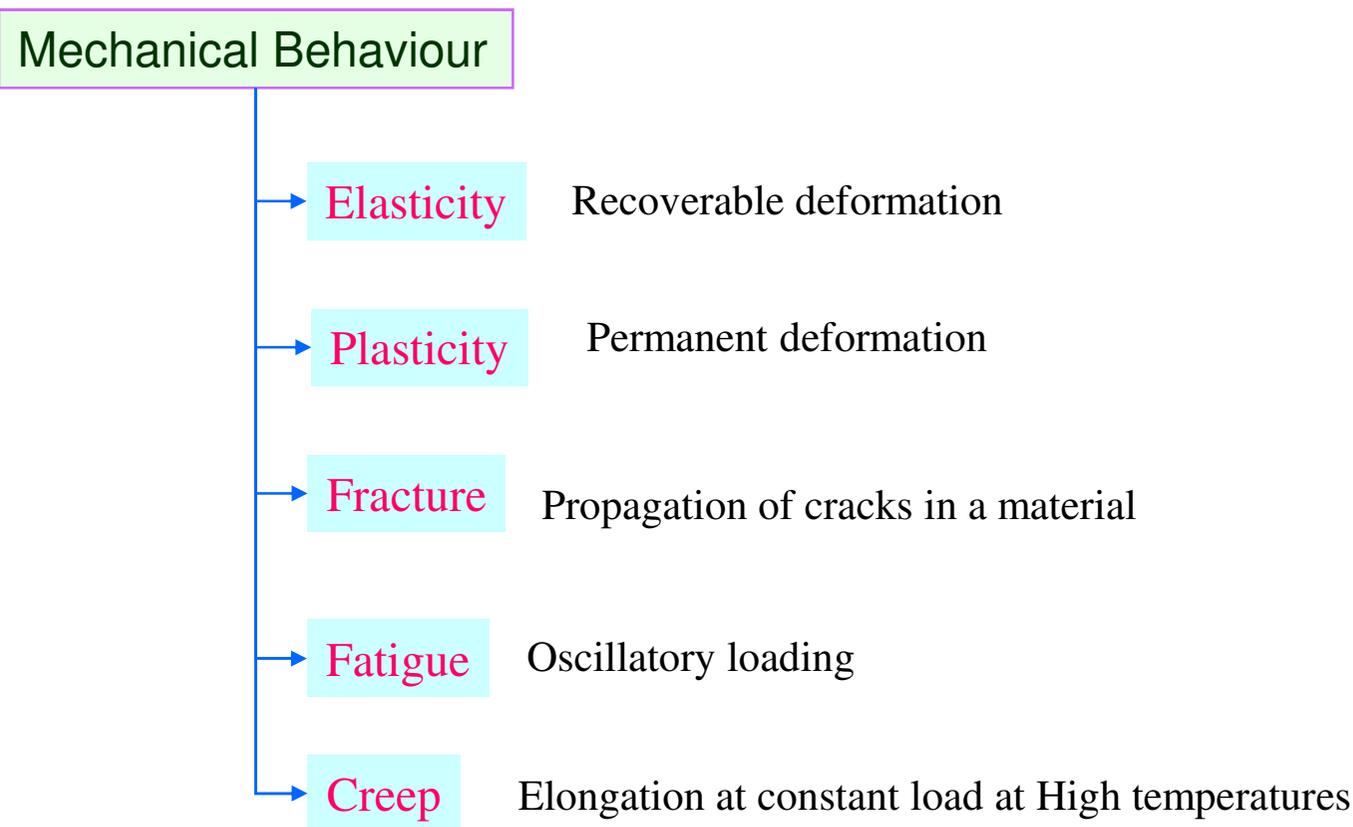


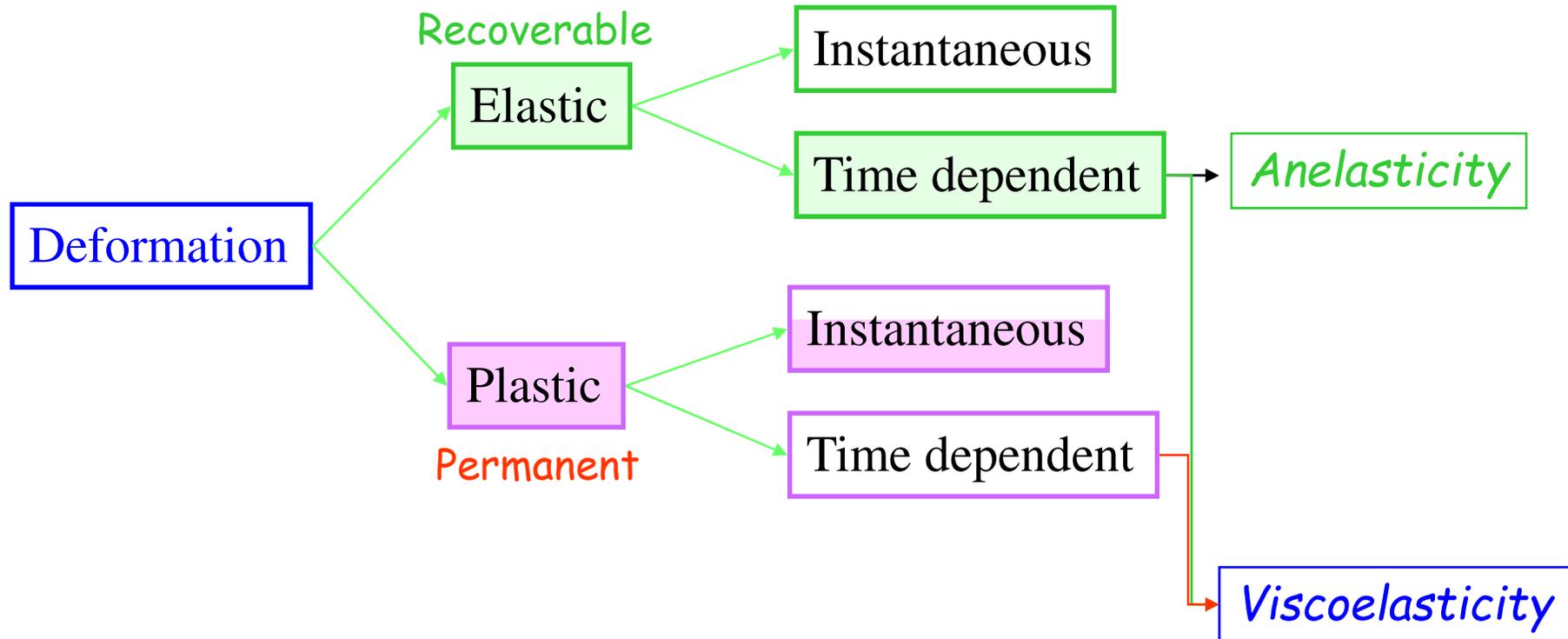
What kind of mechanical behavior phenomena does one have to understand?

- ❑ Phenomenologically mechanical behaviour can be understood as in the flow diagram below.
- ❑ Multiple mechanisms may be associated with these phenomena (e.g. creep can occur by diffusion, grain boundary sliding etc.).
- ❑ These phenomena may lead to the failure of a material.



Note: above is a 'broad' classification for 'convenience'. E.g. Creep is also leads to plastic deformation!

Classification of Deformation Processes

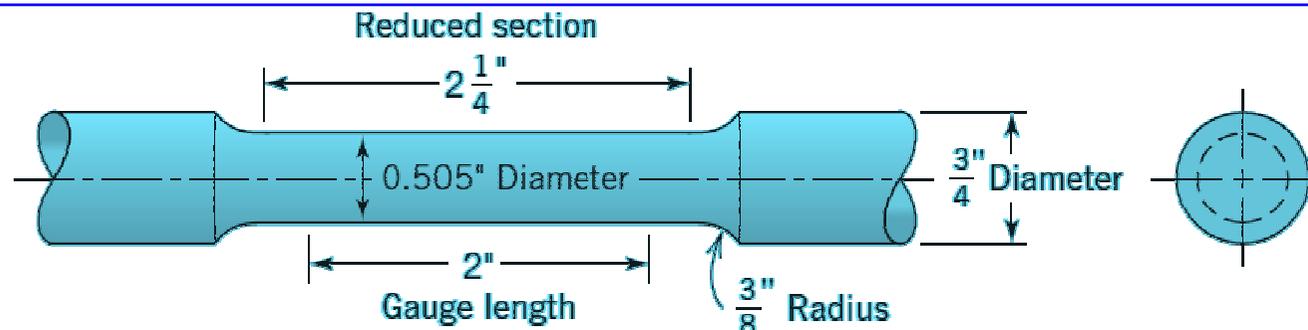


Concepts of Stress & Strain

Solids deform when they are subject to load (can be tensile, compressive or shear). They can maintain or lose their shape

Tension Tests

- ❑ Most common mechanical stress–strain tests which is used to ascertain several mechanical properties of materials.
- ❑ A specimen is deformed, usually to fracture, with a gradually increasing uniaxial tensile load applied along the long axis of a specimen.
- ❑ The tensile testing machine is designed to elongate the specimen at a constant rate, and to continuously and simultaneously measure the instantaneous applied load (with a load cell) and the resulting elongations (using an extensometer).
- ❑ The output of such a tensile test is recorded (usually on a computer) as *load or force versus elongation*



A standard tensile specimen with circular cross section

Concepts of Stress & Strain

Engineering stress : Tensile stress

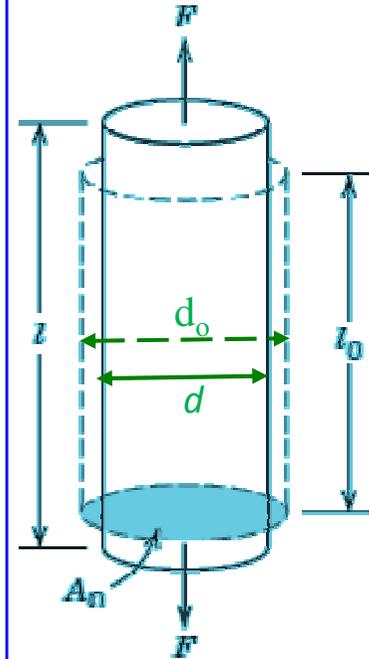
$$\sigma = \frac{F}{A_o} \quad \text{SI Unit: Megapascals}$$

Engineering strain : Tensile strain

$$\varepsilon = \frac{l - l_o}{l_o} = \frac{\Delta l}{l_o}$$

Lateral Strain : $\varepsilon_l = \frac{d - d_o}{d_o} = \frac{\Delta d}{d_o}$ *Strain is always dimensionless*

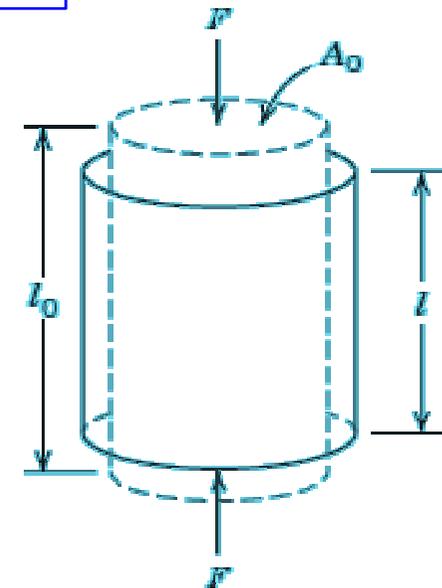
Where l_o and d_o are the original dimensions before any load is applied; l and d are the instantaneous dimensions; Δl and Δd are changes in dimensions.



Compression Tests

Test is conducted in a manner similar to the tensile test, except that the force is compressive and the specimen contracts along the direction of the stress.

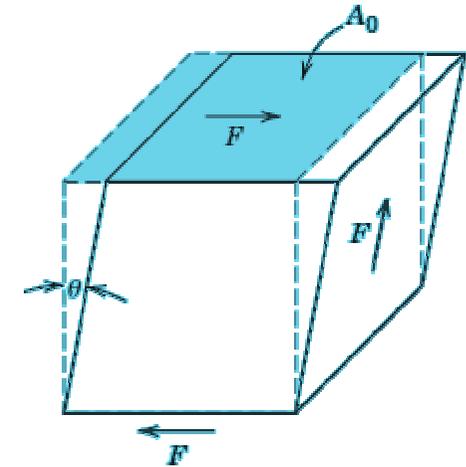
By convention, a compressive force is taken to be negative, which yields a negative stress. Furthermore, since l_o is greater than l , compressive strains is also negative



Concepts of Stress & Strain

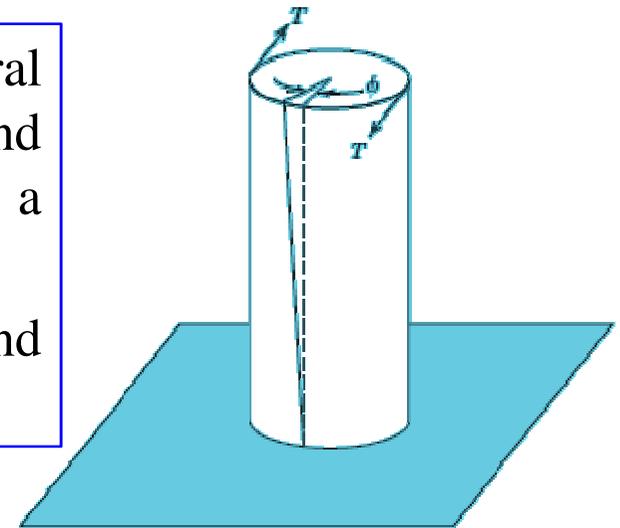
Shear Tests

- ❑ For tests performed using a pure shear force, the shear stress is computed according to
- ❑ Shear stress $\tau = \frac{F}{A_o}$ Shear strain $\gamma = \tan \theta$
- ❑ Where F is the load or force imposed parallel to the upper and lower faces, each of which has an area of A_o . The shear strain γ is defined as the tangent of the strain angle θ .



Torsional Tests

- ❑ Torsion is a variation of pure shear, wherein a structural member is twisted about the longitudinal axis of one end of the member relative to the other end producing a rotational motion .
- ❑ Shear stress τ is a function of the applied torque T and shear strain is related to the angle of twist ϕ .



Tensile Properties

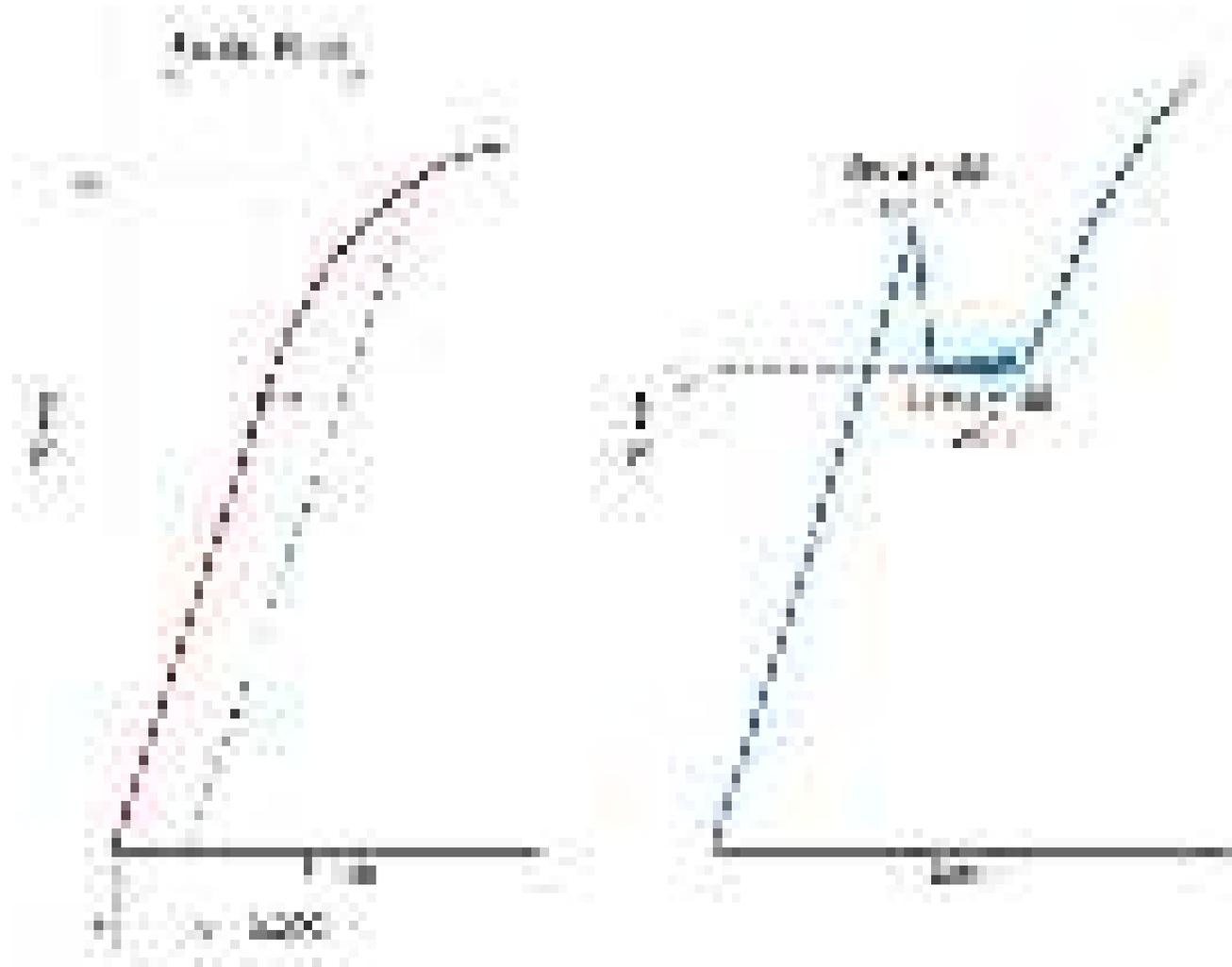
Yielding : Yielding is the beginning of plastic deformation

proportional limit : The point at which there is a deviation from the straight line 'elastic' regime

Yield Strength (σ_y)

- Stress at which noticeable plastic deformation has occurred.
- The magnitude of the yield strength for a metal is a measure of its resistance to plastic deformation.
- For metals that experience gradual elastic–plastic transition, a curve is drawn parallel to the elastic line at a given strain like 0.2% (= 0.002) to determine the yield strength.
- For materials having a nonlinear elastic region the yield strength is defined as the stress required to produce some amount of strain ($\epsilon = 0.005$)
- Some materials elastic–plastic transition is very well defined and occurs abruptly (yield point phenomenon). For these materials yield strength is taken as the average stress that is associated with the lower yield point

Tensile Properties

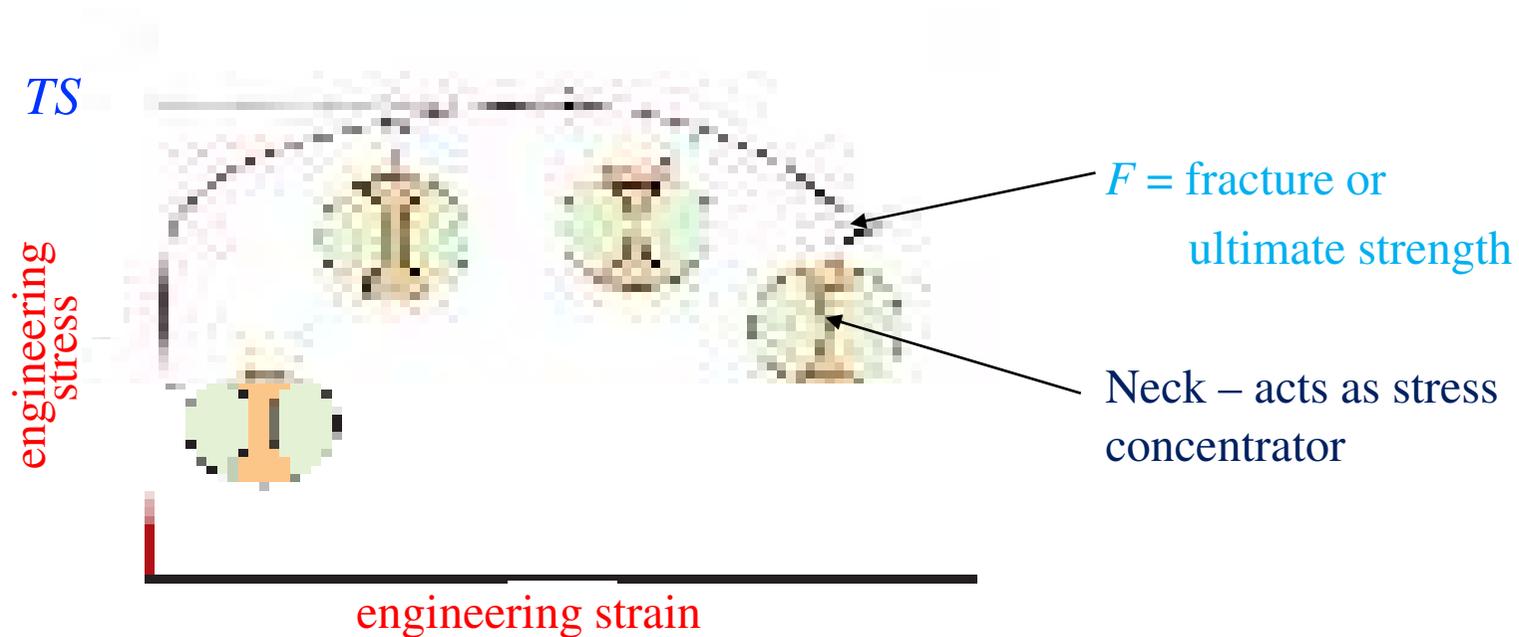


Typical stress– strain behavior for a metal showing elastic and plastic deformations, the proportional limit P , and the yield strength as determined using the 0.002 strain offset method.

Representative stress–strain behavior found for some steels demonstrating the yield point phenomenon.

Tensile Strength (TS)

- ❑ The tensile strength TS (MPa or psi) is the stress at the maximum on the engineering stress–strain curve

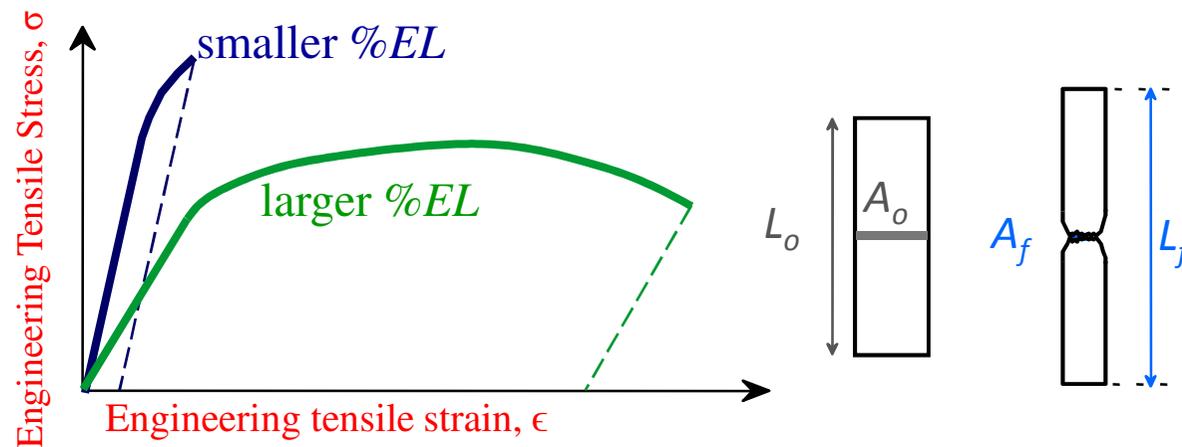


- ❑ Metals : This is the point when noticeable necking starts.
- ❑ Ceramics : Crack propagation starts at this point.
- ❑ Polymers : Polymer backbones are aligned and about to break at this point.

Ductility, %Elongation

- ❑ Ductility may be expressed quantitatively as either *percent elongation* or *percent reduction in area*.
- ❑ The percent elongation %EL is the percentage of plastic strain at fracture

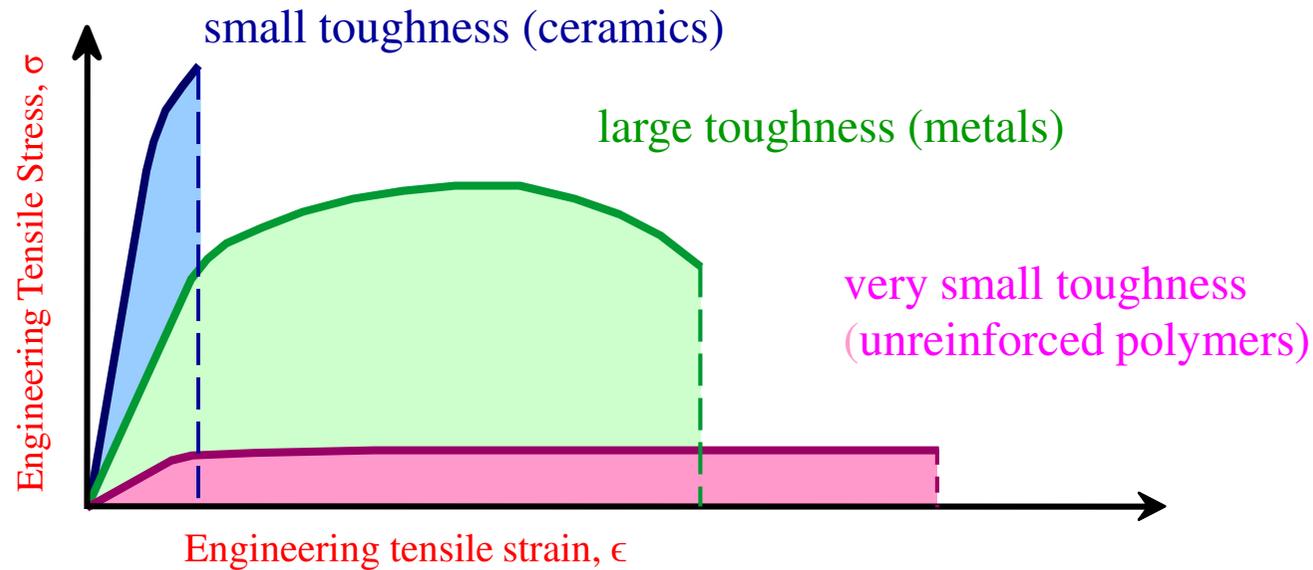
$$\%EL = \frac{L_f - L_o}{L_o} \times 100$$



- ❑ Another ductility measure:
$$\%RA = \frac{A_o - A_f}{A_o} \times 100$$

Toughness

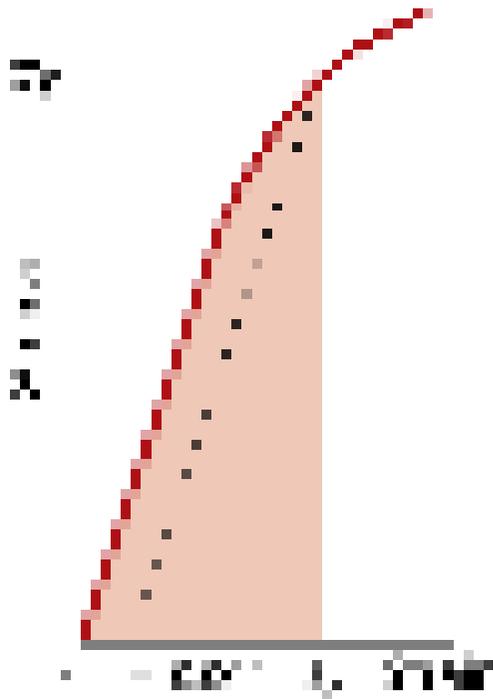
- ❑ Energy required to break a unit volume of material
- ❑ It can be approximated by the area under the stress-strain curve up to the point of fracture.



- ❑ For Brittle fracture: elastic energy
- ❑ For **Ductile** fracture: elastic + plastic energy

Resilience, U_r

- ❑ Resilience is the capacity of a material to absorb energy when it is deformed elastically and then, upon unloading, to have this energy recovered.
- ❑ Modulus of resilience U_r is the strain energy per unit volume required to stress a material from an unloaded state up to the point of yielding.



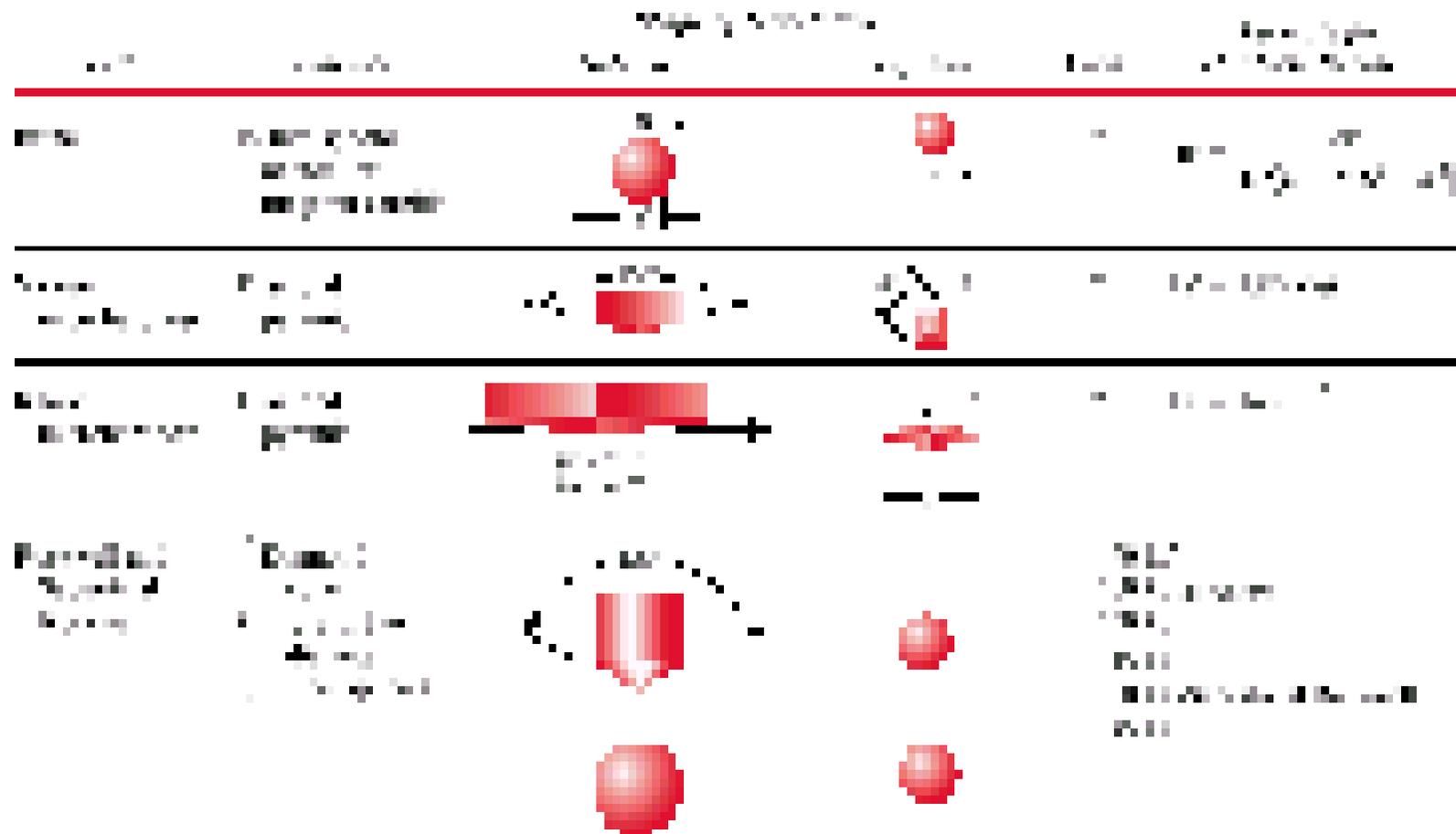
$$U_r = \int_0^{\epsilon_y} \sigma d\epsilon$$

If we assume a linear stress-strain curve this simplifies to

$$U_r \cong \frac{1}{2} \sigma_y \epsilon_y$$

Hardness

- ❑ Resistance to permanently indenting the surface.
- ❑ Large hardness means:
 - ✓ resistance to plastic deformation or cracking in compression.
 - ✓ better wear properties



True Stress & Strain

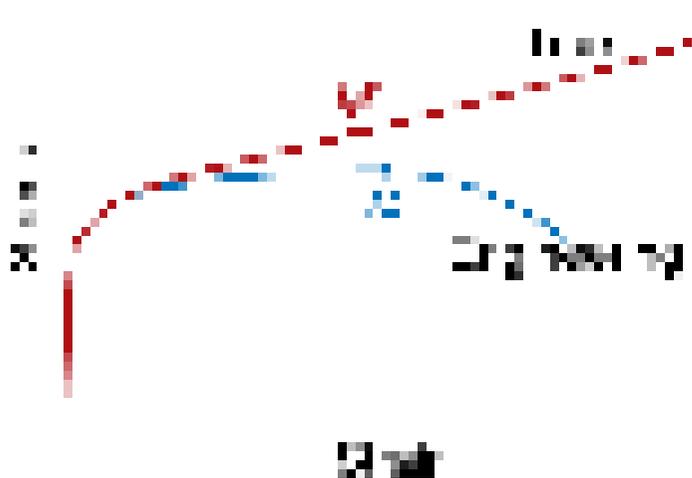
True stress : $\sigma_{True} = \frac{F}{A_i}$

True strain : $\epsilon_{True} = \ln \frac{l_i}{l_o}$

The relation with Eng. Stress and Eng strain is

$$\sigma_T = \sigma (1 + \epsilon)$$
$$\epsilon_T = \ln (1 + \epsilon)$$

Necking begins at point M on the engineering curve, which corresponds to on the true curve. The “corrected” true stress–strain curve takes into account the complex stress state within the neck region.

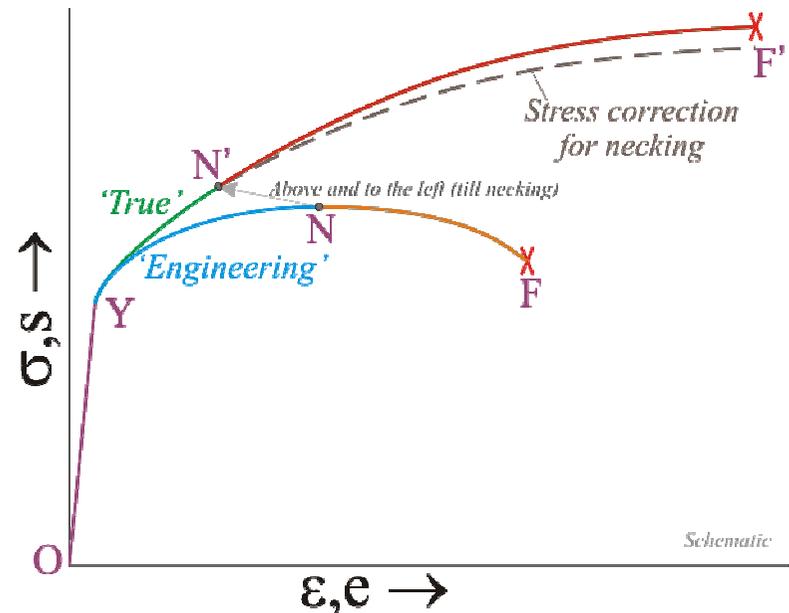
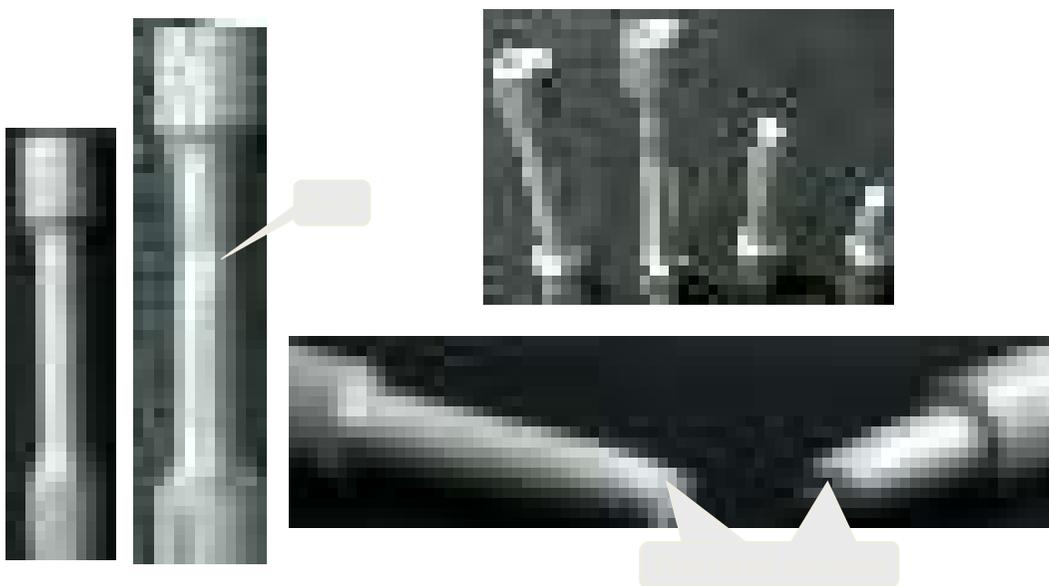


A comparison of typical tensile engineering stress–strain and true stress–strain behaviors

What happens after necking?

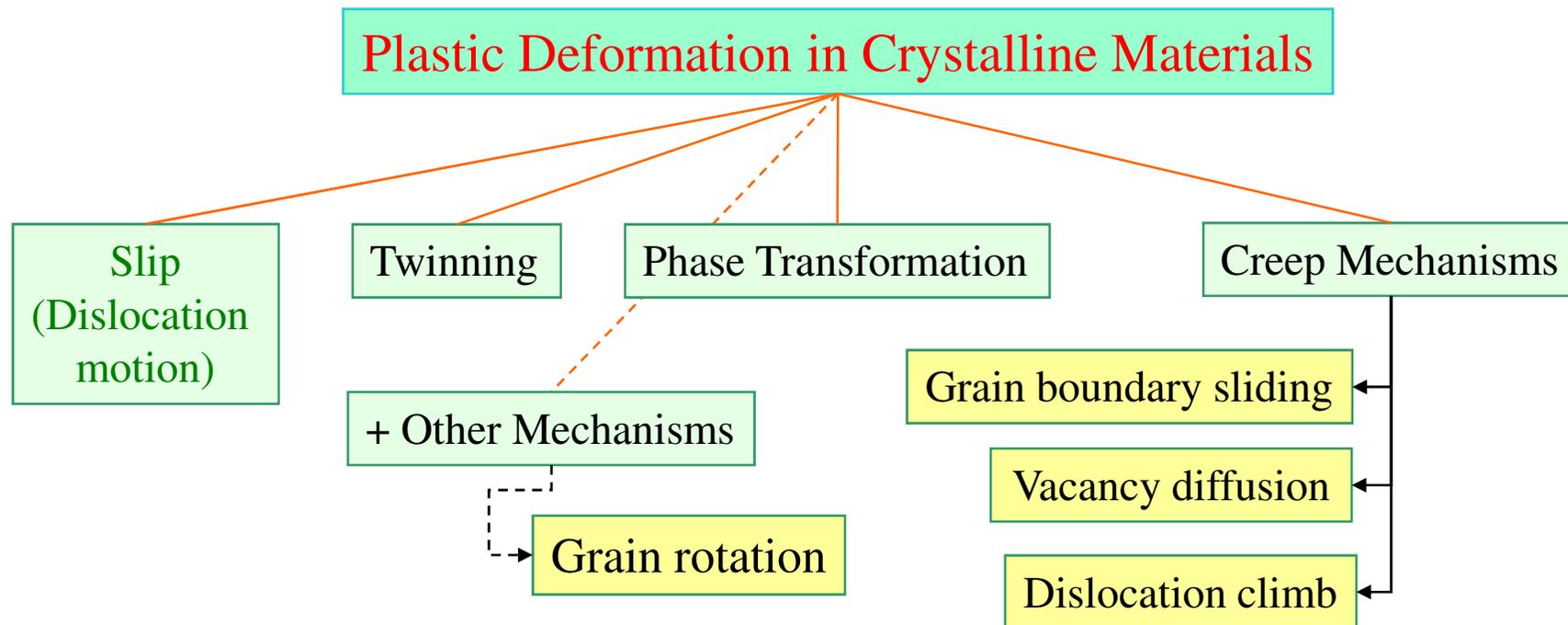
Following factors come in to picture due to necking:

- ❑ Till necking the deformation is ~uniform along the whole gauge length.
- ❑ Till necking points on the σ - ϵ plot lie to the left and higher than the s-e plot (as below).
- ❑ After the onset of necking deformation is localized around the neck region.
- ❑ Formulae used for conversion of 'e' to ' ϵ ' and 's' to ' σ ' cannot be used after the onset of necking. $\sigma = s(1+e)$ $\epsilon = \ln(1+e)$
- ❑ Triaxial state of stress develops and uniaxiality condition assumed during the test *breaks down*.
- ❑ Necking can be considered as an instability in tension.
- ❑ Hence, quantities calculated after the onset of necking (like fracture stress, σ_F) has to be corrected for: (i) **triaxial state of stress**, (ii) **correct cross sectional area**.



Mechanisms/modes of plastic deformation

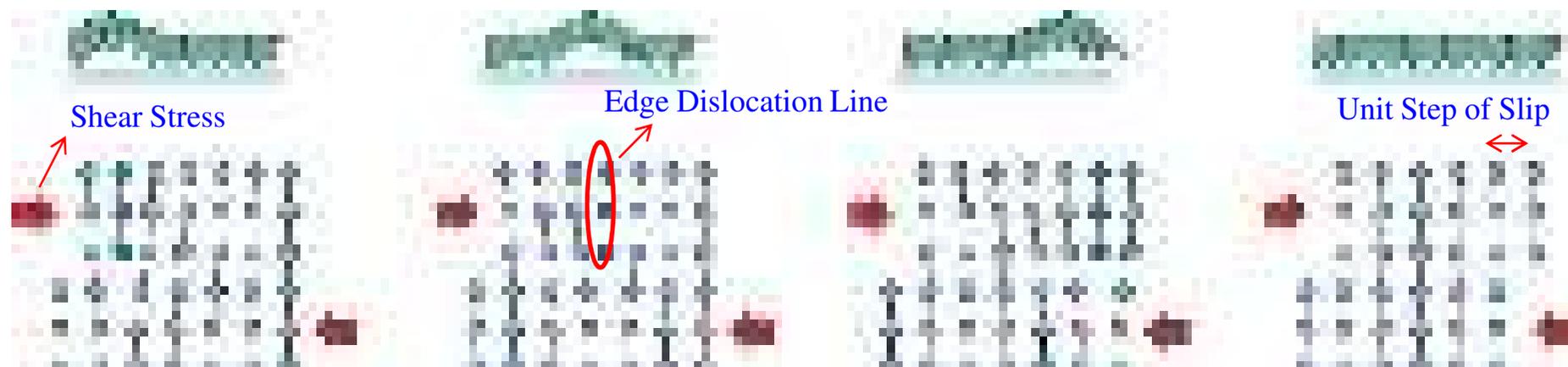
- ❑ Plastic deformation in crystalline solid is accomplished by means of various processes mentioned below; among which slip is the most important mechanism.
- ❑ Plastic deformation of crystalline materials takes place by mechanisms which are very different from that for amorphous materials (glasses). Plastic deformation in amorphous materials occur by other mechanisms including flow (~viscous fluid) and shear banding.



Plastic deformation by dislocation Motion (SLIP)

Basic concepts

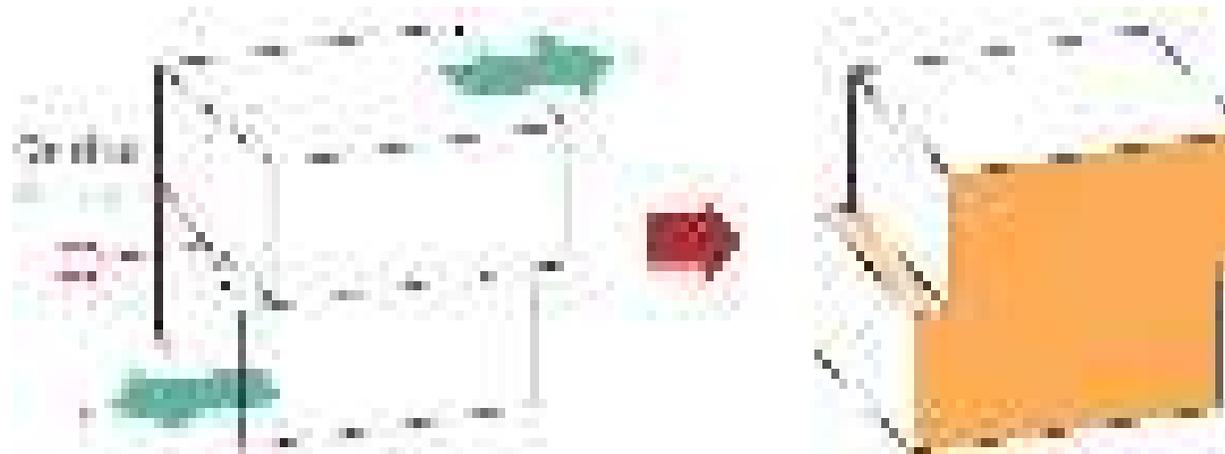
- ❑ SLIP is the most important mechanism of plastic deformation . At low temperatures (especially in BCC metals) twinning may also become important.
- ❑ At the fundamental level plastic deformation (in crystalline materials) by slip involves the motion of dislocations on the slip plane (*creating a step of Burgers vector*).
- ❑ Slip is caused by **shear stresses** (at the level of the slip plane). Hence, a purely hydrostatic state of stress cannot cause slip.
- ❑ A slip system consists of a slip direction lying on a slip plane.
- ❑ Slip is analogous to the mode of locomotion employed by a caterpillar



Direction of Dislocation Motion



Edge dislocation line moves **parallel** to applied stress



Screw dislocation line moves **perpendicular** to applied stress

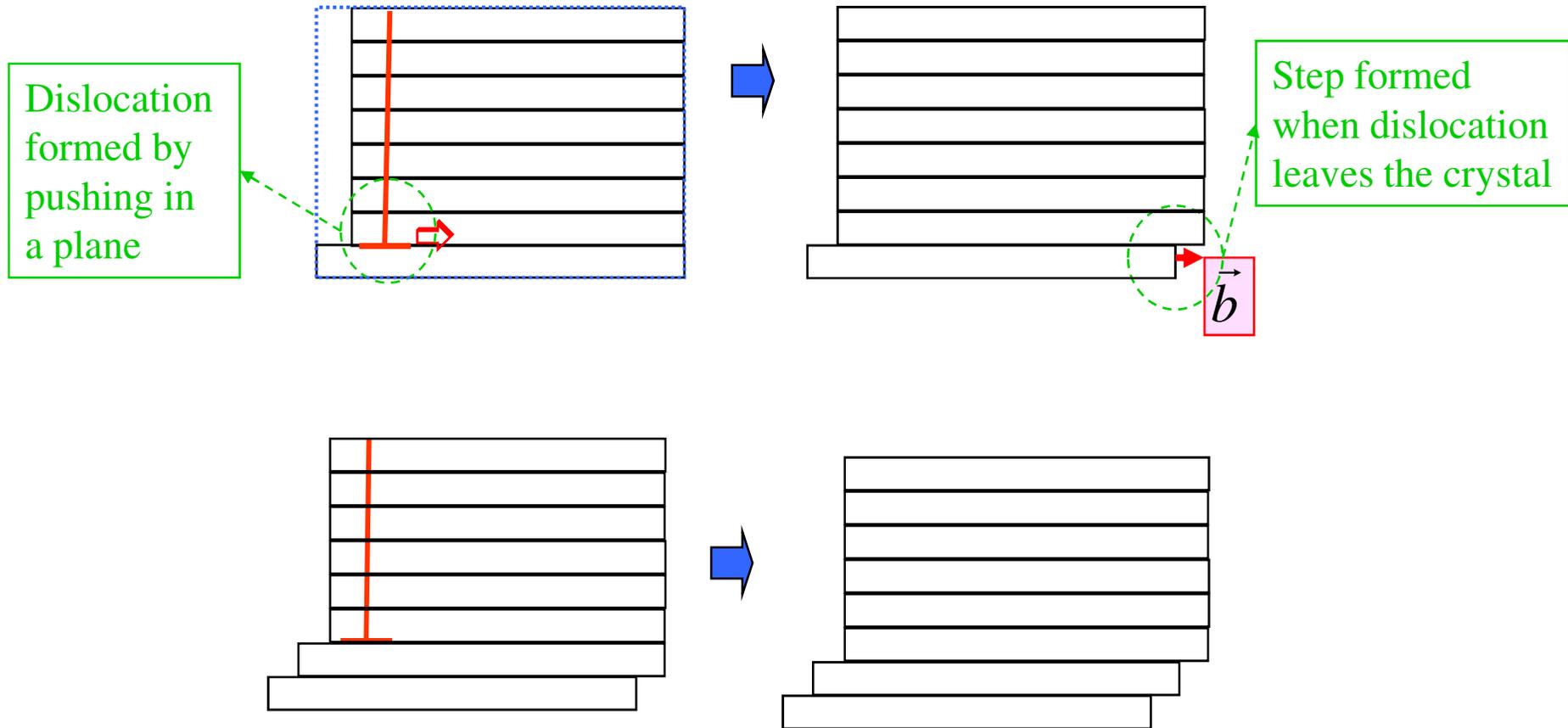
Slip systems

- ❑ Dislocations move more easily on specific planes and in specific directions.
- ❑ Ordinarily, there is a preferred plane (**slip plane**), and specific directions (**slip direction**) along which dislocations move. The combination of slip plane and slip direction is called the **slip system**.
- ❑ The slip system depends on the crystal structure of the metal.
- ❑ The slip plane is the plane that has the **most dense atomic packing** (the **greatest planar density**). The slip direction is most closely packed with atoms (**highest linear density**).
- ❑ In CCP, HCP materials the slip system consists of a close packed direction on a close packed plane.
- ❑ Just the existence of a slip system does not guarantee slip → slip is competing against other processes like twinning and fracture. If the stress to cause slip is very high (i.e. CRSS is very high), then fracture may occur before slip (like in brittle ceramics).
- ❑ For slip to occur in polycrystalline materials, **5 independent slip systems** are required. Hence, materials which are ductile in single crystalline form, may not be ductile in polycrystalline form. CCP crystals (Cu, Al, Au) have excellent ductility.
- ❑ At **higher temperatures** more slip systems may become active and hence polycrystalline materials which are brittle at low temperature, may become ductile at high temperature.

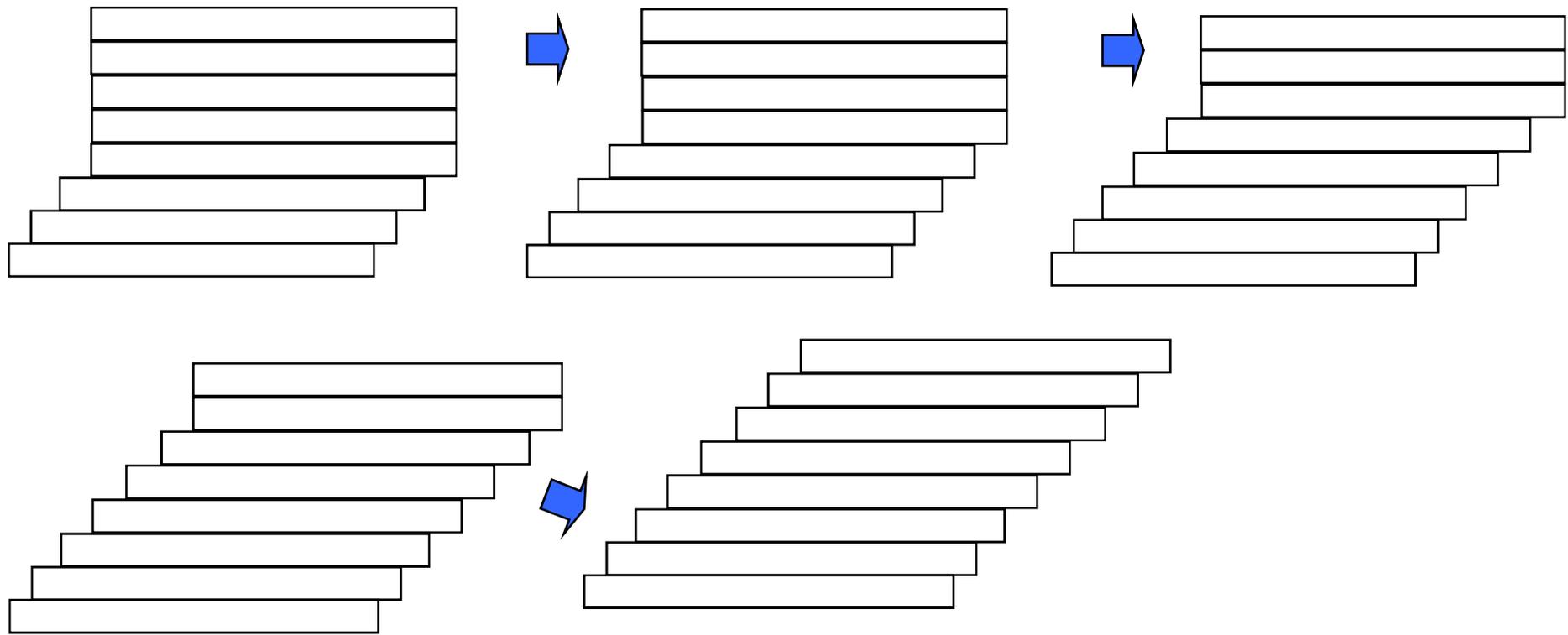
Example of slip systems

| Crystal | Slip plane(s) | Slip direction | Number of slip systems |
|--|---------------------------------|----------------------------------|------------------------|
| FCC | {111} | $\frac{1}{2}\langle 110 \rangle$ | 12 |
| HCP | (0001) | $\langle 11 \bar{2}0 \rangle$ | 3 |
| BCC | {110}, {112}, {123} | $\frac{1}{2}[111]$ | 48 |
| NaCl (<i>Ionic</i>) | {110} {111} not a slip plane | $\frac{1}{2}\langle 110 \rangle$ | 6 |
| C (<i>Diamond cubic</i>) | {111} | $\frac{1}{2}\langle 110 \rangle$ | 12 |
| TiO ₂ (<i>Rutile</i>) | {101} | $\langle 10 \bar{1} \rangle$ | |
| CaF ₂ , UO ₂ , ThO ₂ <i>Fluorite</i> | {001} | $\langle 1 \bar{1}0 \rangle$ | |
| CsCl | {110} | $\langle 001 \rangle$ | |
| NaCl, LiF, MgO <i>Rock Salt</i> | {110} | $\langle 110 \rangle$ | 6 |
| C, Ge, Si <i>Diamond cubic</i> | {111} | $\langle 110 \rangle$ | 12 |
| MgAl ₂ O ₄ <i>Spinel</i> | {111} | $\langle 1 \bar{1}0 \rangle$ | |
| Al ₂ O ₃ <i>Hexagonal</i> | (0001) | $\langle 11 \bar{2}0 \rangle$ | |

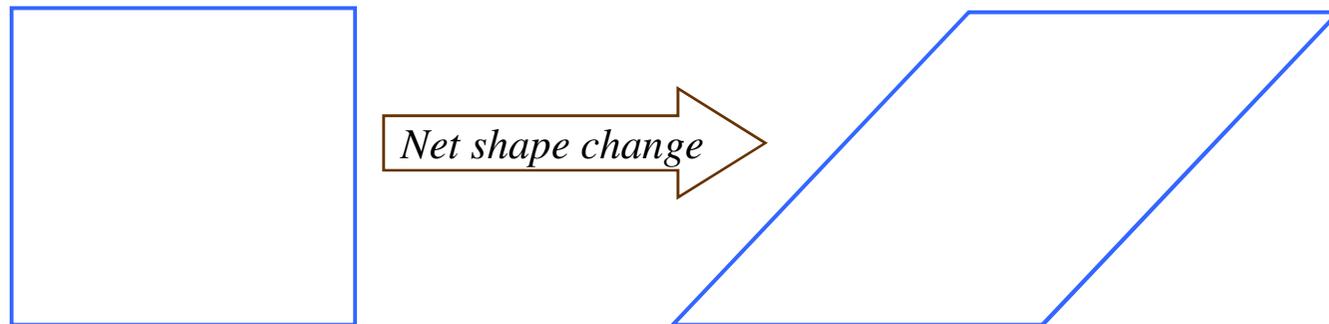
microscopic slip to macroscopic deformation



Now visualize dislocations being punched in on successive planes → moving and finally leaving the crystal

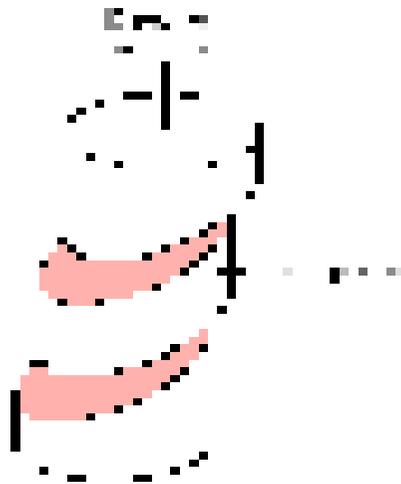


This sequence of events finally leads to deformed shape

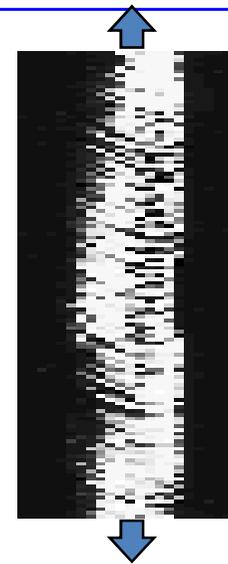


Slip in Single Crystal

- ❑ If a single crystal of a metal is stressed in tension beyond its elastic limit, it elongates slightly and a step appears on the surface due to the relative displacement of one part of the crystal with respect to the others and the elongation stops.
- ❑ Further increase in the load causes movement of another parallel plane, resulting in another step. Similarly number of small steps are formed on the surface of the single crystal that are parallel to one another and loop around the circumference of the specimen.
- ❑ Each step (shear band) results from the movement of a large number of dislocations and their propagation in the slip system.



Macroscopic slip in single crystal

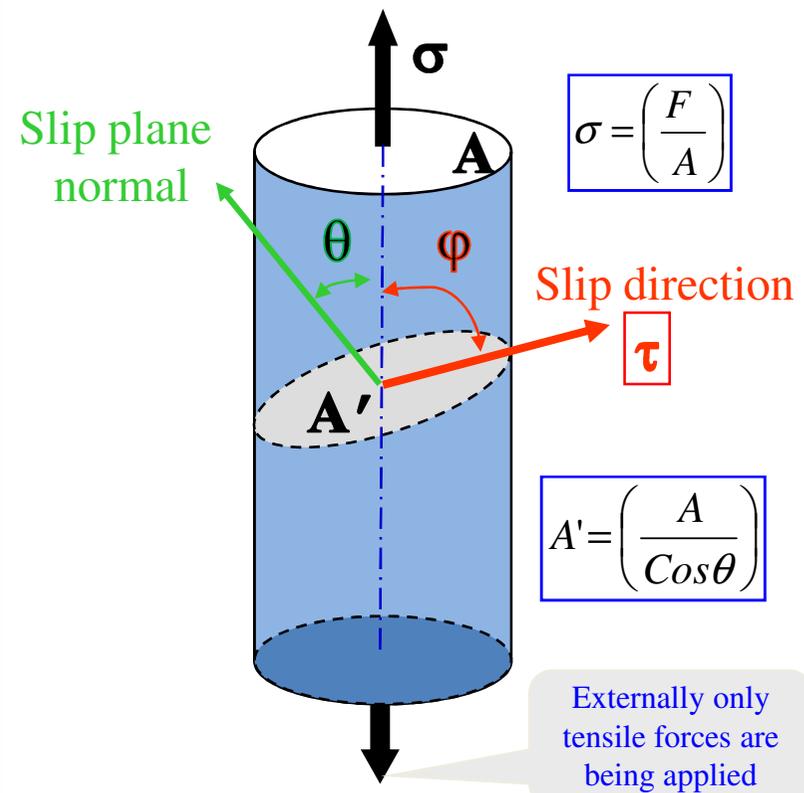


Slip in a zinc single crystal

Critical Resolved Shear Stress (CRSS)

- ❑ Extent of slip in a single crystal depends on the magnitude of shearing stress produced by external loads, geometry of the crystal structure and the orientation of the active slip planes with respect to the shearing stress.
- ❑ Slip begins when the shearing stress on slip plane in the slip direction/Resolved Shear Stress (RSS) reaches a critical value called the Critical Resolved Shear Stress (CRSS) and plastic deformation starts (*The actual Schmid's law*)

- ❑ Even if we apply an tensile force on the specimen → the shear stress resolved onto the slip plane is responsible for slip.
- ❑ The stress at which slip starts in a crystal depends on the relative orientation of the stress axis with respect to the slip plane and the slip direction.
- ❑ When a tensile stress σ is applied to a crystal, as illustrated in figure, the shear stress τ resolved on a slip plane whose normal makes an angle of θ with the stress axis, along a slip direction inclined at an angle of ϕ to the stress axis.



Critical Resolved Shear Stress (CRSS)

$$\text{Stress} = \left(\frac{\text{Force}}{\text{Area}} \right)$$

$$\tau = \left(\frac{F \cos \alpha}{A / \cos \theta} \right)$$

$$\tau_{RSS} = \sigma \cos \theta \cos \phi$$

Schmid factor

- ❑ τ_{RSS} is maximum ($P/2A$) when $\phi = \lambda = 45^\circ$
- ❑ If the tension axis is normal to slip plane i.e. $\lambda = 90^\circ$ or if it is parallel to the slip plane i.e. $\phi = 90^\circ$ then $\tau_{RSS} = 0$ and slip will not occur as per Schmid's law.

Schmid's law

Slip is initiated when

$$\tau_{RSS} \geq \tau_{CRSS}$$

- ❑ τ_{CRSS} is a material parameter, which is determined from experiments

Yield strength of a single crystal

$$\sigma_y = \frac{\tau_{CRSS}}{\cos \theta \cos \phi}$$

Solved Example 1

Consider a single crystal of BCC iron oriented such that a tensile stress is applied along a [010] direction.

- (a) Compute the resolved shear stress along a (110) plane and in a [111] direction when a tensile stress of 52 MPa (7500 psi) is applied. If slip occurs on a (110) plane and in a $[\bar{1}11]$ direction, and the critical resolved shear stress is 30 MPa (4350 psi), calculate the magnitude of the applied tensile stress necessary to initiate yielding.

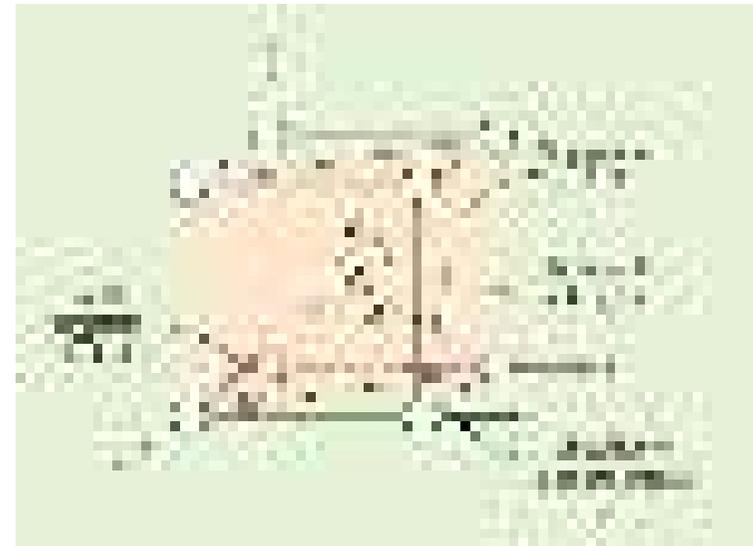
Solution

- a. Determine the value of the angle between the normal to the (110) slip plane (i.e., the [110] direction) and the [010] direction using $[u_1v_1w_1] = [110]$, $[u_2v_2w_2] = [010]$ and the following equation.

$$\theta = \cos^{-1} \left(\frac{u_1u_2 + v_1v_2 + w_1w_2}{\sqrt{(u_1^2 + v_1^2 + w_1^2)(u_2^2 + v_2^2 + w_2^2)}} \right)$$

$$\phi = \cos^{-1} \left(\frac{(1)(0) + (1)(1) + (0)(0)}{\sqrt{[(1)^2 + (1)^2 + (0)^2][(0)^2 + (1)^2 + (0)^2]}} \right)$$

$$= \cos^{-1} \left(\frac{1}{\sqrt{2}} \right) = 45^\circ$$



Solved Example 1

- Similarly determine the value of λ , the angle between $[\bar{1}11]$ and $[010]$ directions as follows:

$$\lambda = \cos^{-1} \left(\frac{(-1)(0) + (1)(1) + (1)(0)}{\sqrt{[(-1)^2 + (1)^2 + (1)^2][(0)^2 + (1)^2 + (0)^2]}} \right) = \cos^{-1} \left(\frac{1}{\sqrt{3}} \right) = 54.7^\circ$$

- Then calculate the value of τ_{RSS} using the following expression:

$$\begin{aligned} \tau_{RSS} &= \sigma \cos\phi \cos\lambda \\ &= (52 \text{ Mpa})(\cos 45)(\cos 54.7) \\ &= 21.3 \text{ Mpa} \\ &= 13060 \text{ psi} \end{aligned}$$

- Yield Strength σ_Y

$$\sigma_y = \frac{30 \text{ MPa}}{(\cos 45)(\cos 54.7)} = 73.4 \text{ Mpa}$$

Solved Example 2

Determine the tensile stress that is applied along the $[\bar{1}\bar{1}0]$ axis of a silver crystal to cause slip on the (111) $[011]$ system. The critical resolved shear stress is 6 MPa.

Solution:

- Determine the angle ϕ between the tensile axis $[\bar{1}\bar{1}0]$ and normal to $(\bar{1}\bar{1}\bar{1})$ using the following equation.

$$\cos \theta = \left(\frac{u_1 u_2 + v_1 v_2 + w_1 w_2}{\sqrt{(u_1^2 + v_1^2 + w_1^2)(u_2^2 + v_2^2 + w_2^2)}} \right)$$

$$\cos \phi = \left(\frac{(1)(1) + (-1)(-1) + (0)(-1)}{\sqrt{[(1)^2 + (-1)^2 + (0)^2][(1)^2 + (-1)^2 + (-1)^2]}} \right) = \frac{1}{\sqrt{2}\sqrt{3}} = \frac{2}{\sqrt{6}}$$

- Determine the angle λ between tensile axis $[\bar{1}\bar{1}0]$ and slip direction $[0\bar{1}1]$

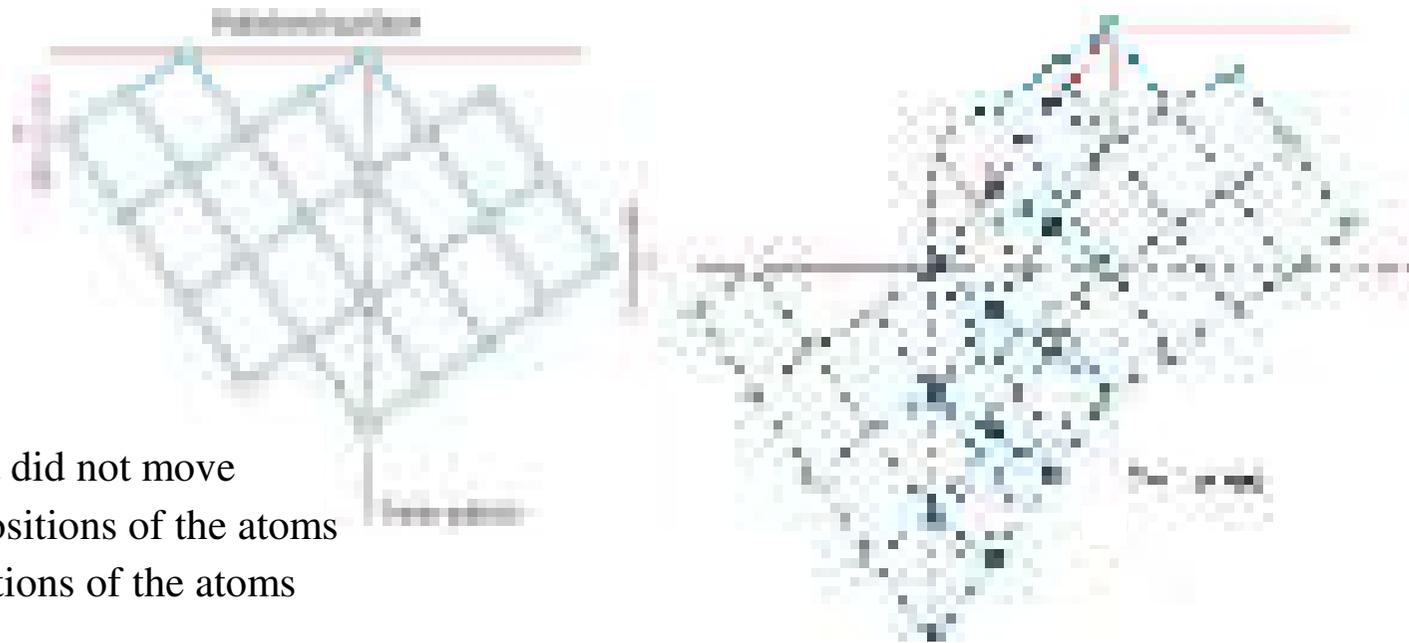
$$\cos \lambda = \left(\frac{(1)(0) + (-1)(-1) + (0)(-1)}{\sqrt{[(1)^2 + (-1)^2 + (0)^2][(0)^2 + (-1)^2 + (-1)^2]}} \right) = \frac{1}{\sqrt{2}\sqrt{2}} = \frac{1}{2}$$

- Then calculate the Tensile Stress using the expression:

$$\sigma = \frac{P}{A} = \frac{\tau_{RSS}}{\cos \phi \cos \lambda} = \frac{6 \text{ MPa}}{\frac{2}{\sqrt{6}} \times \frac{1}{2}} = 6\sqrt{6} = 14.7 \text{ MPa}$$

Plastic deformation by Twin

- ❑ In addition to slip (dislocation movement), plastic deformation can also occur by twinning.
- ❑ Twinning results when a portion of the crystal takes up an orientation that is related to the orientation of the rest of the untwinned lattice in a definite, symmetrical way.
- ❑ Twinned portion of the crystal is a mirror image of the parent crystal and the plane of symmetry between the two portions is called twinning plane.
- ❑ Twinning may favorably reorient slip systems to promote dislocation movement.

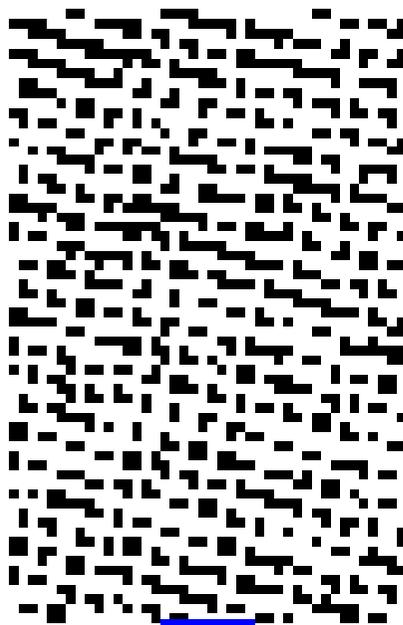


- - Atoms that did not move
- - Original positions of the atoms
- - Final positions of the atoms

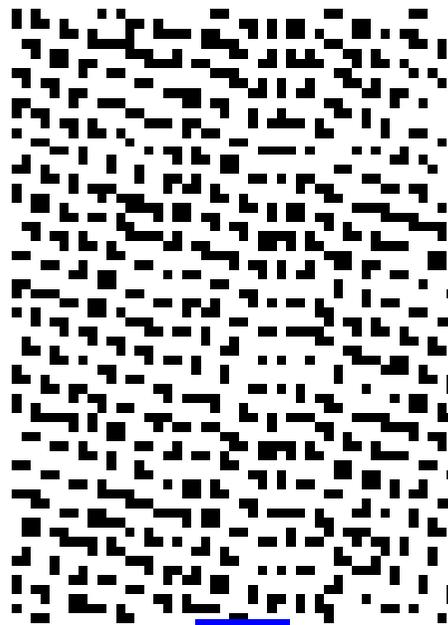
Schematic diagram showing how twinning results from an applied shear stress

Plastic deformation by Twin

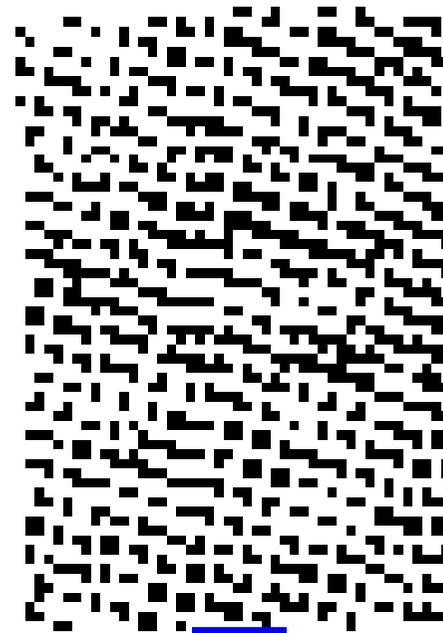
- ❑ Twins are generally of two types: Mechanical Twins and Annealing twins
- ❑ Mechanical twins are generally seen in bcc or hcp metals and produced under conditions of rapid rate of loading and decreased temperature.
- ❑ Annealing twins are produced as the result of annealing. These twins are generally seen in fcc metals.
- ❑ Annealing twins are usually broader and with straighter sides than mechanical twins.



(a)



(b)



(c)

(a) Mechanical Twins (Neumann bands in iron), (b) Mechanical Twins in zinc produced by polishing (c) Annealing Twins in gold-silver alloy

Plastic deformation by Twin

- ❑ Twinning generally occurs when the slip systems are restricted or when the slip systems are restricted or when something increases the critical resolved shear stress so that the twinning stress is lower than the stress for slip.
- ❑ So, twinning generally occurs at low temperatures or high strain rates in bcc or fcc metals or in hcp metals.
- ❑ Twinning occurs on specific twinning planes and twinning directions.

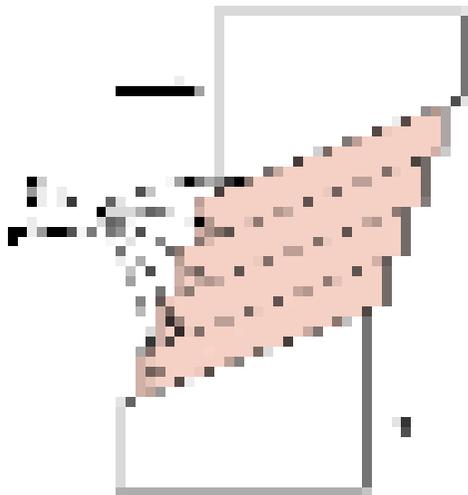
Twin planes and Twin directions

| Crystal Structure | Typical Examples | Twin Plane | Twin Direction |
|-------------------|------------------|----------------|----------------|
| BCC | α -Fe, Ta | (112) | [111] |
| HCP | Zn, Cd, Mg, Ti | $(10\bar{1}2)$ | $[\bar{1}011]$ |
| FCC | Ag, Au, Cu | (111) | [112] |

Difference between Slip and Twin

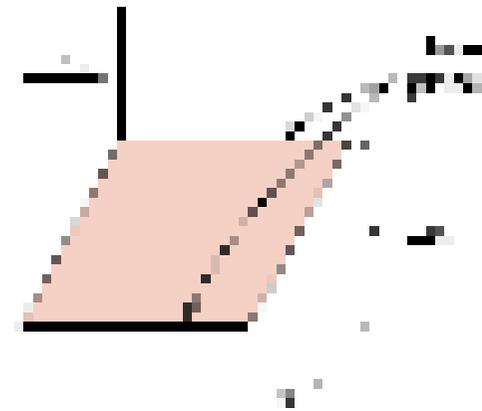
Slip

- The crystallographic orientation above and below the slip plane is the same both before and after the deformation
- Slip occurs in distinct atomic spacing multiples
- Slip Leaves a series of steps (lines)
- Normally slip results in relatively large deformations
- Mostly seen in FCC and BCC structure, as they have more slip systems



Twin

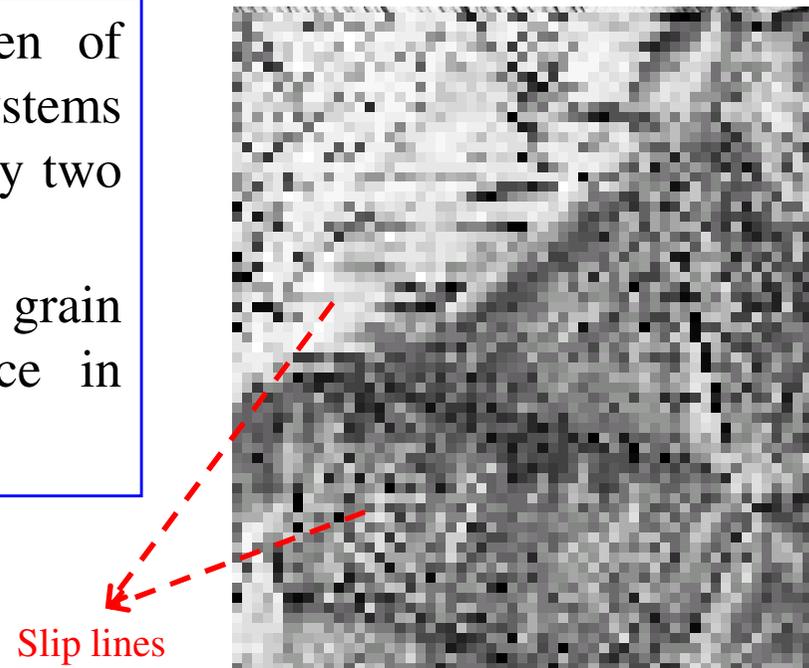
- Orientation difference is seen across the twin plane
- the atomic displacement for twinning is less than the inter-atomic separation
- Twinning leaves small but well defined regions of the crystal deformed
- Only small deformations result for twinning
- Is most important for HCP structure , because of its small number of slip system



Plastic deformation of Polycrystalline Materials

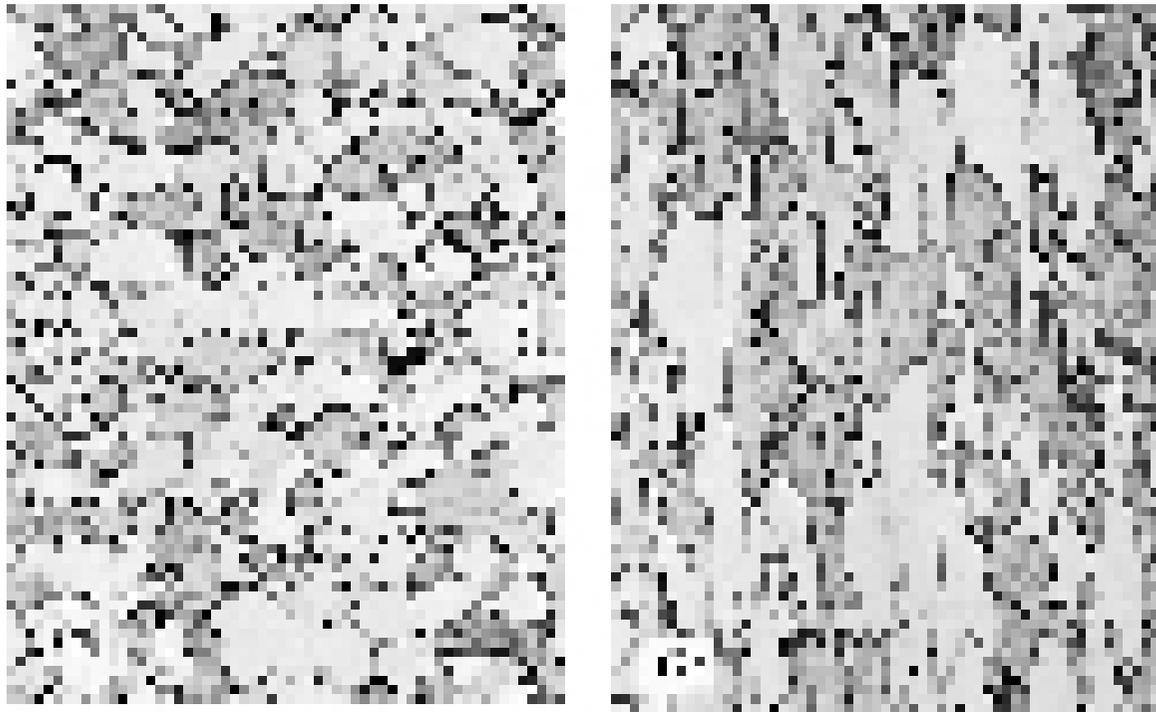
- ❑ Plastic deformation in polycrystalline materials is very complex than those in the single crystals due to the presence of grain boundaries, different orientation of neighboring crystals, presence of several phases etc.
- ❑ Due to random crystallographic orientations, the slip planes and slip direction varies from one grain to another
- ❑ As a result the resolved shear stress τ_{RSS} will vary from one crystal to another and the dislocations will move along the slip systems with favorable orientation (i.e. the highest resolved shear stress).

- ❑ When a polished polycrystalline specimen of copper is plastically deformed, two slip systems operate for most of the grains (evidenced by two sets of parallel yet intersecting sets of lines).
- ❑ Slip lines are visible, and the variation in grain orientation is indicated by the difference in alignment of the slip lines for several grains.



Plastic deformation of Polycrystalline Materials

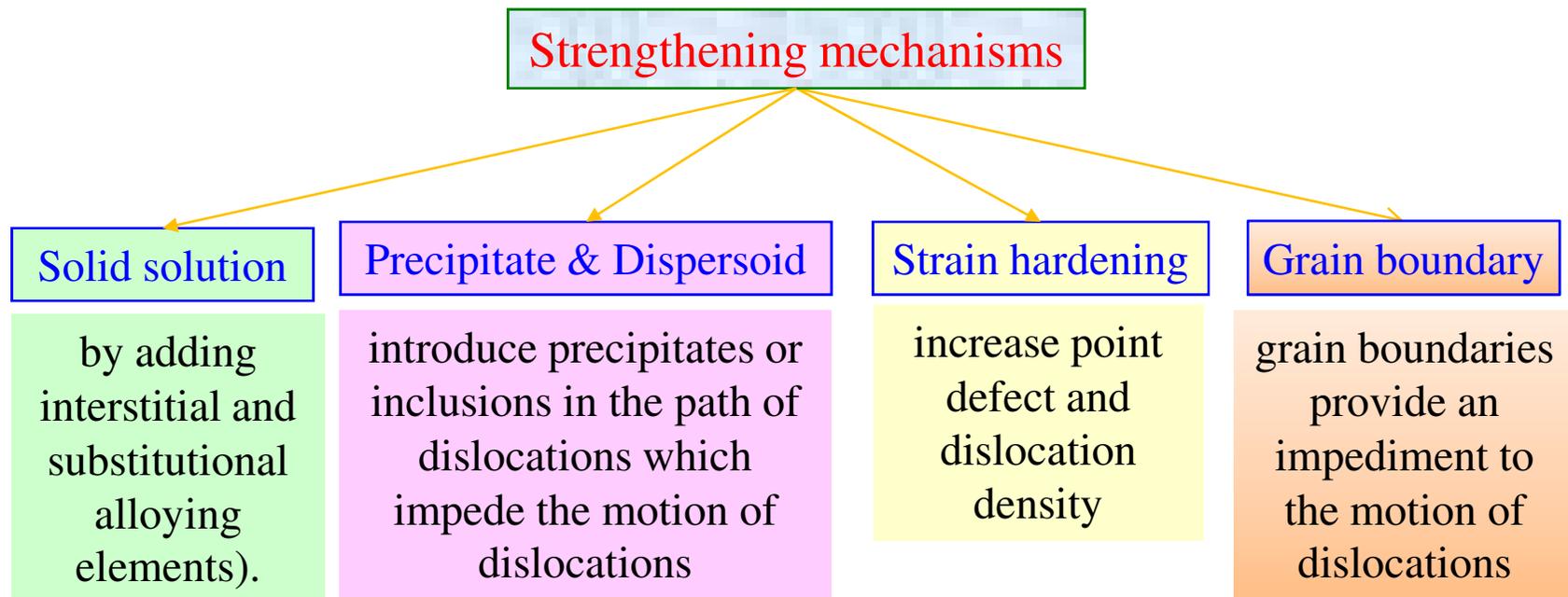
- ❑ During deformation, mechanical integrity and coherency are maintained along the grain boundaries; i.e. the grain boundaries usually do not come apart or open up.
- ❑ As a consequence, each individual grain is constrained, to some degree in the shape it may assume by its neighboring grains.



Alteration of the grain structure of a polycrystalline metal as a result of plastic deformation (a) Before deformation the grains are equiaxed. (b) After deformation elongated grains are produced

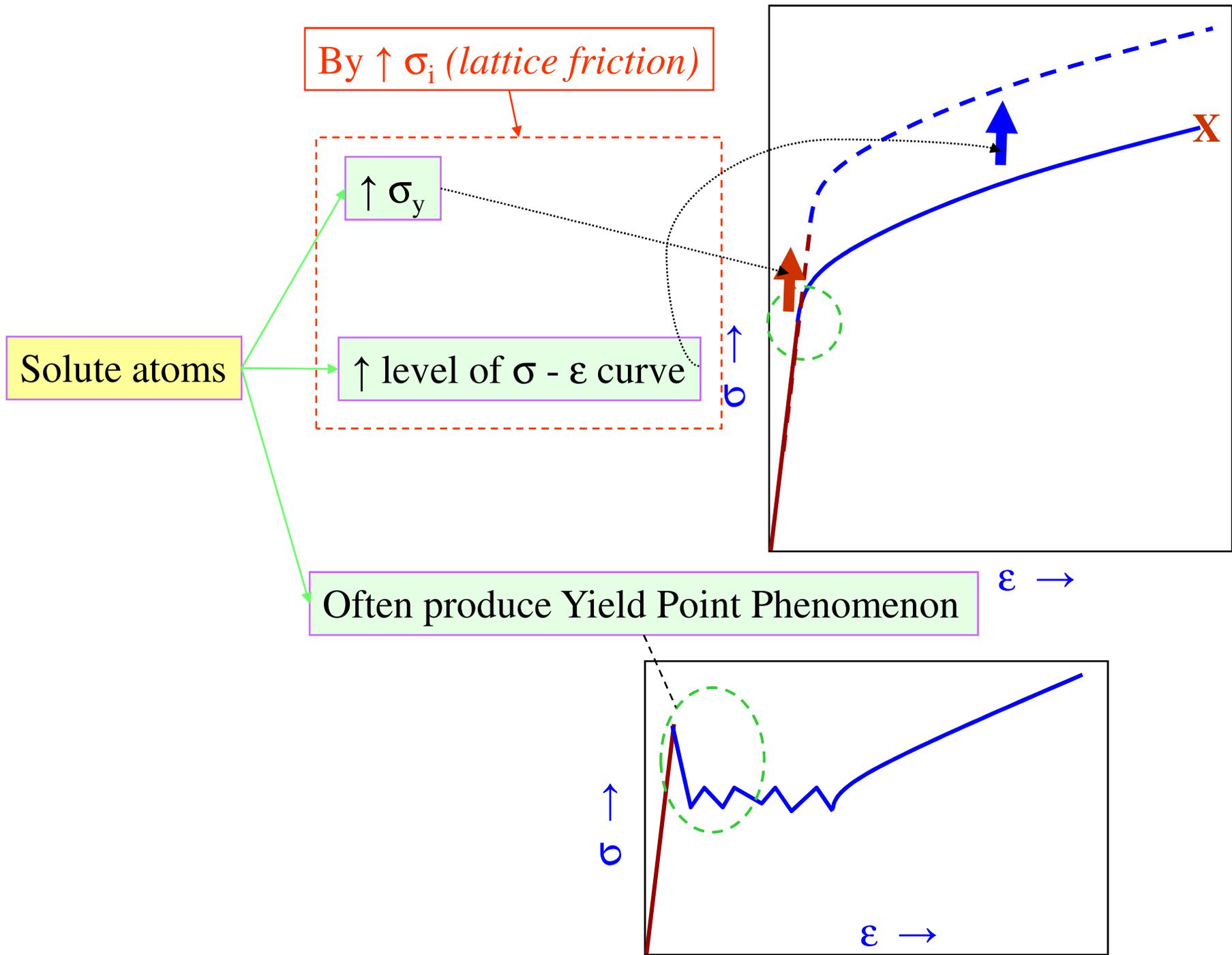
Strengthening Mechanisms

- ❑ The ability of a metal to deform depends on the ability of the dislocations to move and the slip of dislocations weakens the crystal. Hence we have two strategies to strengthen the crystal/material:
 - **completely remove dislocations** → difficult, but dislocation free whiskers have been produced (*however, this is not a good strategy as dislocations can nucleate during loading*)
 - **Increase resistance to the motion of dislocations** or **put impediments** to the motion of dislocations → this can be done in many ways as listed below.



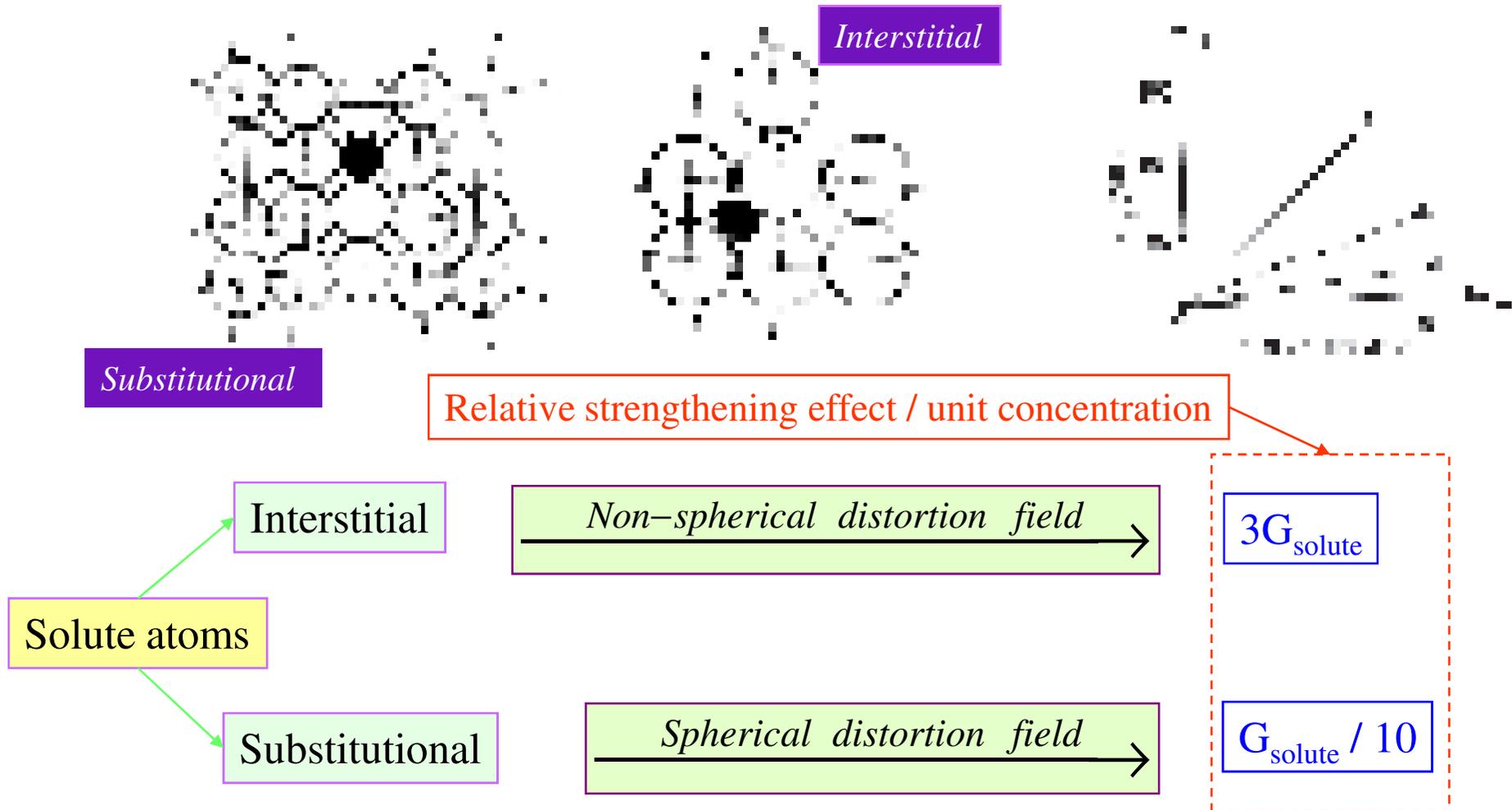
Solid Solution Strengthening

- ❑ The introduction of solute atoms into solid solution in the solvent-atom lattice invariably produces an alloy which is stronger than the pure metal
- ❑ Two types of solid solutions:
 - ⇒ **Substitutional solid solutions** → Solute atoms occupy lattice points in the solvent lattice (Hume Rothery's rules are to be satisfied)
 - ⇒ **Interstitial solid solutions** → Solute atoms occupy interstitial positions in the solvent lattice (Carbon, Nitrogen, Boron, Oxygen, Hydrogen are the common interstitial solutes)
- ❑ The stress fields around solute atoms interact with the stress fields around the dislocation.
- ❑ This interaction provides frictional resistance to dislocations motion and static locking of dislocations
- ❑ The factors playing an important role on strengthening effect:
 - ⇒ Size of the solute
 - ⇒ Concentration of solute
 - ⇒ Elastic modulus of the solute (*higher the elastic modulus of the solute greater the strengthening effect*)
 - ⇒ Nature of distortion produced by solute atoms (*Spherical or Non-spherical*)



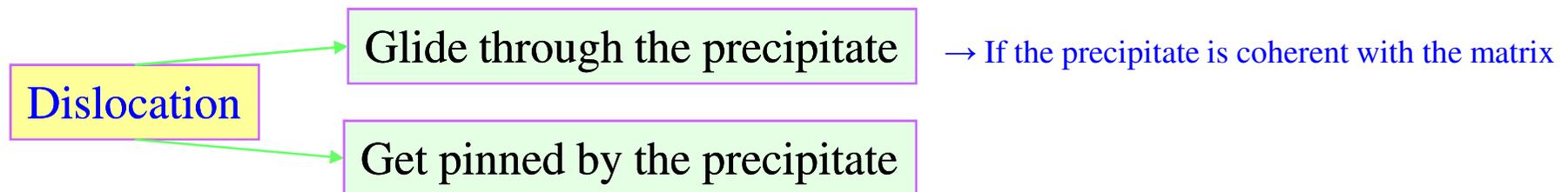
Relative strengthening effect of Interstitial and Substitutional atoms

- ❑ Interstitial solute atoms have a non-spherical distortion field and can elastically interact with both edge and screw dislocations. Hence they give a higher hardening effect (per unit concentration) as compared to substitutional atoms which have (approximately) a spherical distortion field.

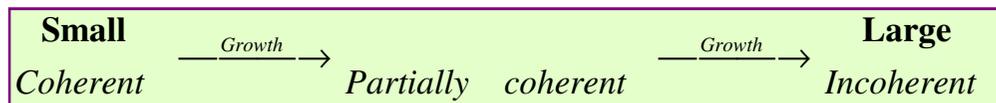


Hardening of Precipitates

- ❑ Precipitates may be coherent, semi-coherent or incoherent. Coherent (& semi-coherent) precipitates are associated with coherency stresses.
- ❑ Dislocations cannot glide through incoherent precipitates.
- ❑ Inclusions behave similar to incoherent precipitates in this regard (precipitates are part of the system, whilst inclusions are external to the alloy system).
- ❑ A pinned dislocation (at a precipitate) has to either climb over it (which becomes favourable at high temperatures) or has to bow around it.



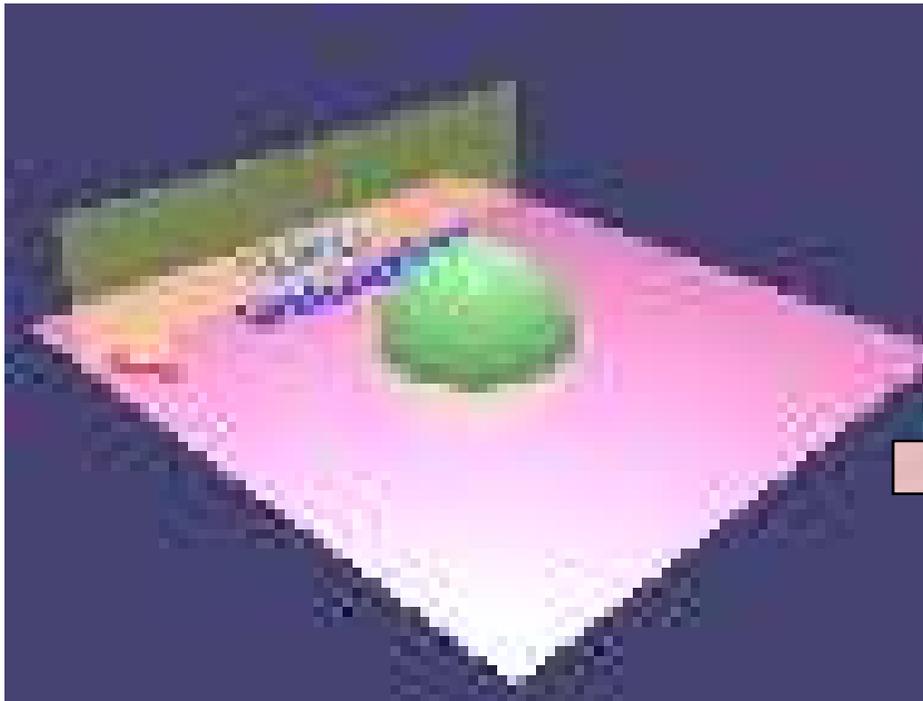
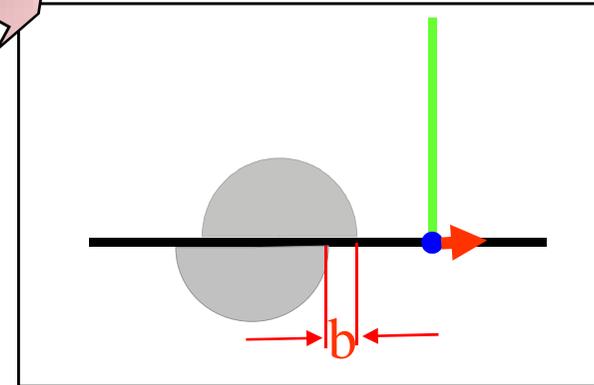
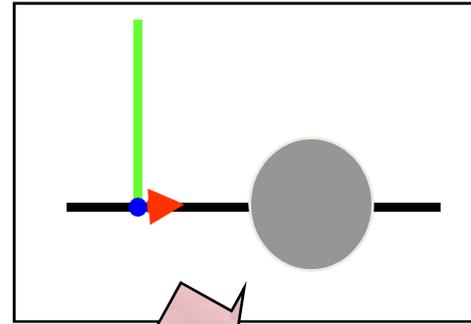
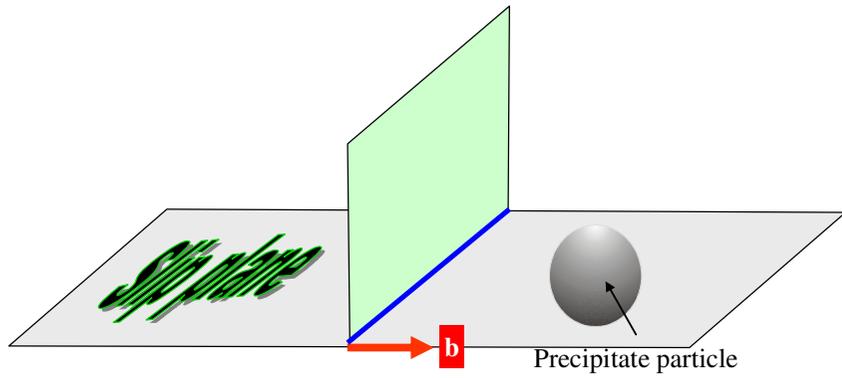
- Only if slip plane is continuous from the matrix through the precipitate \Rightarrow precipitate is *coherent* with the matrix.
- Stress to move the dislocation through the precipitate is \sim that to move it in the matrix (though it is usually higher as precipitates can be intermetallic compounds).
- Usually during precipitation the precipitate is coherent only when it is small and becomes incoherent on growth.



- Glide of the dislocation causes a displacement of the upper part of the precipitate w.r.t the lower part by \mathbf{b} $\rightarrow \sim$ *cutting of the precipitate*.

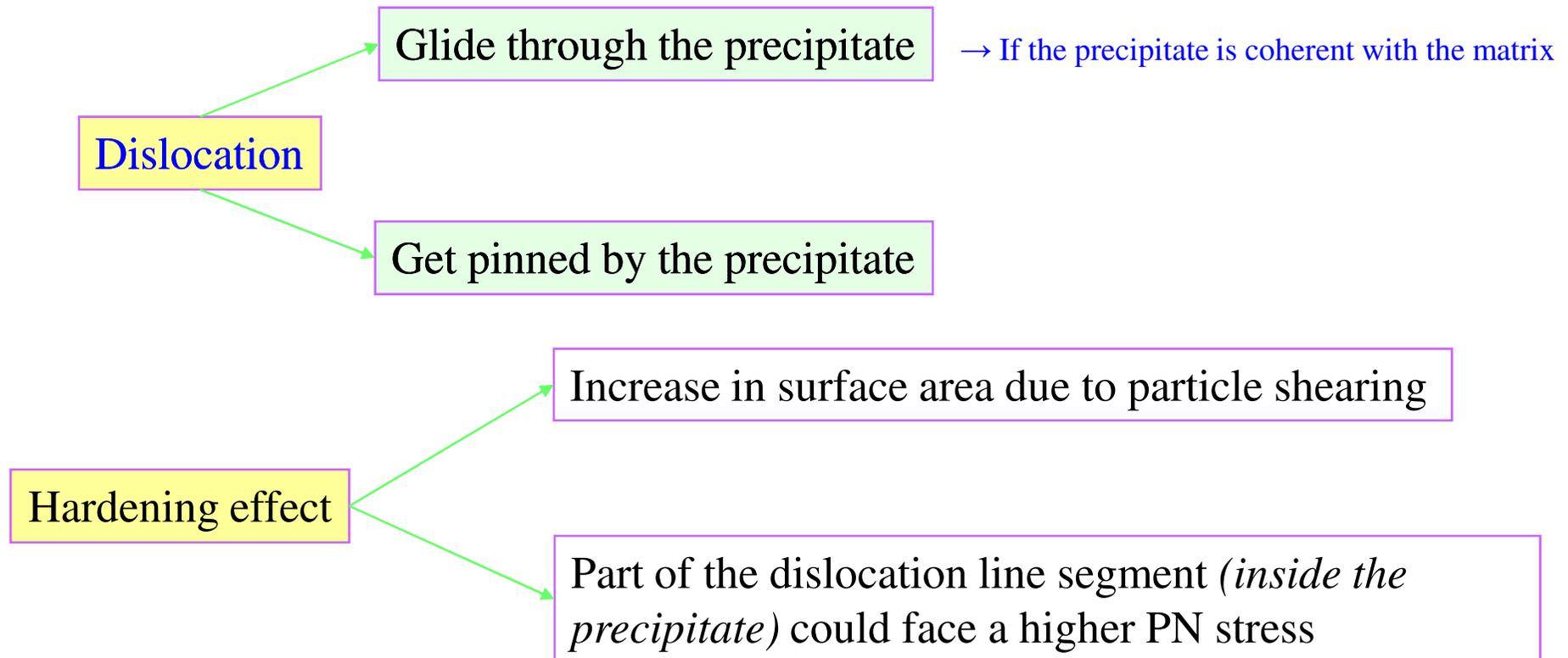
Schematic views

→ edge dislocation glide through a coherent precipitate



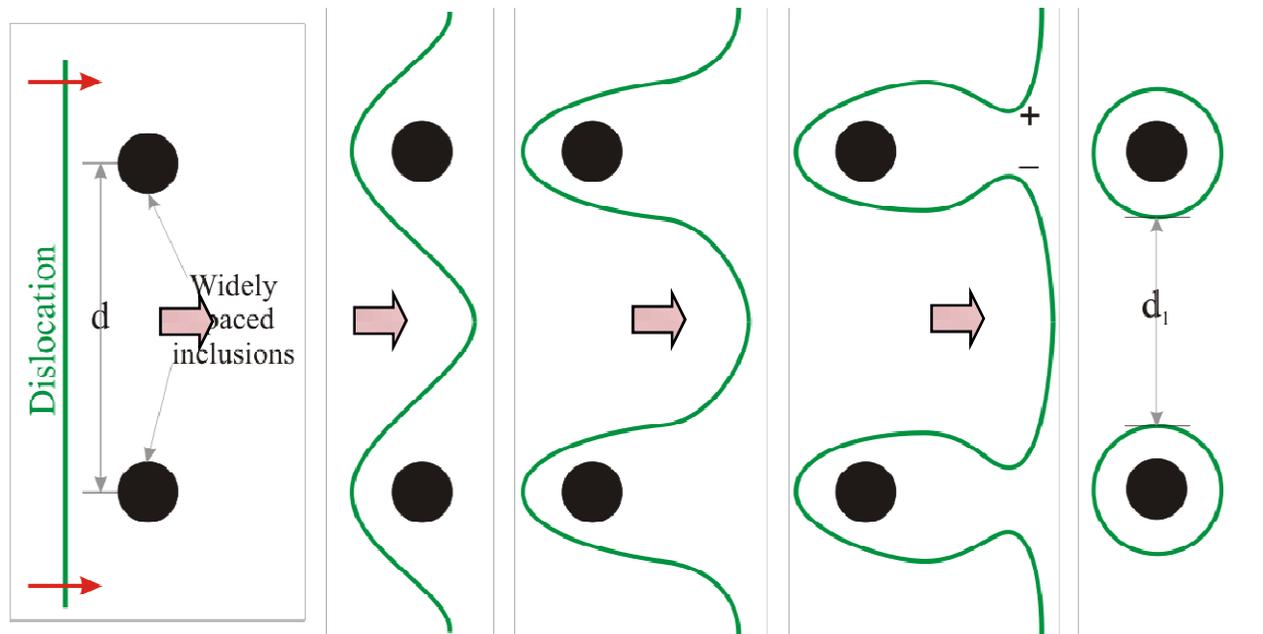
If the particle is sheared, then how does the hardening effect come about?

- We have seen that as the dislocation glides through the precipitate it is sheared.
- If the precipitate is sheared, then how does it offer any resistance to the motion of the dislocation? I.e. how can this lead to a hardening effect?
- The hardening effect due to a precipitate comes about due to many factors (many of which are system specific). The important ones are listed in the tree below.



Orowan bowing mechanism : Pinning effect

- ❑ Dislocations can bow around widely separated inclusions. In this process they leave dislocation loops around the inclusions, thus leading to an increase in dislocation density. This is known as the Orowan bowing mechanism as shown in the figure below. (*This is in 'some sense' similar to the Frank-Read mechanism*).
- ❑ The next dislocation arriving (similar to the first one), feels a repulsion from the dislocation loop and hence the stress required to drive further dislocations increases. Additionally, the effective separation distance (through which the dislocation has to bow) reduces from 'd' to 'd₁'.



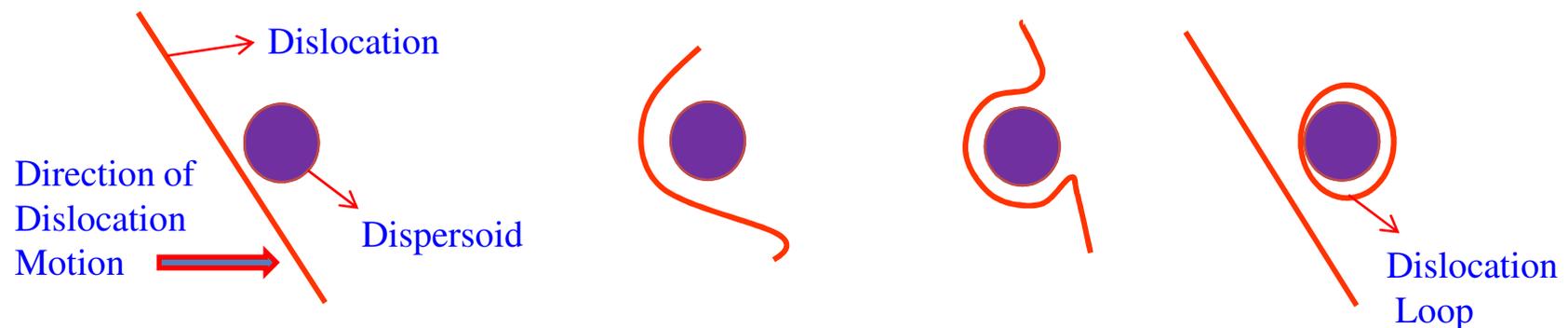
Precipitate Hardening effect

The hardening effect of precipitates can arise in many ways as below:

- ❑ **Lattice Resistance:** the dislocation may face an increased lattice friction stress in the precipitate.
- ❑ **Chemical Strengthening:** arises from additional interface created on shearing
- ❑ **Stacking-fault Strengthening:** due to difference between stacking-fault energy between particle and matrix when these are both FCC or HCP (when dislocations are split into partials)
- ❑ **Modulus Hardening:** due to difference in elastic moduli of the matrix and particle
- ❑ **Coherency Strengthening:** due to elastic coherency strains surrounding the particle
- ❑ **Order Strengthening:** due to additional work required to create an APB in case of dislocations passing through precipitates which have an ordered lattice

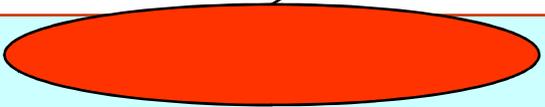
Strengthening by Dispersoids

- ❑ In dispersion hardening, the hard particles are mixed with matrix powder and consolidated and processed by powder metallurgy techniques.
- ❑ Example: *Thoria dispersed Nickel* → Fine particles of Thoria are dispersed in the nickel matrix and the inter particle distance is enough to hinder the dislocation movement thereby increasing the strength up to 0.9 times T_m (T_m in $^{\circ}\text{C}$).
- ❑ In dispersion hardening, dispersoids are incoherent with the matrix and dislocations cannot glide through these dispersoids and gets pinned.
- ❑ A pinned dislocation (at a precipitate) has to either climb over it (which becomes favorable at high temperatures) or has to bow around it (Orowan's Mechanism of Dispersion Hardening)
- ❑ Dislocation loop exert a back stress on dislocation which needs to be overcome for additional slip to take place and this causes hardening.



Strain Hardening : Forest Dislocations

What causes **Strain hardening**? → multiplication of dislocations

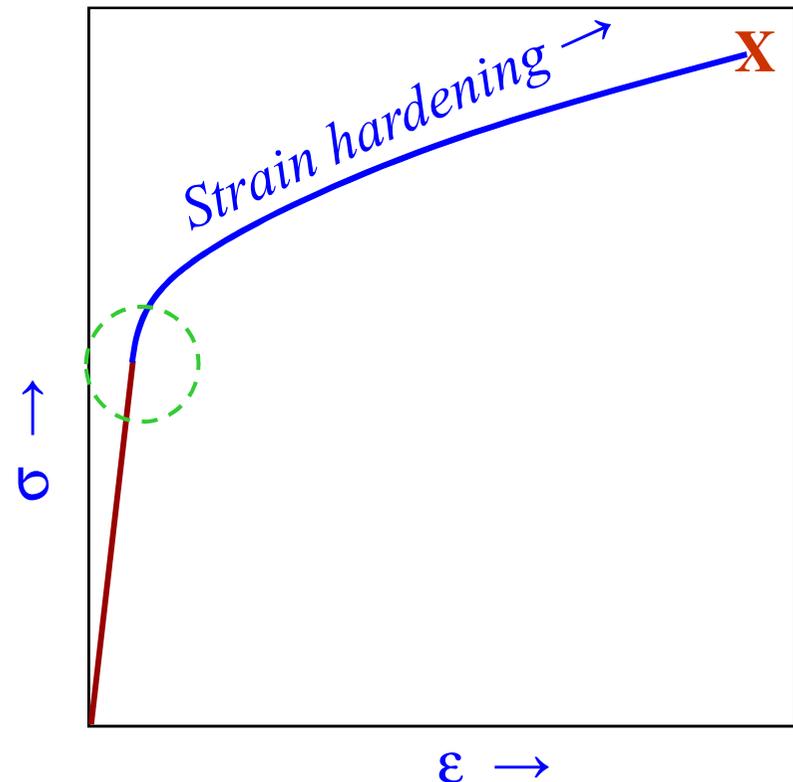
Annealed material $\xrightarrow{\text{Cold work}}$ 
 $\rho_{\text{dislocation n}} \sim (10^6 - 10^9)$ \rightarrow $\rho_{\text{dislocation n}} \sim (10^{12} - 10^{14})$

Strain hardening

- Why increase in dislocation density ?
- Why strain hardening ?

If dislocations were to leave the surface of the crystal by slip / glide then the dislocation density should decrease on plastic deformation →
but observation is contrary to this

This implies some sources of dislocation multiplication / creation should exist



Some specific sources/methods of formation/multiplication of dislocations include

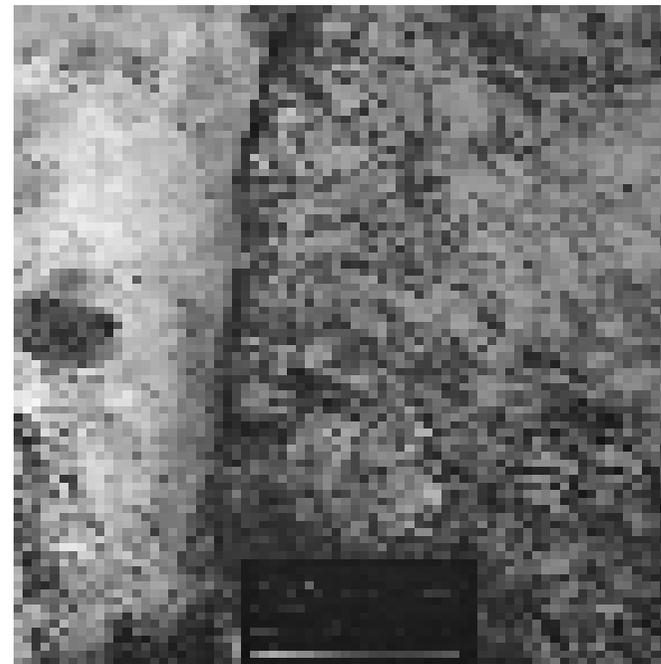
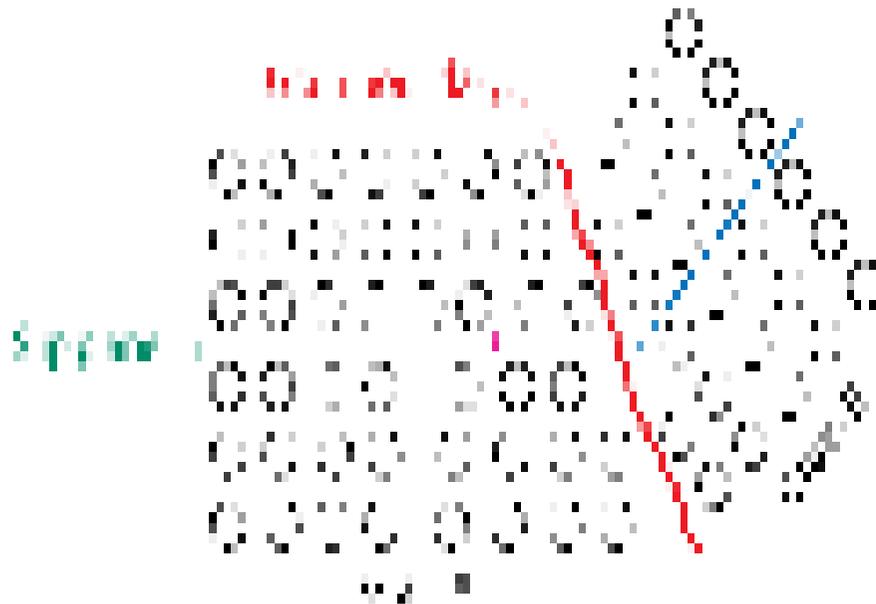
- ❑ It is difficult to obtain crystals without dislocations (under special conditions whiskers have been grown without dislocations).
- ❑ Dislocation can arise by/form:
 - Solidification (errors in the formation of a perfect crystal lattice)
 - Plastic deformation (nucleation and multiplication)
 - Irradiation
- ❑ High stresses
 - ▶ Heterogeneous nucleation at second phase particles
 - ▶ During phase transformation
- ❑ Frank-Read source
- ❑ Orowan bowing mechanism

Strain hardening

- ❑ We had noted that stress to cause further plastic deformation (flow stress) increases with strain → strain hardening. This happens at
- ❑ Dislocations moving in non-parallel slip planes can intersect with each other → results in an increase in stress required to cause further plastic deformation ⇒ *Strain Hardening / work hardening*
- ❑ One such mechanism by which the dislocation is immobilized is the Lomer-Cottrell barrier.

Strengthening by Grain Boundary

- ❑ Grain boundary is the boundary between two grains in a polycrystalline aggregate and this is the region of a disturbed lattice which is of few atomic diameters distance.
- ❑ There are two important ways in which grain boundary acts as a barrier to the dislocation
 - ⇒ Difficulty for a dislocation to pass through two different grain orientations (need to change the direction)
 - ⇒ The atomic disorder within a grain boundary region contributes to a discontinuity of slip planes from one grain to other.



Dislocation pile-up at grain boundaries

Hall – Petch Relation

- ❑ A fine grained material is harder and stronger than one that is coarse grained since greater amounts of grain boundaries in the fine grained materials impede dislocation motion.
- ❑ The general relationship between yield stress (tensile strength) and grain size was proposed by Hall and Petch, which is known as Hall-Petch relation.

$$\sigma_{Yield} = \sigma_o + k_y d^{-\frac{1}{2}}$$

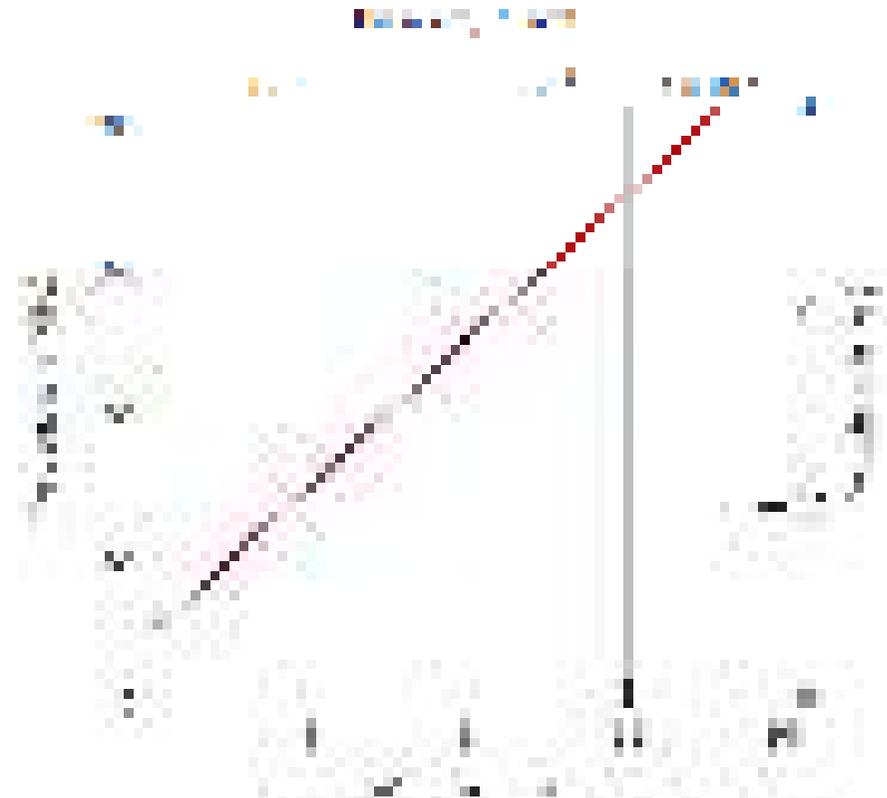
Where,

σ_{yield} = Yield stress

σ_o = Friction stress or resistance to dislocation motion

k_y = Locking parameter or the hardening contribution from the grain boundary

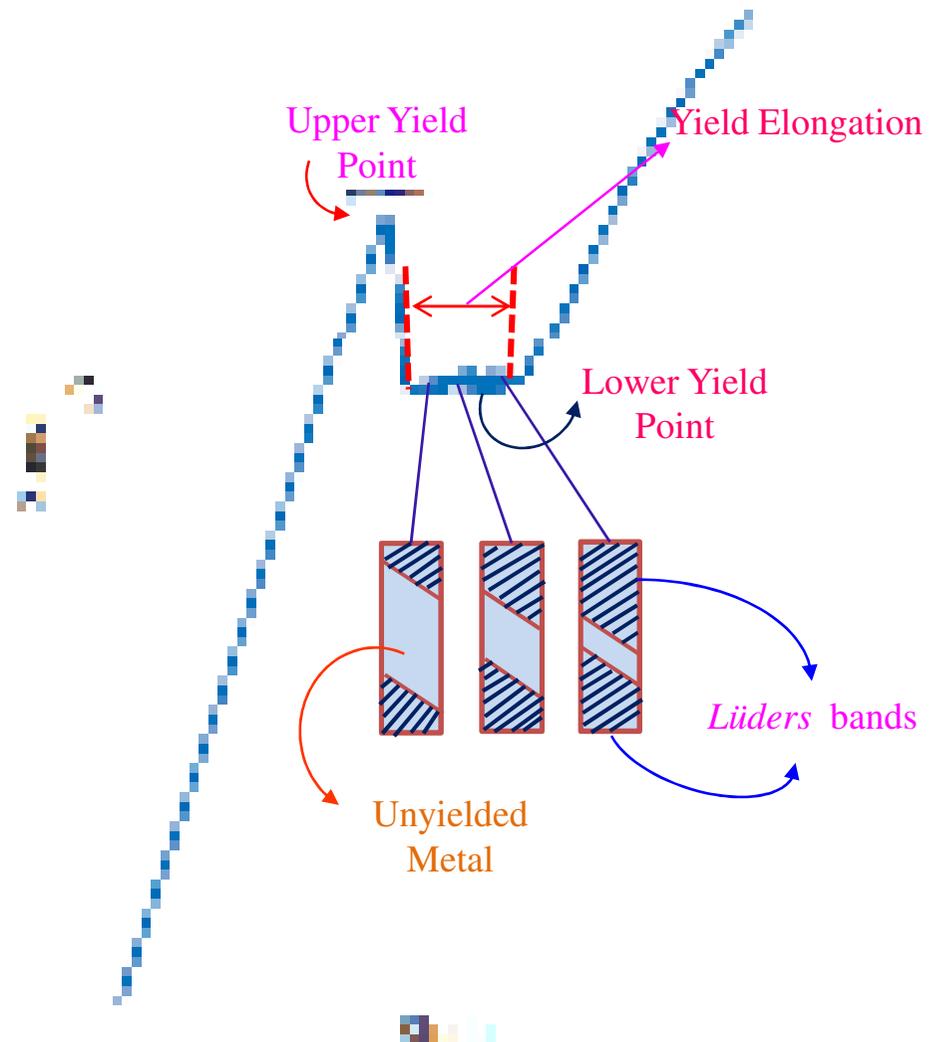
d = Grain diameter



Influence of grain size on yield strength of 70Cu-30Zn Brass

Yield-Point Phenomenon

- ❑ Many metals, particularly low carbon steel, show a localized, heterogeneous type of transition from elastic to plastic deformation which produces a yield point in the stress-strain curve.
- ❑ For these metals, load increases steadily with elastic strain, drops suddenly, fluctuates around a certain value (Plateau region) and then rises with further strain.
- ❑ The load at which sudden drop occurs corresponds to the **upper yield point**, the constant load is called the **lower yield point**, and the elongation that occurs at constant load is called the **yield-point elongation**.
- ❑ At the upper yield point, plastic deformation is initiated forming a discrete band of deformed metal, known as **Lüders band**/Hartmann lines or stretcher strains
- ❑ Then these bands propagate to cover the entire length of the specimen.



Preferred Orientation (Texture)

- ❑ When a metal undergoes a severe amount of deformation, its crystallographic planes tend to orient themselves in a preferred manner with respect to the direction of maximum strain; in which case the material is said to have a “texture”.
- ❑ The type of preferred orientation which is developed depends mainly on number and type of slip systems available, principal strains, temperature of deformation and type of texture present prior to deformation.
- ❑ For uniaxial deformation or other processes, texture is expressed in terms of miller indices of directions [uvw] aligned along the specimen axis, also called Fiber texture.
- ❑ Fiber texture is symmetrical to the wire axis. BCC metals have a fiber texture with $\langle 110 \rangle$ direction parallel to the wire axis. FCC metals have double fiber texture with both $\langle 111 \rangle$ and $\langle 100 \rangle$ directions parallel to the fiber axis.
- ❑ Texture develops or changes due to: (i) Crystallization/ solidification (from a non-crystalline / liquid state) (ii) Plastic deformation (by slip and twinning) (iii) Annealing (from the same phase) (iv) Phase transformation (from a different phase)
- ❑ Texture resulting from plastic deformation is strongly dependent on available slip and twinning systems but is not affected by processing variables like die angle, roll diameter, speed etc. Thus, same texture is produced whether a rod is made by rolling or drawing.
- ❑ Recrystallization of a cold worked metal produces a texture which is different from and stronger than that existing in the deformed metal. This is called an annealing or Recrystallization texture.

Hot Working

- ❑ Plastic deformation which is carried out under conditions of temperature and strain rate such that recovery processes occur substantially so that large strains can be achieved with essentially no strain hardening.
- ❑ Normally performed at temperature $>0.6T_m$ & at high strain rates in the range of $0.5-500 \text{ s}^{-1}$

Advantages of Hot Working

- ❑ Larger deformation can be accomplished and more rapidly by hot working since the metal is in plastic state.
- ❑ Porosity of the metal is considerably minimized.
- ❑ Concentrated impurities, if any in the metal are disintegrated and distributed throughout the metal.
- ❑ Grain structure of the metal is refined and physical properties is improved.
- ❑ No residual stresses in the material

Disadvantages of Hot Working

- ❑ Poor surface finish and loss of metal due to rapid oxidation or scale formation on the metal surface
- ❑ Close tolerances cannot be maintained.
- ❑ It involves excessive expenditure on account of high cost of tooling. This, however, is compensated by the high production rate and better quality of products.

Warm Working

- Warm working is the plastic deformation of a metal at temperature below the temperature range of recrystallization and above the room temperature i.e. intermediate to hot and cold working.

Advantages compared to Cold Working

- Combines the advantages of both hot and cold working into one operation.
- Fewer number of annealing operation (because of less strain hardening)
- Lesser loads on tooling and equipment
- Greater metal ductility

Advantages compared to Hot Working

- Improved dimensional control,
- Lower energy costs.
- Better precision of components
- Lesser scaling and decarburization on parts
- Better surface finish
- Lesser thermal shock on tooling
- Lesser thermal fatigue to tooling, and so greater life of tooling.

Cold Working

- Plastic deformation which is carried out in a temperature region and over a time interval such that the strain hardening is not relieved is called cold work.
- Normally performed at room temperature but in general $< 0.3T_m$, where recovery is limited and recrystallization does not occur.

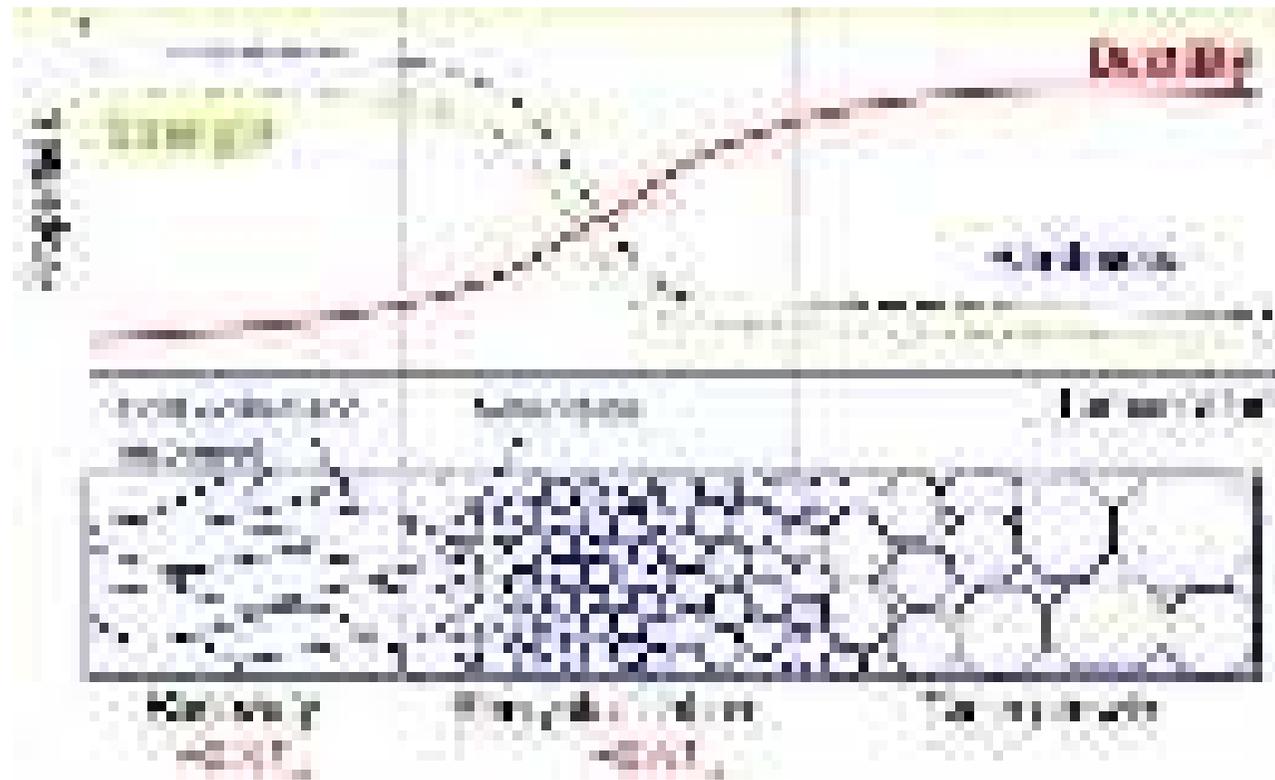
Advantages of Cold Working

- Due to work hardening Strength and hardness of the metal are increased.
- It is an ideal method for increasing hardness of those metals which do not respond to the heat treatment.
- Better dimensional control is possible because the reduction in size is not much.
- Provide fine grain size and good surface finish (No oxidation takes place).
- Handling is easier because of low operating temperature.
- Directional properties can be imparted.

Disadvantages of Cold Working

- Only ductile metals can be shaped through cold working.
- Over-working of metal results in brittleness and it has to be annealed to remove the same.
- Subsequent heat treatment is mostly needed to remove the residual stresses set up during cold working.
- Higher forces and heavier and more powerful equipment are required for deformation.

Recovery, Recrystallization & Grain Growth



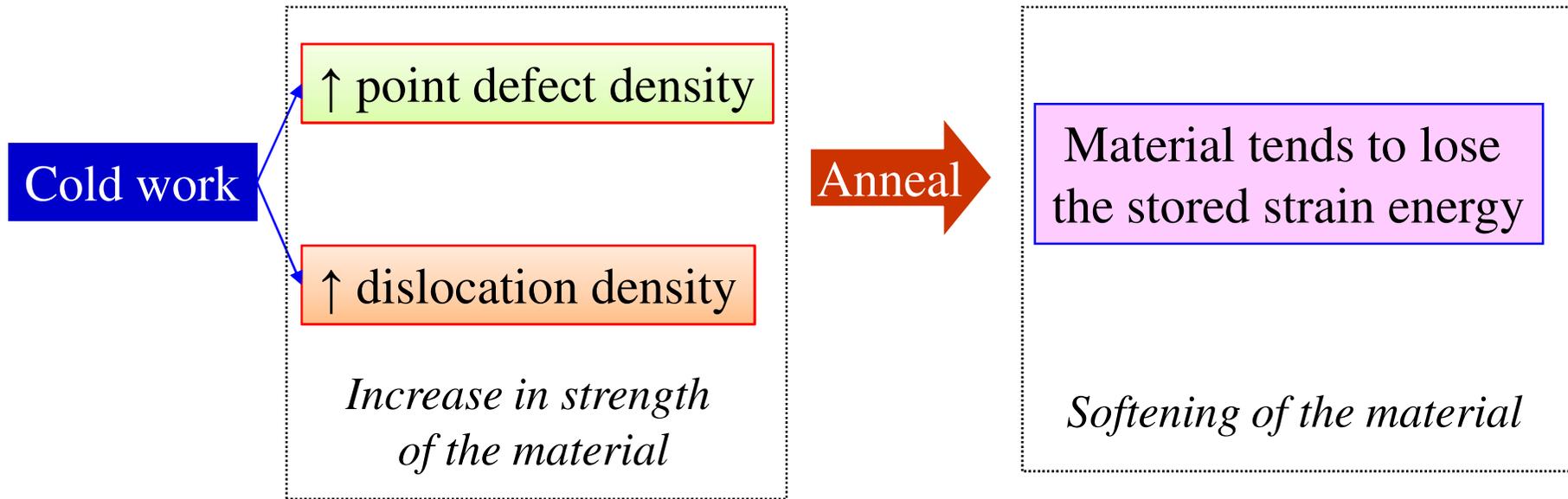
Introduction

Plastic deformation in the temperature range $(0.3 - 0.5) T_m \rightarrow$ **COLD WORK**

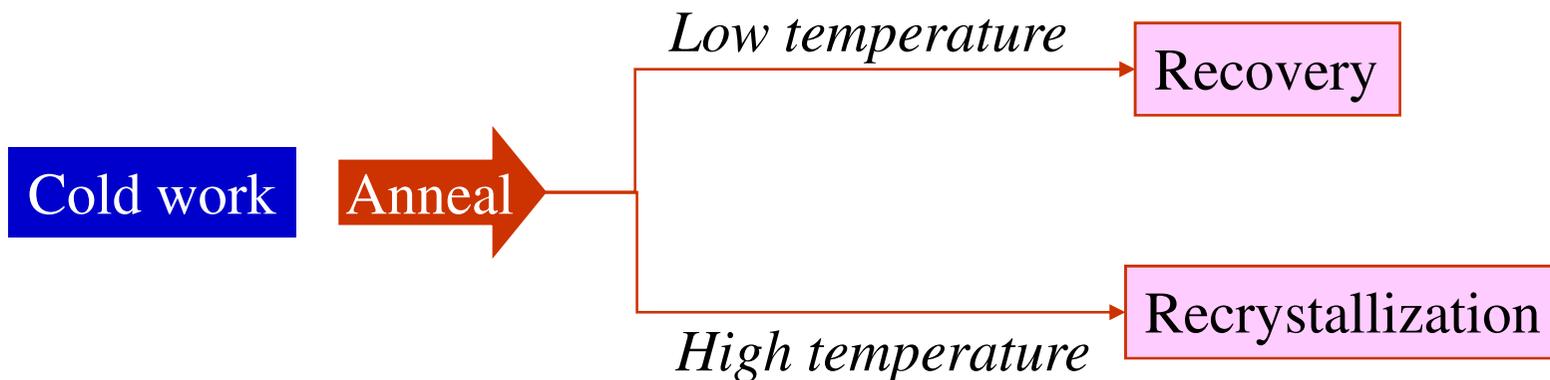
- ❑ Point defects and dislocations have strain energy associated with them
- ❑ (1 -10) % of the energy expended in plastic deformation is stored in the form of strain energy (in these defects) \rightarrow *The material becomes battery of energy..!*
- ❑ The cold worked material is in a micro structurally metastable state.
- ❑ Depending on the severity of the cold work the dislocation density can increase 4-6 orders of magnitude more. The material becomes stronger, but less ductile.
- ❑ The cold worked material is stronger (harder), but is brittle.
- ❑ Heating the material (typically below $0.5T_m$) and holding for sufficient time is a heat treatment process called annealing.
- ❑ Depending on the temperature of annealing processes like Recovery (at lower temperatures) or Recrystallization (at higher temperatures) may take place. During these processes the material tends to go from a micro structurally metastable state to a lower energy state (towards a stable state).
- ❑ Further 'annealing' of the recrystallized material can lead to grain growth.

Annealed material $\xrightarrow{\text{Cold work}}$ *Stronger material*
 $\rho_{\text{dislocation}} \sim (10^6 - 10^9)$ $\rho_{\text{dislocation}} \sim (10^{12} - 10^{14})$

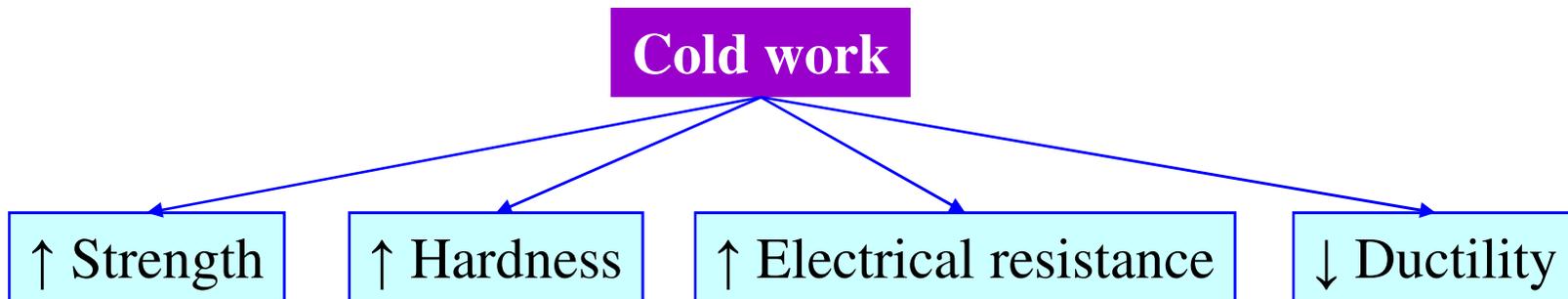
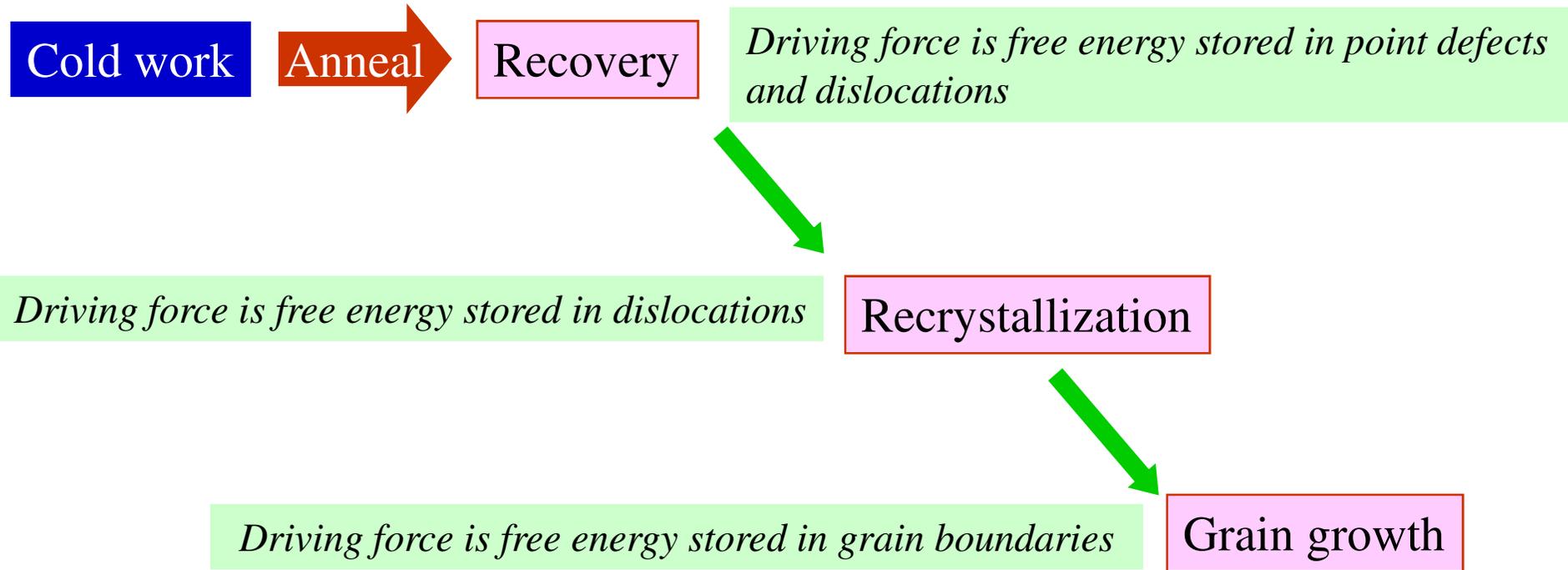
Introduction



- ❑ During cold work the point defect density (vacancies, self interstitials...) and dislocation density increase. Typical cold working techniques are rolling, forging, extrusion etc.
- ❑ Cold working is typically done on ductile metals (e.g. Al, Cu, Ni)



Overview of processes taking place during annealing of cold worked material and the driving force for these processes



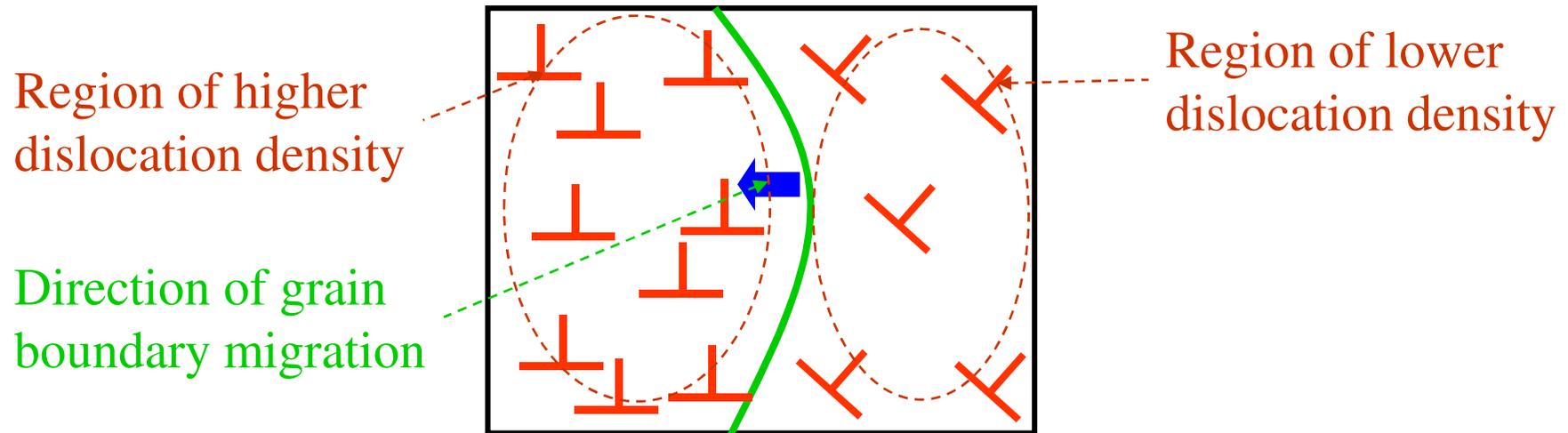
Changes occur to almost all **physical** and **mechanical** properties

Recovery

- ❑ Recovery takes place at low temperatures of annealing
- ❑ “Apparently no change in microstructure”
- ❑ Excess point defects created during Cold work are absorbed:
 - ▶ at surface or grain boundaries
 - ▶ by dislocation climb
- ❑ Random dislocations of opposite sign come together and annihilate each other
- ❑ Dislocations of same sign arrange into low energy configurations:
 - ▶ Edge → Tilt boundaries
 - ▶ Screw → Twist boundaries
 - ➔ **POLYGONIZATION**
- ❑ Overall reduction in dislocation density is small
- ❑ At the early stage of annealing of cold formed metals, external thermal energy permits the dislocations to move and form the boundaries of a polygonized subgrain structure while the dislocation density stays almost unchanged.
- ❑ This process also removes the residual stresses formed due to cold working significant. The recovering of physical and mechanical properties varies with the temperature and time.

Recrystallization

- ❑ $T_{\text{recrystallization}} \in (0.3 - 0.5) T_m$
- ❑ “Nucleation” and growth of new, strain free crystals
- ❑ Nucleation of new grains in the usual sense may not be present and grain boundary migrates into a region of higher dislocation density
- ❑ $\Delta G (\text{recrystallization}) = G (\text{deformed material}) - G (\text{undeformed material})$
- ❑ $T_{\text{Recrystallization}}$ is the temperature at which 50 % of the material recrystallizes in 1 hour



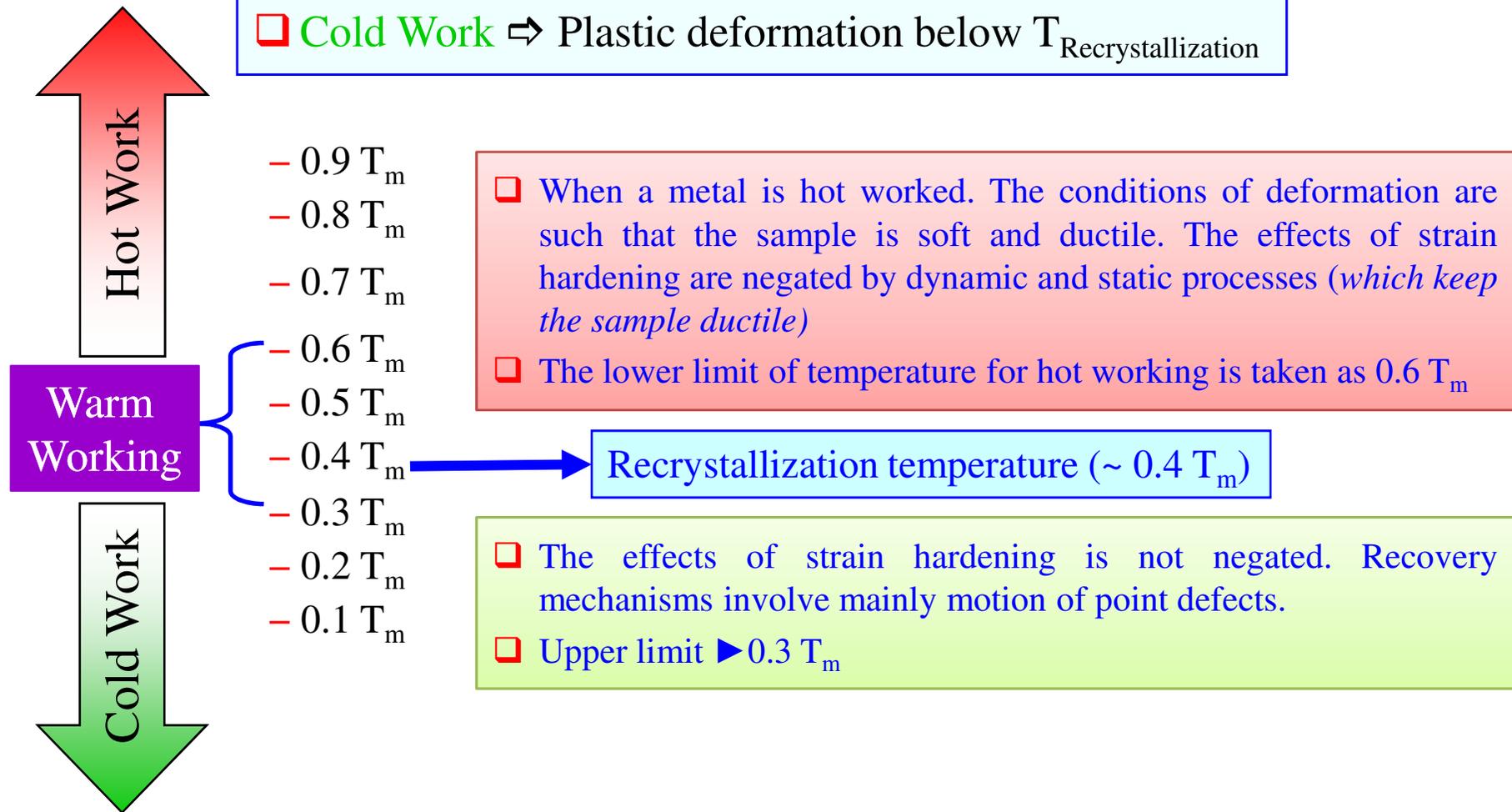
Recrystallization

- ❑ Deformation $\uparrow \Rightarrow$ recrystallization temperature ($T_{\text{recrystallization}}$) \downarrow
- ❑ Initial grain size $\downarrow \Rightarrow$ recrystallization temperature \downarrow
- ❑ High cold work + low initial grain size \Rightarrow finer recrystallized grains
- ❑ \uparrow cold work temperature \Rightarrow lower strain energy stored
 $\Rightarrow \uparrow$ recrystallization temperature
- ❑ Rate of recrystallization = exponential function of temperature
- ❑ $T_{\text{recrystallization}}$ = strong function of the purity of the material
 - $T_{\text{recrystallization}}$ (very pure materials) $\sim 0.3 T_m$
 - $T_{\text{recrystallization}}$ (impure) $\sim (0.5 - 0.6) T_m$
 - ▶ $T_{\text{recrystallization}}$ (99.999% pure Al) $\sim 75^\circ\text{C}$
 - $T_{\text{recrystallization}}$ (commercial purity) $\sim 275^\circ\text{C}$
- ❑ The impurity atoms segregate to the grain boundary and retard their motion \rightarrow *Solute drag* (can be used to retain strength of materials at high temperatures)
- ❑ Second phase particles also pin down the grain boundary during its migration

Hot Work and Cold Work

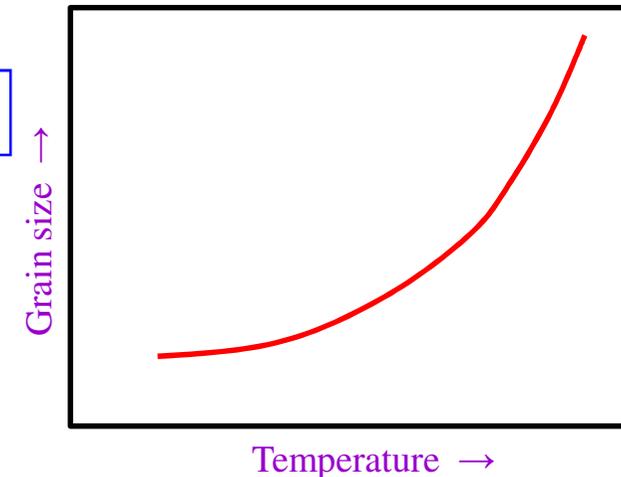
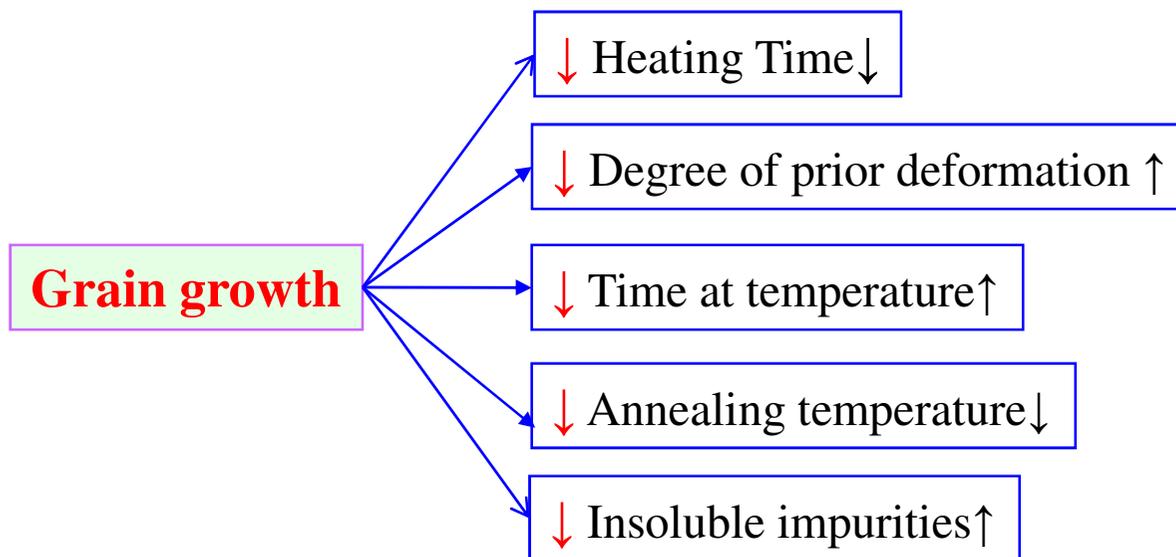
Often the range is further subdivided into Hot, Cold and Warm working as in the figure

- ❑ **Hot Work** \Rightarrow Plastic deformation above $T_{\text{Recrystallization}}$
- ❑ **Cold Work** \Rightarrow Plastic deformation below $T_{\text{Recrystallization}}$



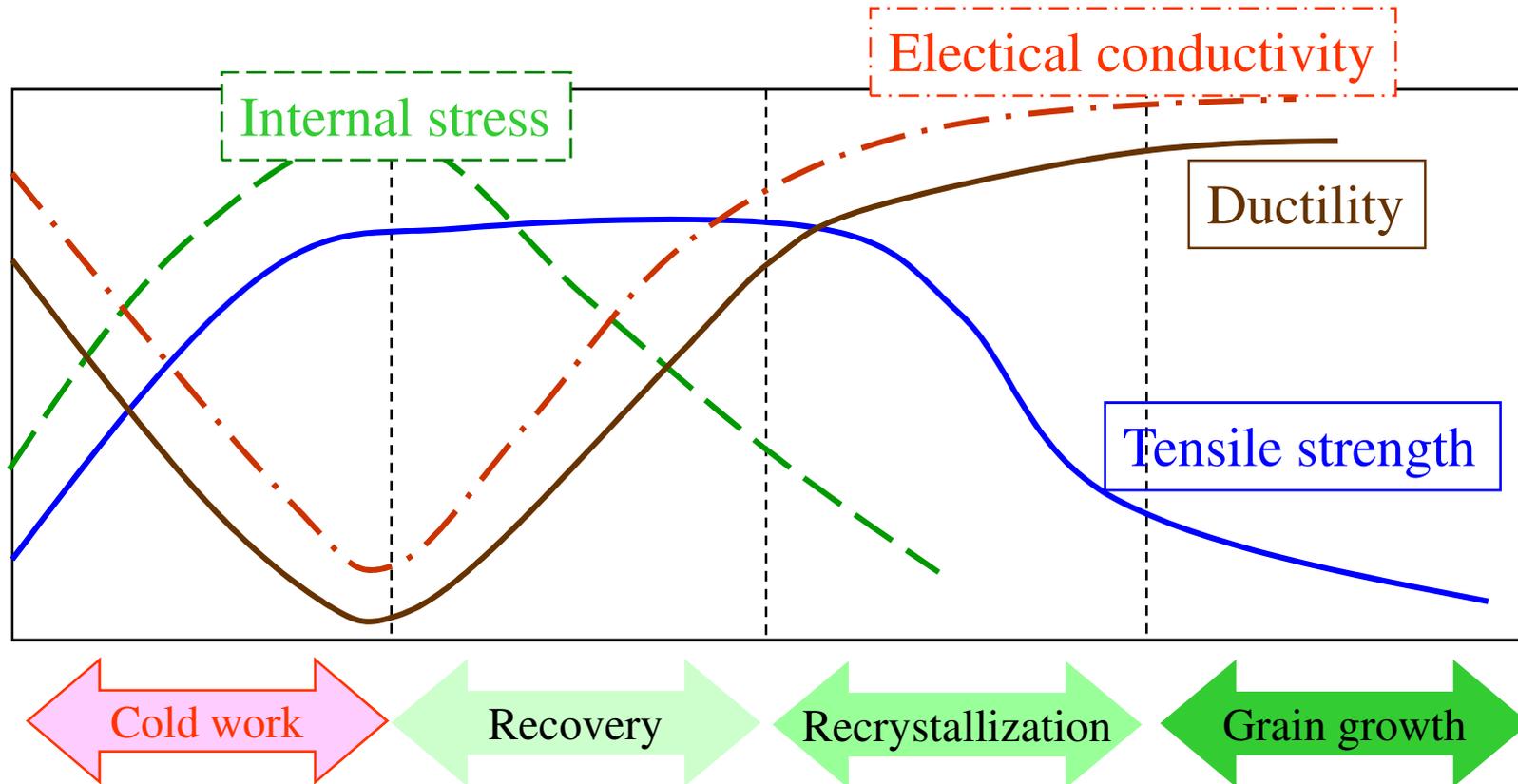
Grain Growth

- ❑ Large grains have lower free energy than small grains. This is associated with the reduction of the amount of grain boundary.
- ❑ Therefore, under ideal conditions, the lower energy state for a metal would be as a single crystal. This is driving force for grain growth.
- ❑ Opposing this force is the rigidity of the lattice. As the temperature increases, the rigidity of the lattice decreases and the rate of grain growth is more rapid.
- ❑ At any given temperature there is a maximum grain size at which these two effects are in equilibrium



Effect of temperature on recrystallized grain size

Summary

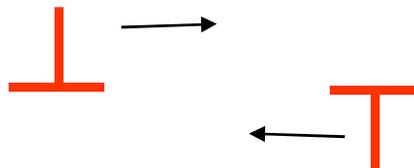


Questions ?

1. Cite the primary differences between elastic, anelastic, and plastic deformation behaviors.
2. Define Slip and Slip system. Give the slip systems of BCC, FCC and HCP
3. Define Twinning. Give the preferred twinning plane and twinning directions of BCC, FCC and HCP
4. It is possible to have both slip and twinning occur in the same grain? Explain
5. Which properties would be affected by preferred orientation and why?
6. Explain the reason for the increase in ductility of most metals as the temperature is raised.
7. A piece of copper originally 305 mm (12 in.) long is pulled in tension with a stress of 276 MPa (40,000 psi). If the deformation is entirely elastic, what will be the resultant elongation? [E for copper is 110 Gpa]
8. Make a schematic plot showing the tensile engineering stress–strain behavior for a typical metal alloy to the point of fracture. Now superimpose on this plot a schematic compressive engineering stress–strain curve for the same alloy. Explain any differences between the two curves.

Questions ?

9. Which of the following is the slip system for the simple cubic crystal structure? Why? $\{100\} \langle 110 \rangle$, $\{110\} \langle 110 \rangle$, $\{100\} \langle 010 \rangle$, $\{110\} \langle 111 \rangle$.
10. Explain the difference between resolved shear stress and critical resolved shear stress. Derive the expression for critical resolved shear stress.
11. Would you expect a crystalline ceramic material to strain harden at room temperature? Why or why not?
12. Briefly explain why some metals (i.e., lead and tin) do not strain harden when deformed at room temperature.
13. Sometimes $\cos\phi \cos\lambda$ in CRSS equation is termed the Schmid factor. Determine the magnitude of the Schmid factor for an FCC single crystal oriented with its $[120]$ direction parallel to the loading axis.
14. Consider two edge dislocations of opposite sign and having slip planes that are separated by several atomic distances as indicated in the diagram. Briefly describe the defect that results when these two dislocations become aligned with each other.



Questions ?

15. Is it possible for two screw dislocations of opposite sign to annihilate each other? Explain your answer.
16. For each of edge, screw, and mixed dislocations, cite the relationship between the direction of the applied shear stress and the direction of dislocation line motion.
17. Consider a single crystal of nickel oriented such that a tensile stress is applied along a $[001]$ direction. If slip occurs on a (111) plane and in a $[\bar{1}01]$ direction and is initiated at an applied tensile stress of 13.9 Mpa. Compute the critical resolved shear stress.
18. A single crystal of a metal that has the BCC crystal structure is oriented such that a tensile stress is applied in the $[100]$ direction. If the magnitude of this stress is 4.0 MPa, compute the resolved shear stress in the $[\bar{1}11]$ direction on each of the (110) , (011) , and $(10\bar{1})$ planes. On the basis of these resolved shear stress values, which slip system(s) is (are) most favorably oriented.
19. List four major differences between deformation by twinning and deformation by slip relative to mechanism, conditions of occurrence, and final result.
20. Briefly explain why HCP metals are typically more brittle than FCC and BCC metals.

Questions ?

21. Describe in your own words the three strengthening mechanisms discussed in this chapter (i.e., grain size reduction, solid-solution strengthening, and strain hardening). Be sure to explain how dislocations are involved in each of the strengthening techniques.
22. Two previously undeformed cylindrical specimens of an alloy are to be strain hardened by reducing their cross-sectional areas (while maintaining their circular cross sections). For one specimen, the initial and deformed radii are 15 mm and 12 mm, respectively. The second specimen, with an initial radius of 11 mm, must have the same deformed hardness as the first specimen; compute the second specimen's radius after deformation.
23. Briefly cite the differences between recovery and recrystallization processes.
24. Explain the differences in grain structure for a metal that has been cold worked and one that has been cold worked and then recrystallized.
25. What is the driving force for recrystallization? And for grain growth?

Introduction

- ❑ An **alloy** is a substance that has metallic properties and is composed of two or more chemical elements, of which at least one is a metal.
- ❑ An alloy system contains all the alloys that can be formed by several elements combined in all possible proportions. If the system is made up of two elements, it is called a *binary alloy system*; three elements, a *ternary alloy system*; etc.
- ❑ Taking only 45 of the most common metals, any combination of two gives 990 binary systems. Combinations of three give over 14,000 ternary systems.
- ❑ However, in each system, a large number of different alloys are possible. If the composition is varied by 1 percent, each binary system will yield 100 different alloys.
- ❑ *Since commercial alloys often contain many elements, it is apparent that the number of possible alloys is almost infinite.*
- ❑ **Alloys** may be homogeneous (uniform) or mixtures. If the alloy is homogeneous it will consist of a single phase, and if it is a mixture it will be a combination of several phases.
- ❑ The uniformity of an alloy phase is not determined on an atomic scale, such as the composition of each unit lattice cell, but rather on a much larger scale.

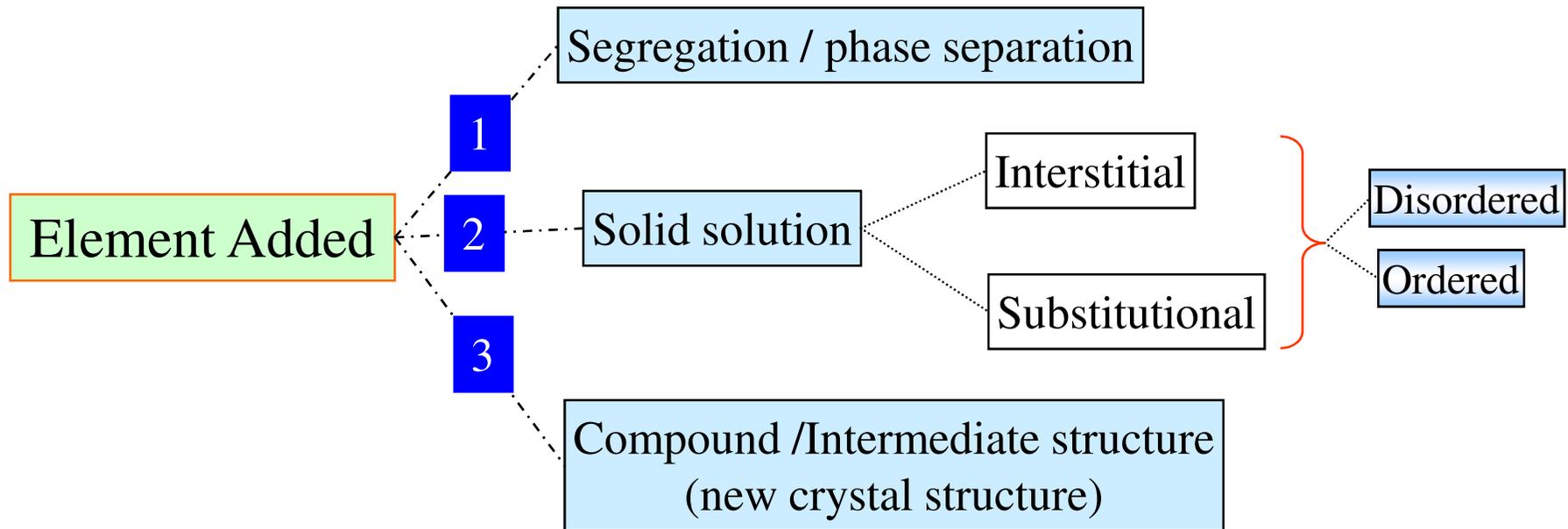
Phase

- ❑ A phase is anything which is homogeneous and physically distinct.
- ❑ Any structure which is visible as physically distinct microscopically may be considered as a phase
- ❑ For most pure elements the term *phase* is synonymous with state. There is, therefore, for pure elements, a gaseous, liquid, and solid phase.
- ❑ Some metals are allotropic in the solid state and will have different solid phases. When the metal undergoes a change in crystal structure, it undergoes a phase change since each type of crystal structure is physically distinct.
- ❑ In a pure material when other elements are added intentionally they are called alloying elements*
- ❑ Alloying elements are added to improve certain properties of the pure element
- ❑ The alloying element can be accommodated in one of the three possibilities as shown in the figure below

* *When added small quantity it is often called doping*

'In Principle' there is no difference between an 'impurity' and 'alloying'

Classification of alloys

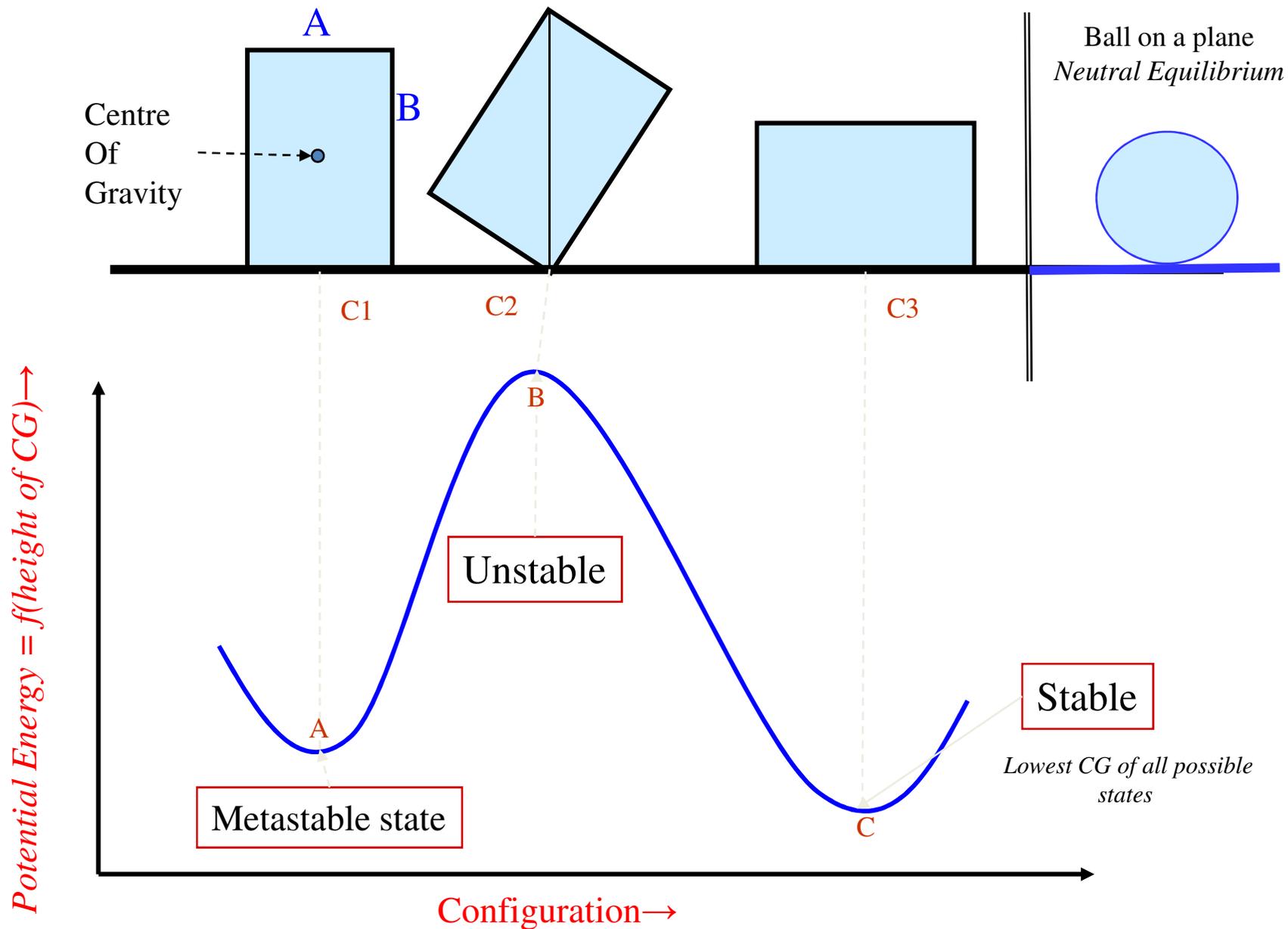


1 Segregation / phase separation

- The added element does not dissolve* in the parent/matrix phase →
 - in may form a separate phase**
 - in a **polycrystal** it may go to the grain boundary
 - in may segregate to other defects like **dislocation cores** etc.
- The solubility in the case of a substitutional solid solution is given by **Hume-Rothery rules** (considered soon)

- ❑ Any solution is composed of two parts: a solute and a solvent. The solute is the minor part of the solution or the material which is dissolved, while the solvent constitutes the major portion of the solution.
- ❑ *The most common solutions involve water as the solvent, such as sugar or salt dissolved in water.*
- ❑ There are three possible conditions for a solution: **unsaturated**, **saturated**, and **supersaturated**.
- ❑ If the solvent is dissolving less of the solute than it could dissolve at a given temperature and pressure, it is said to be **unsaturated**.
- ❑ If it is dissolving the limiting amount of solute, it is **saturated**.
- ❑ If it is dissolving more of the solute than it should, under equilibrium conditions, the solution is **supersaturated**.
- ❑ The supersaturated condition is an unstable one, and given enough time or a little energy, the solution tends to become stable or saturated by rejecting or precipitating the excess solute.
- ❑ *A solid solution is simply a solution in the solid state and consists of two kinds of atoms combined in one type of space lattice.*
- ❑ *There are two types solid solutions, substitutional and interstitial.*

Mechanical Equilibrium of a Rectangular Block



Substitutional Solid Solution

- ❑ In this type of solution, the atoms of the solute substitute for atoms of the solvent in the lattice structure of the solvent.
- ❑ For example, silver atoms may substitute for gold atoms without losing the f.c.c structure of gold, and gold atoms may substitute for silver atoms in the f.c.c lattice structure of silver.
- ❑ All alloys in the silver-gold system consist of an f.c.c lattice with silver and gold atoms distributed at random through the lattice structure. This entire system consists of a continuous series of solid solutions.
- ❑ Several factors are now known, largely through the work of *Hume-Rothery*, that control the range of solubility in alloy systems.

Empirical (precise) rules for the formation of substitutional solid solution

- ❑ The solute and solvent atoms do not differ by more than 15% in diameter
- ❑ The electro-negativity difference between the elements is small
- ❑ The valency and crystal structure of the elements is same

Additional rule

- ❑ Element with higher valency is dissolved more in an element of lower valency rather than vice-versa

Hume Rothery Rules

- ❑ CRYSTAL-STRUCTURE FACTOR : complete solid solubility of two elements is never attained unless the elements have the same type of crystal lattice structure.
- ❑ RELATIVE-SIZE FACTOR : The size factor is favorable for solid solution formation when the difference in atomic radii is less than about 15%

$$\text{mismatch} = \left(\frac{r_{\text{solute}} - r_{\text{solvent}}}{r_{\text{solvent}}} \right) \times 100 \leq 15$$

- ❑ VALENCY RULE : a metal will dissolve a metal of higher valency to greater extent than one of lower valency. The solute and solvent atoms should typically have the same valance in order to achieve maximum solubility.
- ❑ ELECTRONEGATIVITY RULE : Electro negativity difference close to '0' gives maximum solubility. The more electropositive one element and the more electronegative the other, the greater is the likelihood that they will form an inter metallic compound instead of a substitutional solid solution. The solute and the solvent should lie relatively close in the electrochemical series.



Please Read Carefully!

Hume Rothery Rules

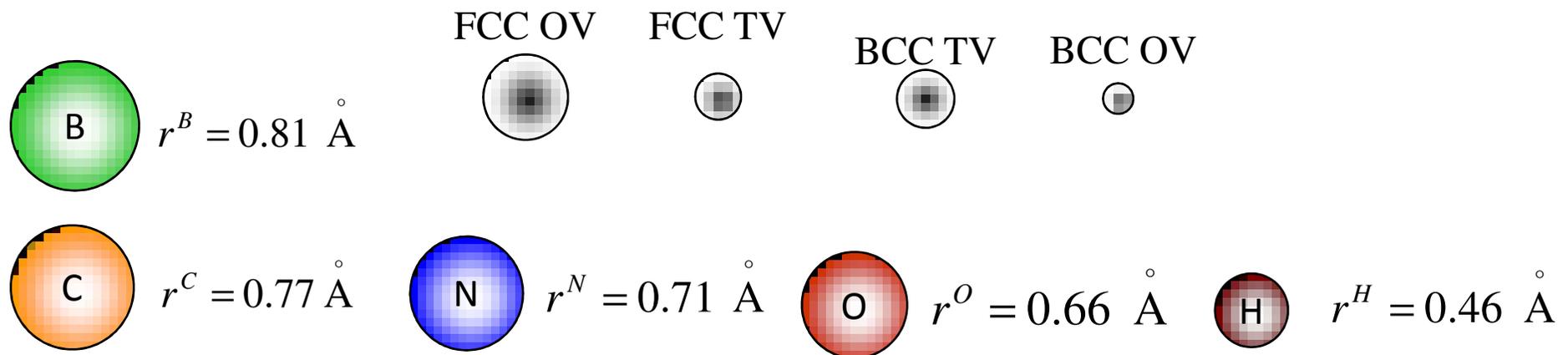
Examples of pairs of elements satisfying Hume Rothery rules and forming complete solid solution in all proportions

| System | | Crystal structure | Radius of atoms (Å) | Valency | Electronegativity |
|--------|----|-------------------|---------------------|---------|-------------------|
| Ag-Au | Ag | FCC | 1.44 | 1 | 1.9 |
| | Au | FCC | 1.44 | 1 | 2.4 |
| Cu-Ni | Cu | FCC | 1.28 | 1 | 1.9 |
| | Ni | FCC | 1.25 | 2 | 1.8 |
| Ge-Si | Ge | DC | 1.22 | 4 | 1.8 |
| | Si | DC | 1.18 | 4 | 1.8 |

A continuous series of solid solutions may not form even if the above conditions are satisfied
e.g. Cu- γ Fe

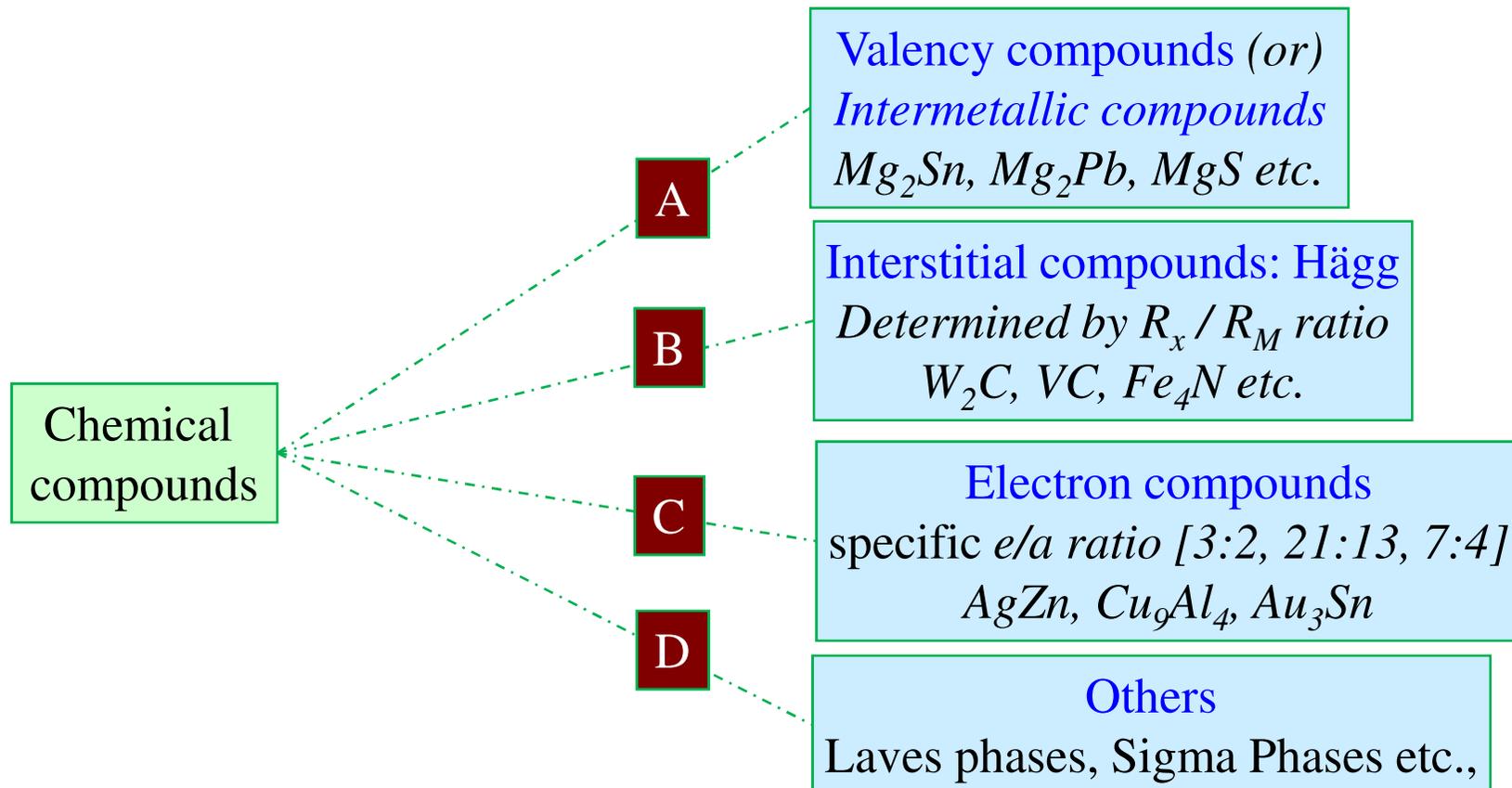
Interstitial Solid Solutions

- ❑ The second species added goes into the voids of the parent lattice
- ❑ E.g. Octahedral and tetrahedral voids in CCP, HCP (& BCC) crystals (E.g. of solvents: Fe, Mo, Cr etc.)
- ❑ E.g. B ($r = 0.97 \text{ \AA}$) C ($r = 0.77 \text{ \AA}$), N ($r = 0.71 \text{ \AA}$), O ($r = 0.66 \text{ \AA}$), H ($r = 0.46 \text{ \AA}$)
- ❑ If the solute atom has a diameter $< 0.59 r_{\text{host}}$ then extensive solubility is expected (*may or may not happen!*)
- ❑ Solubility for interstitial atoms is more in transition elements (Fe, Ti, V, Zr, Ni, W, U, Mn, Cr) \rightarrow due to electronic structure (*incomplete inner shell*)
- ❑ C is especially insoluble in most non-transition elements



3 Compound /Intermediate structure

- ❑ Chemical compounds are combination of positive and negative valence elements. Intermetallic compounds can be very different from the normal chemical compounds (e.g. H₂O).
- ❑ Most compounds like pure metals, the cooling curve for a compound is similar to that for a pure metal.



A

Valency compounds (Intermetallic compounds)

The following includes features distinguishing them from solid solutions

- ❑ Different crystal lattice as compared to the components
- ❑ Most chemical compounds have complex crystal structures
- ❑ Each component has a specific location in the lattice
- ❑ Composition can be specified by a simple formula $\rightarrow A_nB_m : Mg_2Sn, Mg_2Pb, Ni_3(Al, Ti)$
(m,n are small whole numbers)
- ❑ Different properties than the components
- ❑ Constant melting point and dissociation temperature
- ❑ Accompanied by substantial thermal effect
- ❑ Typically formed by elements with very different electronic and crystal structures
- ❑ The bonding in intermetallic compounds is usually metallic
- ❑ The bonding between a metal and a non-metal could also be metallic
- ❑ A large number of intermetallic compounds do not obey valency rules or have a constant composition (*thus distinguishing them from usual chemical compounds*)

In some sense the tendency to form compounds is opposite of that to form solid solutions!

B

Interstitial compounds: Hägg Phases

- ❑ Transition metals form compounds with elements with small atomic size (H, C, N, B)
- ❑ Formulae:
 - $M_4X \rightarrow Fe_4N, Mn_4N$
 - $M_2X \rightarrow W_2C, Mo_2C, Fe_2N$
 - $MX \rightarrow WC, VC, TiC, NbC, TiN$
- ❑ The crystal structure depends on R_x/R_M ratio
 - If $\triangleright R_x/R_M < 0.59 \rightarrow$ **Simple crystal lattices** (Cubic, Hexagonal)
Non-metal occupies specific interstitial sites in the cubic or hexagonal crystal
 - If $\triangleright R_x/R_M > 0.59 \rightarrow$ **Complex crystal structures** (e.g. Fe_3C)
- ❑ Apart from size factor **valency** of the interstitial atom also seems to play some role
- ❑ Typically interstitial phases have a **variable composition** (*the chemical formula indicates the maximum amount of non-metal in the structure*)
- ❑ Properties include:
 - \triangleright High electrical conductivity (with decreasing conductivity with increasing temperature as for a metal)
 - \triangleright Metallic lustre
 - \triangleright Many of the interstitial phases are hard (e.g. WC, VC)
 - \triangleright The carbides have high melting point
 - \triangleright Some covalent character to the bonding in some of these phases

Interstitial solid solutions on the other hand have much lower content of the interstitial atoms and the crystal structure of the parent is retained

C

Electron Compounds

- ❑ It has a definite ratio of valence electrons to atoms and are therefore called electron compounds.
- ❑ These compounds are formed usually in:
 - **Monovalent metals** (Cu, Ag, Au, Li, Na)
 - **Transition metals** (Fe, Co, Mn)
 - Other metals with valency values between 2-5
- ❑ Alloys of Cu, Ag, Au frequently form electron compounds
- ❑ These compounds have specific ratios for: **number of valence electrons/atoms** →
 - **3:2 - B.C.C** → (E.g. AgCd , AgZn , Cu_3Al , FeAl etc.,)
 - **21:13 – complex CUBIC** → (E.g. Ag_5Cd_8 , Cu_9Al_4 , $\text{Fe}_5\text{Zn}_{21}$, $\text{Ni}_5\text{Zn}_{21}$ etc.,)
 - **7:4 – H.C.P** → (E.g. AuZn_3 , AgCd_3 , Cu_3Si , Ag_3Sn)
- ❑ These compounds can form over a wide range of compositions
- ❑ For example, in the compound AgZn , the atom of silver has one valence electron while that of zinc has two valence electrons so that the two atoms of the compound will have three valence electrons, or an electron-to-atom ratio of 3:2.
- ❑ Consider, In the compound Cu_9Al_4 , each atom of copper has one valence electron and each atom of aluminium three valence electrons, so that the 13 atoms that make up the compound have 21 valence electrons, or an electron-to-atom ratio of 21:13.

D

Others..!

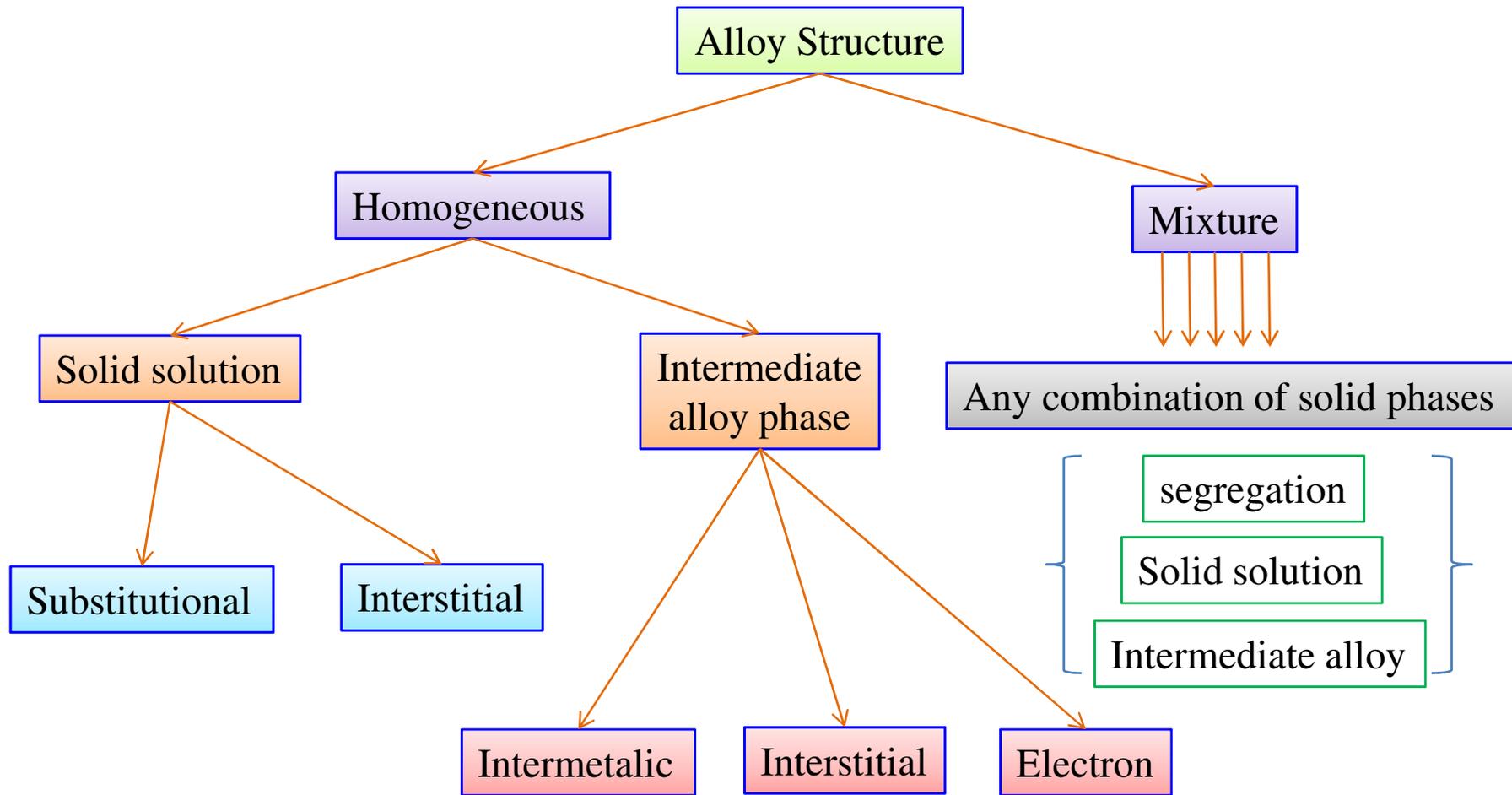
Laves Phases

- ❑ Laves phases have a general formula of AB_2 , for exmple $MgCu_2$ (cubic), $MgZn_2$ (hexagonal), $MgNi_2$ (hexagonal).

Sigma Phases

- ❑ Sigma phases has a very complex crystal structure and is very brittle. This phase can act as a source of embrittlement in some alloys such as steels.

Summary



Introduction

- ❑ Phase diagrams are an important tool in the armory of an materials scientist
- ❑ In the simplest sense a phase diagram demarcates regions of existence of various phases. (*Phase diagrams are maps*)
- ❑ Phase diagrams are also referred to as “**equilibrium diagrams**” or “**constitutional diagrams**”. This usage requires special attention: through the term used is “equilibrium”, in practical terms the equilibrium is *not global equilibrium but Microstructural level equilibrium*.
- ❑ Broadly two kinds of phase diagrams can be differentiated* → those involving time and those which do not involve time.
- ❑ In this chapter we shall deal with the phase diagrams not involving time.
This type can be further sub classified into:
 - ✓ Those with composition as a variable (e.g. **T** vs. **%Composition**)
 - ✓ Those without composition as a variable (e.g. **P** vs. **T**)
- ❑ Time-Temperature-Transformation (TTT) diagrams and Continuous-Cooling-Transformation (CCT) diagrams involve time. These diagrams will be considered in the chapter on Heat treatment.

**This is form a convenience in understanding point of view*

Definitions

Components of a system

- ❑ Independent chemical species which comprise the system. These could be **Elements, Ions, Compounds**

Example: **Au-Cu system** : Components → Au, Cu (elements)

Ice-water system : Component → H₂O (compound)

Al₂O₃-Cr₂O₃ system : Components → Al₂O₃, Cr₂O₃

Phase

- ❑ A physically homogeneous and distinct portion of a material system (e.g. gas, crystal, amorphous...)
- ❑ **Gases** : Gaseous state always a single phase → mixed at atomic or molecule level.
- ❑ **Liquids**: Liquid solution is a single phase → e.g. NaCl in H₂O **and** Liquid mixtures consists of two or more phases → e.g. Oil in water (*no mixing at the atomic level*)
- ❑ **Solids**: In general due to several compositions and crystals structures many phases are possible.
 - ✓ For the same composition different crystal structures represent different phases. E.g. **Fe (BCC) and Fe (FCC)** are different phases

Definitions

What kinds of phases exist?

- Based on state → Gas, Liquid, Solid
- Based on atomic order → Amorphous, Quasi-crystalline, Crystalline
- Based on band structure → Insulating, Semi-conducting, Semi-metallic, Metallic
- Based on Property → Para-electric, Ferromagnetic, Superconducting
- Based on stability → Stable, Metastable, Unstable
- Also sometimes- Based on size/geometry of an entity → Nanocrystalline, mesoporous, layered.

Phase transformation

- Phase transformation is the change of one phase into another. For example
 - ✓ Water → Ice and α -Fe (BCC) → γ -Fe (FCC)

Grain

- The single crystalline part of polycrystalline metal separated by similar entities by a grain boundary

Definitions

Solute

- ❑ The component of either a liquid or solid solution that is present to a lesser or minor extent; the component that is dissolved in the solvent.

Solvent

- ❑ The component of either a liquid or solid solution that is present to a greater or major extent; the component that dissolves the solute.

System

- ❑ System, has two meanings. First, “system” may refer to a specific body of material or object. Or, it may relate to the series of possible alloys consisting of the same components, but without regard to alloy composition

Solubility Limit

- ❑ For many alloy systems and at some specific temperature, there is a maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution; this is called a Solubility Limit.

Definitions

Microstructure

- ❑ (Phases + defects + residual stress) & their distributions
- ❑ Structures requiring magnifications in the region of 100 to 1000 times. (or) The distribution of phases and defects in a material.

Phase diagram

- ❑ Map that gives relationship between phases in equilibrium in a system as a function of T, P and composition. *Map demarcating regions of stability of various phases*

Variables/Axis of phase diagrams

- ❑ The axes can be:
 - ✓ Thermodynamic (T, P, V)
 - ✓ Kinetic (t) or Composition variables (C, %X)
- ❑ In single component systems (unary systems) the usual variables are T & P
- ❑ In phase diagrams used in materials science the usual variables are T & %X
- ❑ In the study of phase transformation kinetics TTT diagrams or CCT diagrams are also used where the axes are T & t

Definitions

System Components

Phase diagrams and the systems they describe are often classified and named for the number (in Latin) of components in the system:

| Number of components | Name of system or diagram |
|----------------------|---------------------------|
| <i>One</i> | Unary |
| <i>Two</i> | Binary |
| <i>Three</i> | Ternary |
| <i>Four</i> | Quaternary |
| <i>Five</i> | Quinary |
| <i>Six</i> | Sexinary |
| <i>Seven</i> | Septenary |
| <i>Eight</i> | Octanary |
| <i>Nine</i> | Nonary |
| <i>Ten</i> | Decinary |

Coordinates of Phase Diagrams

❑ Phase diagrams are usually plotted with temperature, in degrees centigrade or Fahrenheit, as the ordinate and the alloy composition in weight percentage as the abscissa.

❑ The weight % of component A:

$$W_A = \frac{\text{weight of component A}}{\Sigma \text{ Weight of all components}} \times 100$$

❑ The atom (or mol)% of component A

$$X_A = \frac{\text{number of atoms (or mols) of component A}}{\Sigma \text{ number of atoms (or mols) of all components}} \times 100$$

❑ The Conversion from weight percentage to atomic percentage may be made by the following formulas:

$$\text{Atomic percent of A} = \frac{X}{X + Y \left(\frac{M}{N} \right)} \times 100$$

$$\text{Atomic percent of B} = \frac{Y \left(\frac{M}{N} \right)}{X + Y \left(\frac{M}{N} \right)} \times 100$$

M = atomic weight of metal A & N = atomic weight of metal B

X = weight percentage of metal A & Y = weight percentage of metal B

Experimental Methods

Thermal Analysis

A plot is made of temperature vs. time, at constant composition, the resulting cooling curve will show a change in slope when a phase change occurs because of the evolution of heat by the phase change. This method seems to be best for determining the initial and final temperature of solidification. Phase changes occurring solely in the solid state generally involve only small heat changes, and other methods give more accurate results.

Metallographic Methods

This method consists in heating samples of an alloy to different temperatures, waiting for equilibrium to be established, and then quickly cooling to retain their high temperature structure. The samples are then examined microscopically. This method is difficult to apply to metals at high temperatures because the rapidly cooled samples do not always retain their high temperature structure, and considerable skill is then required to interpret the observed microstructure correctly.

X-ray diffraction

Since this method measures lattice dimensions, it will indicate the appearance of a new phase either by the change in lattice dimension or by the appearance of a new crystal structure. This method is simple, precise, and very useful in determining the changes in solid solubility with temperature

Gibbs Phase Rule

- ❑ The phase rule connects the Degrees of Freedom, the number of components in a system and the number of phases present in a system via a simple equation.
- ❑ To understand the phase rule one must understand the variables in the system along with the degrees of freedom.
- ❑ We start with a general definition of the phrase “degrees of freedom”.

Degrees of Freedom

The degree of freedom, F , are those externally controllable conditions of temperature, pressure, and composition, which are independently variable and which must be specified in order to completely define the equilibrium state of the system.

**For a system in
equilibrium**

$$F = C - P + 2$$

or

$$F - C + P = 2$$

F – Degrees of Freedom
 C – Number of Components
 P – Number of Phases

The degrees of freedom cannot be less than zero so that we have an upper limit to the number of phases that can exist in equilibrium for a given system.

Gibbs Phase Rule

Variables in a phase diagram

- C – No. of components
- P – No. of phases
- F – No. of degrees of freedom
- Variables in the system = Composition variables + Thermodynamic variables
- Composition of a phase specified by (C – 1) variables (*If the composition is expressed in %ages then the total is 100% → there is one equation connecting the composition variables and we need to specify only (C - 1) composition variables*)
- No. of variables required to specify the composition of all phases: P(C – 1) (*as there are P phases and each phase needs the specification of (C – 1) variables*)
- Thermodynamic variables = P + T (usually considered) = 2 (*at constant pressure (e.g. atmospheric pressure) the thermodynamic variable becomes 1*)
- Total no. of variables in the system = P (C – 1) + 2
- F < no. of variables → F < P (C – 1) + 2

Gibbs Phase Rule

- For a system in equilibrium the chemical potential of each species is same in all the phases
 - ✓ If $\alpha, \beta, \gamma \dots$ are phases, then: $\mu_A(\alpha) = \mu_A(\beta) = \mu_A(\gamma) \dots$
 - ✓ Suppose there are 2 phases (α and β phases) and 3 components (A, B, C) in each phase then : $\mu_A(\alpha) = \mu_A(\beta)$, $\mu_B(\alpha) = \mu_B(\beta)$, $\mu_C(\alpha) = \mu_C(\beta) \rightarrow$ i.e. there are three equations. For each component there are $(P - 1)$ equations and for C components the total number of equations is $C(P - 1)$. In the above example the number of equations is $3(2 - 1) = 3$ equations.
 - ✓ $F = (\text{Total number of variables}) - (\text{number of relations between variables})$
 $= [P(C - 1) + 2] - [C(P - 1)] = C - P + 2$
 - ✓ In a single phase system $F = \text{Number of variables}$
 - ✓ $P \uparrow \rightarrow F \downarrow$ (For a system with fixed number of components as the number phases increases the degrees of freedom decreases.)

$$F = C - P + 2$$

It is worthwhile to clarify a few terms at this stage:

- ❑ Components 'can' go on to make a phase (*of course one can have single component phases as well e.g. BCC iron phase*)
- ❑ Phases 'can' go on to make a microconstituent.
- ❑ Microconstituents 'can' go on to make a microstructure (*of course phases can also directly go on to make a microstructure*)

Gibbs Phase Rule

A way of understanding the Gibbs Phase Rule : $P + F = C + 2$

The degrees of freedom can be thought of as the difference between *what you (can) control and what the system controls*

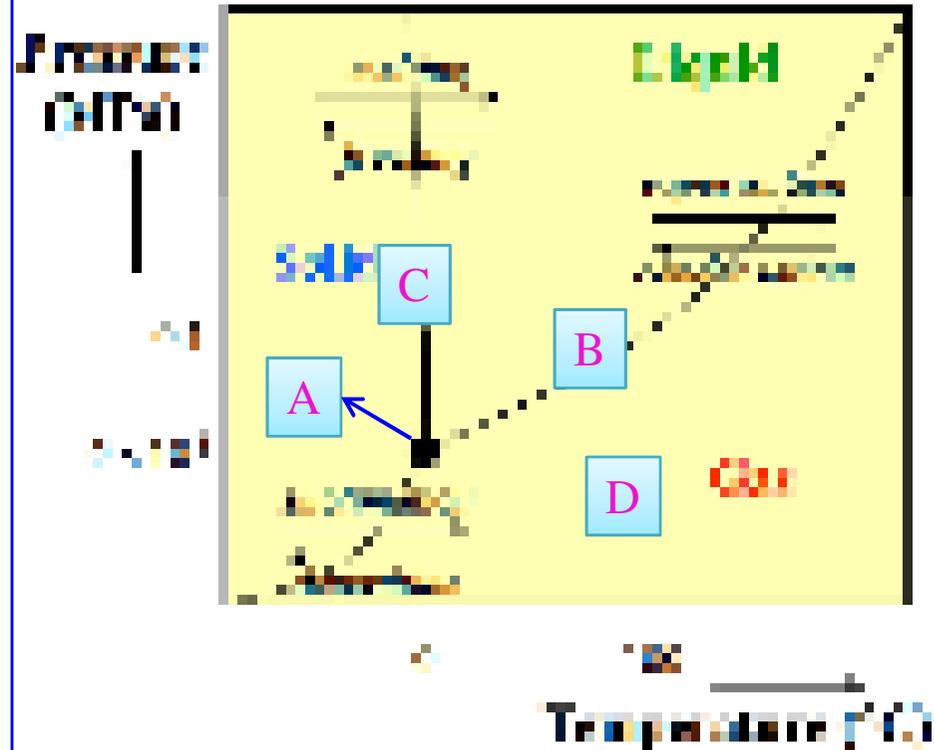
$$\begin{array}{c} \boxed{F} \\ \uparrow \\ \boxed{\text{Degrees of freedom}} \end{array} = \begin{array}{c} \boxed{C+2} \\ \uparrow \\ \boxed{\text{What you can control}} \\ \text{Can control the no. of} \\ \text{components added and P\&T} \end{array} - \begin{array}{c} \boxed{P} \\ \uparrow \\ \boxed{\text{What the system controls}} \\ \text{System decided how many} \\ \text{phases to produce given the} \\ \text{conditions} \end{array}$$

Variation of the number of degrees of freedom with number of components and number of phases

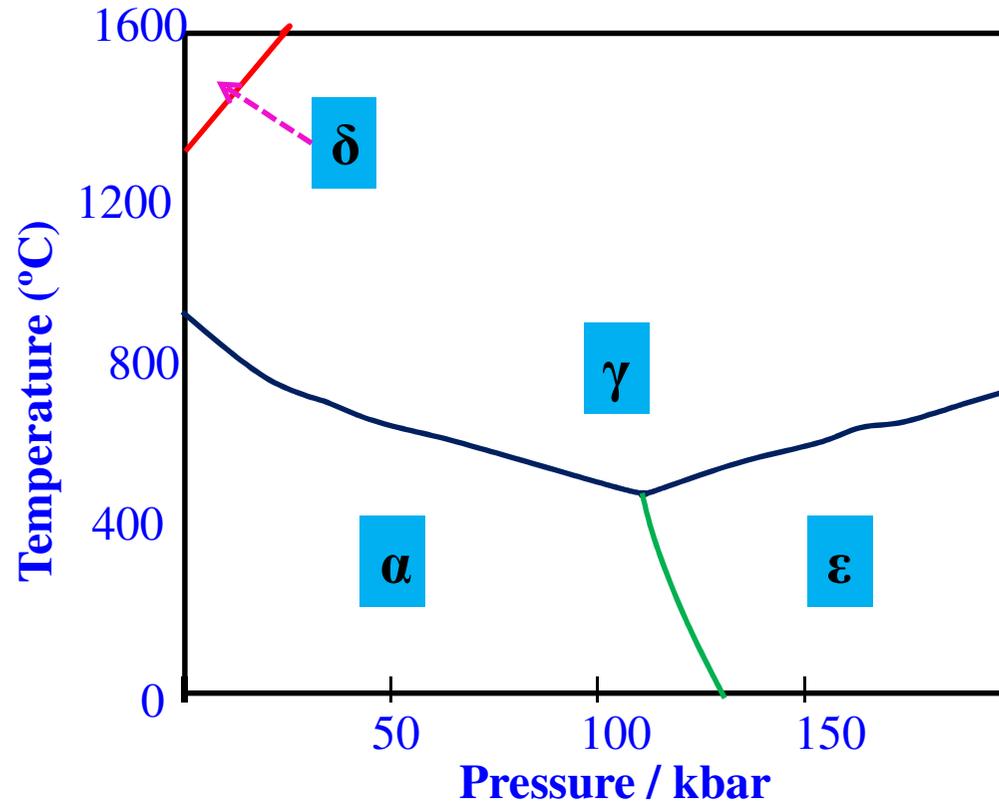
| $C = 2$ | No. of Phases | Total Variables $P(C-1)+2$ | Degrees of freedom $C-P+2$ | Degrees of freedom $C-P+1$ |
|---------|---------------|-------------------------------|-------------------------------|-------------------------------|
| | 1 | 3 | 3 | 2 |
| | 2 | 4 | 2 | 1 |
| | 3 | 5 | 1 | 0 |
| | 4 | 6 | 0 | <i>Not possible</i> |

Unary Phase Diagram

- ❑ Let us start with the simplest system possible: the unary system wherein there is just one component.
- ❑ Though there are many possibilities even in unary phase diagram (in terms of the axis and phases), we shall only consider a T-P unary phase diagram.
- ❑ Let us consider the water (H_2O) unary phase diagram
- ❑ The Gibbs phase rule here is: $F=C-P+2$ (2 is for T&P) (no composition variables here)
- ❑ Along the 2 phase co-existence (at B & C) lines the degree of freedom (F) is 1 \rightarrow i.e. we can choose either T or P and the other will be automatically fixed.
- ❑ The 3 phase co-existence points (at A) are invariant points with $F=0$. (Invariant point implies they are fixed for a given system).
- ❑ The single phase region at point D, T and P can both be varied while still being in the single phase region with $F = 2$.



Unary Phase Diagram



The above figure represents the phase diagram for pure iron. The triple point temperature and pressure are 490°C and 110 kbars, respectively. α , γ and ϵ refer to ferrite, austenite and ϵ -iron, respectively. δ is simply the higher temperature designation of α .

Binary Phase Diagram

- ❑ Binary implies that there are two components.
- ❑ Pressure changes often have little effect on the equilibrium of solid phases (unless of course we apply 'huge' pressures).
- ❑ Hence, binary phase diagrams are usually drawn at 1 atmosphere pressure.
- ❑ The Gibbs phase rule is reduced to:
- ❑ Variables are reduced to : $F = C - P + 1$ (*1 is for T*).
- ❑ T & Composition (*these are the usual variables in materials phase diagrams*)

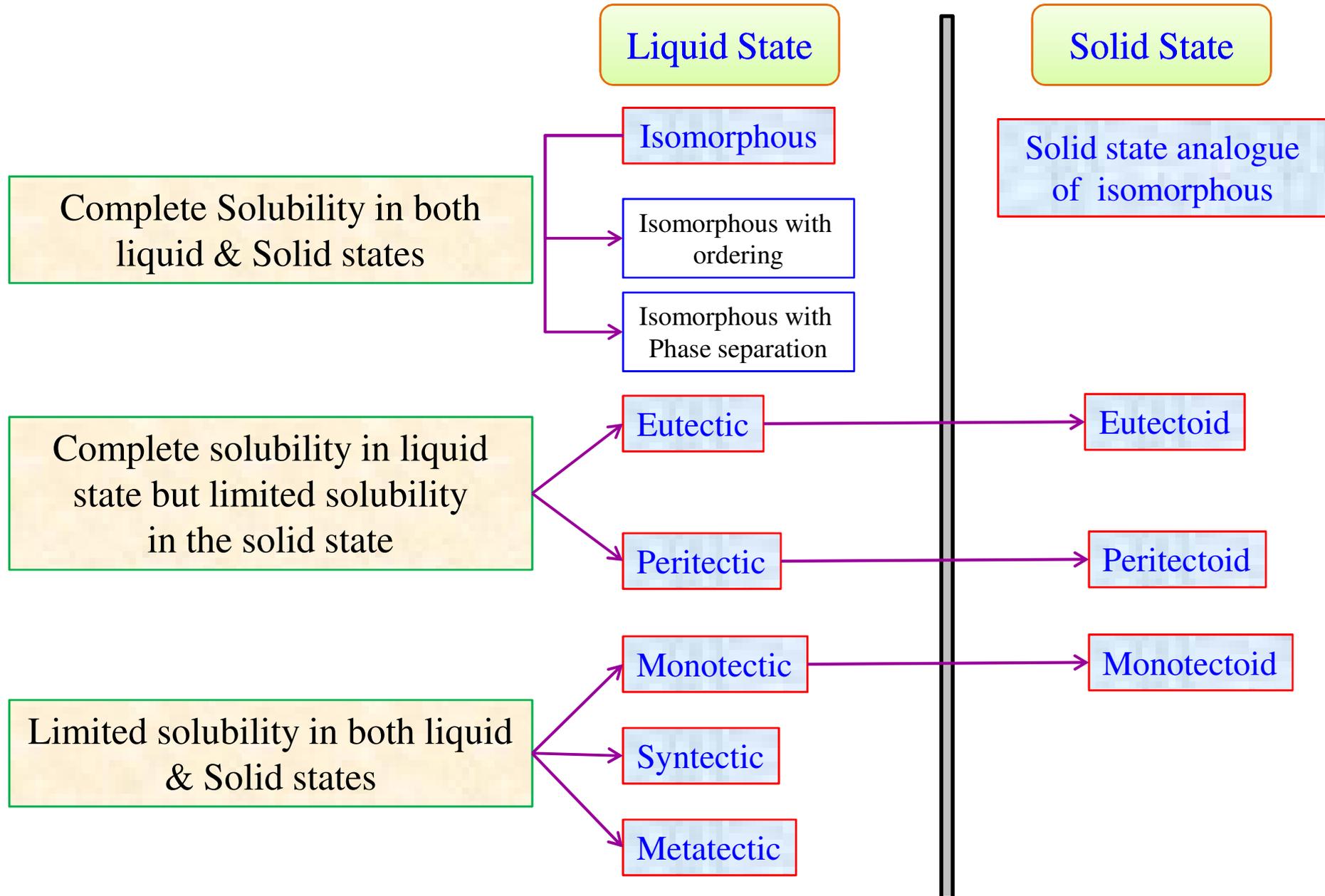
Phase rule for condensed phases

$$F = C - P + 1$$

For T

- ❑ In the next page we consider the possible binary phase diagrams. These have been classified based on:
 - ✓ Complete solubility in both liquid & solid states
 - ✓ Complete solubility in both liquid state, but limited solubility in the solid state
 - ✓ Limited solubility in both liquid & solid states

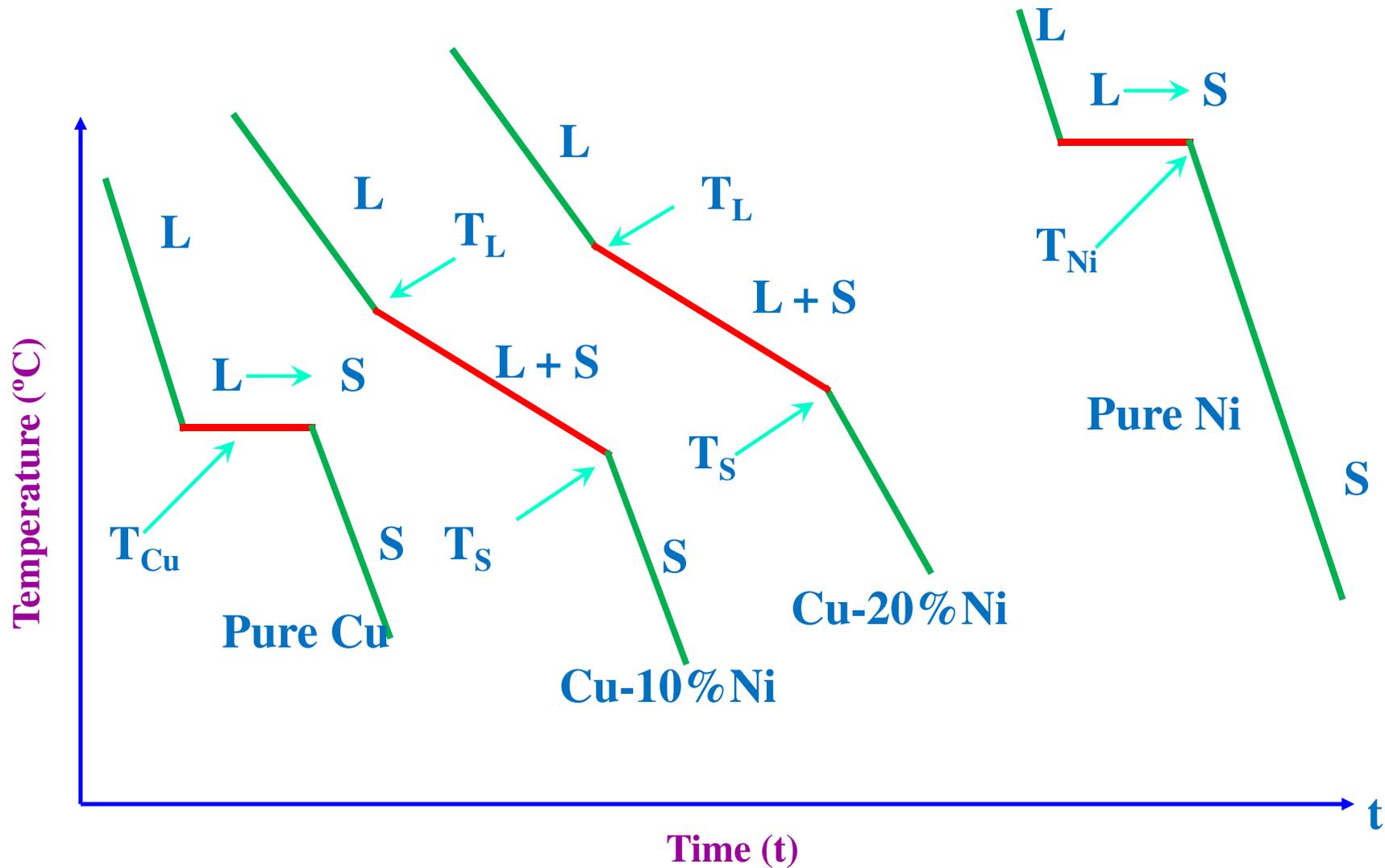
Overview of possible Binary Phase Diagram



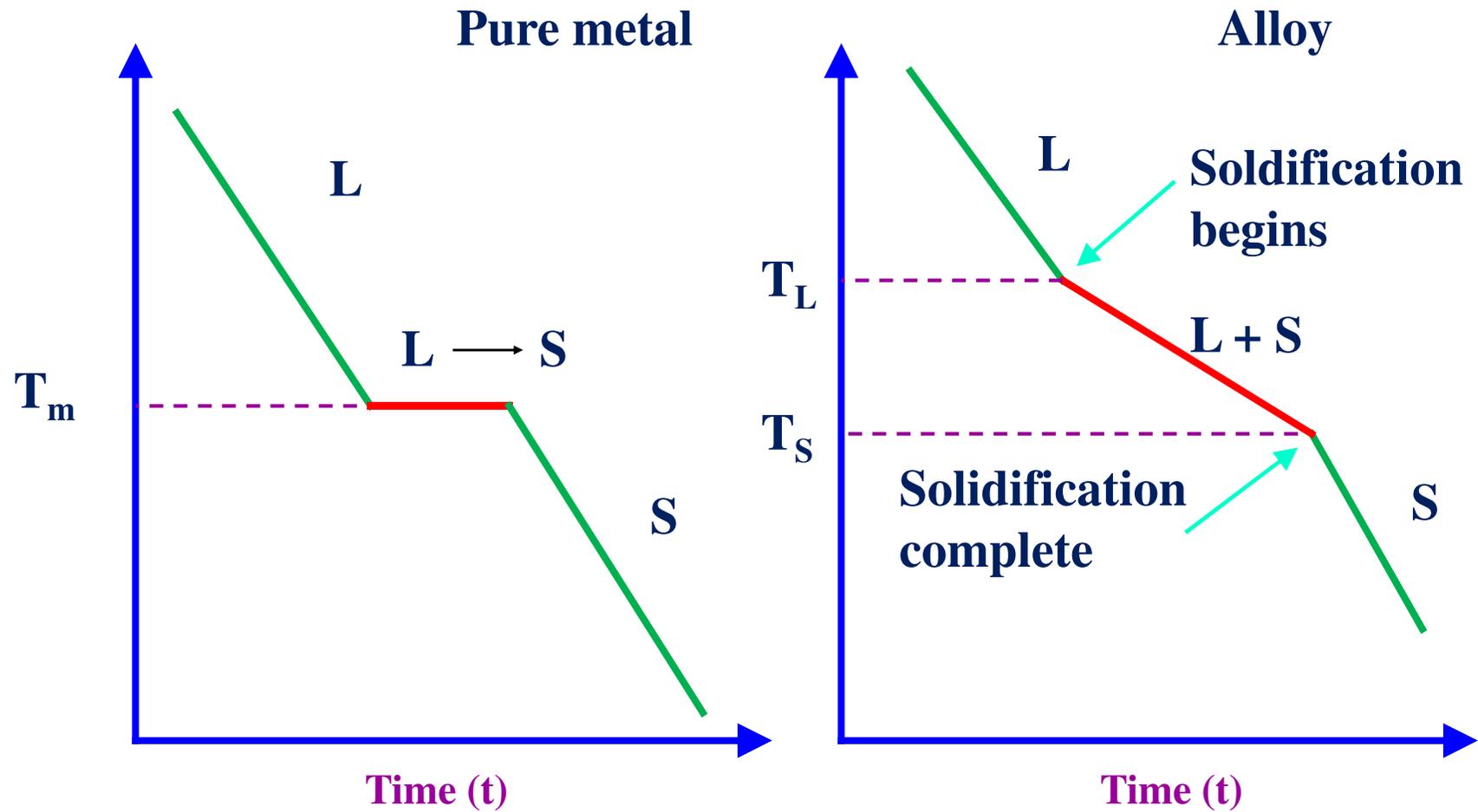
Isomorphous Phase Diagram

- ❑ Isomorphous phase diagrams form when there is complete solid and liquid solubility.
- ❑ Complete solid solubility implies that the crystal structure of the two components have to be same and Hume-Rothery rules to be followed.
- ❑ Examples of systems forming isomorphous systems: Cu-Ni, Ag-Au, Ge-Si, Al_2O_3 - Cr_2O_3
- ❑ Both the liquid and solid contain the components A and B.
- ❑ In binary phase diagrams between two single phase regions there will be a two phase region → In the isomorphous diagram between the liquid and solid state there is the (Liquid + Solid) state.
- ❑ The Liquid + Solid state is NOT a semi-solid state → it is a solid of fixed composition and structure, in equilibrium with a liquid of fixed composition.
- ❑ In some systems (e.g. Au-Ni system) there might be phase separation in the solid state (i.e., the complete solid solubility criterion may not be followed) → these will be considered as a variation of the isomorphous system (with complete solubility in the solid and the liquid state).

cooling curves : Isomorphous system

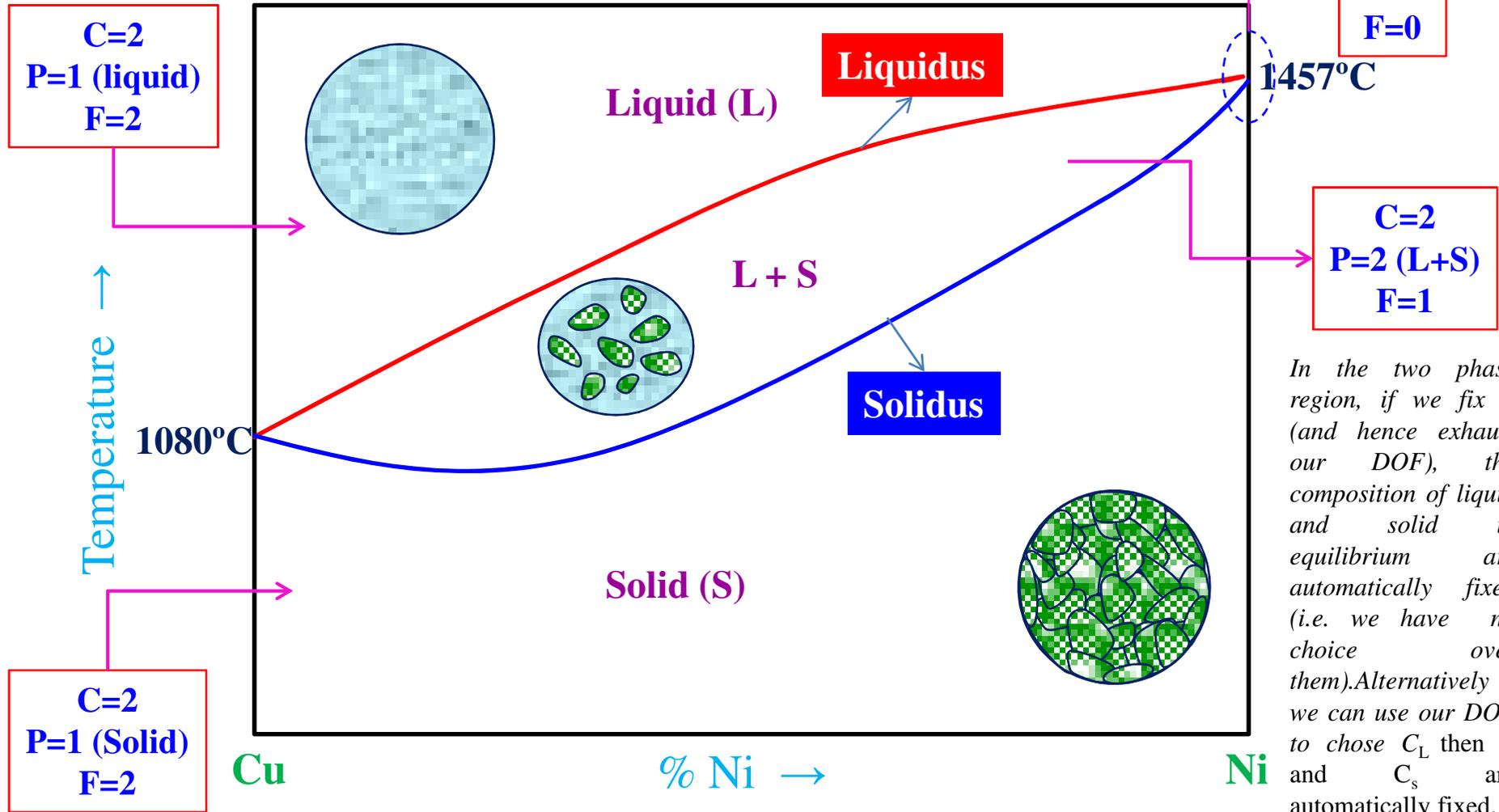


Revision : Solidification (cooling) curves



Isomorphous Phase Diagram

T and Composition can both be varied while still being in the single phase region



In the two phase region, if we fix T (and hence exhaust our DOF), the composition of liquid and solid in equilibrium are automatically fixed (i.e. we have no choice over them). Alternatively we can use our DOF to chose C_L then T and C_s are automatically fixed.

T and Composition can both be varied while still being in the single phase region

Tie line and Lever rule

Chemical Composition of Phases

Tie Line Rule

- ❑ To determine the actual chemical composition of the phases of an alloy, in equilibrium at any specified temperature in a two phase region, draw a horizontal temperature line, called a *tie line*, to the boundaries of the field. These points of intersection are dropped to the base line, and the composition is read directly.

Relative Amounts of Each Phase

Lever Rule

- ❑ To determine the relative amounts of the two phases in equilibrium at any specified temperature in a two phase region, draw a vertical line representing the alloy and a horizontal temperature line to the boundaries of the field.
- ❑ The vertical line will divide the horizontal line into two parts whose lengths are inversely proportional to the amount of the phases present. This is also known as *Lever rule*.
- ❑ The point where the vertical line intersects the horizontal line may be considered as the *fulcrum* of a lever system.
- ❑ The relative lengths of the lever arms multiplied by the amounts of the phases present must balance.

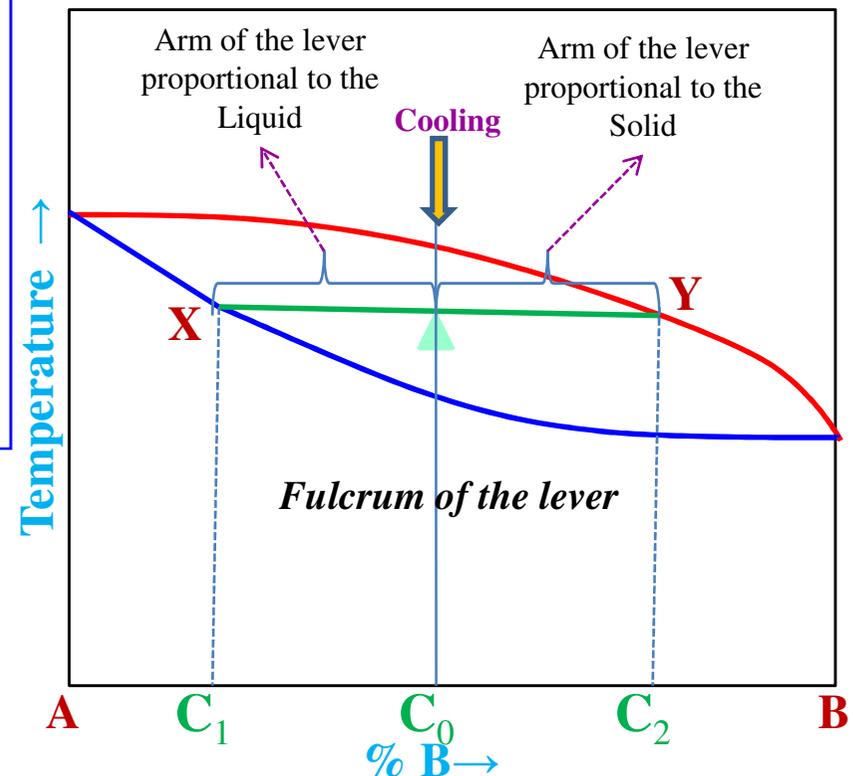
Tie line and Lever rule

- ❑ We draw a horizontal line (called the Tie Line) at the temperature of interest (say T_0). Let Tie line is XY.
- ❑ Solid (crystal) of composition C_1 coexists with liquid of composition C_2
- ❑ Note that tie lines can be drawn only in the two phase coexistence regions (fields). Though they may be extended to mark the temperature.
- ❑ To find the fractions of solid and liquid we use the lever rule.

- ❑ The portion of the horizontal line in the two phase region is akin to 'lever' with the fulcrum at the nominal composition (C_0)
- ❑ The opposite arms of the lever are proportional to the fraction of the solid and liquid phase present (this is lever rule)

$$f_{liquid} = \frac{C_0 - C_1}{C_2 - C_1}$$

$$f_{solid} = \frac{C_2 - C_0}{C_2 - C_1}$$



Tie line and Lever rule

Example

At $C_o = 35$ wt% Ni

At T_A : Only Liquid (L)

$$W_{liquid} = 100 \text{ wt}\%, W_{solid} = 0$$

At T_D : Only Solid (S)

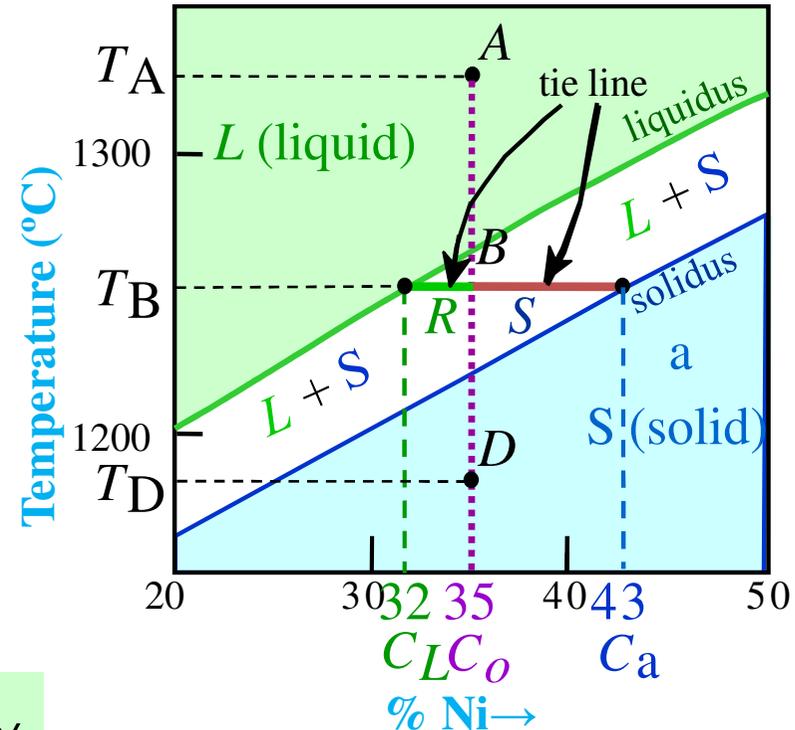
$$W_L = 0, W_{solid} = 100 \text{ wt}\%$$

At T_B : Both S and L

$$W_L = \frac{S}{R + S} = \frac{43 - 35}{43 - 32} = 73 \text{ wt}\%$$

$$W_S = \frac{R}{R + S} = 27 \text{ wt}\%$$

Cu - Ni System

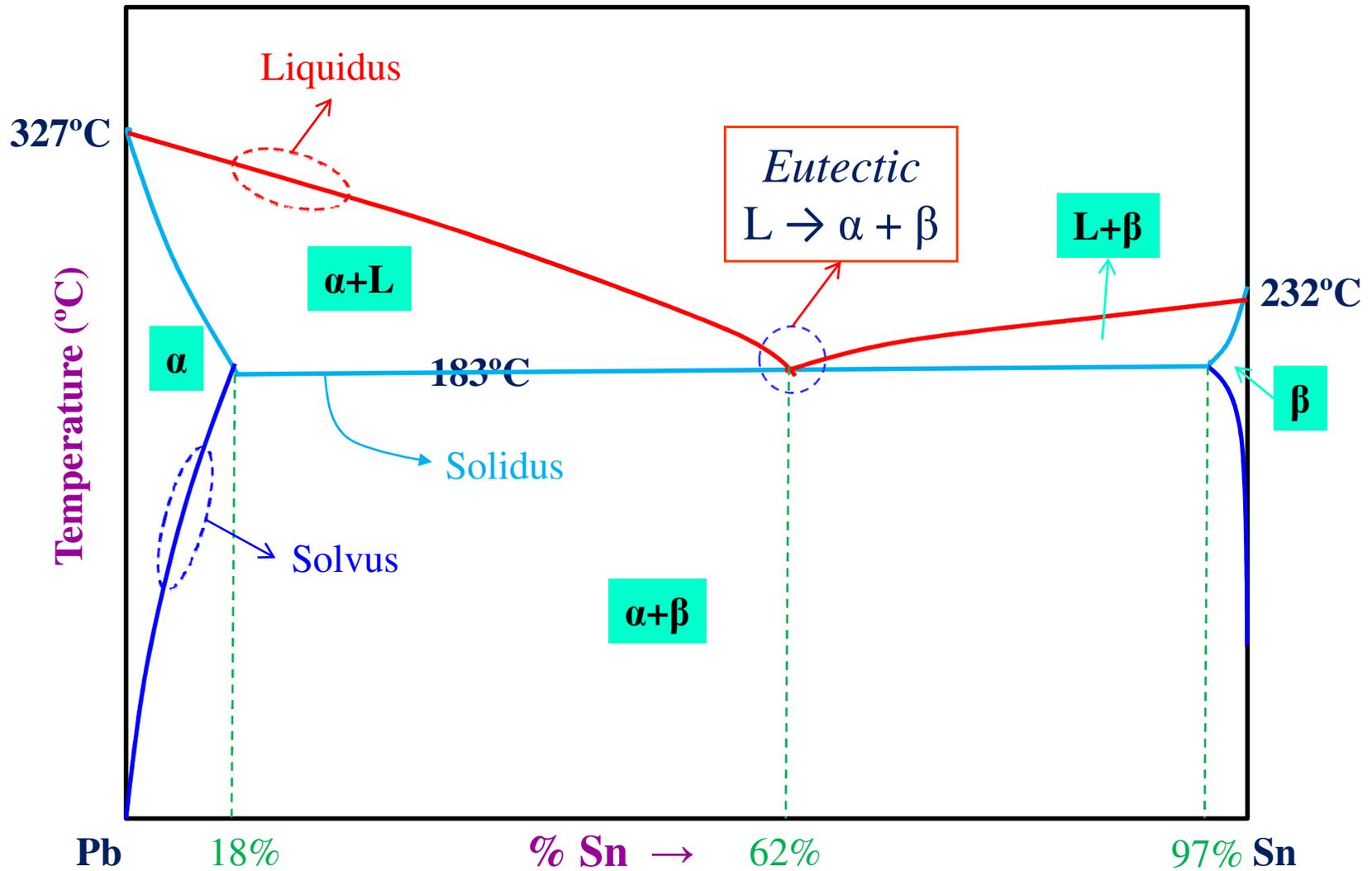


Notice: as in a lever “the opposite leg” controls with a balance (fulcrum) at the ‘base composition’ and $R+S$ = tie line length = difference in composition limiting phase boundary, at the temp of interest

Eutectic Phase Diagram

- ❑ Very few systems exhibit an isomorphous phase diagram (usually the solid solubility of one component in another is limited).
- ❑ Often the solid solubility is severely limited – through the solid solubility is never zero (due to entropic reasons).
- ❑ In a Simple eutectic system (binary), there is one composition at which the liquid freezes at a single temperature. This is in some sense similar to a pure solid which freezes at a single temperature (unlike a pure substance the freezing produces a two solid phases both of which contain both the components).
- ❑ The term **Eutectic** means easy melting → The alloy of eutectic composition freezes at a lower temperature than the melting points of the constituent components.
- ❑ *This has important implications → e.g. the Pb-Sn eutectic alloy melts at 183°C, which is lower than the melting points of both Pb (327°C) and Sn (232°C) → Can be used for soldering purposes (as we want to input least amount of heat to solder two materials).*
- ❑ In the next page we consider the Pb-Sn eutectic phase diagram.

Eutectic Phase Diagram



Eutectic reaction at 183°C



Example : Cu-Ag Eutectic System

❑ Raoult's law states that the freezing point of a pure substance will be lowered by the addition of a second substance provided the latter is soluble in the pure substance when liquid and insoluble when solidified. The amount of lowering of the freezing point is proportional to the molecular weight of the solute.

- Limited solubility:

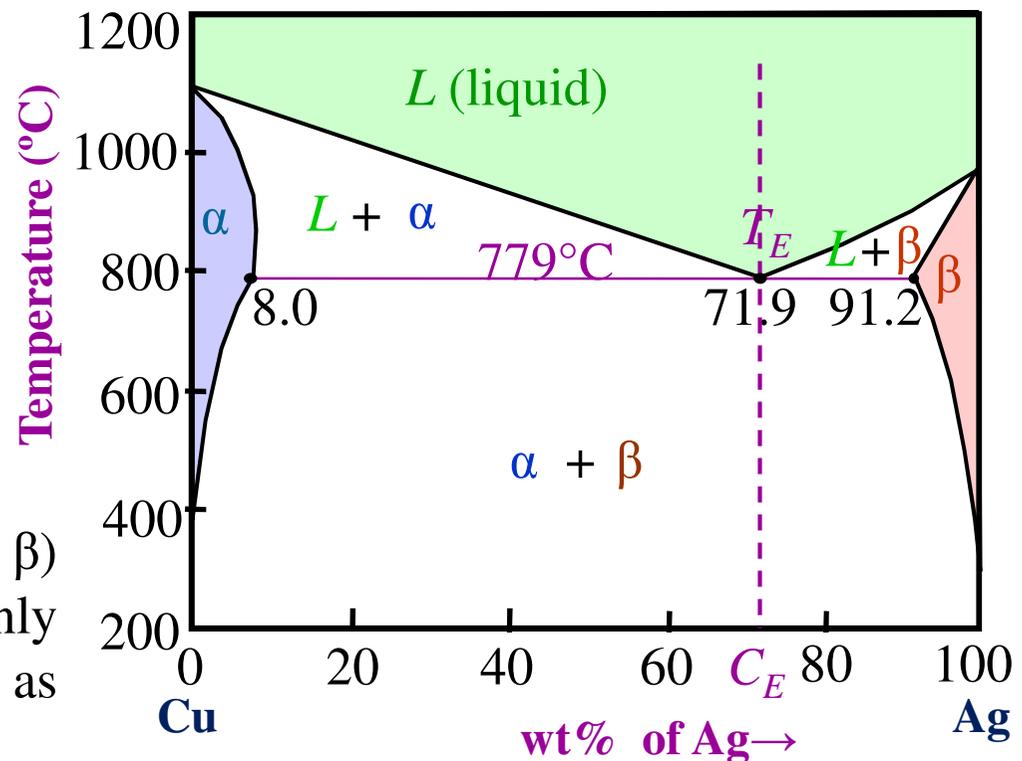
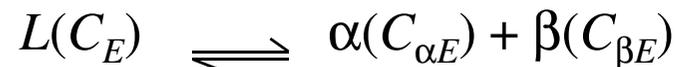
- α : mostly Cu

- β : mostly Ag

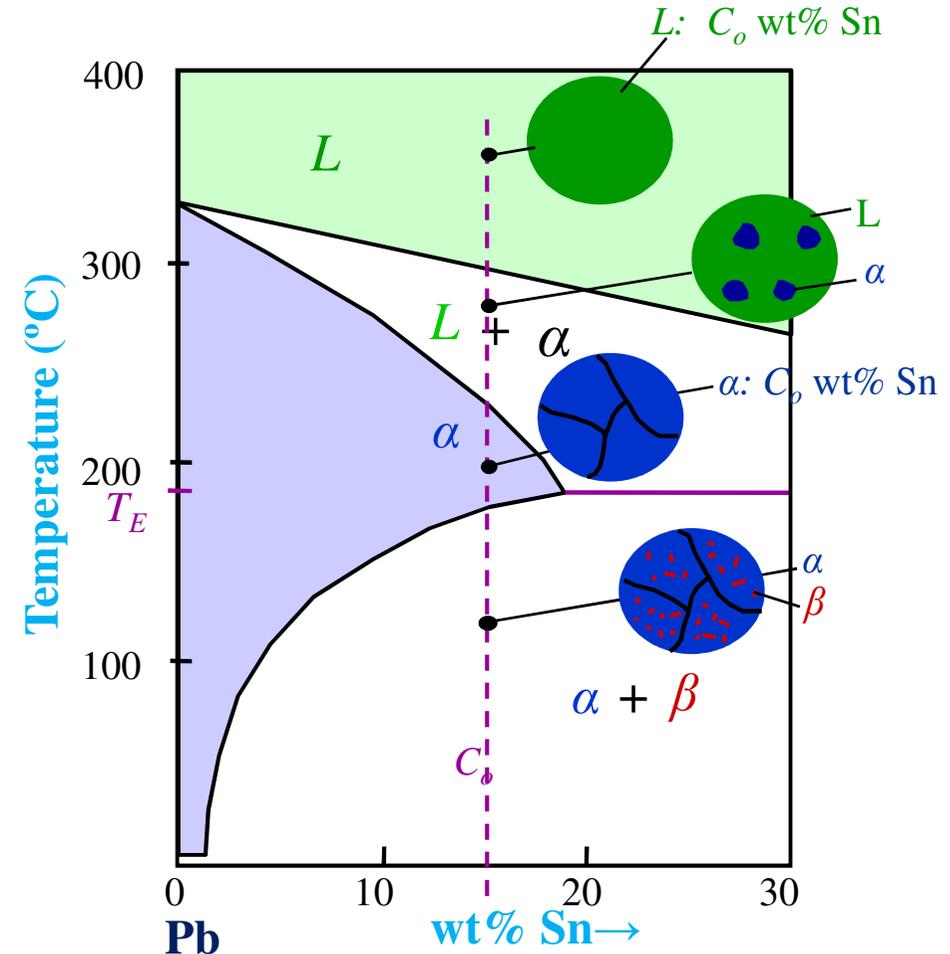
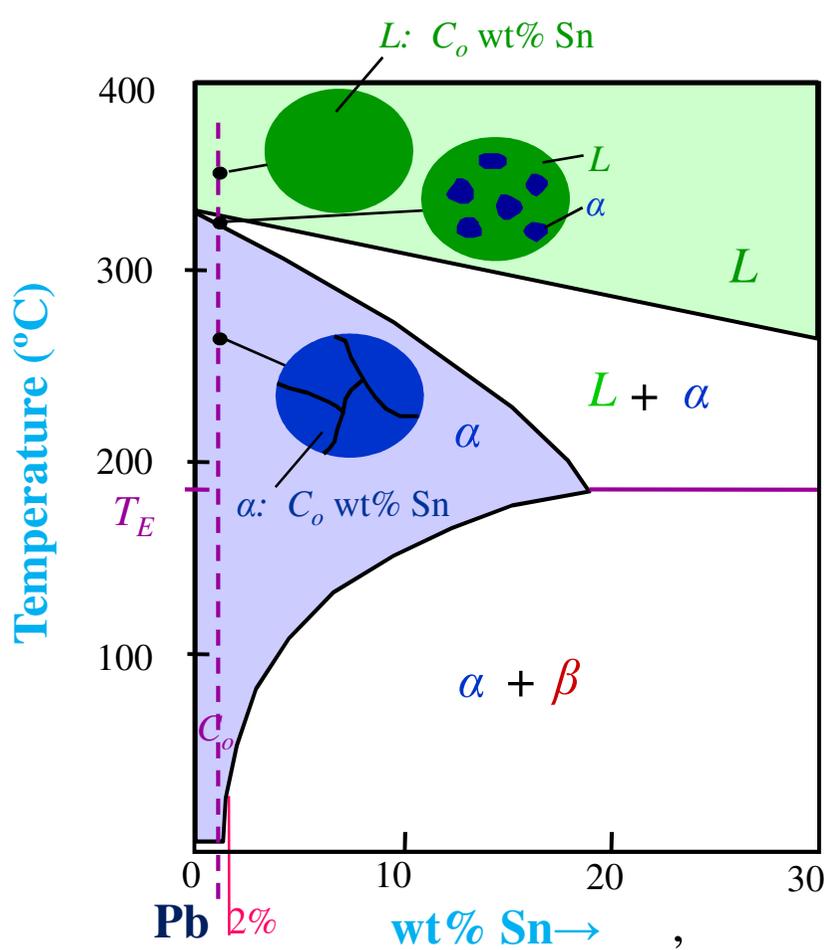
- T_E : No liquid below T_E

- C_E : Min. melting T_E

Three single phase regions – (L, α , β) exist at 71.9% Ag at 779°C commonly known as Eutectic. The reaction is as follows...!



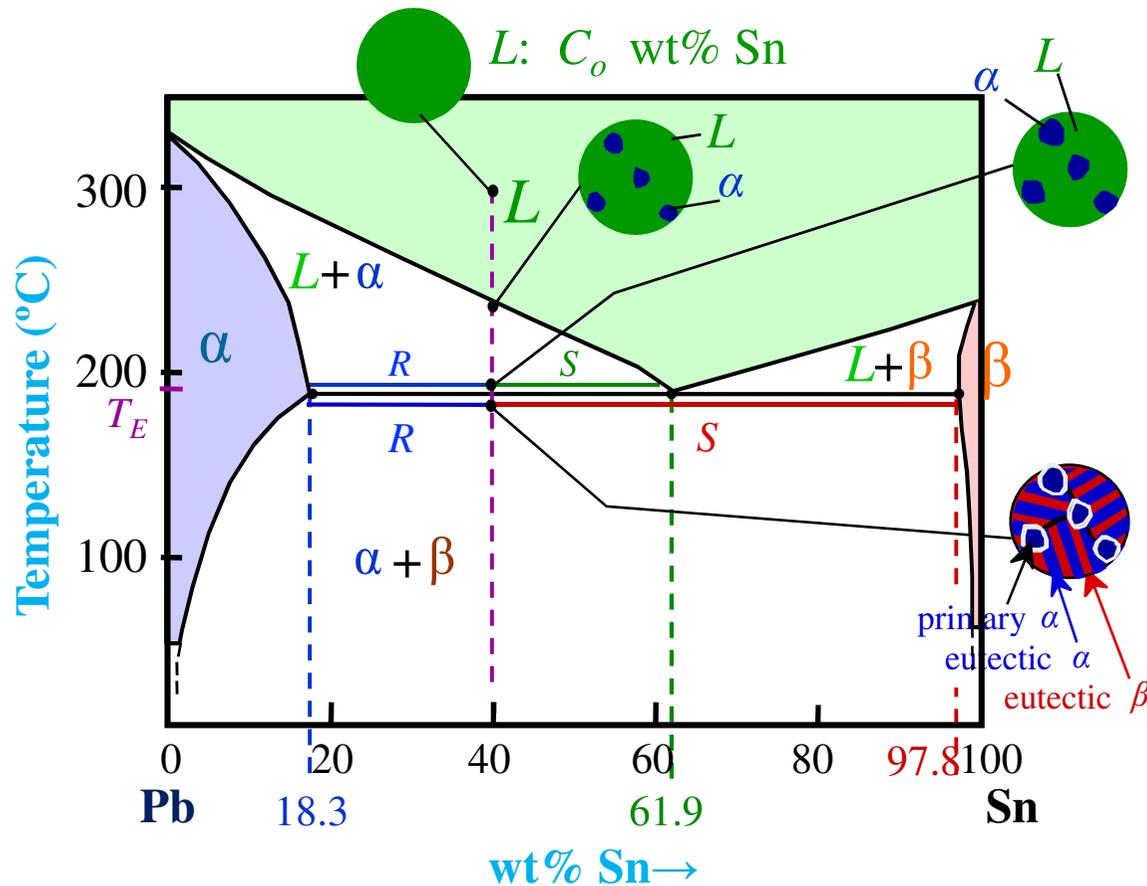
Microstructural Characteristics of Eutectic System



- ❑ To reiterate an important point: Phase diagram do not contain microstructural information (i.e. they cannot tell you what is the microstructures produced by cooling. Often microstructural information is overlaid on phase diagram for convenience. Hence, strictly cooling is not in the domain of phase diagram – but we can overlay such information keeping in view the assumptions involved.

Microstructural Characteristics of Eutectic System

- 18.3 wt% Sn < C_o < 61.9 wt% Sn
- Microstructure consists a crystals and a eutectic microstructure



→ Just above T_E :

$$C_\alpha = 18.3 \text{ wt\% Sn}$$

$$C_L = 61.9 \text{ wt\% Sn}$$

$$W_\alpha = \frac{S}{R + S} = 50 \text{ wt\%}$$

$$W_L = (1 - W_\alpha) = 50 \text{ wt\%}$$

→ Just below T_E :

$$C_\alpha = 18.3 \text{ wt\% Sn}$$

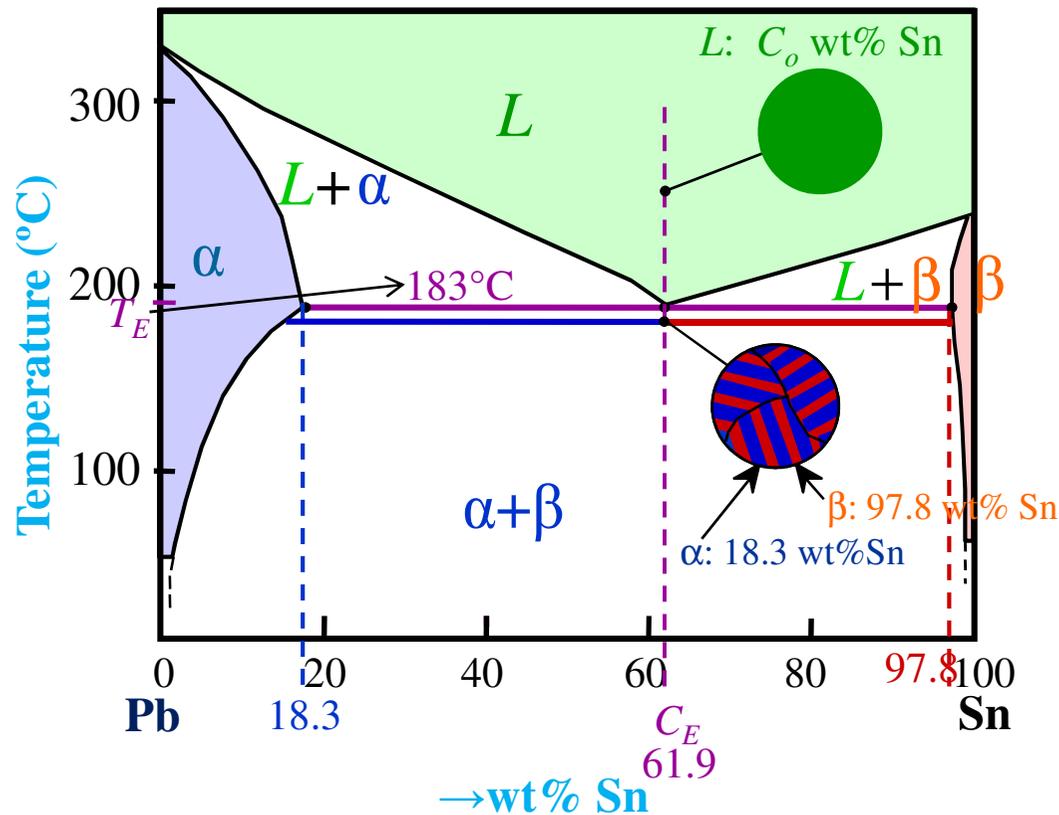
$$C_\beta = 97.8 \text{ wt\% Sn}$$

$$W_\alpha = \frac{S}{R + S} = 72.6 \text{ wt\%}$$

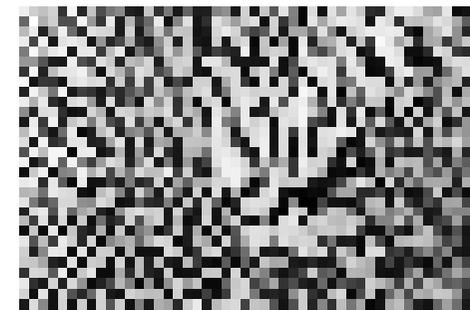
$$W_\beta = 27.4 \text{ wt\%}$$

Microstructural Characteristics of Eutectic System

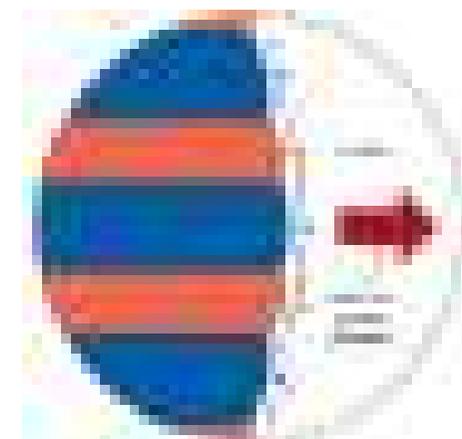
- ❑ $C_o = C_E$
- ❑ Microstructure represents Eutectic microstructure (lamellar structure) alternating layers (lamellae) of a and b crystals.



Pb-Sn Eutectic Microstructure

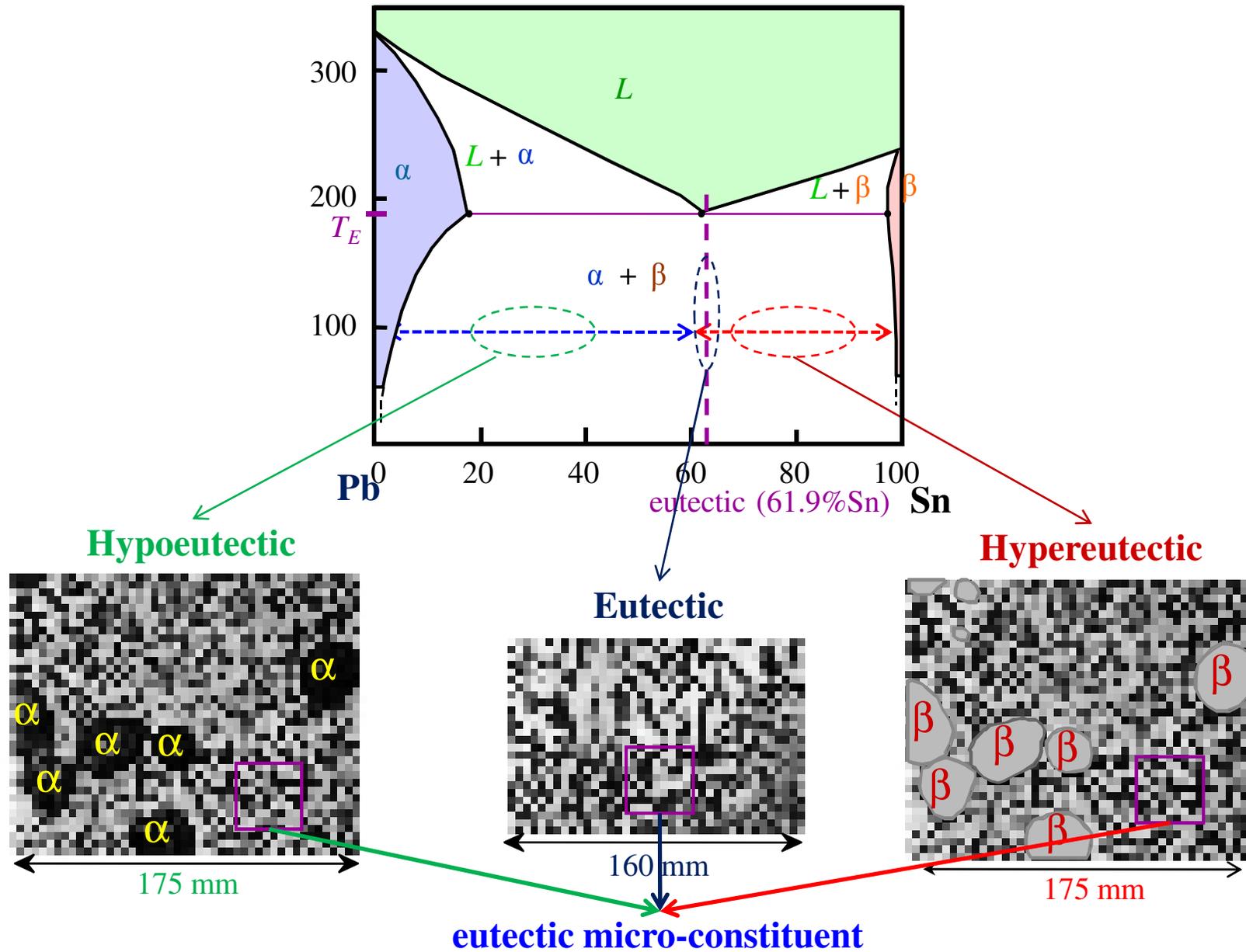


160 μ m



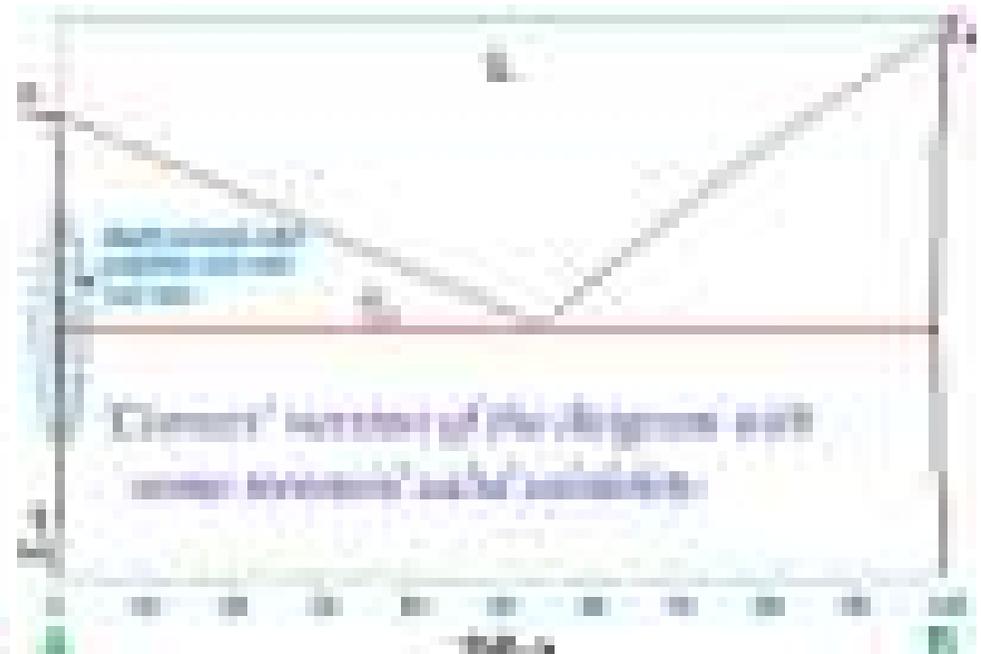
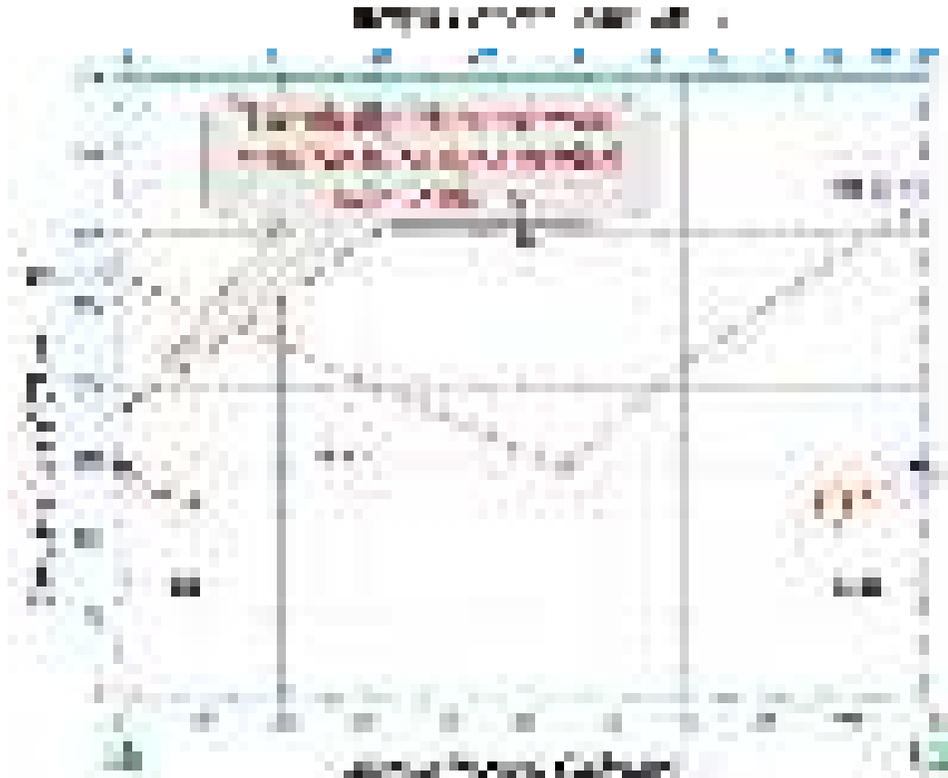
45.1% α and 54.8% β

Hypo Eutectic – Eutectic – Hyper Eutectic

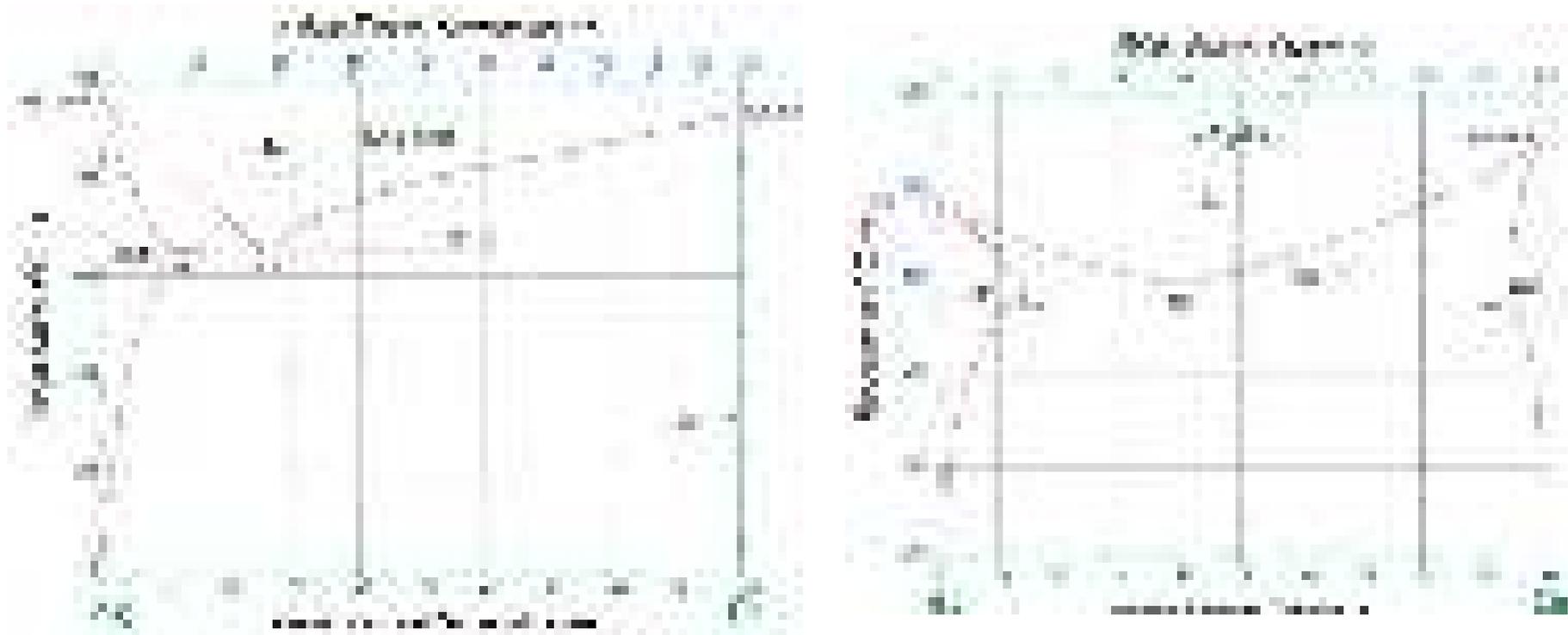


Special Eutectic Systems

- ❑ Consider the eutectic system *without terminal solid solubility* : **Bi-Cd**
- ❑ Technically it is incorrect to draw eutectic phase diagrams with zero solid solubility.
- ❑ This would imply that a pure component (say Bi in the example considered) melts over a range of temperatures (from 'p' to 271 °C) → which is wrong.
- ❑ Also let us consider an example of a point 'p' (which lies on the 'eutectic line' PQ). At 'p' the phase rule becomes : $F = C - P + 1 = 1 - 3 + 1 = -1$!!!



Special Eutectic Systems



- ❑ Note that the above is an alternate way of arriving at the obvious contradiction that at 'P' on one hand we are saying that there is a pure component and on the other hand we are considering a three phase equilibrium (which can happen only for Bi-Cd alloys).
- ❑ In Eutectic systems, at Eutectic point E \rightarrow 3 phases co-exist : L, α & β
- ❑ The number of components in a binary phase diagram is 2 \rightarrow the number of DOF $F=0$
- ❑ This implies that the Eutectic point is an **Invariant Point** \rightarrow For a given system it occurs at a fixed composition and temperature.

Application of Lever rule in Eutectic System

Solved Example

For a 40 wt% Sn-60 wt% Pb alloy at 150°C, find the phases present: α and β , Composition of phases

$$C_o = 40 \text{ wt\% Sn}$$

$$C_a = 11 \text{ wt\% Sn}$$

$$C_b = 99 \text{ wt\% Sn}$$

The relative amount of each phase by using lever rule

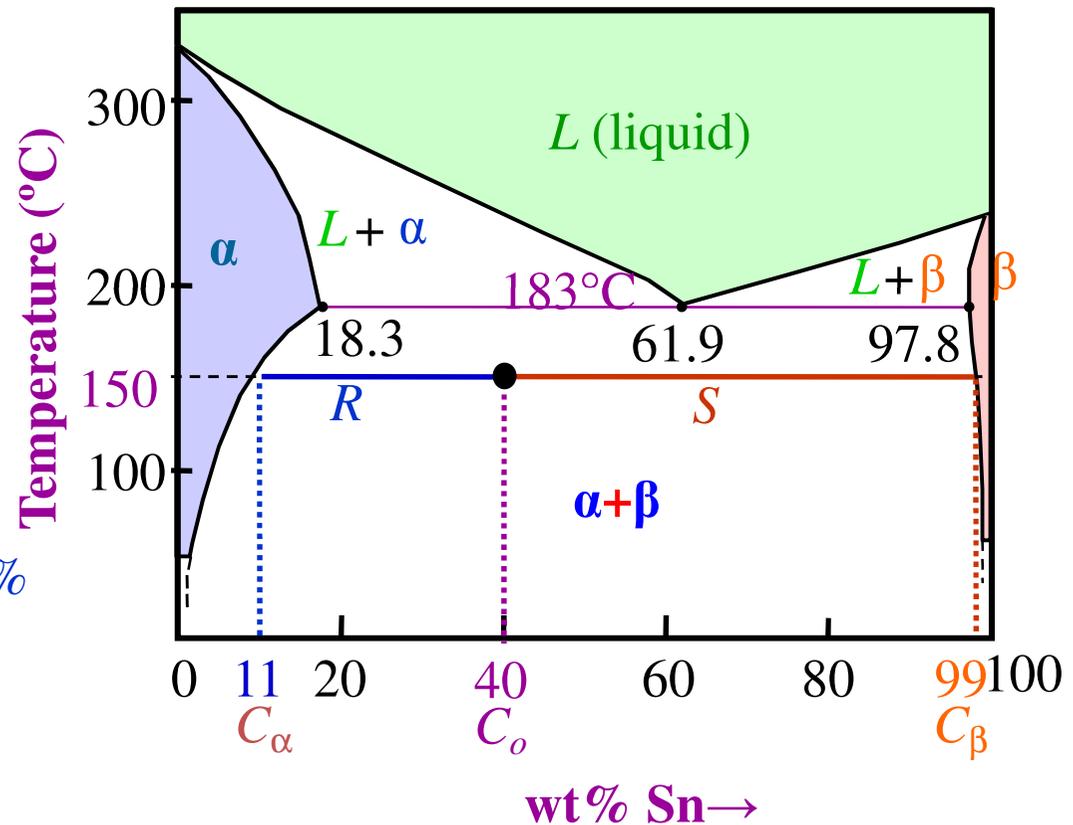
$$W_a = \frac{S}{R+S} = \frac{C_\beta - C_o}{C_\beta - C_\alpha}$$

$$= \frac{99 - 40}{99 - 11} = \frac{59}{88} = 67 \text{ wt\%}$$

$$W_\beta = \frac{R}{R+S} = \frac{C_o - C_\alpha}{C_\beta - C_\alpha}$$

$$= \frac{40 - 11}{99 - 11} = \frac{29}{88} = 33 \text{ wt\%}$$

Pb-Sn Phase Diagram



Application of Lever rule in Eutectic System

Solved Example

For a 40 wt% Sn-60 wt% Pb alloy at 220°C, find the phases present: α and Liquid, Composition of phases

$$C_O = 40 \text{ wt\% Sn}$$

$$C_a = 17 \text{ wt\% Sn}$$

$$C_L = 46 \text{ wt\% Sn}$$

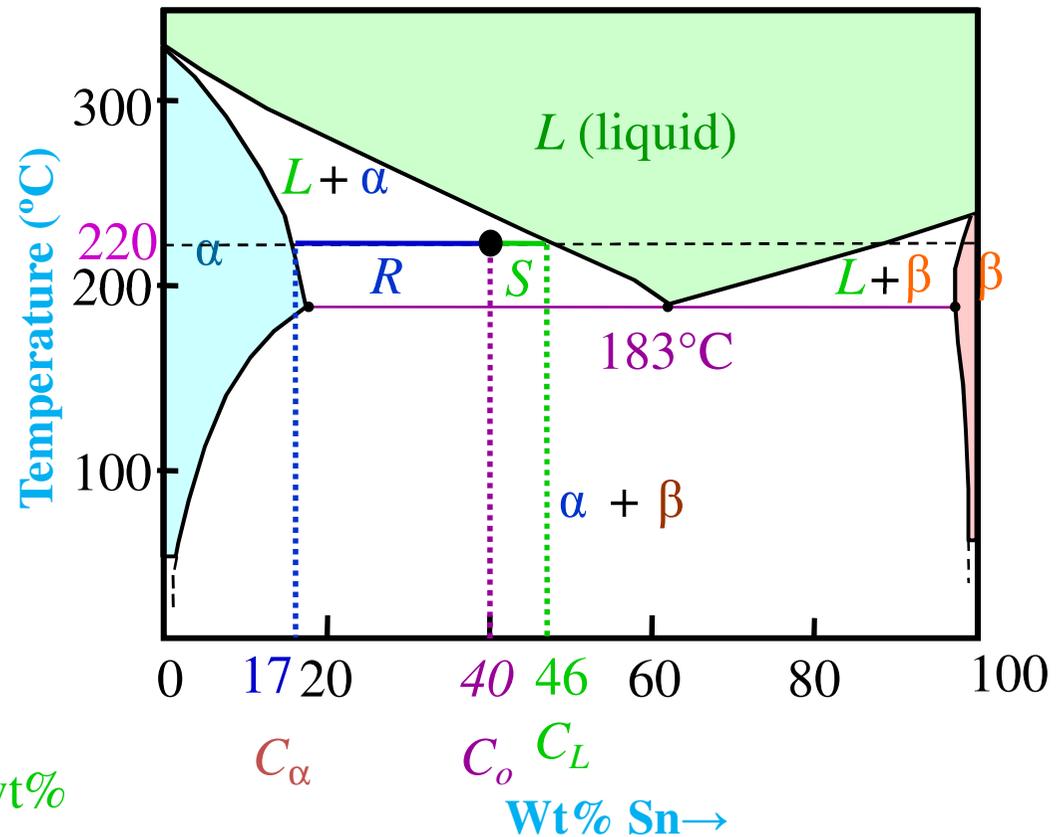
The relative amount of each phase by using lever rule

$$W_a = \frac{C_L - C_O}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17}$$

$$= \frac{6}{29} = 21 \text{ wt\%}$$

$$W_L = \frac{C_O - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 79 \text{ wt\%}$$

Pb-Sn Phase Diagram



Solved Example

During the solidification of a off eutectic (Pb-Sn) composition (C_0), 90 vol.% of the solid consisted of the eutectic mixture and 10vol.% of the proeutectic β phase. What is the value of C_0 ?

Density data for β and α

$$\rho_\alpha = 10300 \text{ Kg/m}^3$$

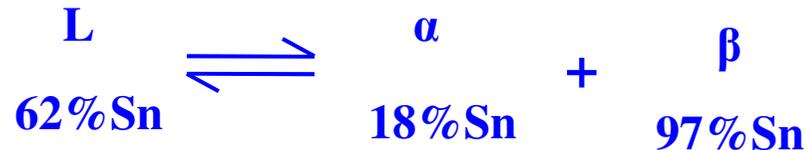
$$\rho_\beta = 7300 \text{ Kg/m}^3$$

Eutectic Data

183 °C

62 wt% Sn

Let us start with some observations: ♦Pb is heavier than Sn and hence the density of α is more than that of β ♦Since the proeutectic phase is $\beta \rightarrow$ the composition is hypereutectic (towards the Sn side) ♦ The volume fraction (in %) are usually calculated by taking the area fractions by doing metallography (microstructure) and then converting it into volume fractions (usually volume fraction is assumed to be equal to area fraction



Using the fact that there is 10 Vol% β phase :

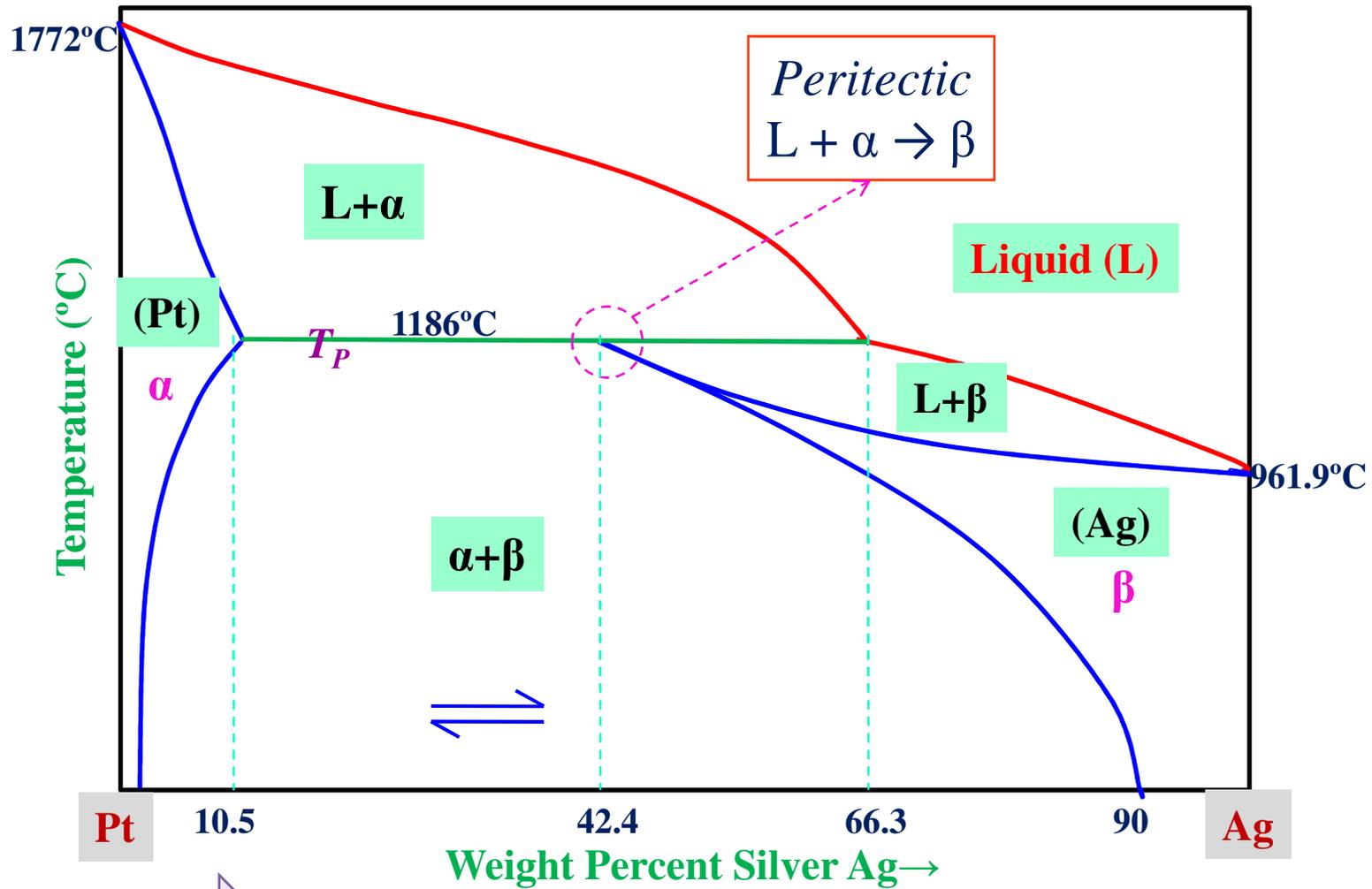
$$\text{Wt. fraction of proeutectic } \beta = \left[\frac{\text{Wt. of } \beta}{\text{Wt. of the alloy}} \right] = \frac{0.1 \times 7300}{(0.1 \times 7300) + (0.9 \times \rho_{\text{eutectic mix}})}$$

$$\text{Where, } \rho_{\text{eutectic mix}} = 10300 \left(\frac{97 - 62}{97 - 18} \right) + 7300 \left(\frac{62 - 18}{97 - 18} \right) = 4563 + 4066 = 8629 \text{ Kg / m}^3$$

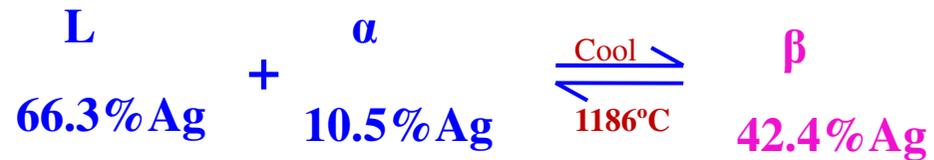
Substituting in equation (1): Wt. fraction of proeutectic $\beta = 0.086$

$$\text{U sin gleverrule : } 0.086 = \frac{C_0 - 0.62}{0.97 - 0.62}, C_0 = 0.650 = 65.0\%$$

Peritectic Phase Diagram



Peritectic Reaction



Peritectic Phase Diagram

- ❑ Like the eutectic system, the Peritectic reaction is found in systems with complete liquid solubility but limited solid solubility.
- ❑ In the Peritectic reaction the liquid (L) reacts with one solid (α) to produce another solid (β). $L + \alpha \rightarrow \beta$
- ❑ Since the solid β forms at the interface between the L and the α , further reaction is dependent on solid state diffusion. Needless to say this becomes the rate limiting step and hence it is difficult to 'equilibrate' peritectic reactions (as compared to say eutectic reactions).

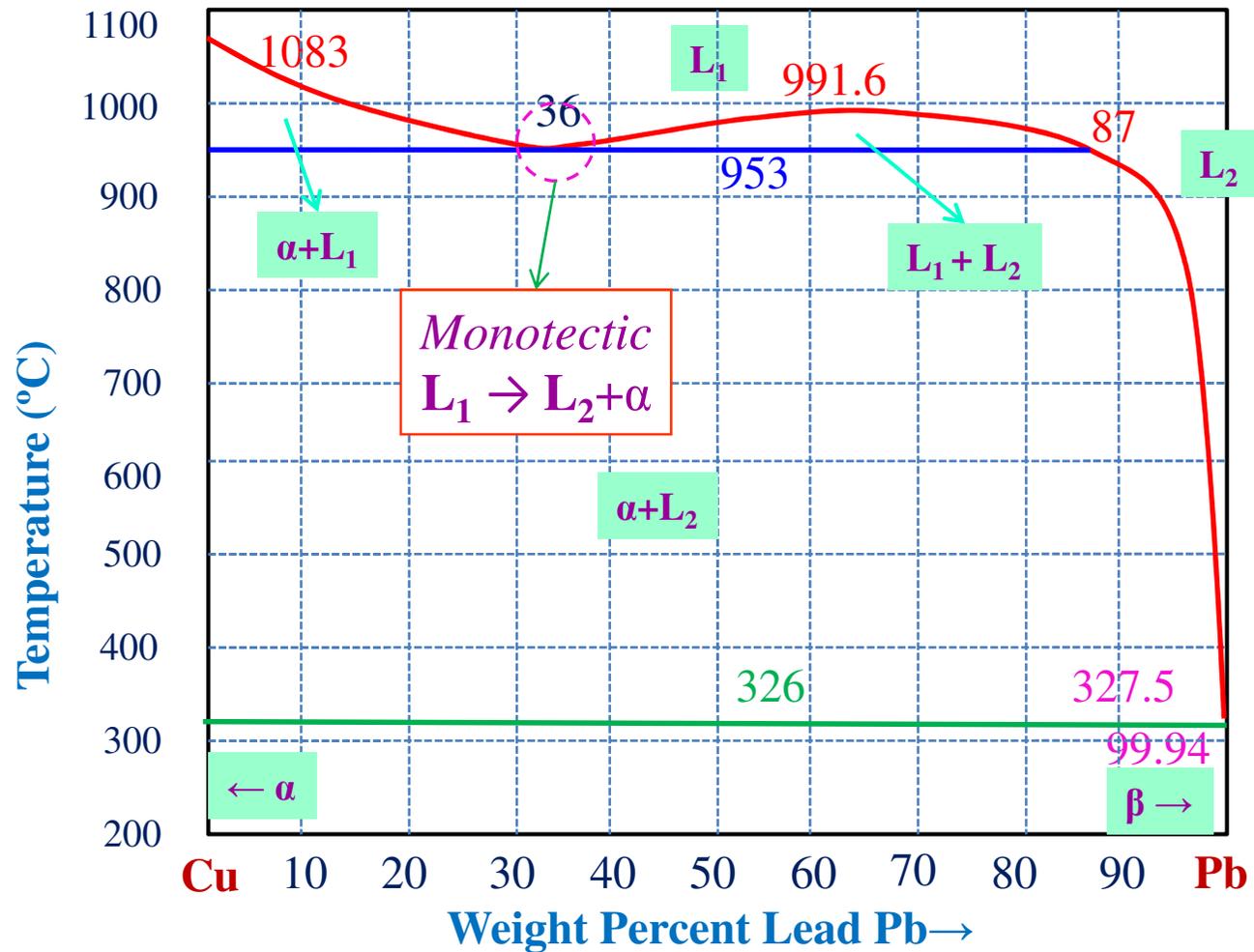


- ❑ In some Peritectic reactions (e.g. the Pt-Ag system – previous page). The (pure) β phase is not stable below the Peritectic temperature ($T_P = 1186$ °C for Pt- Ag system) and splits into a mixture of ($\alpha + \beta$) just below T_P .

Monotectic Phase Diagram

- ❑ In all the types discussed previously, it was assumed that there was complete solubility in the liquid state. It is quite possible, however, that over a certain composition range two liquid solutions are formed that are not soluble in each other.
- ❑ Another term for solubility is miscibility. Substances that are not soluble in each other, such as oil and water, are said to be immiscible. Substances that are partly soluble in each other are said to show a miscibility gap, and this is related to Monotectic Systems.
- ❑ When one liquid forms another liquid, plus a solid, on cooling, it is known as a *Monotectic Reaction*.
- ❑ It should be apparent that the Monotectic reaction resembles the eutectic reaction, the only difference being that one of the products is a liquid phase instead of a solid phase.
- ❑ An example of an alloy system showing a Monotectic reaction is that between *copper and lead* given in next page. Notice that in this case the $L_1 + L_2$ is closed.
- ❑ Also, although the terminal solids are indicated as α and β , the solubility is actually so small that they are practically the pure metals, copper and lead.

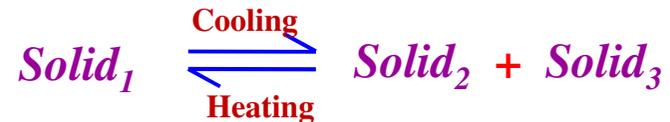
Monotectic Phase Diagram



In Cu-Zn Phase diagram the eutectoid reaction occurs
At 560 °C with 75% Zn

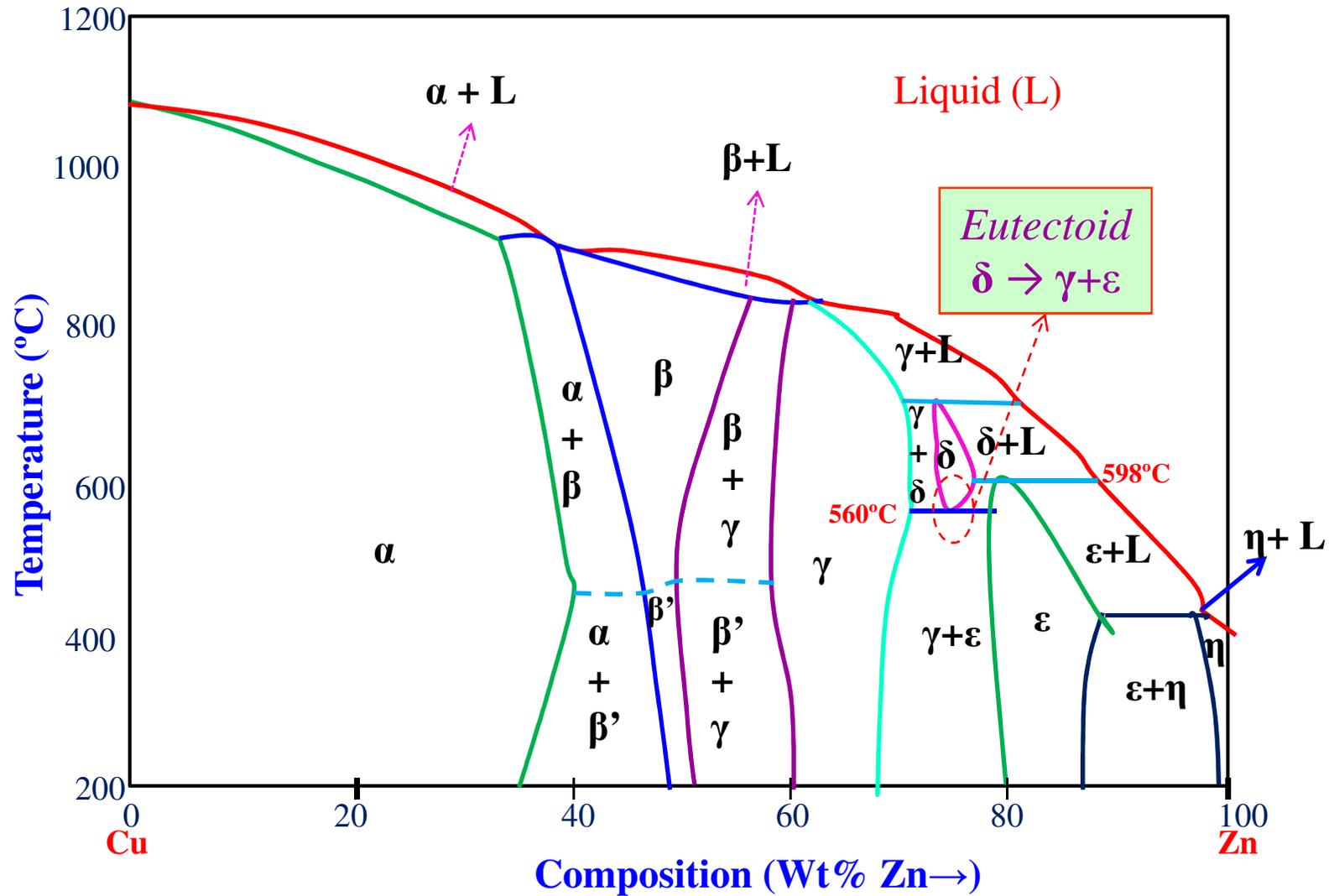
The Eutectoid Reaction

- ❑ This is a common reaction in the solid state. It is very similar to the eutectic reaction but does not involve the liquid. In this case, a solid phase transforms on cooling into two new solid phases. The general equation may be written as..!



- ❑ The resultant Eutectoid mixture is extremely fine, just like the eutectic mixture. Under the microscope both mixtures generally appear the same, and it is not possible to determine microscopically whether the mixture resulted from a eutectic reaction or eutectoid reaction.
- ❑ An **equilibrium diagram of Cu-Zn**, illustrating the eutectoid reaction is shown in figure (*see in next page*).
- ❑ In copper (Cu) – Zinc (Zn) system contains two terminal solid solutions i.e. these are extreme ends of phase diagram α and η , with four intermediate phases called β , γ , δ and ϵ . The β' phase is termed an ordered solid solution, one in which the copper and zinc atoms are situated in a specific and ordered arrangement within each unit cell.

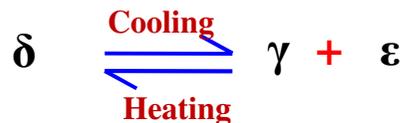
Cu-Zn Phase Diagram - Eutectoid Reaction



Cu-Zn Phase Diagram - Eutectoid Reaction

- ❑ In the diagram, some phase boundary lines near the bottom are dashed to indicate that their positions have not been exactly determined. The reason for this is that at low temperatures, diffusion rates are very slow and inordinately long times are required for the attainment of equilibrium.
- ❑ Again only single- and two- phase regions are found on the diagram, and the same and we can utilize the lever rule for computing phase compositions and relative amounts.
- ❑ The commercial material brasses are copper-rich copper-zinc alloys: for example, cartridge brass has a composition of 70 wt% Cu-30 wt% Zn and a microstructure consisting of a single α phase.

In Cu-Zn Phase diagram the eutectoid reaction occurs at 560 °C with 75% Zn



Cu 70, Zn 30 (wt%),
recrystallized
annealing twins



The Peritectoid Reaction

- ❑ This is a fairly common reaction in the solid state and appears in many alloy systems. The peritectoid reaction may be written as



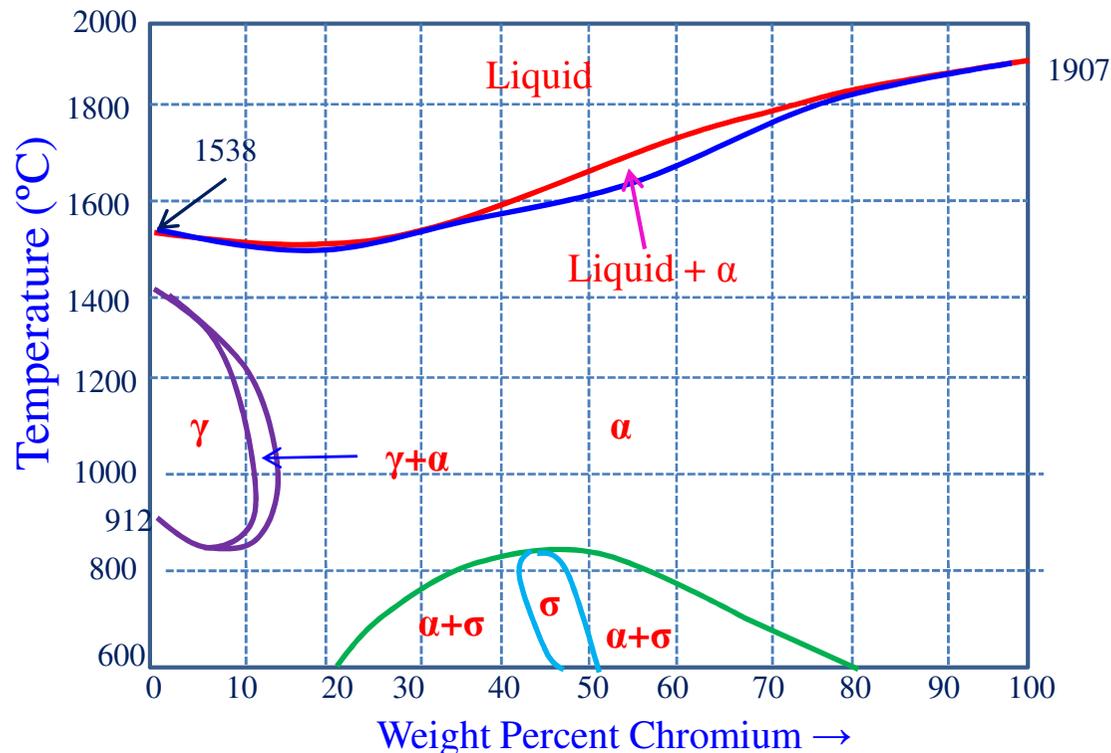
- ❑ The new solid phase is usually an intermediate alloy, but it may also be a solid solution. The peritectoid reaction has the same relationship to the peritectic reaction as the eutectoid has to the eutectic. Essentially, it is the replacement of a liquid by a solid.
- ❑ The peritectoid reaction occurs entirely in the solid state and usually at lower temperatures than the peritectic reaction, the diffusion rate will be slower and there is less likelihood that equilibrium structures will be reached.
- ❑ Consider Silver (Ag) – Aluminium (Al) phase diagram (*in next page*) containing a peritectoid reaction.
- ❑ If a 7% Al alloy is rapidly cooled from the two phase area just above the peritectoid temperature the two phases will be retained, and the microstructure will show a matrix of γ with just a few particles of α . When we cool at below the peritectoid temperature by holding we get single phase μ .

Summary of Invariant reactions

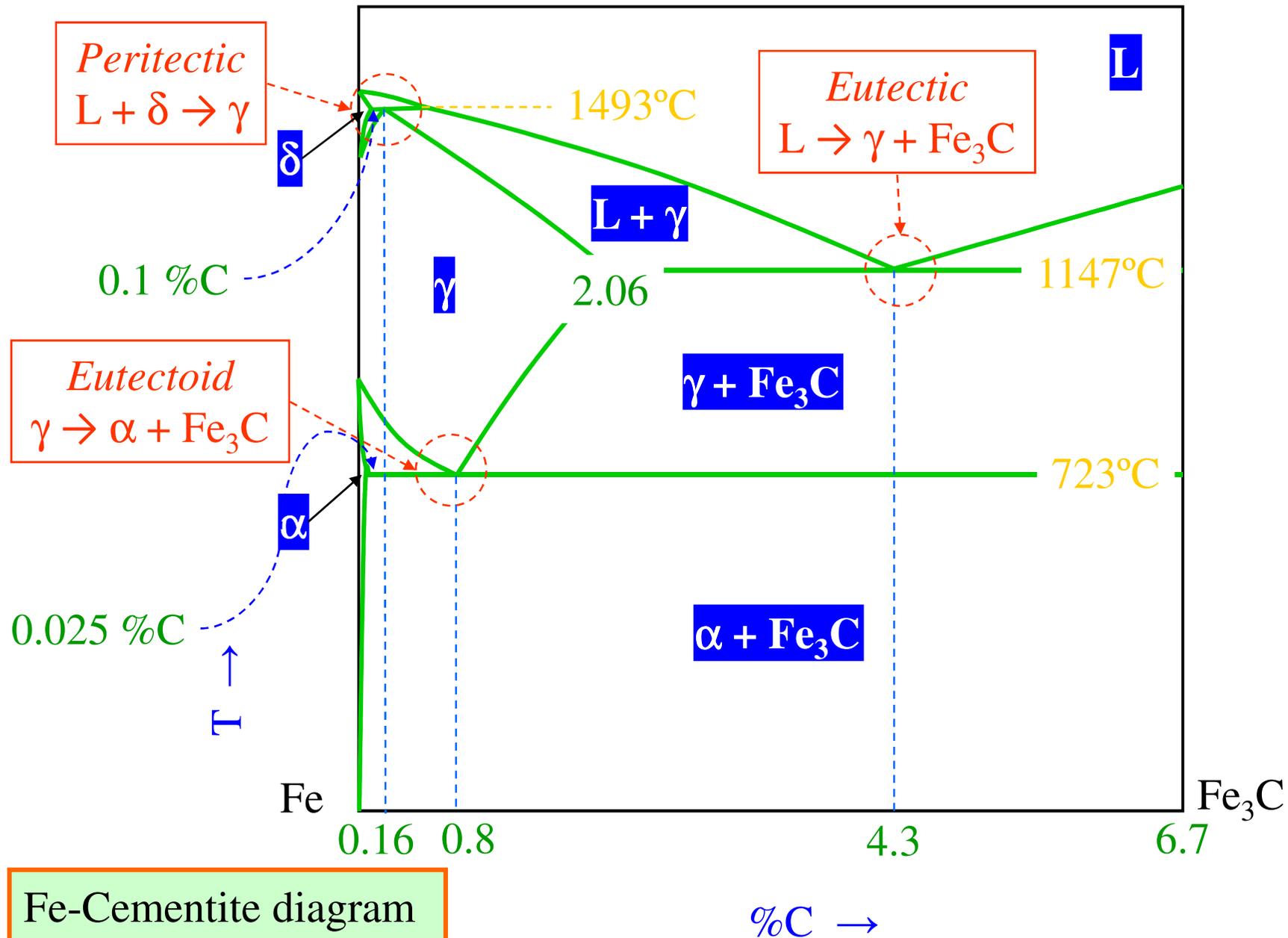
| Name of reaction | Phase equilibrium | Schematic representation |
|--------------------|---------------------------------------|--------------------------|
| Eutectic | $L \leftrightarrow S_1 + S_2$ | |
| Peritectic | $S_1 + L \leftrightarrow S_2$ | |
| Monotectic | $L_1 \leftrightarrow S_1 + L_2$ | |
| Eutectoid | $S_1 \leftrightarrow S_2 + S_3$ | |
| Peritectoid | $S_1 + S_2 \leftrightarrow S_3$ | |
| Monotectoid | $S_{1a} \leftrightarrow S_{1b} + S_2$ | |
| Metatectic | $S_1 \leftrightarrow S_2 + L$ | |
| Syntectic | $L_1 + L_2 \leftrightarrow S$ | |

Allotropic Transformations

- ❑ As we discussed earlier that several metals may exist in more than one type of crystal structure depending upon temperature, Iron, Tin, Manganese and Cobalt are examples of metals which exhibit this property, known as *Allotropy*.
- ❑ On an equilibrium diagram, this allotropic change is indicated by a point or points on the vertical line which represents the pure metal. This is illustrated in below figure. In this diagram, the gamma solid solution field is 'looped'. The pure metal Fe and alloys rich in Fe undergo two transformations.



Allotropic Transformations: Fe-Fe₃C System



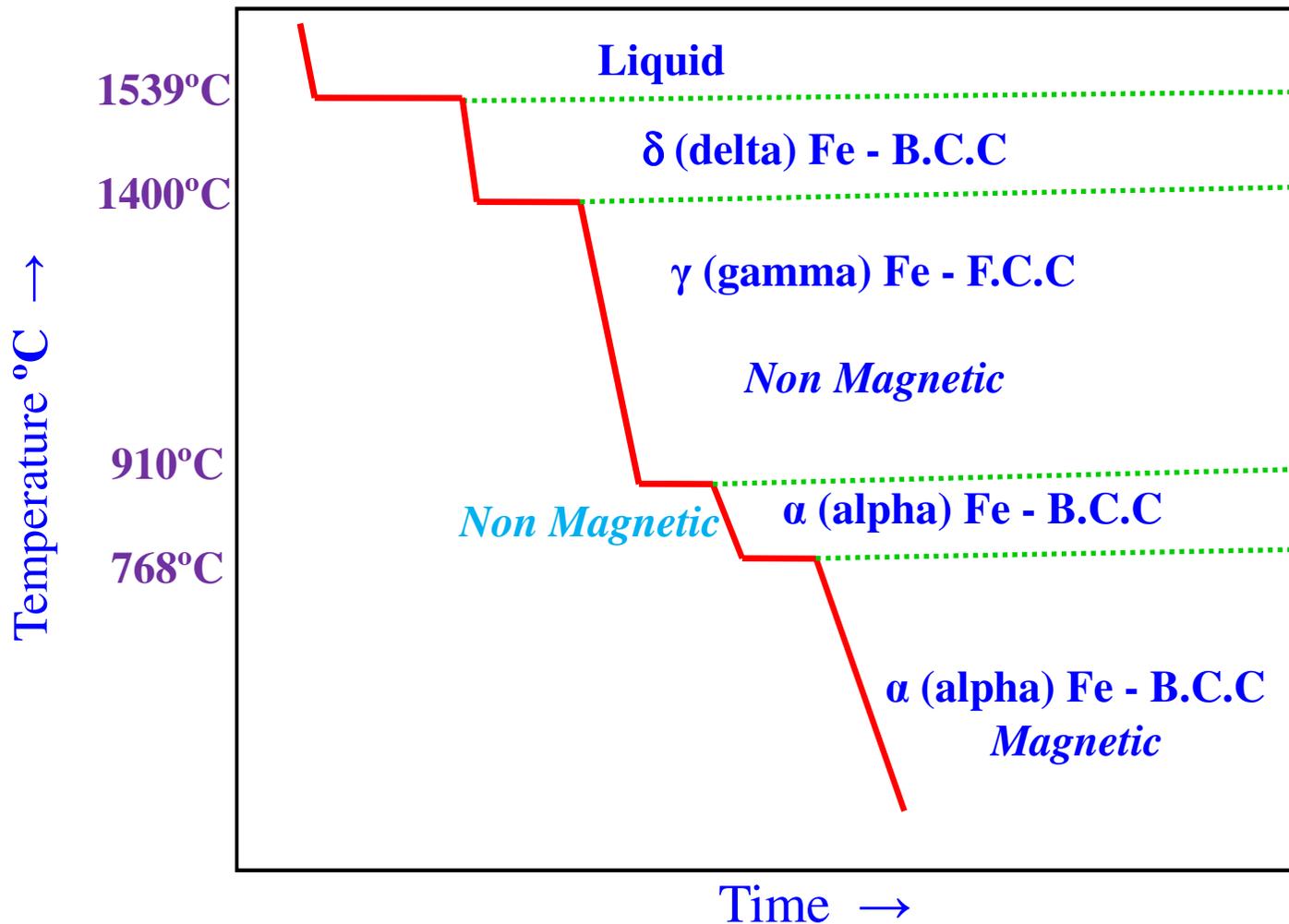
Note



- ❑ Some of the equilibrium diagrams discussed under the simple types are the same as actual ones. Many alloy systems have diagrams which show more than one type of reaction and are generally more complex than the simple types.
- ❑ However, even the most complex diagrams show mainly the reactions that have been covered. The student should be able to label a phase diagram completely; understand the significance of every point, line and area; determine the various reactions that occur at the horizontal lines; and describe the slow cooling and microstructure of any alloy on a binary equilibrium diagram.

Allotropic Transformations in Iron

- Iron is an allotropic metal, which means that it can exist in more than one type of lattice structure depending upon temperature. A cooling curve for pure iron is shown below:



Allotropic Transformations in Iron

There are three more allotropes for pure iron that form under different conditions

ϵ -iron

The iron having hexagonal close packed structure. This forms at extreme pressure, 110 k bars and 490°C. It exists at the centre of the Earth in solid state at around 6000°C and 3 million atmosphere pressure.

FCT-iron

This is face centered tetragonal iron. This is coherently deposited iron grown as thin film on a {100} plane of copper substrate

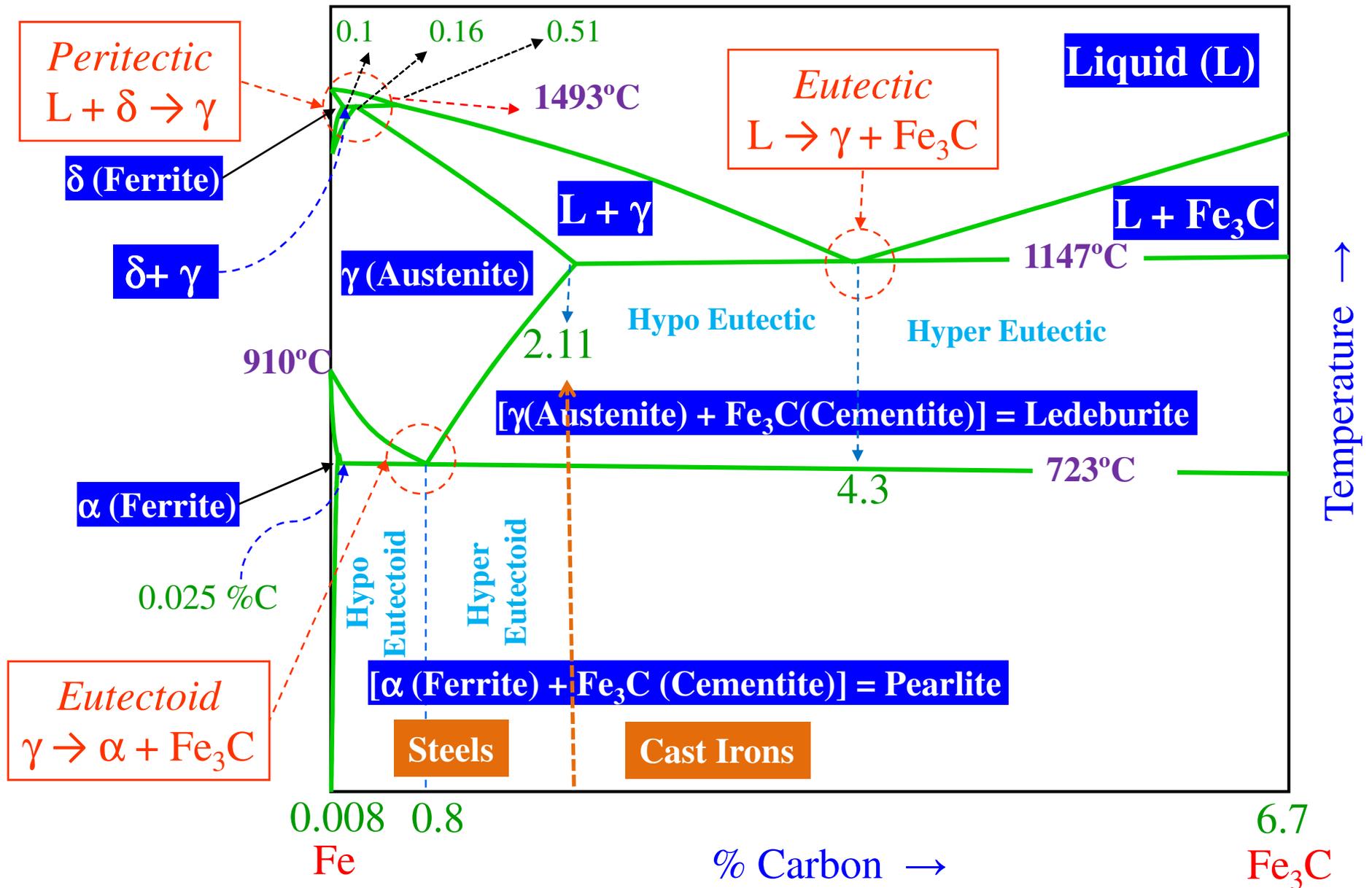
Trigonal-iron

Growing iron on mis-fiting {111} surface of a face centered cubic copper substrate.

Iron – Cementite Phase Diagram

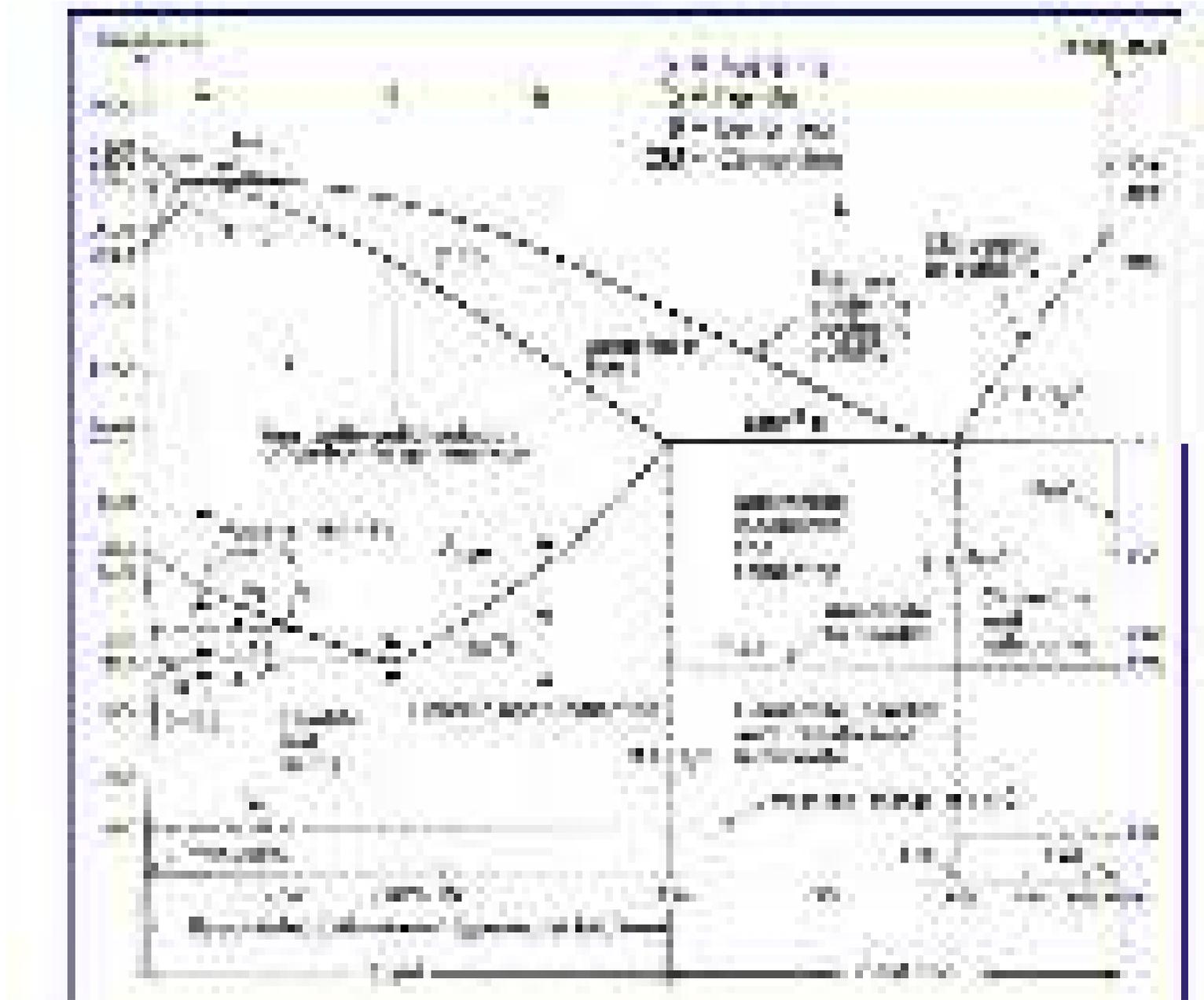
- ❑ The Fe-C (or more precisely the Fe-Fe₃C) diagram is an important one. Cementite is a metastable phase and ‘strictly speaking’ should not be included in a phase diagram. But the decomposition rate of cementite is small and hence can be thought of as ‘stable enough’ to be included in a phase diagram. Hence, we typically consider the Fe-Fe₃C part of the Fe-C phase diagram.
- ❑ A portion of the Fe-C diagram – the part from pure Fe to 6.67 wt.% carbon (*corresponding to cementite, Fe₃C*) – is *technologically very relevant*.
- ❑ Cementite is not an equilibrium phase and would tend to decompose into Fe and graphite. This reaction is sluggish and for practical purpose (at the microstructural level) cementite can be considered to be part of the phase diagram. Cementite forms as it nucleates readily as compared to graphite.
- ❑ Compositions up to 2.1% C are called steels and beyond 2.1% are called cast irons. *In reality the classification should be based on ‘castability’ and not just on carbon content.*
- ❑ Heat treatments can be done to alter the properties of the steel by modifying the microstructure → we will learn about this in coming chapters.

Iron – Cementite Phase Diagram



Iron – Cementite Phase Diagram

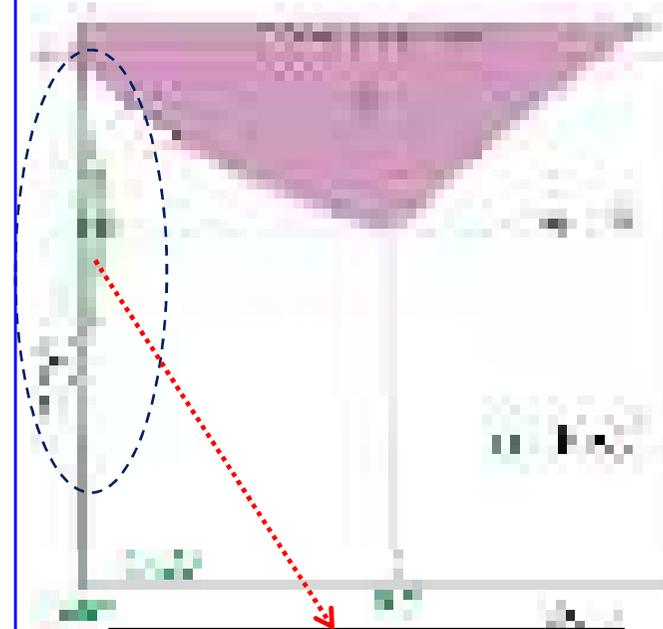
more detailed view of Fe-Fe₃C.....!



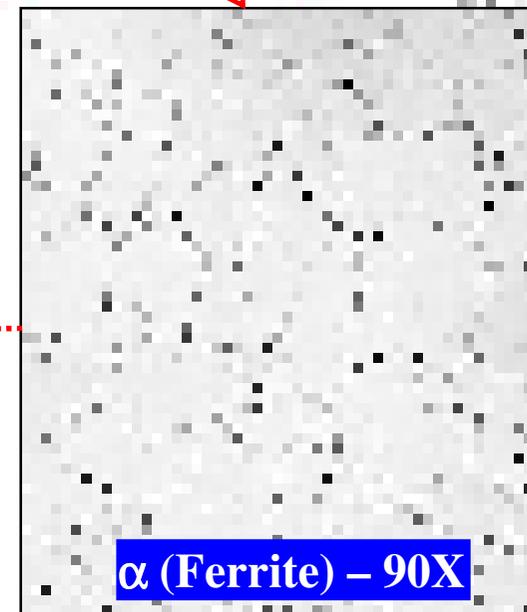
**Characteristics of phases appeared in
Fe-Fe₃C phase diagram**

Ferrite (α)

- ❑ It is an interstitial solid solution of a small amount of carbon dissolved in α iron. The maximum solubility is 0.025%C at 723°C and it dissolves only 0.008%C at room temperature. *It is the softest structure that appears on the diagram*
- ❑ The crystal structure of ferrite (α) is B.C.C
- ❑ Tensile strength – 40,000 psi or 275 Mpa
- ❑ Elongation – 40% in 2 in.
- ❑ Hardness - < 90 HRB



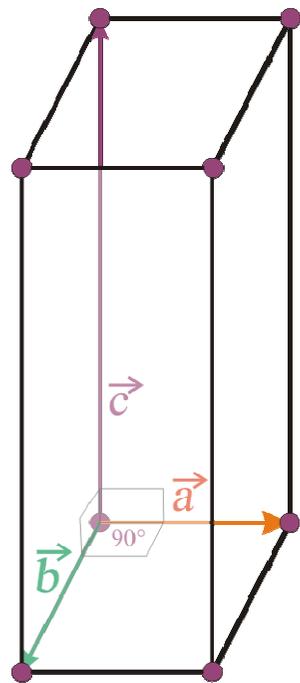
α (Ferrite) contains
B.C.C structure



α (Ferrite) – 90X

Cementite (Fe_3C)

- ❑ Cementite or iron carbide, chemical formula Fe_3C , contains 6.67% C by weight and it is a metastable phase.
- ❑ It is typically hard and brittle interstitial compound of low tensile strength (approx. 5000 psi) but high compressive strength.
- ❑ It is the hardest structure that appears on the diagram.
- ❑ Its crystal structure is orthorhombic

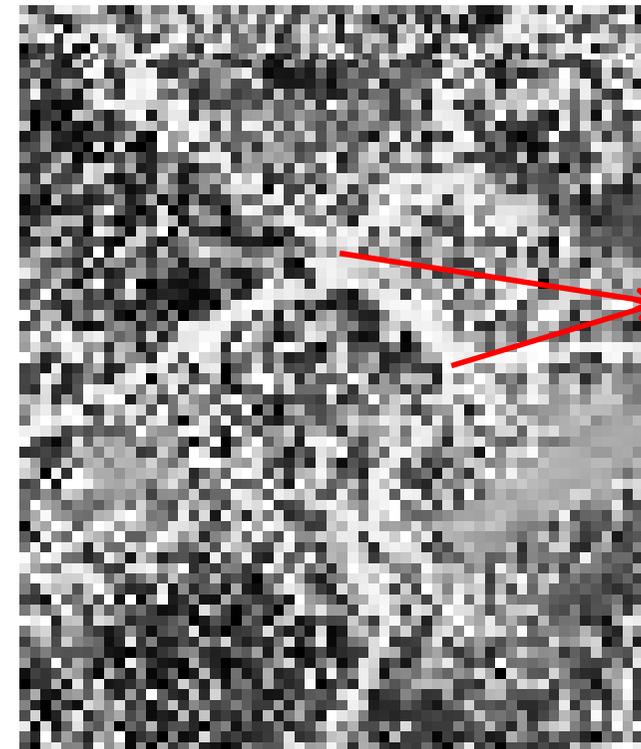


Orthorhombic

$$a \neq b \neq c$$
$$\alpha = \beta = \gamma = 90^\circ$$

**Carbon
(4 atoms)**

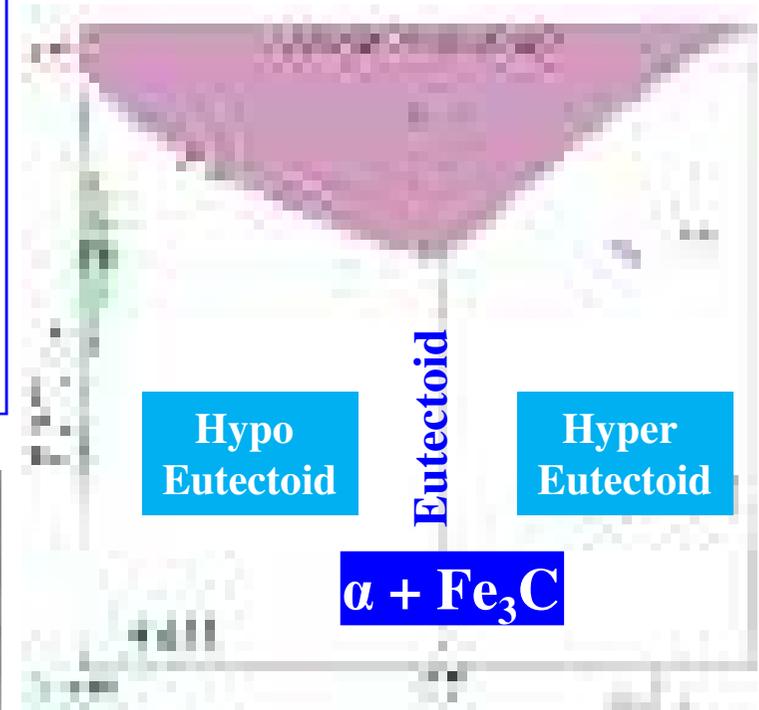
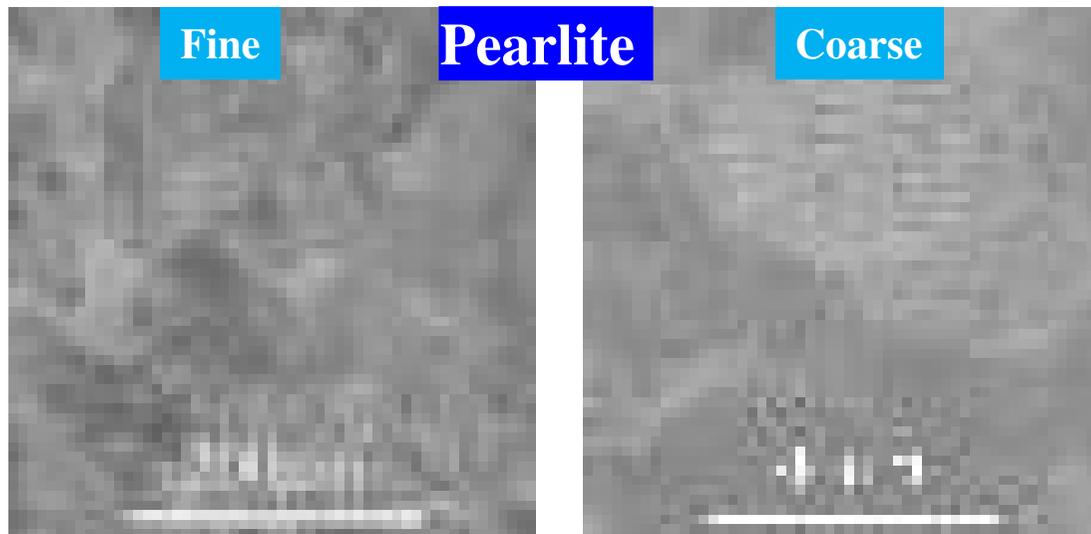
**Iron
(12 atoms)**



Cementite network

Pearlite ($\alpha + \text{Fe}_3\text{C}$)

- ❑ Pearlite is the eutectoid mixture containing 0.80 %C and is formed at 723°C on very slow cooling.
- ❑ It is very fine platelike or lamellar mixture of ferrite and cementite. The fine fingerprint mixture called pearlite is shown in below figure.



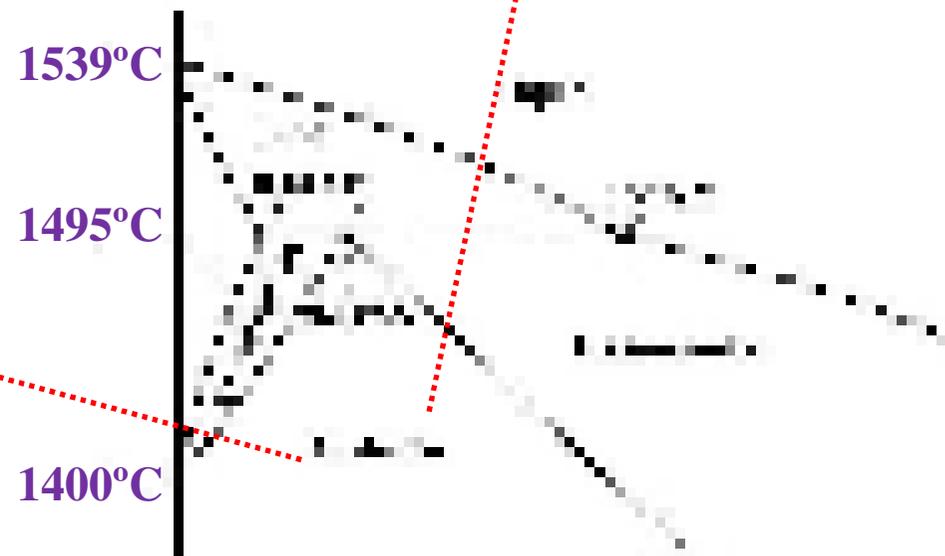
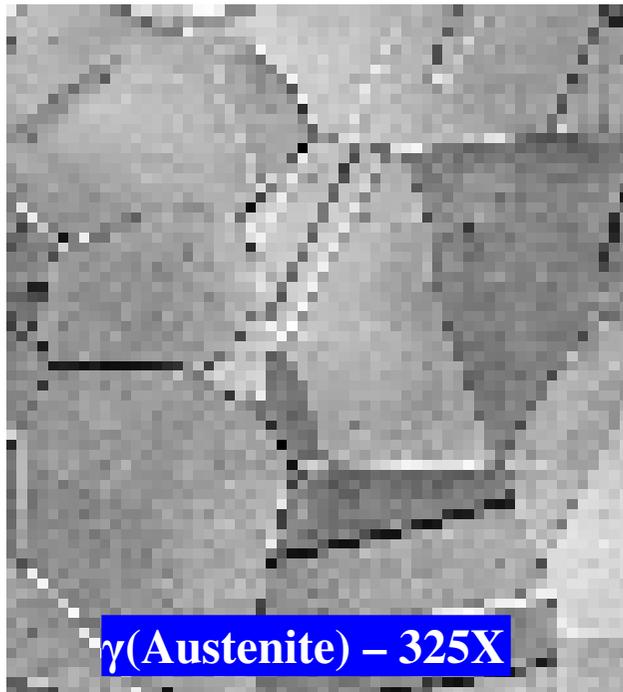
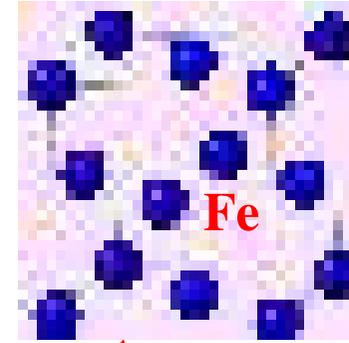
Remember...!

Pearlite is not a phase but combination of two phases (ferrite + cementite)

- ❑ Tensile strength – 120,000 psi or 825 Mpa
- ❑ Elongation – 20 percent in 2 in.
- ❑ Hardness – HRC 20, HRB 95-100, or BHN 250-300

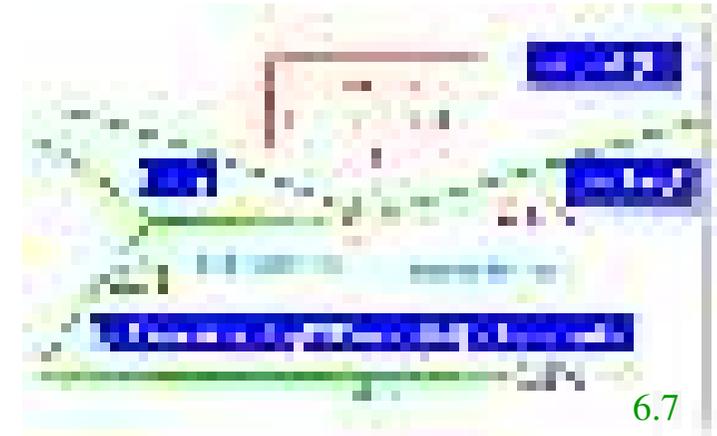
Austenite (γ)

- ❑ It is an interstitial solid solution of a small amount of carbon dissolved in γ iron. The maximum solubility is 2.1% C at 1147°C.
- ❑ The crystal structure of Austenite (γ) is F.C.C
- ❑ Tensile strength – 150,000 psi or 1035 Mpa
- ❑ Elongation – 10% in 2 in.
- ❑ Hardness - 40 HRC and Toughness is high.



Ledeburite ($\gamma + \text{Fe}_3\text{C}$)

- ❑ Ledeburite is the eutectic mixture of austenite and cementite. It contains 4.3% C and is formed at 1147°C
- ❑ Structure of ledeburite contains small islands of austenite are dispersed in the carbide phase.
- ❑ Not stable at room temperature

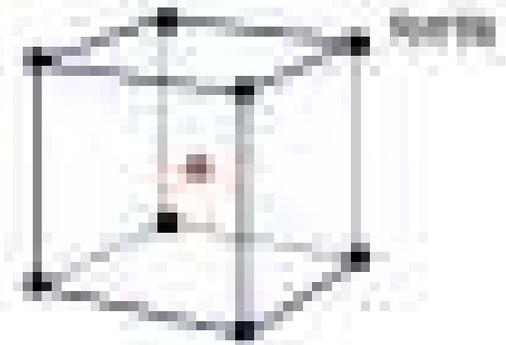


The pearlite is resolved in some regions where the sectioning plane makes a glancing angle to the lamellae. The ledeburite eutectic is highlighted by the arrows. At high temperatures this is a mixture of austenite and cementite formed from liquid. The austenite subsequently decomposes to pearlite.

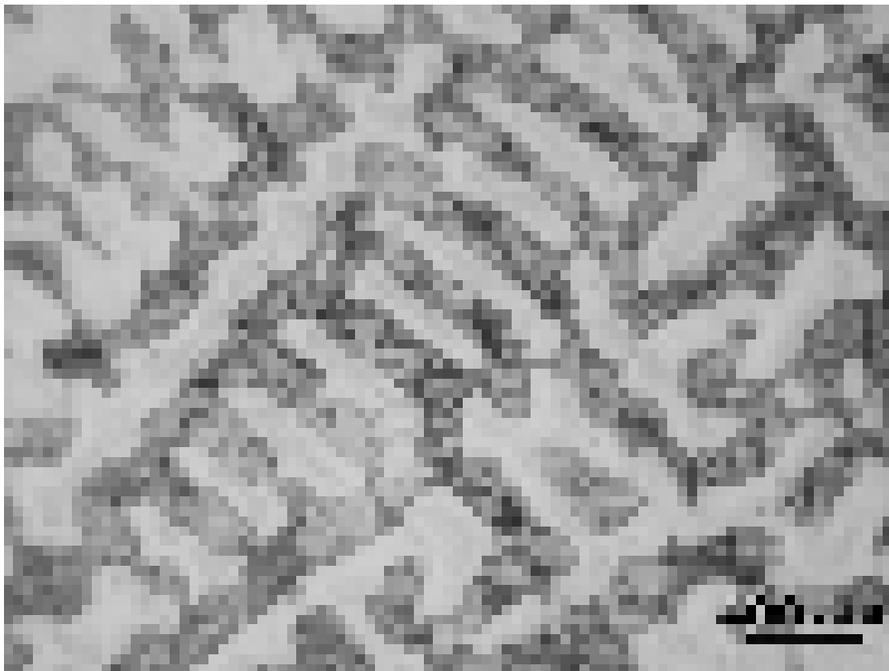


Ferrite (δ)

❑ Interstitial solid solution of carbon in iron of body centered cubic crystal structure. (δ iron) of higher lattice parameter (2.89\AA) having solubility limit of 0.09 wt% at 1495°C with respect to austenite. The stability of the phase ranges between $1394\text{-}1539^\circ\text{C}$.



❑ This is not stable at room temperature in plain carbon steel. However it can be present at room temperature in alloy steel specially duplex stainless steel.

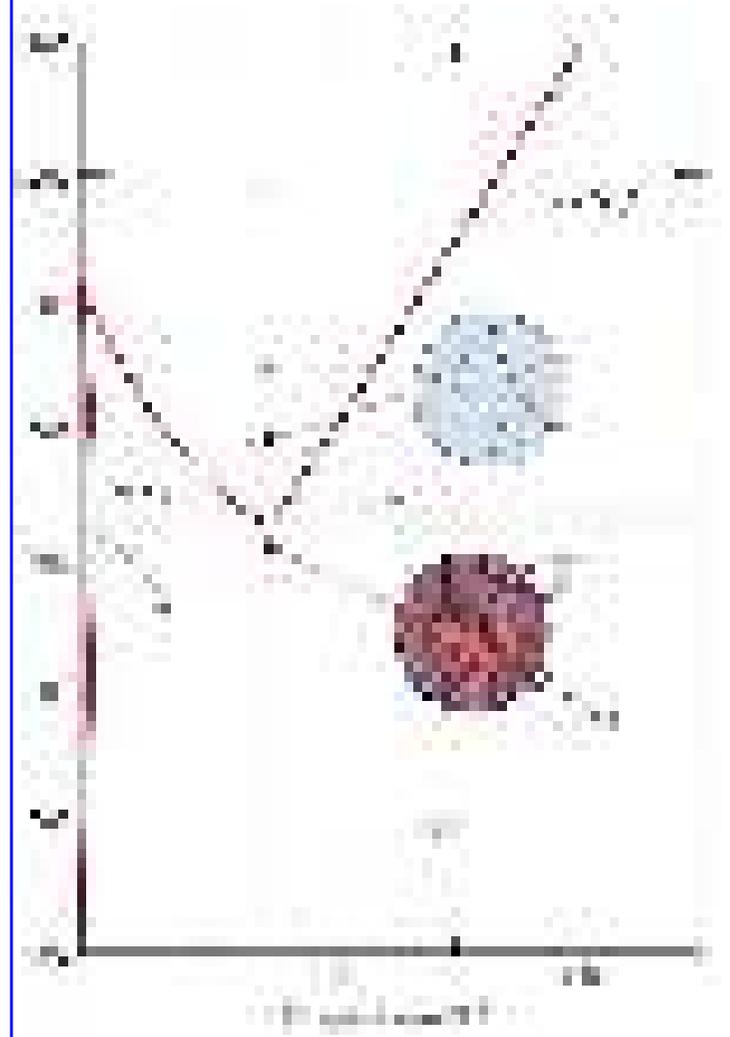


δ -ferrite in dendrite form
in as-cast Fe-0.4C-2Mn-
0.5Si-2Al-0.5Cu

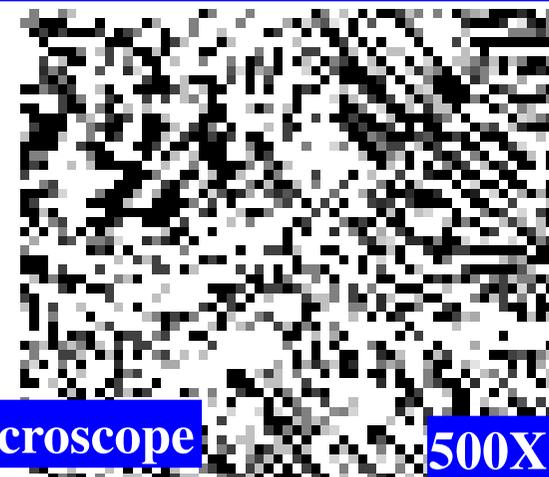
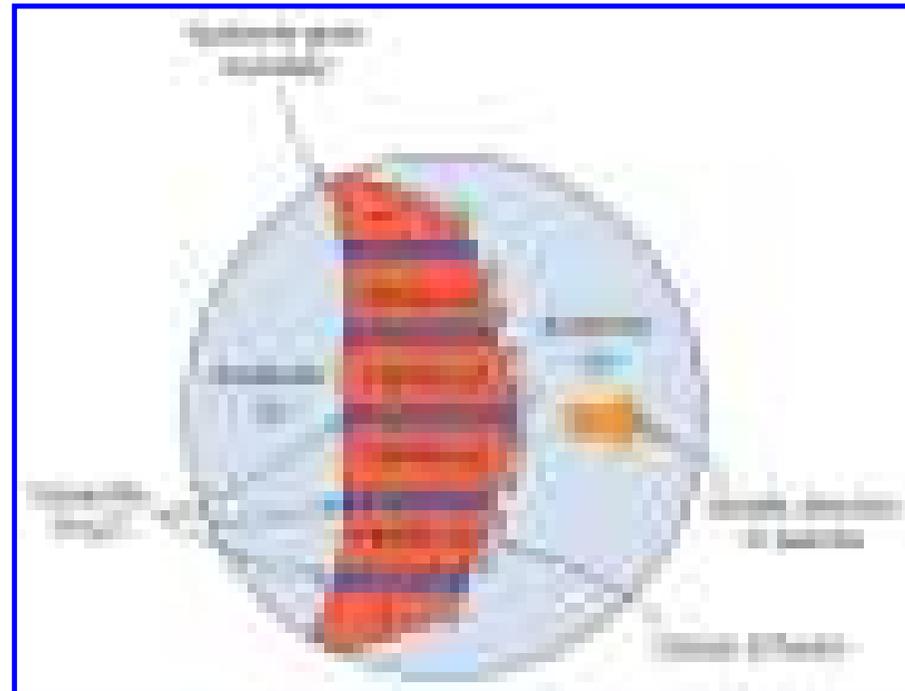
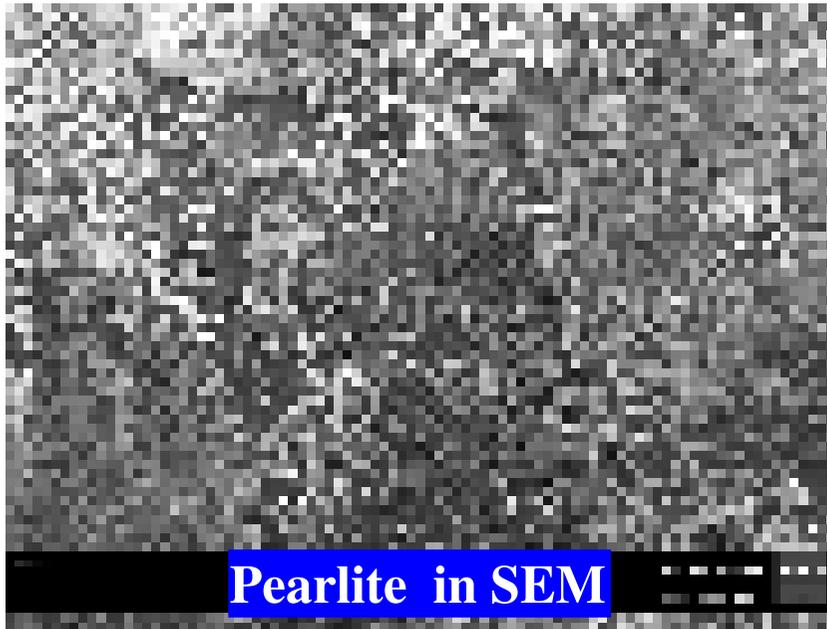
**Microstructures involved in
eutectoid mixture**

Eutectoid reaction

- ❑ Phase changes that occur upon passing from the γ region into the $\alpha + \text{Fe}_3\text{C}$ phase field.
- ❑ Consider, for example, an alloy of eutectoid composition (0.8% C) as it is cooled from a temperature within the γ phase region, say 800°C – that is, beginning at point ‘a’ in figure and moving down vertical xx' . Initially the alloy is composed entirely of the austenite phase having composition 0.8 wt.% C and then transformed to $\alpha + \text{Fe}_3\text{C}$ [pearlite]
- ❑ The microstructure for this eutectoid steel that is slowly cooled through eutectoid temperature consists of alternating layers or lamellae of the two phases α and Fe_3C
- ❑ The pearlite exists as grains, often termed “colonies”; within each colony the layers are oriented in essentially the same direction, which varies from one colony to other.
- ❑ The thick light layers are the ferrite phase, and the cementite phase appears as thin lamellae most of which appear dark.

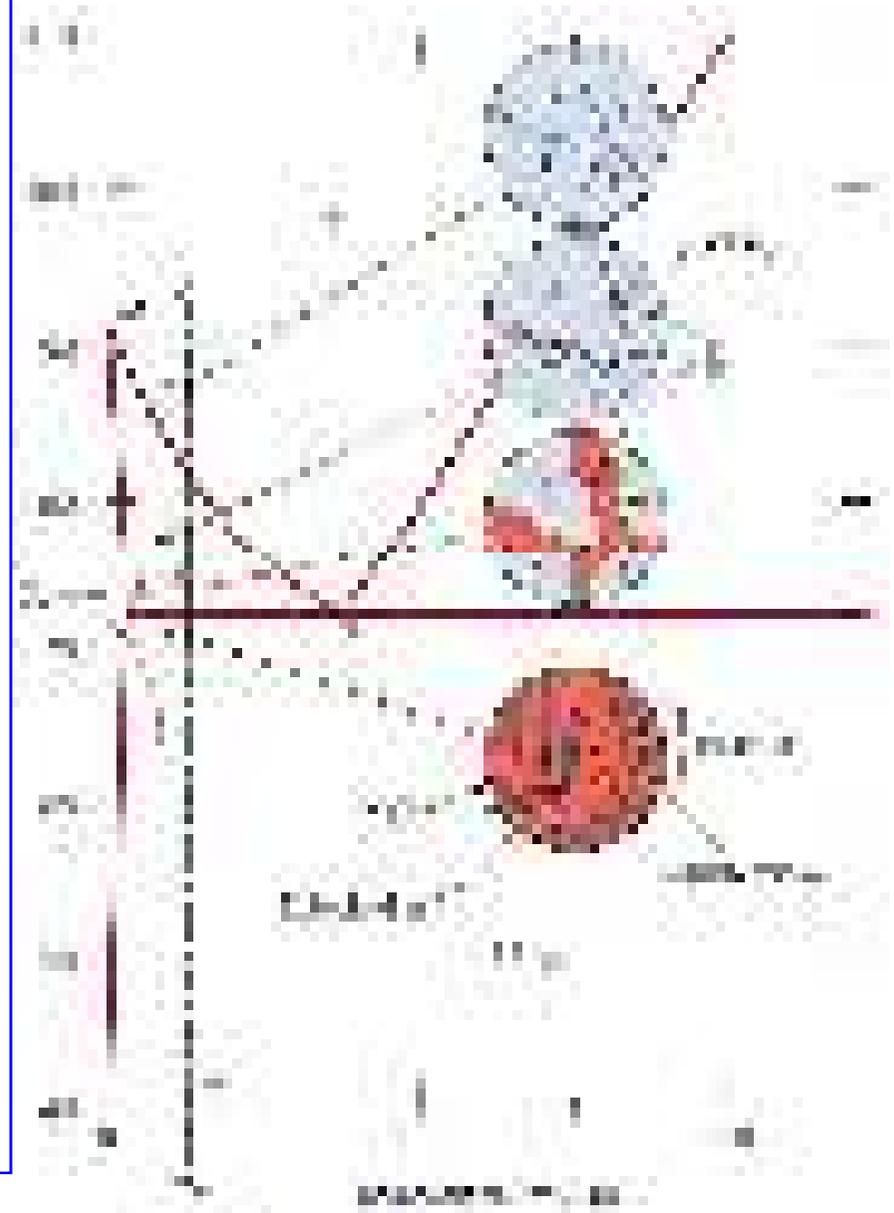


Eutectoid structure



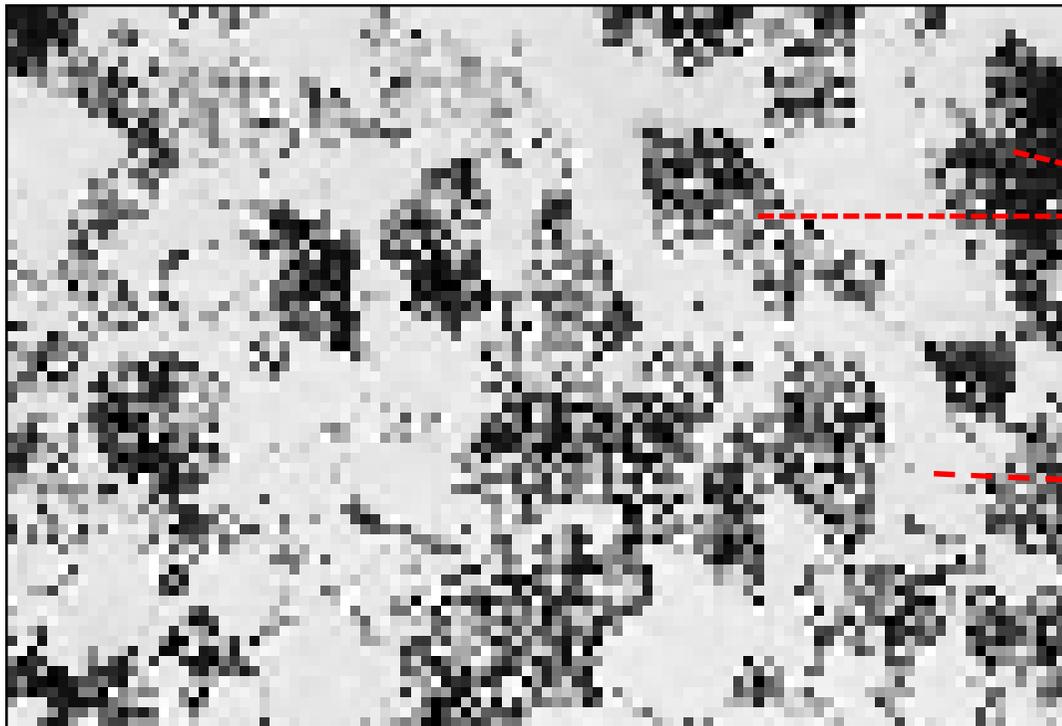
Hypo eutectoid region

- ❑ Hypo eutectoid region – 0.008 to 0.8 %C
- ❑ Consider vertical line yy' in figure, at about 875°C, point c , the microstructure will consist entirely of grains of the γ phase.
- ❑ In cooling to point d , about 775°C, which is within the $\alpha+\gamma$ phase region, both these phases will coexist as in the schematic microstructure. Most of the small α particles will form along the original γ grain boundaries.
- ❑ Cooling from point d to e , just above the eutectoid but still in the $\alpha+\gamma$ region, will produce an increased fraction of the α phase and a microstructure similar to that also shown: the α particles will have grown larger.



Hypo eutectoid region

- ❑ Just below the eutectoid temperature, at point **f**, all the γ phase that was present at temperature **e** will transform pearlite. Virtually there is no change in α phase that existed at point **e** in crossing the eutectoid temperature – it will normally be present as a continuous matrix phase surrounding the isolated pearlite colonies.
- ❑ Thus the ferrite phase will be present both in the pearlite and also as the phase that formed while cooling through the $\alpha+\gamma$ phase region. The ferrite that is present in the pearlite is called eutectoid ferrite, whereas the other, is termed proeutectoid (meaning pre- or before eutectoid) ferrite.

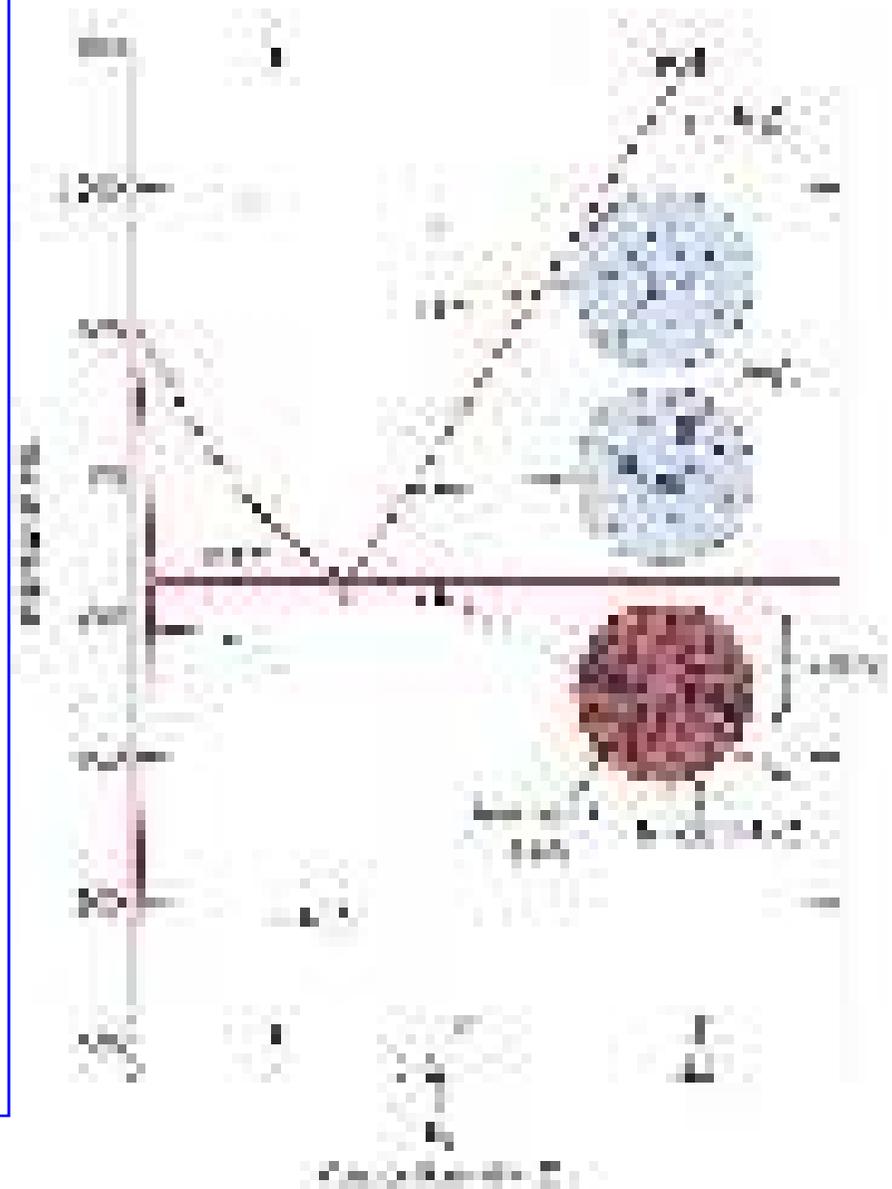


Pearlite

Pro-eutectoid ferrite

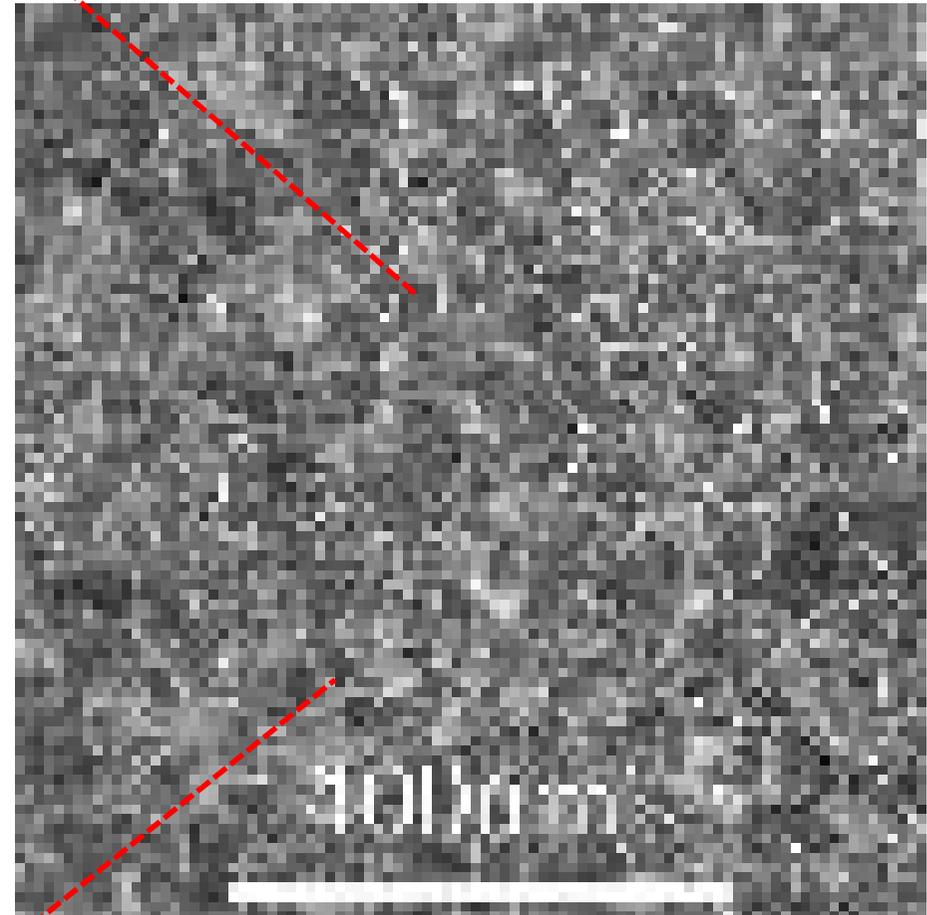
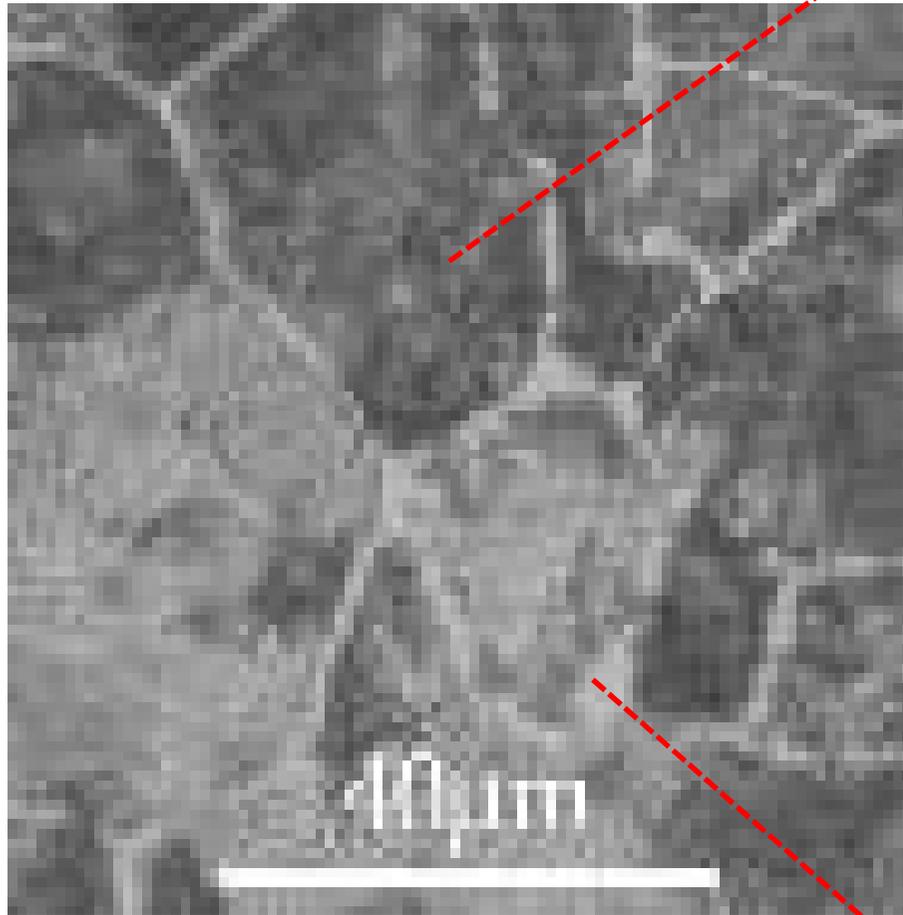
Hyper eutectoid region

- ❑ Hyper eutectoid region – 0.8 to 2.1 %C
- ❑ Consider an alloy of composition C_1 in figure that, upon cooling, moves down the line zz' . At point g only the γ phase will be present and the microstructure having only gamma grains.
- ❑ Upon cooling into the $\gamma + Fe_3C$ phase field – say to point h – the cementite phase will begin to form along the initial γ grain boundaries, similar to the α phase in point d . this cementite is called *proeutectoid cementite* that which forms before the eutectoid reaction.
- ❑ As the temperature is lowered through the eutectoid to point I , all remaining austenite of eutectoid composition is converted into pearlite; thus the resulting microstructure consists of pearlite and proeutectoid cementite as microconstituents.



Hyper eutectoid region

Pearlite



Cementite network

Application of Lever rule in Fe-Fe₃C phase diagram

Solved Example

For a 99.6 wt% Fe-0.40 wt% C at a temperature just below the eutectoid, determine the following:

- a) The amount of Fe₃C, ferrite (α) and pearlite
- b) The amount of pearlite and proeutectoid ferrite (α)

a) The amount of Fe₃C and ferrite (α)

$$\text{Percentage of Fe}_3\text{C} = \frac{0.4 - 0.025}{6.67 - 0.025} * 100$$

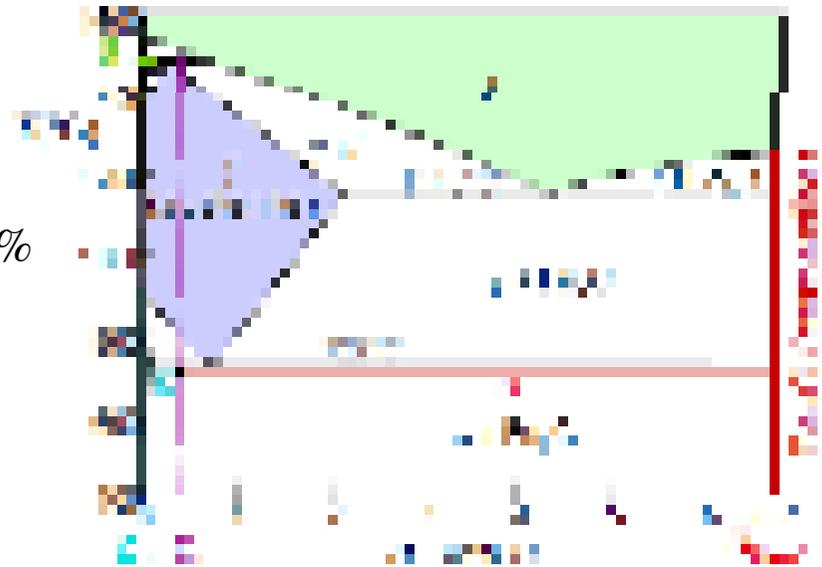
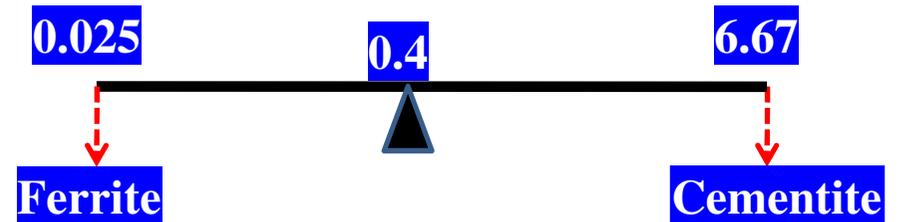
Percentage of Fe₃C in 0.4 %C steel is 5.64 %

Percentage of Ferrite (α) in 0.4 %C steel = (100- 5.64)%

Percentage of ferrite in 0.4 %C steel = 94.36%

or

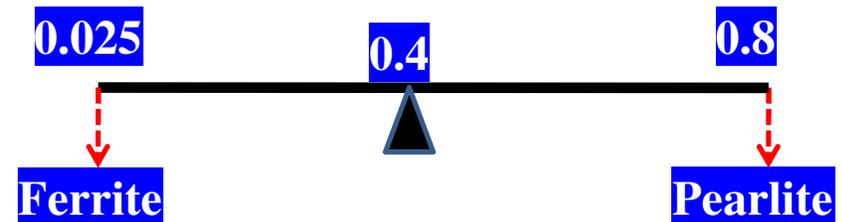
$$\text{Percentage of ferrite} = \frac{6.67 - 0.4}{6.67 - 0.025} * 100 = 94.36\%$$



b) Phase fraction of pearlite and proeutectoid ferrite (α)

$$\text{Percentage of pearlite} = \frac{0.4 - 0.025}{0.8 - 0.025} * 100$$

Percentage of pearlite = 48 %



Percentage of proeutectoid ferrite (α) in 0.4 % C steel = (100- 48) %

Percentage of proeutectoid ferrite (α) = 52 %

or

$$\text{Percentage of proeutectoid ferrite} = \frac{0.8 - 0.4}{0.8 - 0.025} * 100 = 52\%$$