धातुशास्त्रम्

METALLURGY

MECHANICAL RESPONSE OF METALS AND ALLOYS
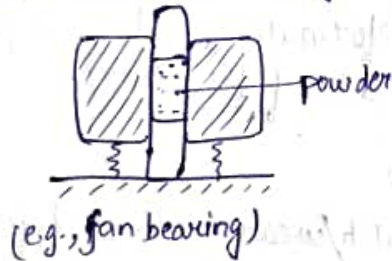
Materials

- Metals
- Polymers ⎫ classification
- Composites ⎬ based on , Solids
- Ceramics ⎭ structure
- Semi-conductor

Processing ← Casting/Foundry, forming, Machining, welding, Powder Metallurgy

Nuclear, Atomic, Cube HCP Mono-clinic Crystal, Micro, Macro → Structure

Processing ↓ Structure ↓ Properties ↓ Performance

→ Processing

 # Power Metallurgy

powder

(e.g., fan bearing)
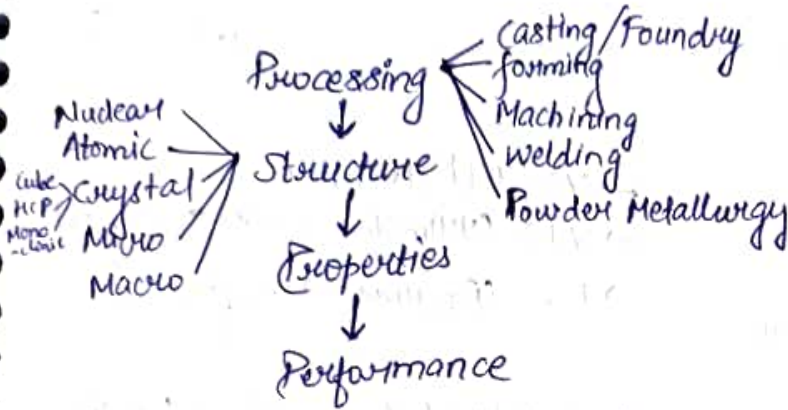
Self lubricating bearing

 # Foundry

 # Stainless steel
⎧ Fe, C, Ni, Cr
⎩ Cr forms protecting layer (Cr_2O_3)

 # Forming

Punch

Die

 # Machining

 # Welding
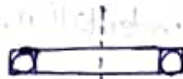
→ Structure

- Nuclear
- Atomic
- Crystal ← Cube ← BCC / FCC ; HCP ; Monoclinic
- Micro
- Macro
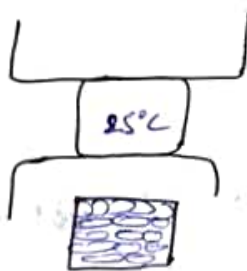
25°C — Forged grain
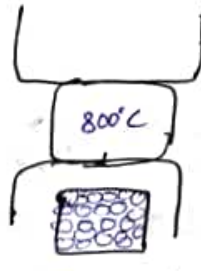
800°C — Fine grain ↓ more strength

→ Grain size and shape can affect the properties of materials.
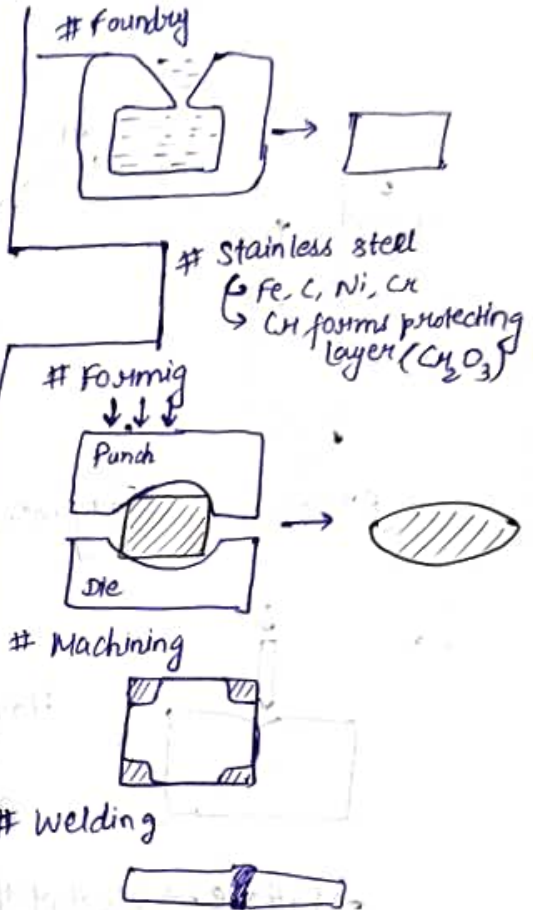
Steel ≠ Steel
casting ≠ forming
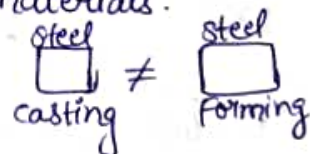
⇒ Difference in microstructure.

→ Yield stress,

$$\sigma_y = \sigma_i + \frac{k}{\sqrt{d}}$$ ← grain diameter

→ **Properties**
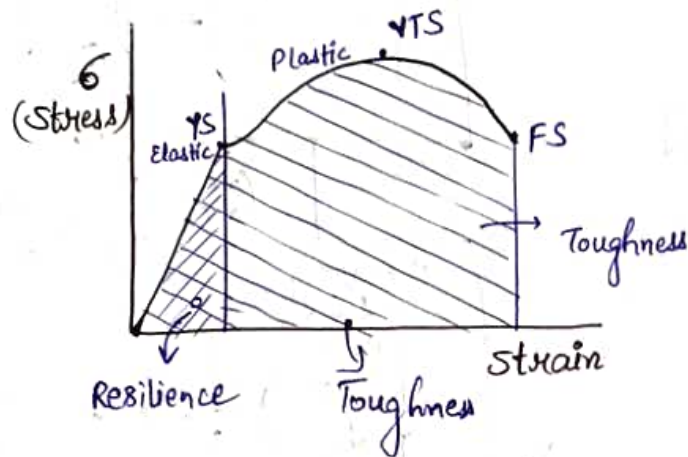- → Mechanical ← Tensile strength, Yield strength, Hardness
- → Physical
- → chemical

(Resistance to external stress)

Resilience   Toughness

→ YS (Yield strength)
→ UTS (Ultimate Tensile Strength)
→ FS (Fracture Strength)

→ Ductility or % Elongation length
→ **Malleability** → property of material by which it can withstand large plastic deformation under compressi... loads prior of fractures.
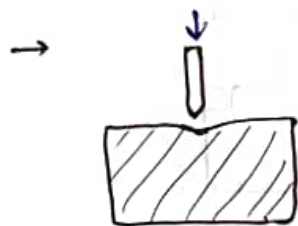
$$Hardness \propto \frac{1}{Depth \ of \ penetration}$$

↓

Persistance to indentation, scratch/wear or local deformat...

→ **Fatigue** → Most of the materials fail due to this (due to dynamic loading).
→ Premature failure of material when subjected to dynamic/ fluctuating loads.

100 MPa
+20
-20
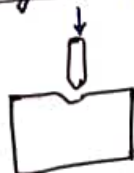
→ **Ductility** → property of material by which it can withstand large plastic deformation prior of fracture in tensile loads.

→ **Creep:** Elongation

W
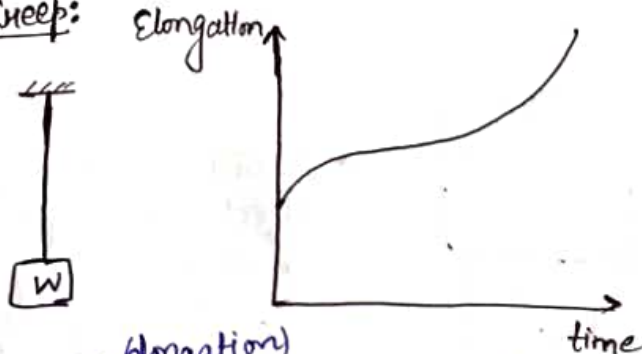
↳ Failure of a material under constant load/stress at higher temperature.

↳ steel doesn't undergo deformation at room temp. because its melting point is very high (>1000°c).

Metallurgy

- The science and technology of metals and alloys
 - physical metallurgy, mechanical metallurgy, process metallurgy, etc.

Physical Metallurgy: with the physical and mechanical properties of metals as affected by composition, processing and environmental conditions.

Mechanical Metallurgy: The science that studies the response of metals to applied forces.

Process Metallurgy: Processing of ores to metals.

→ **Materials Science:** Study of the properties of solid materials and how those properties are determined by material's composition and structure, both macroscopic and microscopic.
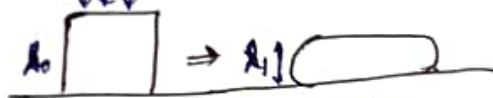
in 10,000 seconds
1000 s
100 s
10 s
1 s

$$\frac{l_1 - l_0}{l_0} = e$$
↓
same strain

Strain rate ∝ Resistance (Hardness)
to deformation

17-05-2023

$$Strength \propto \frac{1}{ductility \ (or) \ toughness}$$
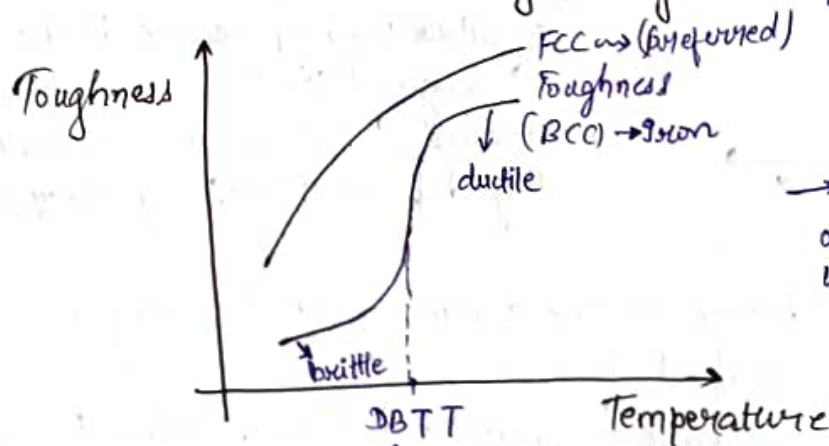
↘ Resistance to bulk deformation

Toughness: Energy required (withstand) prior to failure

→ Most materials with FCC structure are used for sub-zero applications which don't have sharp DBTT.

Toughness

FCC ∿ (preferred)
Toughness
↓ (BCC) → iron
ductile

brittle

DBTT   Temperature
↓
(Ductile to Brittle)
Transition Temp.
↳ Depends on crystal structure, alloying, chemical composition, etc.

Eg.

P_0 : Applied load , S_0 : shear force at basal plane

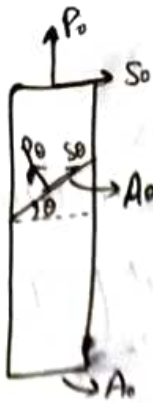$$\sigma_0 = \frac{\text{load}}{\text{area}} = \frac{S_0}{A} = 0 \qquad T = \frac{\text{shear load}}{\text{area}}$$

$$\sigma_0 = P_0/A_0$$

$$T_0 = S_0/A_0$$

$$\sigma_\theta = P_0/A_\theta$$

$$T_\theta = S_\theta/A_\theta$$

Find $\sigma_0, T_0, \sigma_\theta, T_\theta$.

Soln: $S_0 = \cancel{P_0 \sin 0}$ 0 .

$$\sigma_\theta = \frac{P_0 \cos\theta}{A_0/\cos\theta} = \sigma_0 \cos^2\theta$$

$$\cancel{T_0 \sigma_0 \cos\theta}$$
$$T_0 = \sigma_0 \sin\theta \cos\theta$$

$$P_\theta = P_0 \cos\theta$$
$$S_\theta = P_0 \sin\theta$$

$$A_\theta = \frac{A}{\cos\theta}$$

Shear stress ↓
responsible for deformation

$$T_\theta = \sigma_0 \sin\theta \cos\theta_0$$
$$T_\theta = \sigma_0/2$$
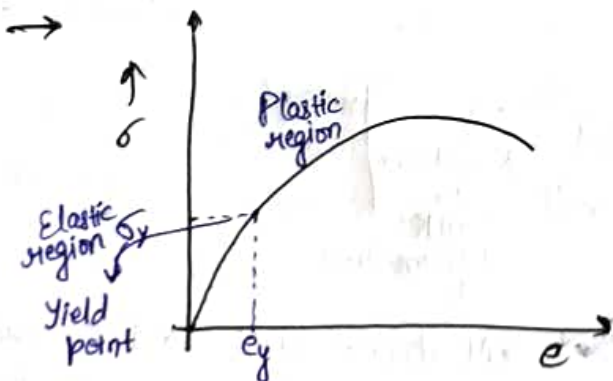
→ Till elastic limit, intermolecular forces of attraction help restore to the original state.

→ Normal forces donot contribute in any deformation (only shear forces do).

<u>Plastic deformation</u>: change in the arrangement (e.g., neighbours) of atoms due to mechanical forces.

↳ During this, bond breakage happens and then bonding takes place.

→ <u>slip plane</u>: Plane along which slip is favourable.

<u>highest planar density</u> ↳ ∴ whole plane of atoms shift. So, the bonds broken will have strength equal to ∴ bond energy × no. of atoms in a plane, which is high ...
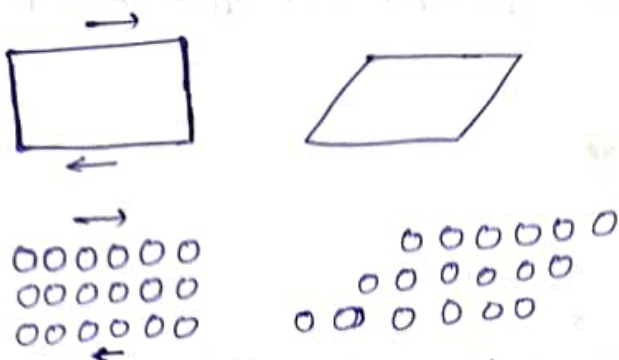
→ **Elastic deformation**
↓
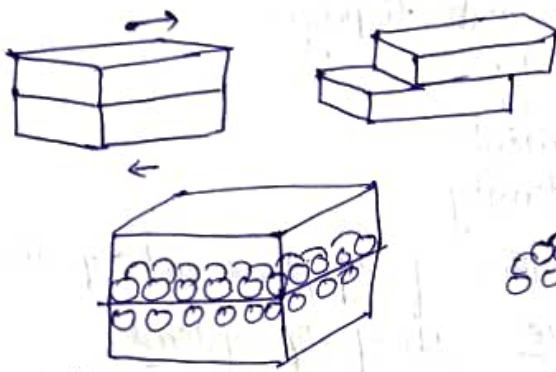Shear force leads to elastic deformation, body regains its shape after removal of force.
↳ Till yield point, body show elastic deformation
↳ No bond breakage.

→ **Slip direction:** dirce of movement
↓
highest linear densities

Plastic deformation

Dislocations
slipping:

→ All atoms of the plane slip.
(if no dislocation)
↓
More force is required for perfect crystal

extra half plane
⊥ (+ve dislocation): Missing atoms in the lower half.
missing half plane
T (-ve dislocation)

Without ⊥

F
|
d
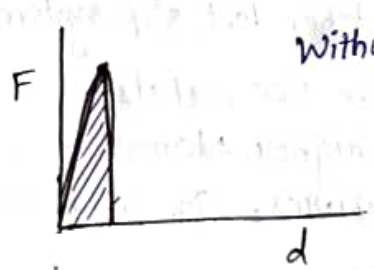
→ Energy required will be equal regardless of presence of dislocations

with ⊥

F
|
d
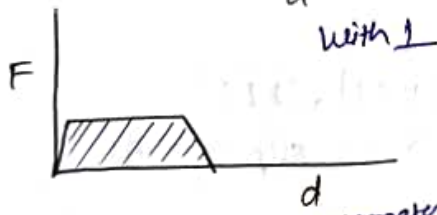
→ Movement of dislocation causes plastic deformation.

a → lattice parameter
→ Compressive strain

b < a (due to dislocation)

c > a

→ dislocation line (into the plane)
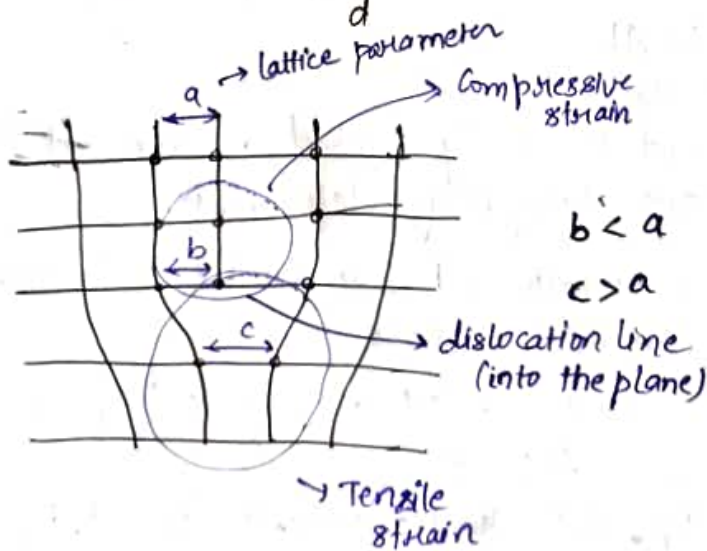
Tensile, compressive strain
↓
due to imbalanced forces

→ Tensile strain

→ For choosing/changing/deforming material, material with dislocation is preferred.
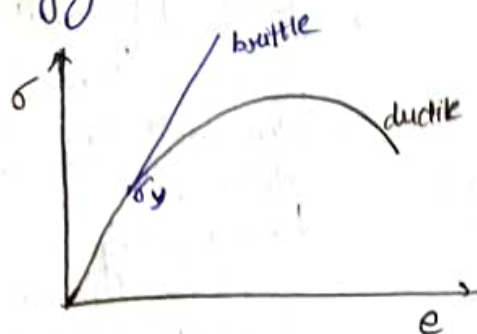
Slip System

→ **Slip plane:** Plane allowing easiest slippage.
　　↳ highest planar density

lesser interatomic distances →**Slip direction:** Dirn of movement
　　↳ highest linear density.

Slip systems → combination of slip plane and slip direction.

Crystal structure	No. of slip systems
FCC	12
BCC	48
HCP	3

→ For a material to be ductile – 5 independent slip systems.

→ FCC metals are less stronger than BCC metals
　↳ FCC structures have planes of higher planar density and higher linear density than BCC structures. So, smaller force can easily dislocate.

FCC: planes: $(1\,1\,1)$, $(1\,\bar{1}\,\bar{1})$, $(\bar{1}\,1\,\bar{1})$, $(\bar{1}\,\bar{1}\,1)$
　　↳ 4 planes, 3 sides ⇒ 12 slip systems

FCC → Ag, Au, Cu, Al
BCC – Fe, W, Cr, Mo.

→ Slip planes are not so closely packed as compared to FCC metals—
Need high shear strength for deformation.

→ FCC metals have relatively lower ductile to brittle transition temperature than BCC metals.

→ Dislocations can easily wander at higher temp. as atoms have thermal energy to dislocate.
　↳ At sub-zero temp., dislocations are more difficult, in addition to lower thermal energy.

↳ BCC structures will have longer distances to shift, making shifting difficult ⟹ Sharper transition temp. and lower ductility.

slip plane $\vec{n}$ normal, Applied force, $F = \sigma A$, Cross-sectional area = A
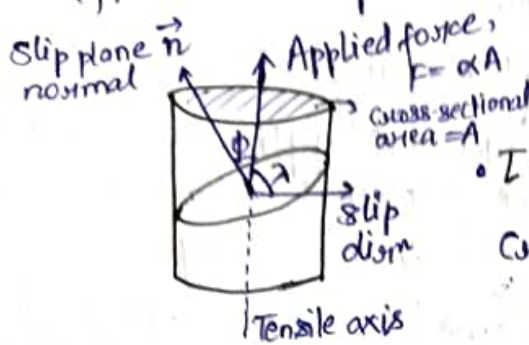
- Min^m stress to cause yielding, $\phi = \lambda = 45°$
- $\tau_{CRSS} = 0$ for $\lambda = \phi = 90°$ (No slip, no fracture)
- $\tau = \dfrac{F \cos\phi \cos\lambda}{A} = \sigma \boxed{\cos\phi \cos\lambda}$

slip dirn.

Tensile axis

Critically Resolved Shear Stress — Schimid factor

yield point

→ Metals with dislocations have lower strength.
    ↳ Dislocations move plastically on mechanical loading.
    ↳ Designing requires higher strength.
    Manufacturing requires lower strength.

→ By heat treatment, we can alter the internal structure, not the shape of material.
    ↳ Used to increase/decrease the strength (hard/soft).

→ Dislocations can't move from one grain to the other.
    ↳ get piled up at the grain boundaries.

⊥⊥⊥⊥⊥ | ⟶ ⊥⊥⊥⊥⊥ | → micro crack forms
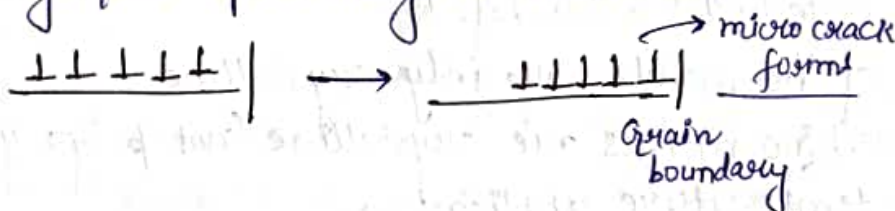
Grain boundary

→ In the vicinity of a crack, a series of dislocations are always found.

Characteristics:
    { Structure
    Processing
    Performance
    Properties

→ More grain boundaries, more strength.

→ Structure sensitive properties: Hardness, Yield strength, tensile strength, ductility, fatigue, creep, electrical & thermal properties.

→ Structure insensitive properties: Young's Modulus, Melting point, Specific heat, Refractive index, Dielectric constant. → depends on lattice parameter

→ Physical properties: Density, Thermal, Magnetic, Optical, Electrical

→ Mechanical properties: Strength, Ductility, Hardness, Impact strength, Fatigue, Creep, Wear.

Hardness

↳ Resistance to localised plastic deformation.

→ Grain structure is not uniform after casting:

Outermost: Finer grains

Middle: Columnar grains

Centre: Bigger grains

⎫
⎬
⎭

structural applications don't use the products of casting b/c it has non-uniformity

⬇

Formed products are used instead.

→ Super alloy : 8-10 components → dendritic structure b/c of higher no. of components.

↓

Welded component has bigger grain size.

→ Some resistance (some metals having atomic impurities) to movement of dislocations can increase strength.

→ Pure metals have higher ductility but lower strength, hence can be easily deformed.

→ Perfect lattice: no plastic deformation, no ductility, no toughness, very high strength.

→ Grain boundaries : 2D defects.

Most of the metals are poly-crystalline.

→ Gas turbine metals are crystalline (not polycrystalline) for higher temperature applications.
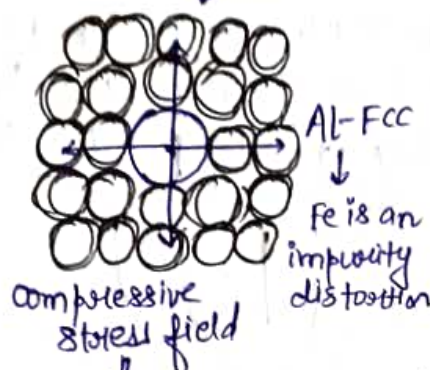
→ Presence of vacancies decrease the free energy of system, hence they are thermodynamically bound to occur.

SOLID SOLUTIONS

Crystal Imperfections: Vacancies, Impurity

Substitutional Impurity → ← Interstitial impurity

Al-FCC ↓ Fe is an impurity distortion

compressive stress field

δize of interstitial atom' > size of void

Local tensile stress field

(for local size of impurity)
→ C, B, N, O, H → occupy voids
(DO NOT SUBSTITUTE)

→ **Mixtures**: Two or more substances which are not chemically united together.

→ **Solution**: Substances which are physically inseparable and are chemically united together.

→ Alloys are solid solution.

→ Addition of foreign element should not change the crystal structure of base metal.
  ↳ In interstitial sites: Interstitial solid soln
    ↳ Substituting lattice points: Substitutional solid soln.
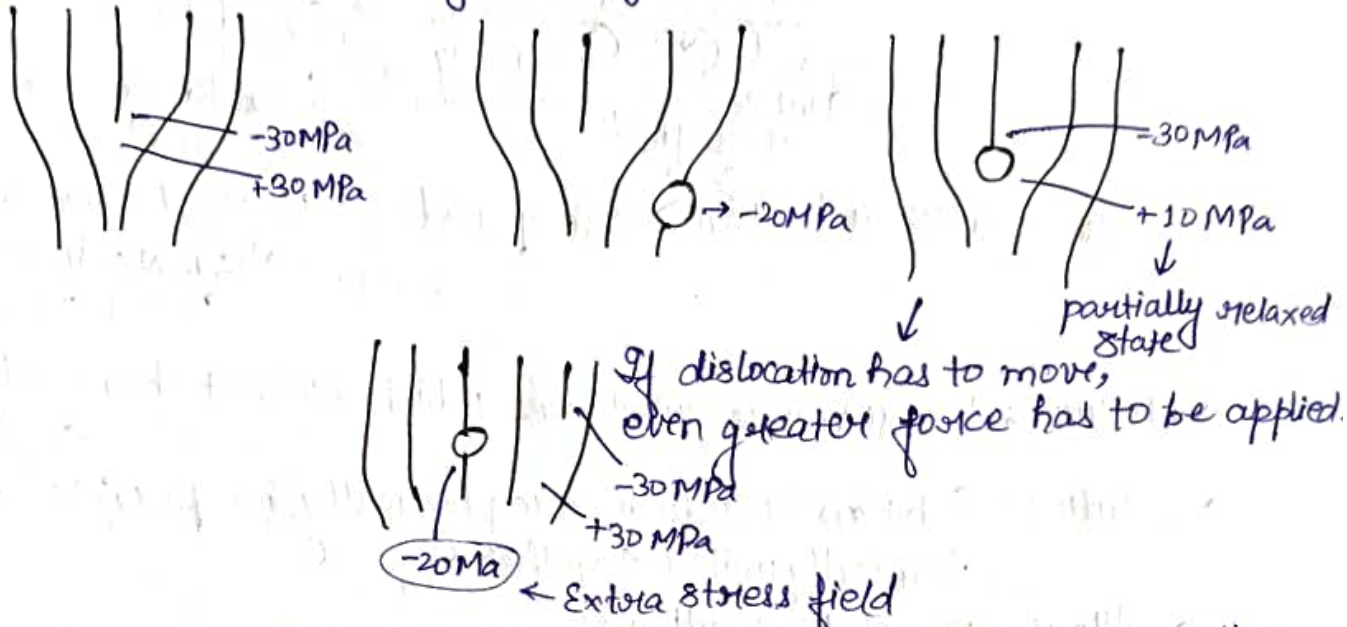
→ Strength $\propto \dfrac{1}{\text{Ductility}}$

Q) why does ductility decreases on alloying?

→ **Phase**: Physically distinct and chemically homogeneous portion of a system with particular chemical composition.

→ CuZn: Intermetallic Compound (defined stoichiometry)
  ↳ Ni_3Al, Ti_3Al, $CuAl_2$

Cu Zn super lattice: has a different boundary
  ↳ regular arrangement
    ↳ Rest of the part of Cu-Zn: Substitutional solid soln

→ **Brass:** Zn is added to Cu (Zn: HCP, Cu: FCC)
 Cu(FCC)   ↓   ↓   ↳ Substitution solid sol^n
       foreign/alloying   host
       element

→ **Steel:** Interstitial solid sol^n of C in Fe.

→ For larger size of substituting atom, it travels towards the tensile stress field below dislocation line by diffusion in liquid state (when alloy is being produced).

−30MPa
+30 MPa

→ −20M Pa

=30MPa
+10 MPa
↓
partially relaxed
state

↓
If dislocation has to move, even greater force has to be applied.

−30 MPa
+30 MPa

−20 Ma
← Extra stress field

→ Greater stress is required to dislocate, resulting in higher strength after substitutional atom is added.

→ Substitutional atom acts as an anchor in the lattice. Hence, alloys have higher strength compared to pure metal.

→ If smaller atoms are added, they have tensile stress field and get attracted to compressive stress field.

→ Interstitial atoms generate compressive stress field, so those atoms get attracted towards tensile stress field under dislocation lines.

Hume-Rothery Rule : For substitutional solid solution

① Atomic Size factor:

→ If the size difference is less than 8%, then there is a complete solid solubility.

→ Partial solubility: There is a range in which solubility is possible.

→ For complete solubility: Any quantity of A can dissolve with any quantity of B.

→ The size difference should be less for less lattice distortion for lower stress field energies.

→ If $\Delta r \% \in (8\%, 15\%) \longrightarrow$ partial solubility

$$\text{Mismatch} = \left(\frac{r_{solute} - r_{solvent}}{r_{solvent}} \right) \times 100\%$$

→ If $\Delta r > 15\% \longrightarrow$ no solubility

Eg., Cu-Ni → complete solubility
Cu-Ag → partial solubility.

→ Alloying increases strength as dislocations can't move easily.

→ Interstitial atom will influence the strength more than what we can get in substitutional solid soln.

② Electrochemical factor :

→ If there are metals which are electropositive and the other one is electronegative, then they will form ionic compound rather than an alloy.

③ Crystal Structure :

→ For complete solid solubility: The solvent and the solute must have same crystal structure.
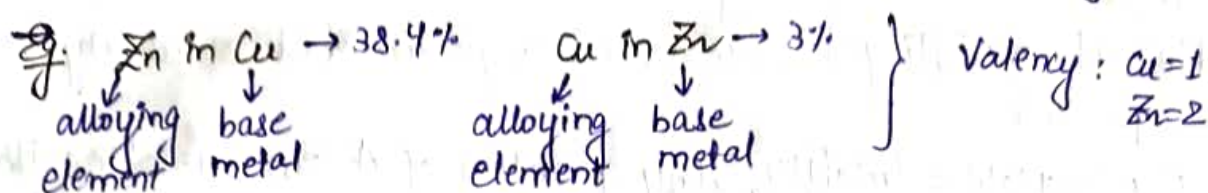
Eg   Cu- Zn → partial
    FCC HCP

    Cu-Ni → complete
    FCC FCC

④ **Valency:**

→ A metal of lower valency is more likely to dissolve the metal of higher valency.
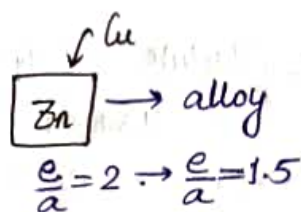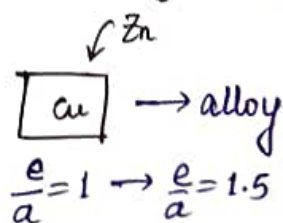
Both solute and solvent shall have equal valency.

Eg. Zn in Cu → 38.4%   Cu in Zn → 3%   } Valency: $Cu = 1$
     ↓   ↓   ↓   ↓ $Zn = 2$
   alloying base   alloying base
   element   metal   element   metal

$\dfrac{e \text{ (electron)}}{a \text{ (atom)}}$ ratio: $\left[\dfrac{e}{a}\right]_{Cu} = \dfrac{1}{1} = 1$, $\left[\dfrac{e}{a}\right]_{Cu} = \dfrac{2}{1} = 2$

valence e^-

Cu-Zn alloy: $\left.\dfrac{e}{a}\right|_{Cu, Zn} = \dfrac{3}{2} = 1.5$

         Zn   Cu
    [Cu] → alloy   [Zn] → alloy
   $\dfrac{e}{a} = 1 \to \dfrac{e}{a} = 1.5$ $\dfrac{e}{a} = 2 \to \dfrac{e}{a} = 1.5$

→ To promote metal bonding, free e^- are needed.
 When Zn is added to Cu, Zn provides more free e^- than Cu, hence increasing metallic bonding and favours alloying.

→ Types of Substitutional solid solution:
      Random, Clustered, Ordered
                            ↳ may become intermetallic
                                compound.

→ For Interstitial Solid soln:
 ↳ Size of solute should be comparable to pore size.
 ↳ Solute should have comparable electronegativity as the base metal.
                    solid
 # For complete ^solubility, solvent & solute must have same crystal
                                            structure.

THERMODYNAMICS

First Law: $\Delta U = Q - W$ (sign conventions); $dU = \delta Q - \delta W$

Second Law: $\Delta S > 0$, $\Delta S = \dfrac{Q_{rev}}{T}$, $ds = \dfrac{\delta Q_{rev}}{T}$

→ Work, $dW = P \cdot dv$

→ Internal energy, $dU = T \cdot ds - P \cdot dv$

→ Enthalpy, $H = U + P \cdot V$ ⟶ how much volume is going to change. ↱ measure of accommodation in volume

$dH = dU + P \cdot dv + v \cdot dP$

$\Rightarrow dH = \delta Q - \delta W + P \cdot dv + v \cdot dP$

$= \delta Q + v \cdot dP = T ds + v dP$

$dH|_P = \delta Q = T \cdot ds$

Most metallurgical processes are carried out at constant pressure.

→ $\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys}$

→ For a process at constant temperature and pressure:

$$\Delta S_{surr} = \dfrac{\delta Q_{surr}}{T} = -\dfrac{\delta Q_{sys}}{T} = -\dfrac{dH_{sys}}{T}$$

→ $dS_{univ} = dS_{sys} - \dfrac{dH_{sys}}{T}$

$-T \, dS_{univ} = -T \cdot dS_{sys} + dH$

Gibbs Free Energy

↳ The component of the total energy of a system that can do work at constant temperature and pressure.

↳ The energy in a physical system that can be converted to do work.

↳ Function of internal energy & randomness/disorderness of system.

$G = H - TS$

$dG = dH - T \cdot ds$
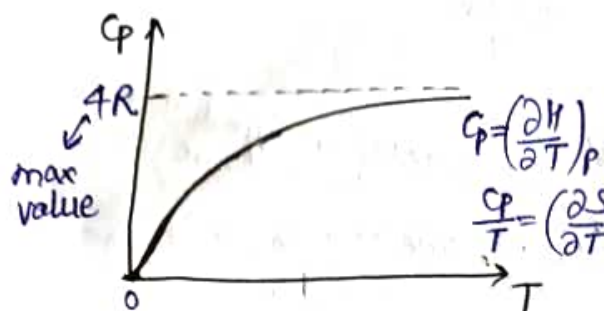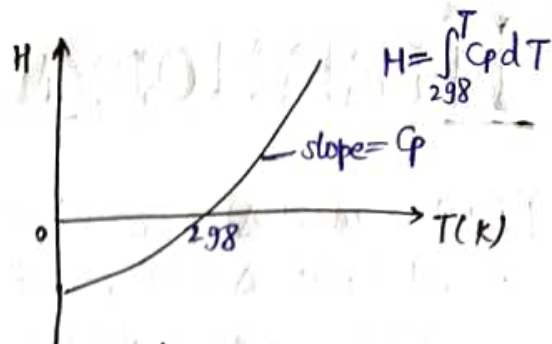
$= dU + P \cdot dv + v \cdot dP - T \cdot ds - S \, dT$

$\boxed{\dfrac{dG}{dT}\Big|_P = -S}$

$\Rightarrow \boxed{dG = v \cdot dP - S \cdot dT}$; dG/dT at constant pressure $= -S$
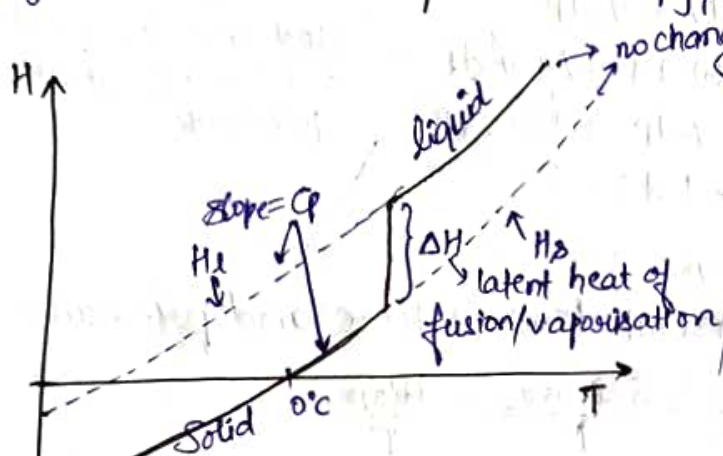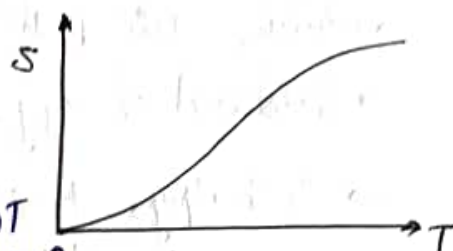↳ Maxwell's equation

→ Free energy: extra energy than what is required, that brings changes to the system.

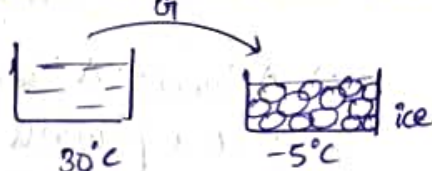→ At any temperature, the stable state is the one that has lowest free energy.

→ Heat capacity: $C_p = \dfrac{dH}{dT}$

$\Rightarrow dH = C_p dT$

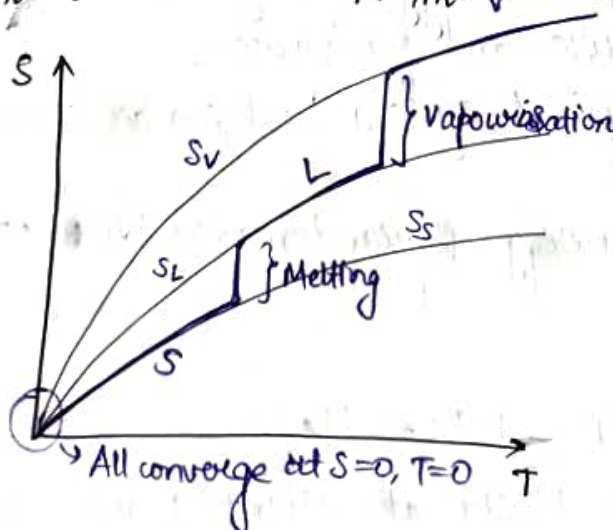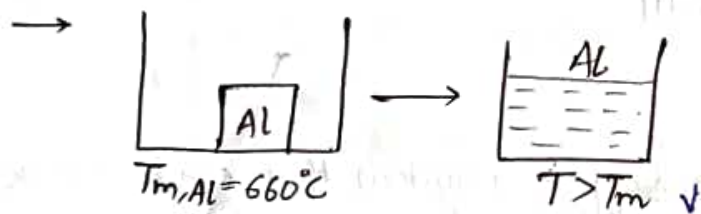$\Rightarrow H = \int_{T_o}^{T_1} C_p dT$

$H = \int_{298}^{T} C_p dT$

slope = C_p

(graph: H vs T(K), starting at 298)

(graph: C_p vs T)

4R ← max value

$C_p = \left(\dfrac{\partial H}{\partial T}\right)_p$

$\dfrac{C_p}{T} = \left(\dfrac{\partial S}{\partial T}\right)_p$; $S = \int_0^T \dfrac{C_p}{T} dT$

$= C_p \int_0^T \dfrac{1}{T} dT = C_p \ln T$

no change in slope

(graph: S vs T)

(graph: H vs T)

liquid

slope = C_p

H_l

ΔH → H_s latent heat of fusion/vaporisation

Solid   0°C   T

→ Extrapolated to get enthalpy of solid after $T > T_m$.

Excess Gibbs energy is used up to make the disordered atom (liquid state) to more ordered state (solid state).

G

(diagram: water at 30°C → ice at −5°C)

30°C   −5°C   ice

(diagram: Al solid → Al liquid)

Al

$T_{m,Al} = 660°C$

AL

$T > T_m$ ✓

(graph: S vs T)

S_V

L   Vapourisation

S_S

S_L Melting

S

→ All converge at $S = 0, T = 0$

S:
① Thermal entropy
② Configuration
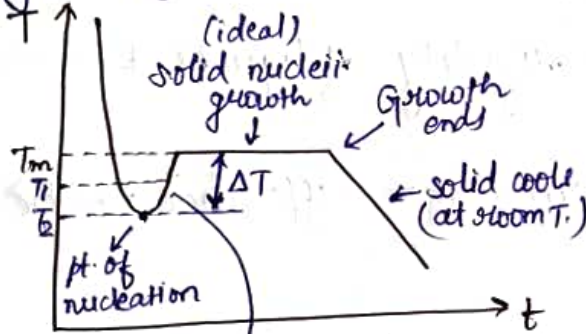   ↓ entropy
   Randomness when two metals are mixed.
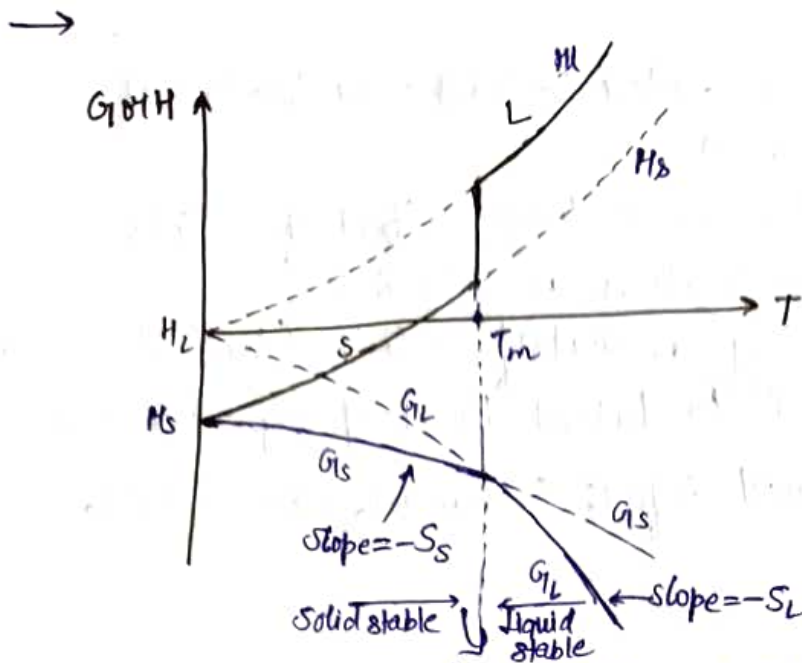
$G = H$ at $T = 0$

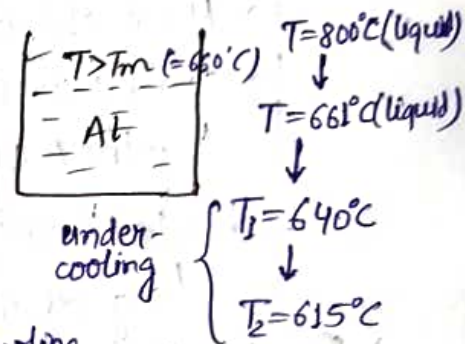$\left.\dfrac{dG}{dT}\right|_P = -S$ ⟹ G always decreases

and $S_L > S_S$

· As $S \uparrow$, magnitude of slope $\uparrow$ with $T\uparrow$

Liquids are more stable than solids, above T_m.

Solidification

→ During casting,

(ideal)
solid nuclei
growth ↓

Growth ends

solid cools
(at room T.)

Pt. of nucleation

still in liquid phase
↓
higher free energy
↳ little excess only which is not able to do work.

$\begin{array}{l} - T > T_m\ (=660^\circ C) \\ - \Delta T \end{array}$ under-cooling

$T = 800^\circ C\ (\text{liquid})$
↓
$T = 661^\circ C\ (\text{liquid})$
↓
$T_1 = 640^\circ C$
↓
$T_2 = 615^\circ C$

ΔT: under cooling Temp.

→ Phase transformation from liquid to solid state:
- property of fluidity is lost and rigidity is introduced
- long range order is introduced.
- viscosity changes by a factor of 10^8 Pa-s.
- Diffusion reduces by several orders of magnitude (liquids have more defects than solids).
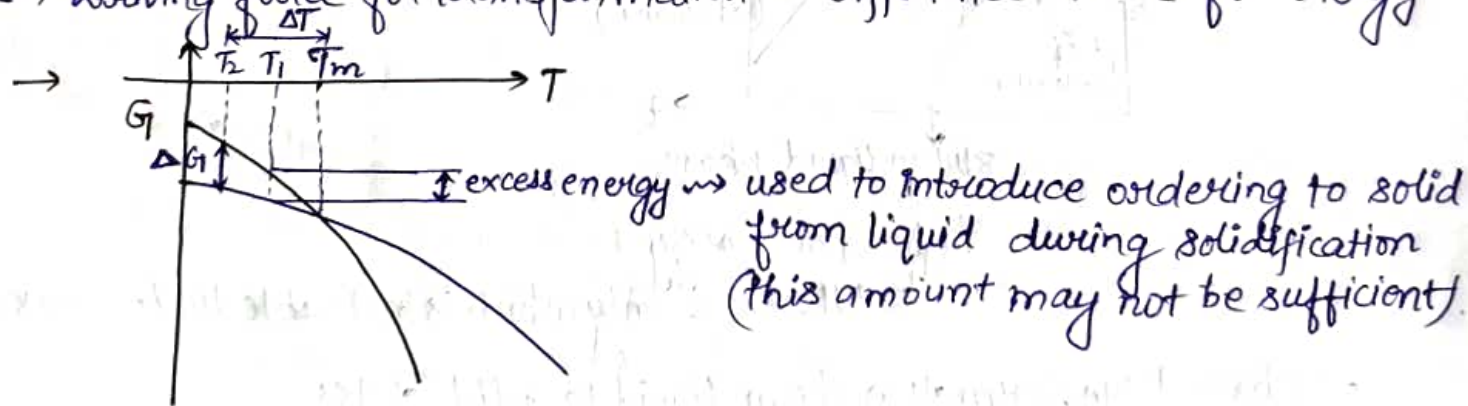
→ Orderliness over distances comparable to interatomic distances is called short-range order, whereas orderliness repeated over infinitely great distances is called long range order.

→ **Liquids:**
- → Neither possess long range order (solids) nor the lack of interaction b/w atoms (gases).
- → Average separation b/w atoms is close to that of solids.
  - → shrinkage during solidification is 2 to 6%.
  - → Similar binding energy as that of solids (low latent heat of fusion as compared to latent heat of vaporisation.
- → Have additional structural defects (vacancies, interstitials, dislocations, etc.)
- → Have higher U and S.
- → Have short-range order.
- → Can be considered as dense gas in which atoms are held together by attractive forces.
- → Hole theory of liquids:
  - ↳ gives insight about rigidity of liquids & voids in liquids.

Nucleation

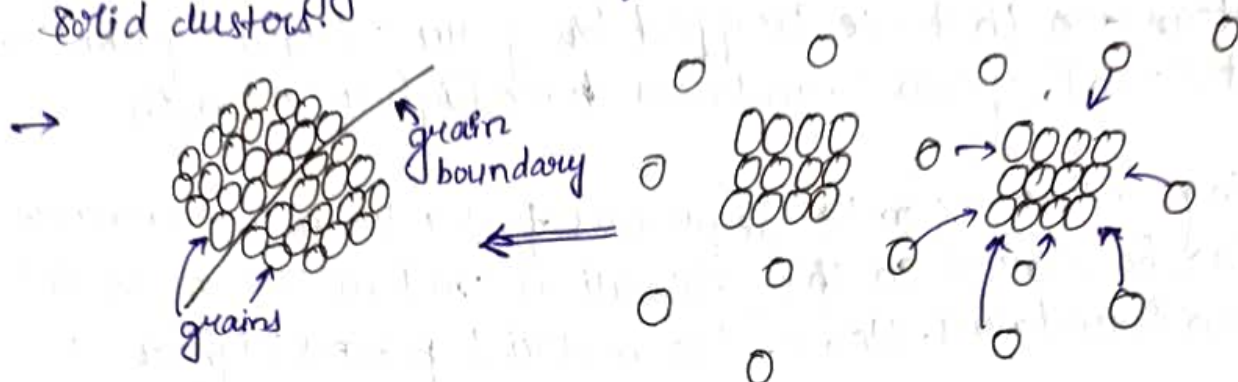→ Driving force for transformation = Difference in the free energy

I excess energy ⟿ used to introduce ordering to solid from liquid during solidification (this amount may not be sufficient).

↳ Solid clusters form at T_2.

↳ Solid clusters release energy (latent heat of fusion), so that causes the rise in temperature after the dip.

solid   O← liquid
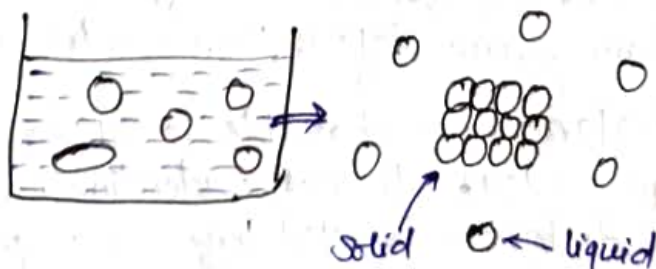
→ A nucleus is essentially a small group of atoms that have taken up arrangement in definite space lattice, is stable and capable of further growth.

→ If the no. of nuclei is large, then energy released will be greater than the energy absorbed from the surroundings to form solid clusters.

→

grain boundary

grains

$$G_{1s} = H_s - T \cdot S_s$$
$$G_{1L} = H_L - TS_L$$
$$(G_{1s} - G_{1L}) = (H_s - H_L) - T(S_s - S_L)$$
$$\Rightarrow \Delta G_1 = \Delta H - T\Delta S$$

At T_m, $\Delta G = 0$

$$\Delta H - T\Delta S = 0$$
$$\Rightarrow \boxed{\Delta S = \frac{\Delta H}{T_m}} , \quad \Delta H : \text{heat of fusion}, H_f \Rightarrow \boxed{\Delta S = \frac{H_f}{T_m}}$$

$$\Delta G = H_f - \frac{H_f}{T_m} \times T = H_f \left(1 - \frac{T}{T_m}\right)$$

$$\Rightarrow \Delta G = H_f \left(\frac{T_m - T}{T_m}\right)$$

$$\Rightarrow \boxed{\Delta G = \frac{H_f \Delta T}{T_m}}$$

we can control grain size
↓
$\Delta T \uparrow \Rightarrow \Delta G \uparrow \Rightarrow$ more solid nuclei
↓
more grain boundaries

→ The release of heat when a metal solidifies indicates that the crystalline phase has a lower Gibbs Free Energy G, than the liquid.

Liquid
Nuclei

Liquid

Crystal that will form grains

Grain boundaries
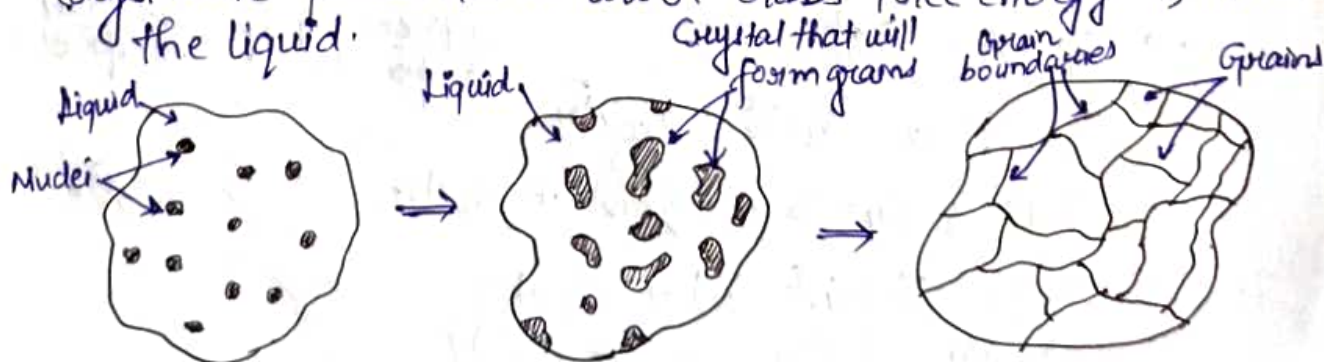
Grains

Grain Boundary:
→ where grains meet in a solid
→ transition region b/w the neighbouring crystals.

High angle grain boundary— orientation diff. b/w adjacent grains $> 15°$
Low angle grain boundary— orientation diff b/w adjacent grains $< 15°$
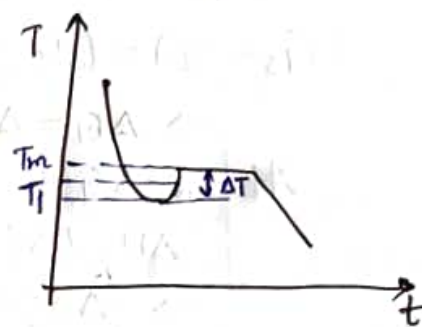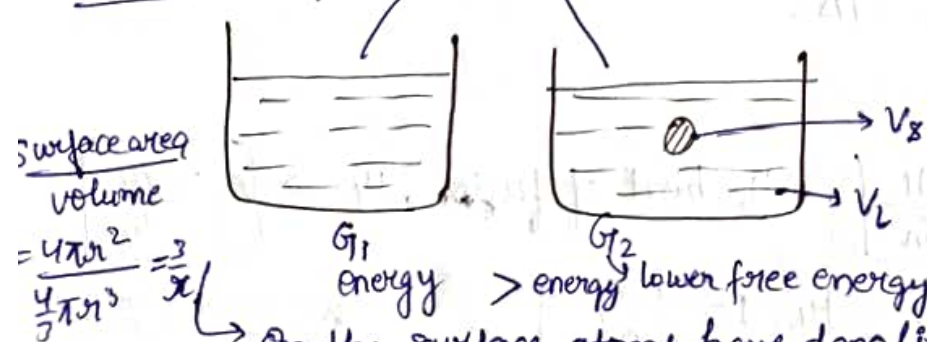
→ Atoms that are trapped b/w grain consitute grain boundary.
→ At room T, grain boundaries have higher strength.

→ During casting, we make the process faster to introduce more grain boundaries so the dislocations can't move across the grain boundaries. Hence, the material possess higher strength.

→ Free energy change per unit volume,

$$G_{1s} - G_{1L} = \Delta G_v = \frac{\Delta H \Delta T}{T_m}$$

$T_1 < T_m:$ for same volume

$\dfrac{\text{surface area}}{\text{volume}}$
$= \dfrac{4\pi r^2}{\frac{4}{3}\pi r^3} = \dfrac{3}{r}$

G_1 G_2
energy > energy lower free energy
→ On the surface, atoms have dangling bonds.
    → once a solid is formed, there is a surface energy associated with it.

→ Surface energy ↑es energy of system
   formation of solid ↓es energy of system.

→ $G_1 = (V_s + V_L) G_2^L$ $\overset{\text{surface energy of solid-liquid}}{\underset{\text{surface area}}{\longleftarrow}}$ interface

$G_2 = V_s G_v^S + V_L G_v^L + \sigma_{SL} A_{SL}$

$\Delta G = G_2 - G_1 = V_s G_v^S + V_L G_v^L + \sigma_{SL} A_{SL} - V_s G_v^L - V_L G_v^L$

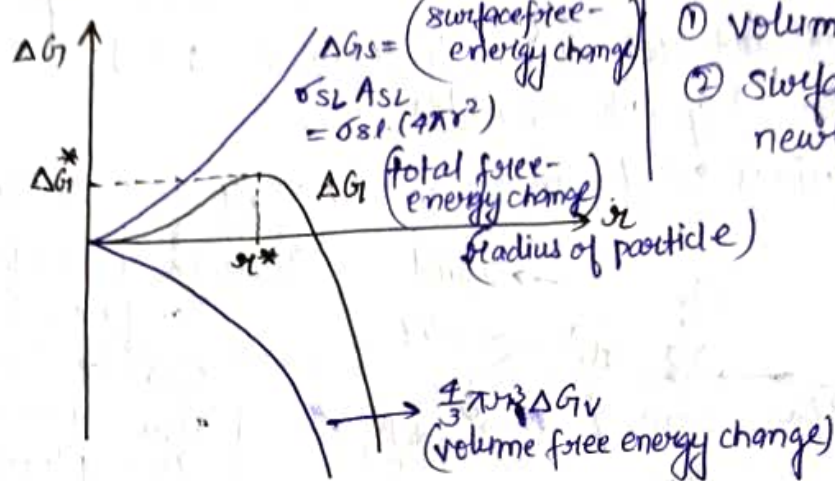$\Rightarrow \Delta G = V_s (G_v^S - G_v^L) + \sigma_{SL} A_{SL}$

$\Rightarrow \boxed{\Delta G = \sigma_{SL} A_{SL} - V_s (G_v^L - G_v^S)}$

$\Rightarrow \boxed{\Delta G = \sigma_{SL} A_{SL} - V_s \Delta G_v}$ $(\Delta G_v = G_v^L - G_v^S > 0)$

→ Solid will be nucleated as sphere as it has minimum surface energy per unit volume for all shapes.

$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \sigma_{SL}$$

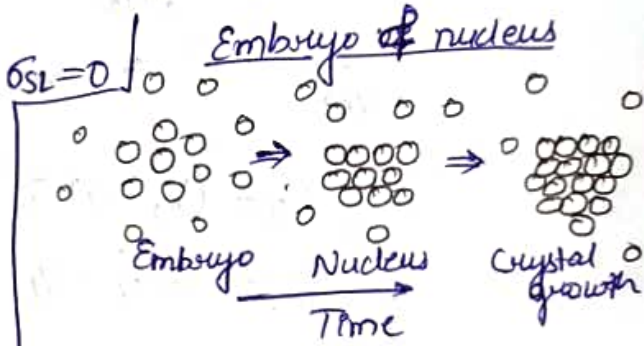$\Delta G_S = \left(\begin{array}{c}\text{surface free-}\\\text{energy change}\end{array}\right)$

$\sigma_{SL} A_{SL} = \sigma_{SL}\cdot(4\pi r^2)$

ΔG $\left(\begin{array}{c}\text{total free-}\\\text{energy change}\end{array}\right)$

r (radius of particle)

$\frac{4}{3}\pi r^3 \Delta G_V$ (volume free energy change)

→ The process of nucleation is controlled by two factors:
① volume free energy change
② surface energy of the newly formed solid

$$\frac{d}{dr}(\Delta G) = -4\pi r^2 \Delta G_V + 8\pi r \sigma_{SL} = 0$$

$$\boxed{r^* = \frac{2\sigma_{SL}}{\Delta G_V}}$$

$$\boxed{r^* = \frac{2\sigma_{SL} T_m}{\Delta H \Delta T}}$$

Embryo & nucleus

Embryo → Nucleus → Crystal growth
$\xrightarrow{\text{Time}}$

$$\Delta G^* = -\frac{4}{3}\pi \times \frac{8\sigma_{SL}^3}{\Delta G_V^{3}} \times \Delta G_V + 4\pi \times \frac{4\sigma_{SL}^2}{\Delta G_V^2} \times \sigma_{SL}$$

$$\Delta G^* = \frac{16\pi}{\Delta G_V^2}\left[-\frac{2}{3}\sigma_{SL}^3 + \sigma_{SL}^3\right] = \frac{16\pi\sigma_{SL}^3}{\Delta G_V^2}$$

$$\boxed{\Delta G^* = \frac{16\pi\sigma_{SL}^3}{\Delta G_V^2}}$$

$$\boxed{\Delta G^* = \frac{16\pi\sigma_{SL}^3 T_m}{3(\Delta H)^2(\Delta T)^2}}$$

Cooling rate ↑ $\Delta T\uparrow \Rightarrow \Delta G^* \downarrow$ $(r^*\downarrow)$

↳ no. of nuclei
↳ finer grain size (higher strength)
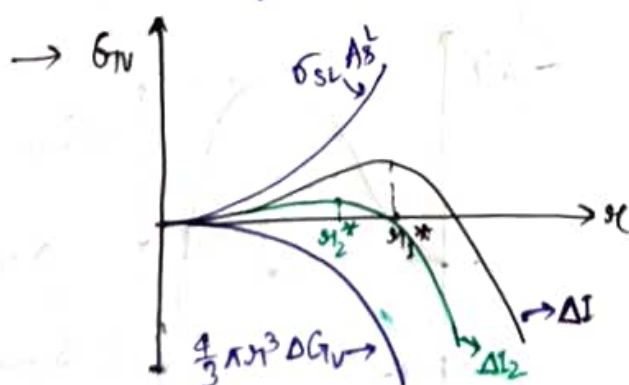
Homogeneous nucleation
↓
contains less solidification
↳ (microgravity)
nucleation in the volume of liquid

→ G_V

$\sigma_{SL} A_S$

r_2^* r_1^*

r

Δl

$\frac{4}{3}\pi r^3 \Delta G_V$
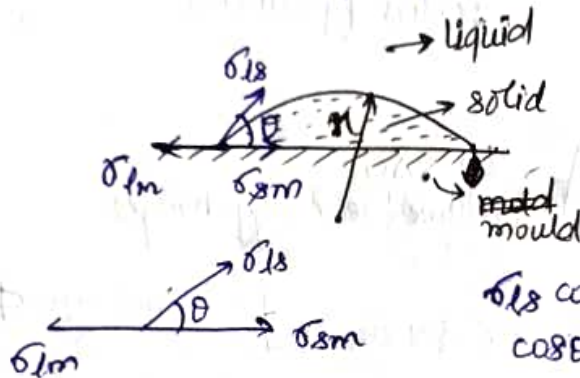
Δl_2

→ **Heterogeneous Nucleation:** Bubbles of CO_2 in a glass of coke form at the walls.

↳ E.g., artificial rain

↳ use something which has similar crystal structure as ice ($h = 10km$, $T = -40°C$)
  ↳ Eg. Silver halides

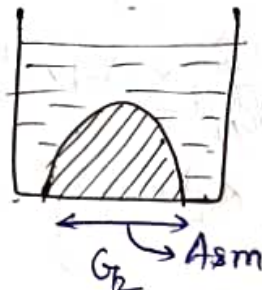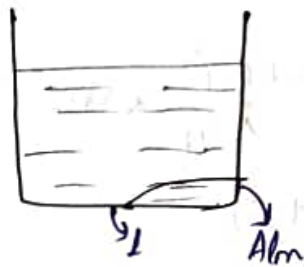→ requires solid platform → energy for nucleation ↓ when there is a surface.

surface energy per unit area:
σ_{lm} = of liquid-mould interface
σ_{sm} = of solid-mould interface
σ_{ls} = of liquid-solid interface

$$\sigma_{ls}\cos\theta + \sigma_{sm} = \sigma_{lm}$$
$$\cos\theta = \frac{(\sigma_{lm} - \sigma_{sm})}{\sigma_{ls}}$$

$$G_1 = (V_s + V_l) G_v^l + A_{lm}\cdot\sigma_{lm}$$

$$G_2 = V_s G_v^s + V_l G_v^l + A_{sl}\sigma_{sl} + A_{sm}\sigma_{sm} + (A_{lm} - A_{sm})\sigma_{lm}$$

$$V_s = \frac{\pi r^3}{3}(2 - 3\cos\theta + \cos^3\theta)$$
$$A_{sl} = 2\pi r^2(1-\cos\theta)$$
$$A_{sm} = \pi r^2\sin^2\theta$$

$$\Delta G_{net} = -\frac{4}{3}\pi r^3 \Delta G_v\left[\frac{2-3\cos\theta+\cos^3\theta}{4}\right] + 4\pi r^2\cdot\sigma_{ls}\left[\frac{2-3\cos\theta+\cos^3\theta}{4}\right]$$

$$\frac{d}{dr}(\Delta G_{net}) = 0 \Rightarrow \boxed{r^*_{het} = \frac{2\sigma_{ls}}{\Delta G_v}} \Rightarrow \boxed{r^*_{het} = r^*_{homo}}$$

Nucleation barrier,

(for het. nucleation) $\boxed{\Delta G^*_{het} = \frac{4\pi\sigma_{ls}^3}{3\Delta G_v^2}(2-3\cos\theta+\cos^3\theta)}$
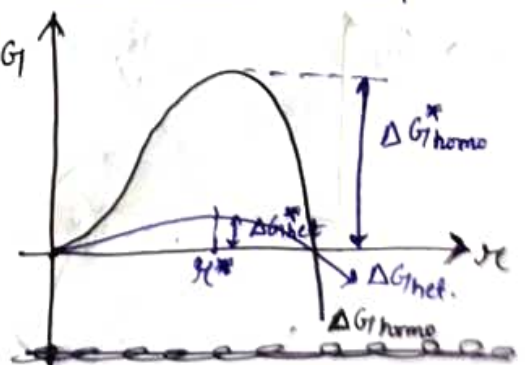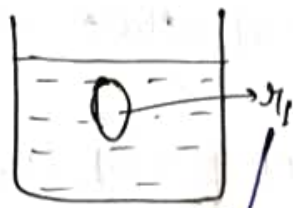
$\boxed{\Delta G^*_{homo} > \Delta G^*_{hetro}}$

↓ depends on wetting angle of the liquid with mould wall.

$\theta: 0° → 180°$
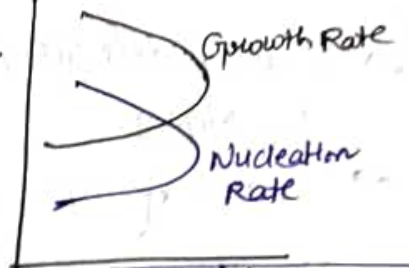$\Delta G^*_{het}: 0 → 1$

If $\theta = 180°$, $\Delta G^*_{het} = \Delta G^*_{homo}$

no. of atoms to be grouped together is greater → greater energy required

n_i → No. of atoms to be grouped together is lower
⇓
Lower energy required

→ **Eyring theory** → theory of holes.
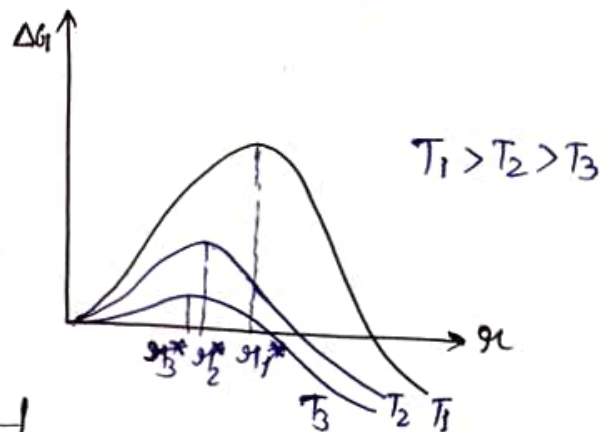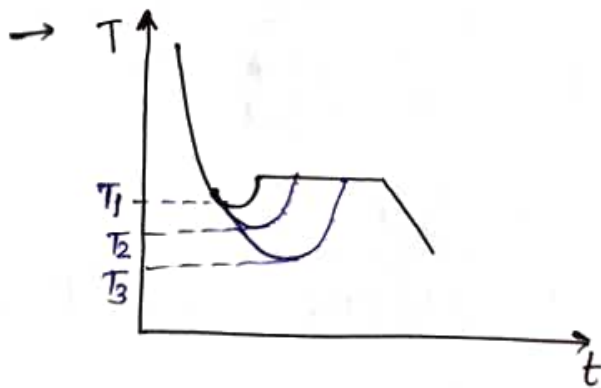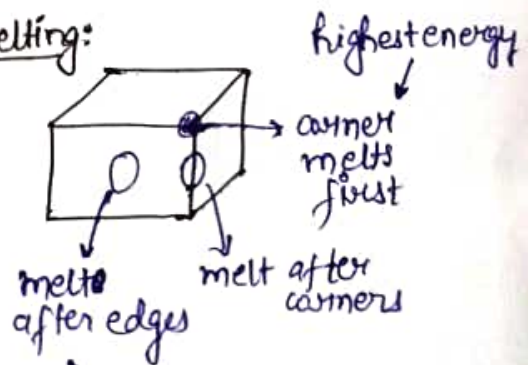→ Liquids do not have any rigidity. On application of shear stress, the molecules occupy the next available voids.
→ Every grain has different orientation.
→ Grain boundary has atoms trapped b/w 2 grains, randomly placed.
←— not all bonds are satisfied
⇓
higher energy

$T_1 > T_2 > T_3$

↑↑↑↑ heating

heating curve

T_m — X
S+L
S
L

Melting:
highest energy
↓
corner melts first

melts after edges

melt after corners
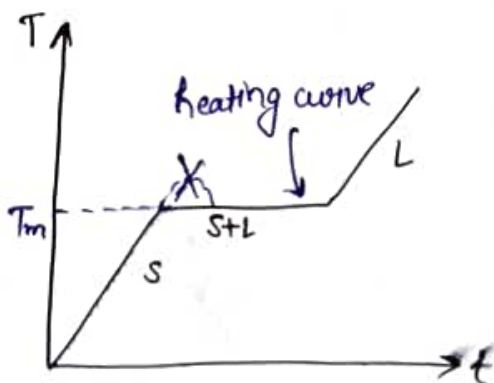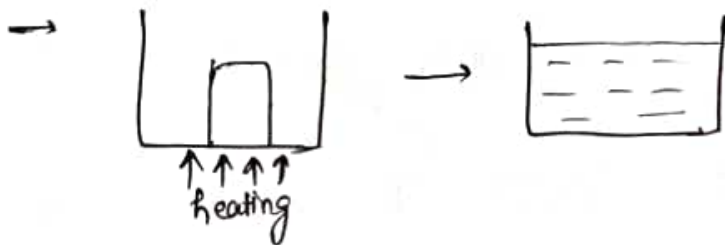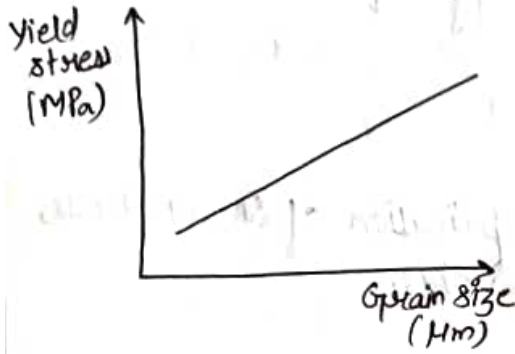
⇓
As heating is started, the particles with highest energy at corners, start melting first without any overheating T.

→ During solidification, metals takeup tree like structure called dendrites.

→ Grains form in the dir^n opposite to the dir^n of heat absorption.

Yield stress v/s Grain size

Hall Petch Relation : $\boxed{\sigma_y = \sigma_i + \dfrac{k}{\sqrt{d}}}$

σ_y : yield stress of a polycrystalline material

σ_i : yield stress at infinite grain size

d : grain size (mean grain diameter)

k : Hall-Petch constant
    ↳ depends on crystal structure

        $K = 0.71$ MN m$^{-1.5}$ for BCC

        $K = 0.11$ MN m$^{-1.5}$ for FCC

Optical Microscopy of Metals

↳ works on the principle of reflection.
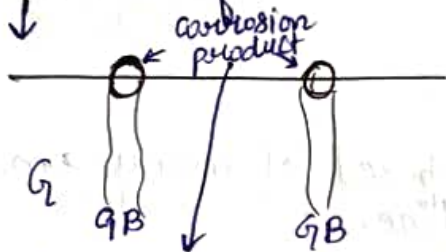↳ Steps in specimen prepation:
  ① Rough grinding
  ② Polishing with emery paper
 ③ Diamond / Alumina polishing
  ④ Etching.

Etching

↳ controlled chemical reaction
↳ chemical is applied on the surface, forming corrosion products on the surface.
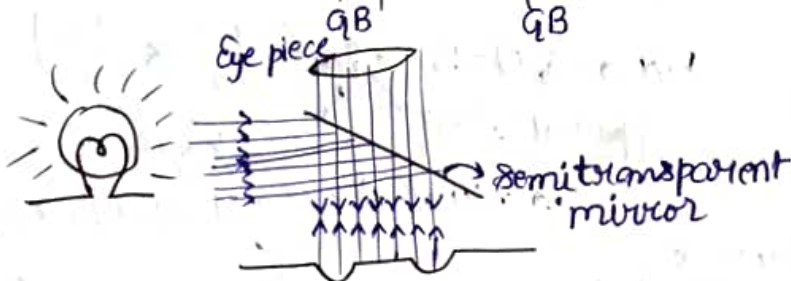
↓

corrosion product

G

GB   GB

The surface is cleaned soon after chemical is applied so only atoms in grain boundaries react.

chemicals are choosen such that the corrosion products don't stick to the surface. After etching, sinking is done.

grooves

GB   GB

Eye piece

semitransparent mirror
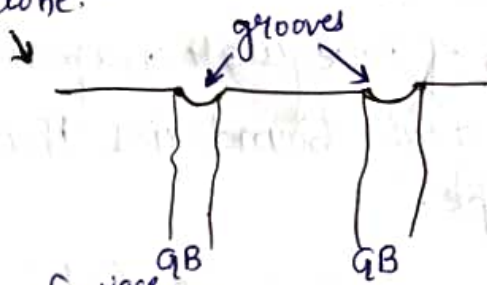
Before etching

After etching

Grain Size Measurement

① Intercept Technique:

Lines are drawn in the photomicrograph, and the no. of grain boundary intercepts, N_ℓ, along a line is counted.

Mean diameter, $\bar{d} = \dfrac{L}{N_\ell M}$, L: Length of intercept
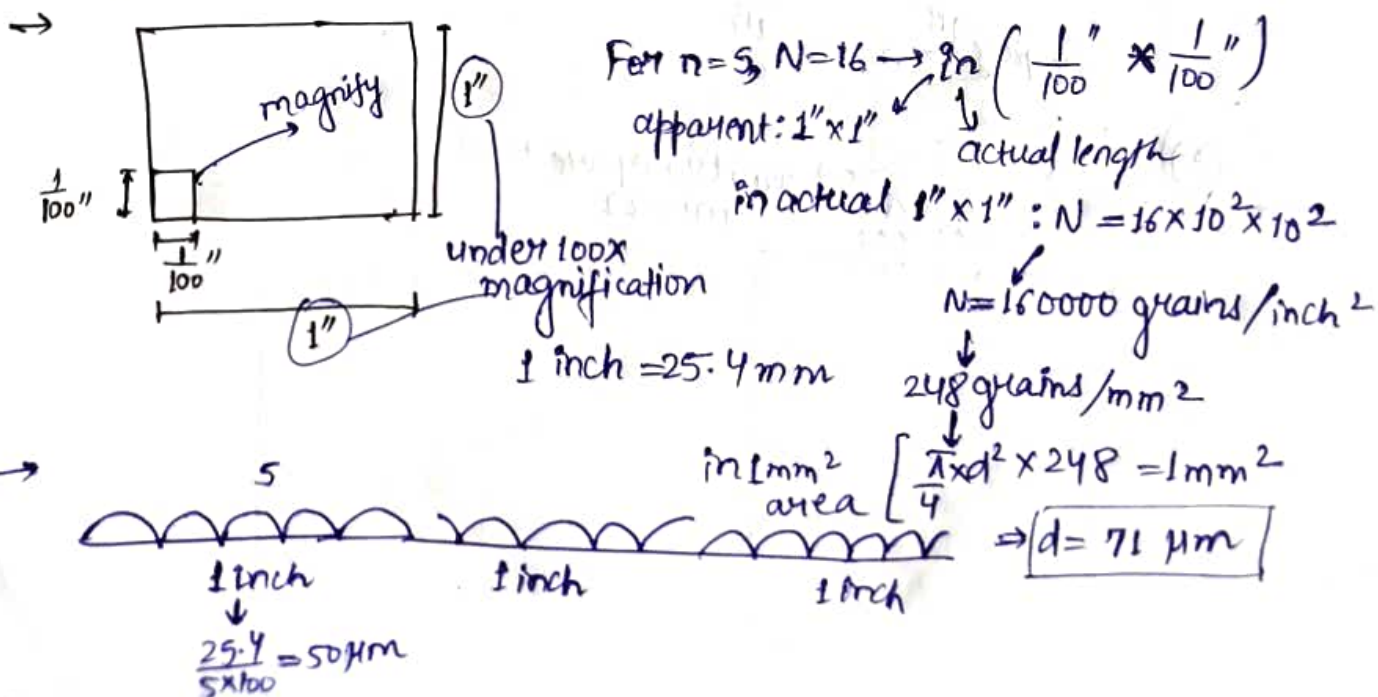N_ℓ: No. of grain boundary intercepts
M: Magnification

② ASTM No.: indicates the average diameter of grains

$$N = 2^{n-1}, \quad N: \text{No. of grains present per square inch under a magnification of 100X}$$

n: ASTM grain size no.

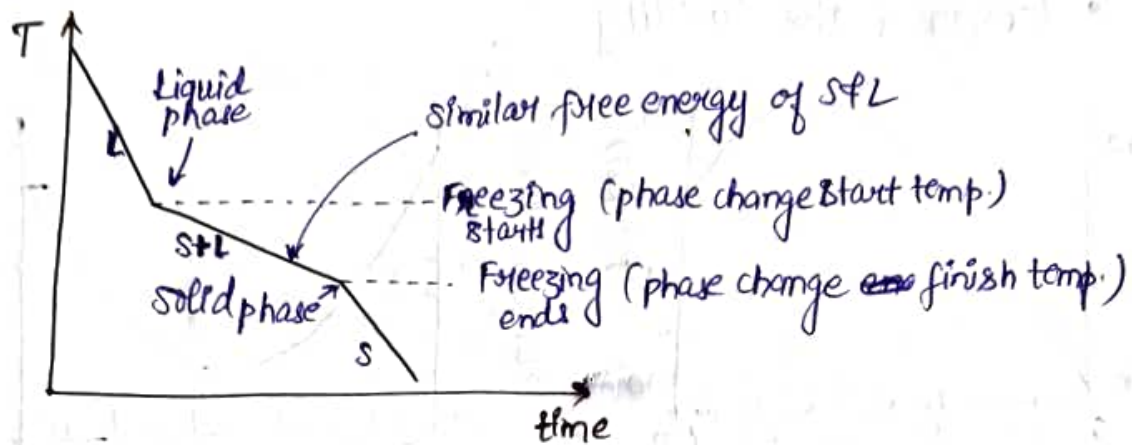→ Fine grains increases the toughness.

Polycrystalline Materials

→ Most crystalline solids are composed of many small crystals or grains termed as polycrystalline.

→ During the solidification of a polycrystalline solids the crystallisation may start at various nuclei with random crystallographic orientations.

→ Upon solidification, grains of irregular shapes may form.

→ The structure will have grain boundaries that could be seen under a microscope.
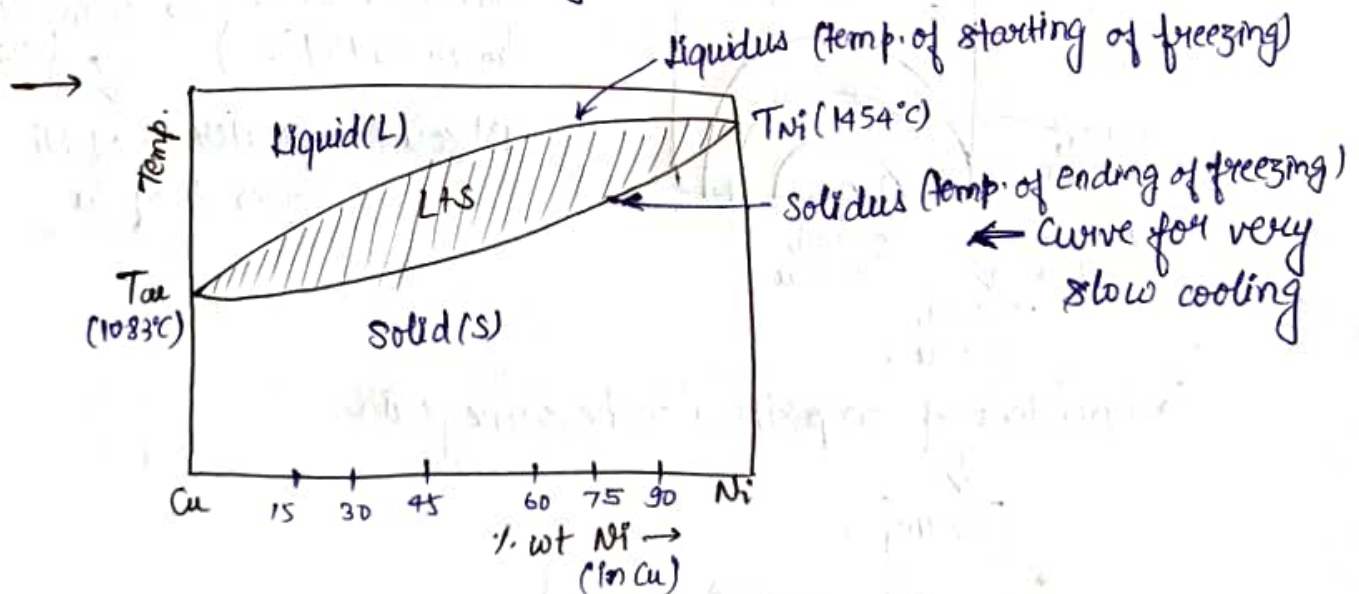
→

For $n=5$, $N=16 \rightarrow$ in $\left(\dfrac{1}{100}'' * \dfrac{1}{100}''\right)$
apparent: $1'' \times 1''$ ← actual length
in actual $1'' \times 1''$: $N = 16 \times 10^2 \times 10^2$

under 100X magnification

1 inch = 25.4 mm

$N = 160000$ grains/inch^2

248 grains/mm^2

in 1 mm^2 area $\left[\dfrac{\pi \times d^2}{4} \times 248 = 1 \text{ mm}^2\right.$

$\Rightarrow \boxed{d = 71 \ \mu m}$

→

5

1 inch   1 inch   1 inch
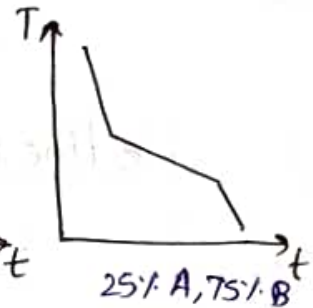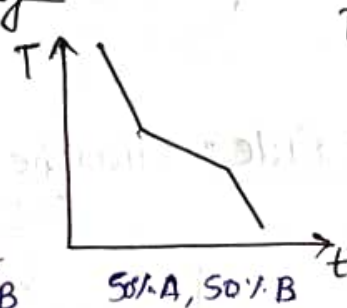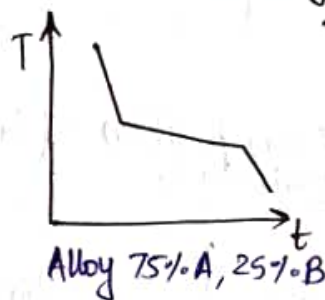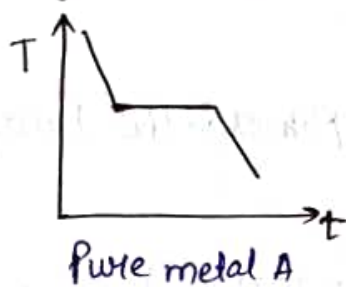
$\dfrac{25.4}{5 \times 100} = 50 \ \mu m$

COOLING CURVE OF AN ALLOY

→ No single melting point for most of the alloys.
  Due to continuous change of composition of the solid and liquid phases.

- Liquid phase
- L
- Similar free energy of S & L
- Freezing (phase change start temp.) start
- S + L
- Solid phase
- Freezing (phase change finish temp.) ends
- S
- time

Cooling curve for Pure Metal and Alloys

Pure metal A   Alloy 75% A, 25% B   50% A, 50% B   25% A, 75% B

- Liquidus (temp. of starting of freezing)
- Liquid (L)
- L + S
- T_{Ni} (1454°C)
- Solidus (temp. of ending of freezing)
  ← Curve for very slow cooling
- T_{cu} (1083°C)
- Solid (S)
- Cu   15   30   45   60   75   90   Ni
- % wt Ni → (In Cu)

→ **Solidus:** Max. temp. at which all the components can be in solid state.
  Liquidus: Min⁻ temp. at which all the components can be in liquid state.

→ A boundary b/w a multi-region and liquid solution — Liquidus.

→ **Binary alloy:** A mixture of 2 metals; constitutes a two-component system.

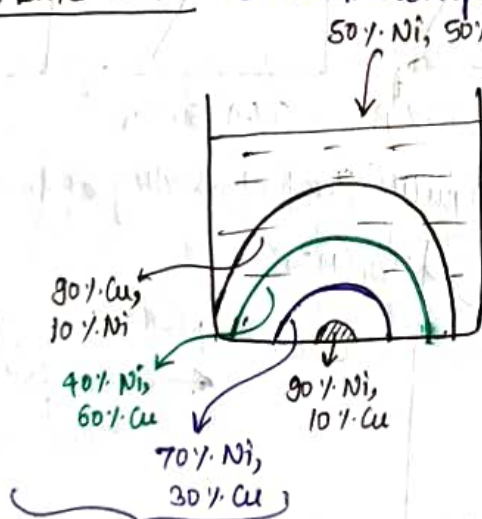→ **Imorphous system:** complete solid solubility of the two components
   (both in liquid and solid phases)

→ Alloying to produce a solid solution usually
   - increases the tensile strength (TS)
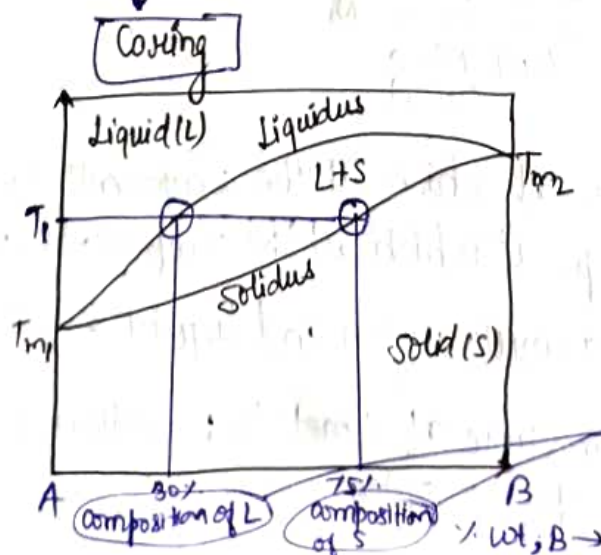   - decreases the ductility
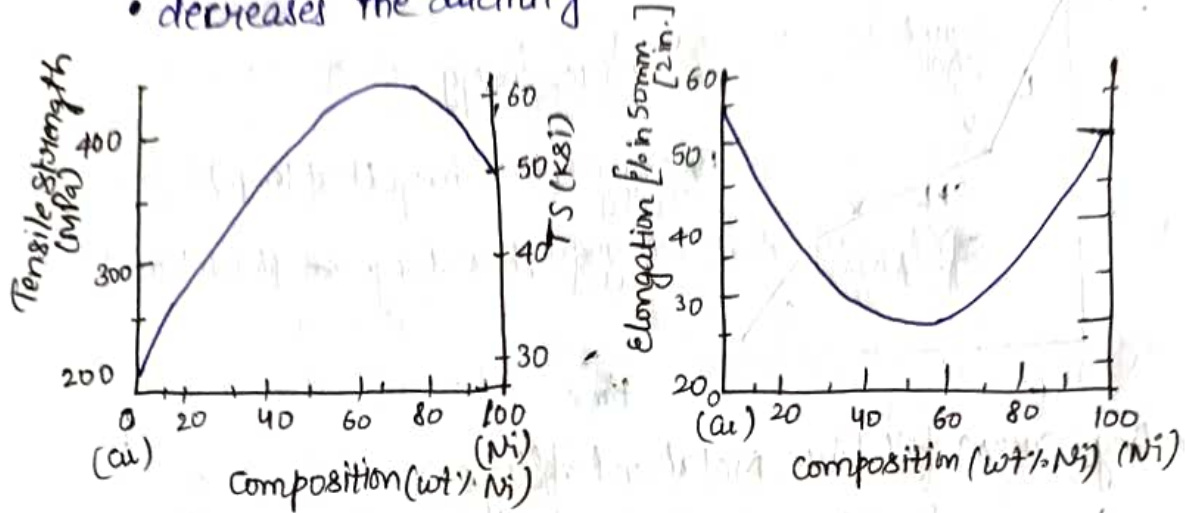
Tie Line Rule: Gives the composition of the phases in the two phase region.

50% Ni, 50% Cu

90% Cu,
10% Ni

40% Ni,
60% Cu

90% Ni,
10% Cu

70% Ni,
30% Cu

$T_{m,\,Cu} = 1083°C$ → cooling down
$T_{m,\,Ni} = 1454°C$ → starts

1st solid: greater % of Ni
            lower % of Cu

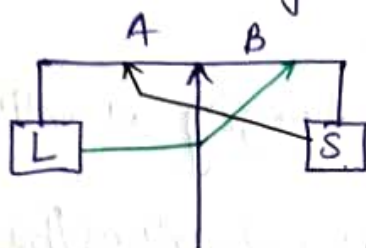↳ Gradient of composition in the same grain
   ↓
   [Coring]
   ↓

In equilibrium at temp. T_1

→ After solidification, heat treatment is used to obtain homogeneous solids. (Homogenisation treatment)
  ↳ The free energy will be equal for all particles once concentration gradient is nullified.

Lever Rule: Amount of co-existing phases in a two phase region at a given temperature.

$A \times L = B \times S$

$\Rightarrow \dfrac{A}{B} = \dfrac{S}{L}$

$\Rightarrow 1 + \dfrac{A}{B} = 1 + \dfrac{S}{L}$

$\Rightarrow \dfrac{B+A}{B} = \dfrac{L+S}{L}$

$\Rightarrow \dfrac{B}{A+B} = W_L$

$W_L = \dfrac{C_S - C_0}{C_S - C_\ell}$, $W_S = \dfrac{C_0 - C_\ell}{C_S - C_\ell}$

where, w_ℓ / w_s: weight fraction of ℓ / s

$\boxed{w_\ell + w_s = 1}$

C_S / C_ℓ : composition of s/ℓ

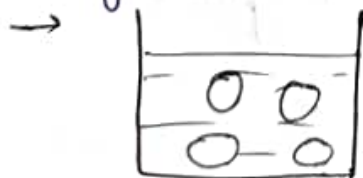C_0 : overall composition of alloy

$W_s \cdot C_s + W_\ell \cdot C_\ell = C_0$

Eg.
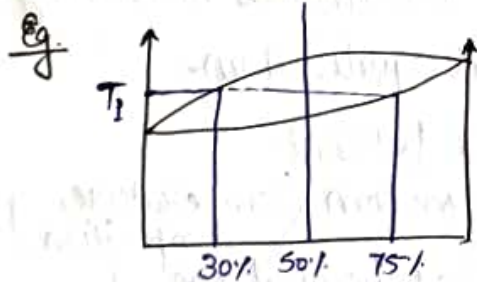
$W_s = \dfrac{20}{20+25} = \dfrac{4}{9}$

$W_L = \dfrac{25}{20+25} = \dfrac{5}{9}$

→ Lever rule and tie line are applicable for binary, homogeneous system.

→

$\boxed{\begin{array}{l} W_\ell + W_s = 1 \\[4pt] \dfrac{\ell}{\ell + s} = W_\ell , \ \dfrac{s}{s+\ell} = W_s \\[4pt] W_\ell\, C_\ell + W_s\, C_s = C_0 \end{array}}$

$W_\ell(C_\ell) + (1 - W_\ell)(C_s) = C_0$

$\Rightarrow W_\ell(C_\ell - C_s) = C_0 - C_s$

$\Rightarrow W_\ell = \dfrac{C_0 - C_s}{C_\ell - C_s}$, $W_s = \dfrac{C_\ell - C_0}{C_\ell - C_s}$ $\Rightarrow$ $\boxed{\begin{array}{l} W_\ell = \dfrac{C_s - C_0}{C_s - C_\ell} \\[6pt] W_s = \dfrac{C_0 - C_\ell}{C_s - C_\ell} \end{array}}$

Phase Diagram

→ Graphical representation of the combinations of temperature and composition for which specific phases exist in equilibrium.

→ For a given temperature & composition, we can use phase diagram to determine:

① the equilibrium phases that are present.

② compositions of the phases.

③ the relative fractions of the phases.

④ to predict temperature at which freezing or melting, beings begins or ends.

⑤ to predict the safe temp. for forming operations/heat treatment.

→ Phase diagrams provide valuable information about melting, casting, crystallisation and other phenomenon.

Phase Rule

→ Phase diagrams and phase equilibria are subject to the laws of thermodynamics.

→ Gibbs phase rule is a criterion that determines how many phases can coexist within a system at equilibrium.

$$P + F = C + 1 \quad , \quad$$

P: No. of phases present

F: degrees of freedom (temperature, composition)
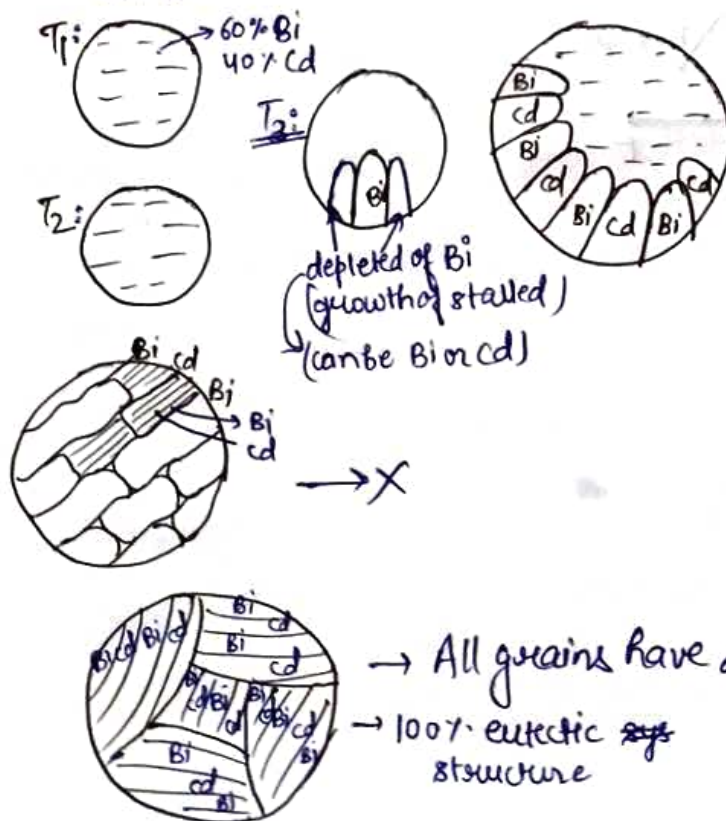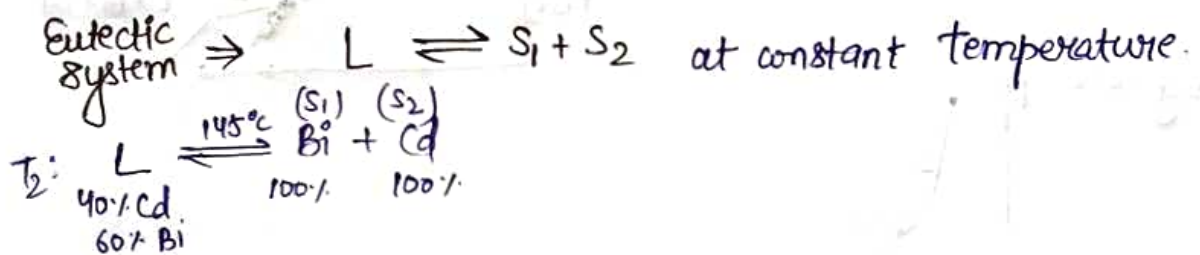
C: components or chemical species

→ A phase is a physically distinct, chemically homogeneous and mechanically separable region of a system.
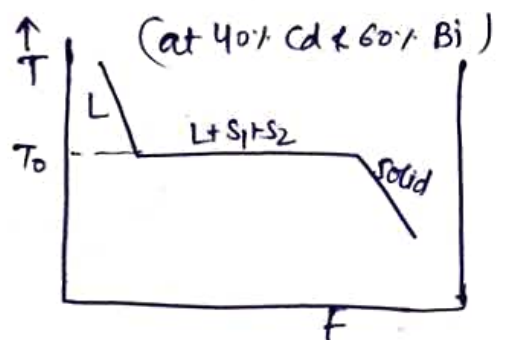
EUTECTIC SYSTEM

→ completely soluble in liquid state but immiscible in solid state (no solubility at all).

→ The freezing starts, but 2 phases are obtained as both solids are immiscible in each other.
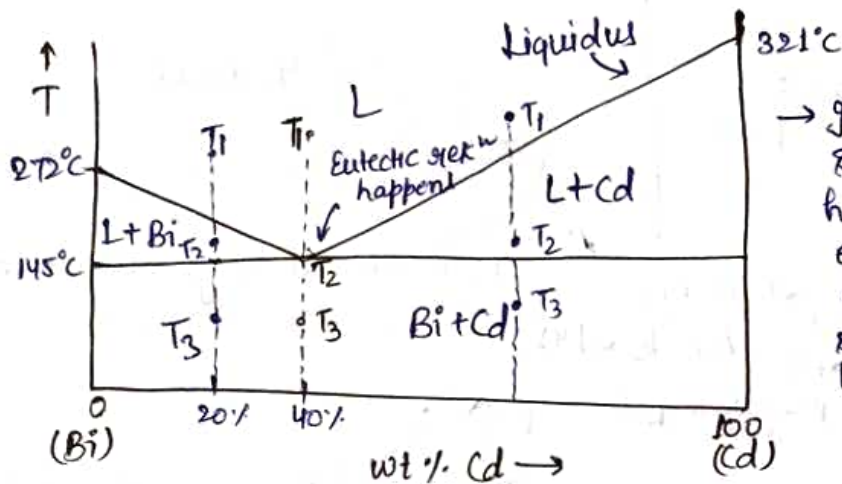
→ In liquid system, due to solubility, the entropy is high, hence has lower free energy. This is why the mp is low, meaning that the system wants to become liquid easily.

Eutectic system → $L \rightleftharpoons S_1 + S_2$ at constant temperature.

T_2: $L \xrightleftharpoons{145°C} \overset{(S_1)}{Bi} + \overset{(S_2)}{Cd}$
   40% Cd   100%   100%
   60% Bi

depleted of Bi
(growth of stalled)
(can be Bi or Cd)

→ X

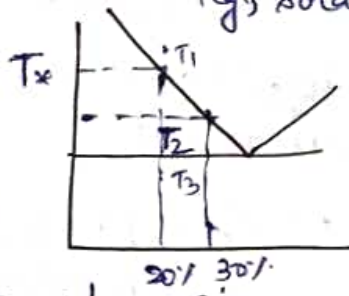Let us say Bi is formed first.

(at 40% Cd & 60% Bi)

→ All grains have alternate Cd & Bi layers.
→ 100% eutectic structure

Congruent Melting Alloy → Alloys having well defined melting point.
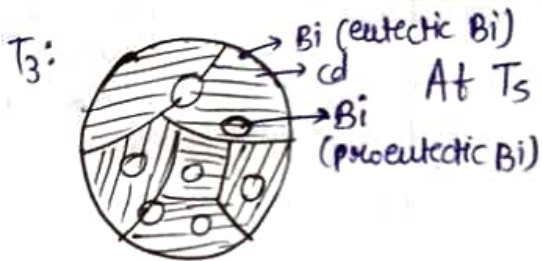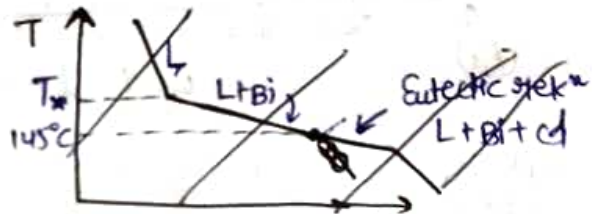(eg, solder)

→ more liquid cadmium

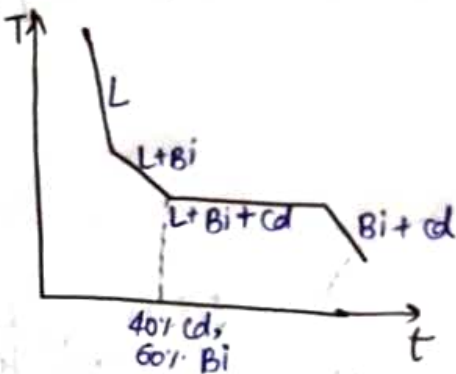cooling curve:

T_1: completely liquid: 20% Cd, 80% Bi

T_2:

→ Bi
→ 35% of Cd

L (40% Cd)

At T_4, it can undergo Eutectic reaction.

T_3:

→ Bi (eutectic Bi)
→ Cd
→ Bi (proeutectic Bi)

At $T_5 < 145°$

T
T_*
145°C
L
L+Bi
Eutectic ηek^u
L+Bi+Cd

→ Cooling curve:

L
L+Bi
L+Bi+Cd
Bi+Cd

40% Cd,
60% Bi
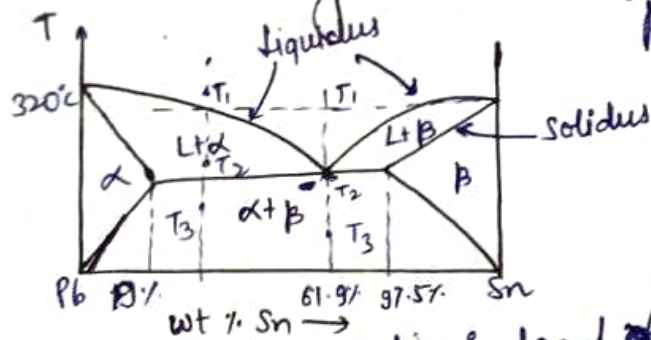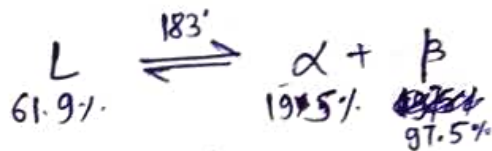
Partial Eutectic System → Completely miscible in liquid state, partially miscible in solid state

max solubility of tin in lead ~~kinim~~ is 19% at 183°C

α: substitutional solid solution of Sn in Pb

$$L \underset{}{\overset{183°}{\rightleftharpoons}} \alpha + \beta$$
$$61.9\% \qquad 19.5\% \quad \cancel{0.5\%}$$
$$\qquad\qquad\qquad 97.5\%$$

⇒ Evolution of grains

⇒ Final microstructure.