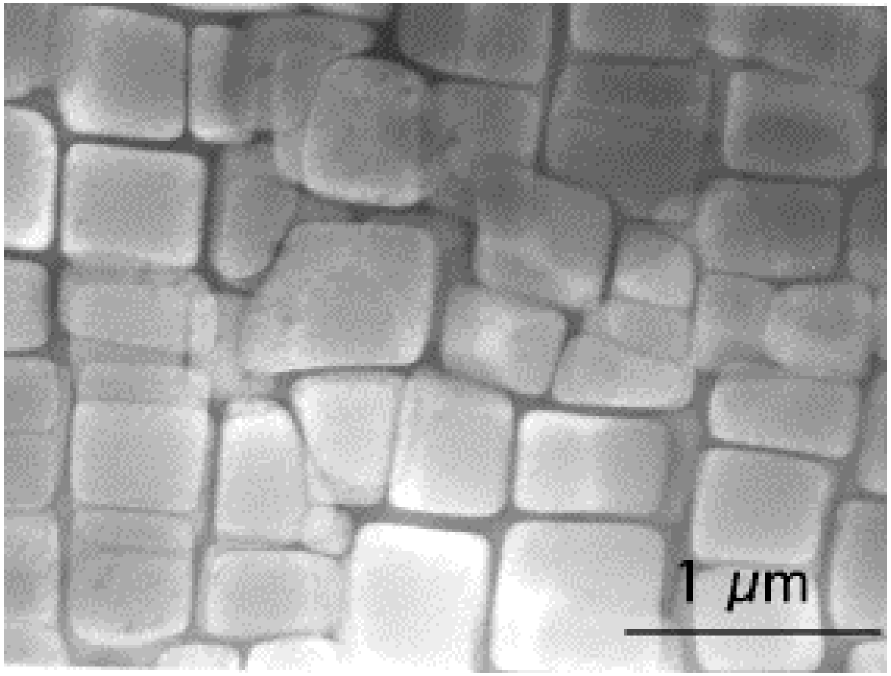
# Properties

- Small lattice misfit between phases leads to small interfacial energy
  - Coarsening driven by interfacial energy
  - Small precipitates stable

- Dislocations find it difficult to move from $\gamma$ into $\gamma'$ because this would disrupt local ordering

- Strength independent of temperature up to 600 C because dislocations trapped on $\gamma'$ phase

# Microstructure



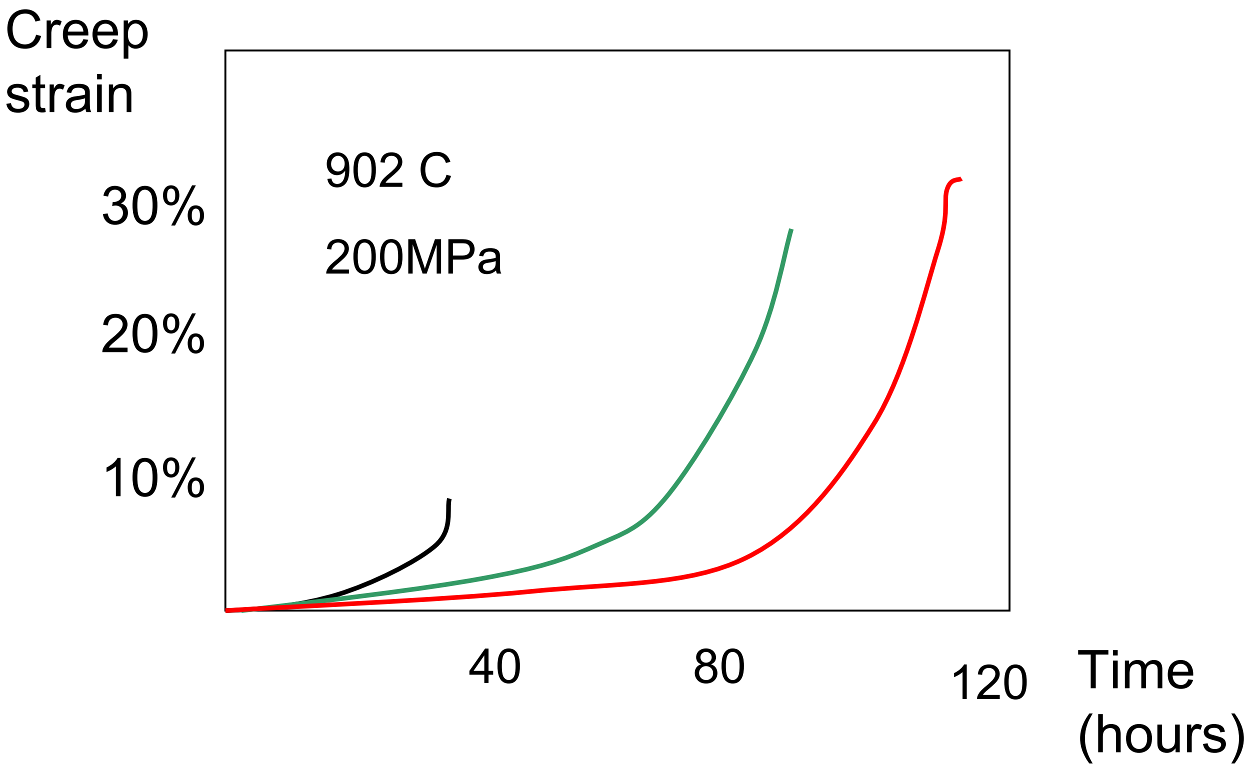
Transmission electron micrograph showing a large fraction of cuboidal γ' particles in a γ matrix. Ni-9.7Al-1.7Ti-17.1Cr-6.3Co-2.3W at%. Hillier, Ph.D. Thesis, University of Cambridge, 1984.

# Alloys

- Al (up to 10%) to add γ’ phase
- Ti – goes into γ’ to give solid solution strengthening
- Cr – goes into γ (Ni) phase to give corrosion resistance and solid solution strengthening
- Co – goes into both γ and γ’ – enhances g’ formation

# Creep Resistance

- Creep resistance improved by
  - – Directional solidification
  - – Single crystal solidification



# What makes metals suitable base for alloys?

- Readily available and cheap
- High melting T
- Cubic crystal structure
- Low density
- Readily dissolves solutes
- Solubility varies strongly with temperature
- Forms hard compounds
- Undergoes an allotropic phase change
- Chemically stable
- Not hazardous