

THEORY & OBJECTIVE

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MATERIAL SCIENCE

THEORY

1.1 INTRODUCTION

Two materials will combine together and form alloy when the conditions of Hume-Rothery Rules are satisfied.

Conditions:

- (i) The difference in atomic radius should be less than 15%.
- (ii) Valency of both the materials should be same.
- (iii) Electronegativity and Electron affinity of both materials should be comparable.
- (iv) Crystal Structures of both materials will be same.

1.2 PHASE DIAGRAM

Phase diagram is a plot on temperature composition space showing stability of various phases. In other words, it tells us what will be the melting point of alloy.

(P) = Number of Phase

(C) = Number of Components

(F) = Number of Degree of Freedom

$$C + 2 = F + P$$

If

$C = 1$; Unitary phase diagram

Example: Carbon phase diagram

1.2.1 Binary Phase Diagram (C = 2)

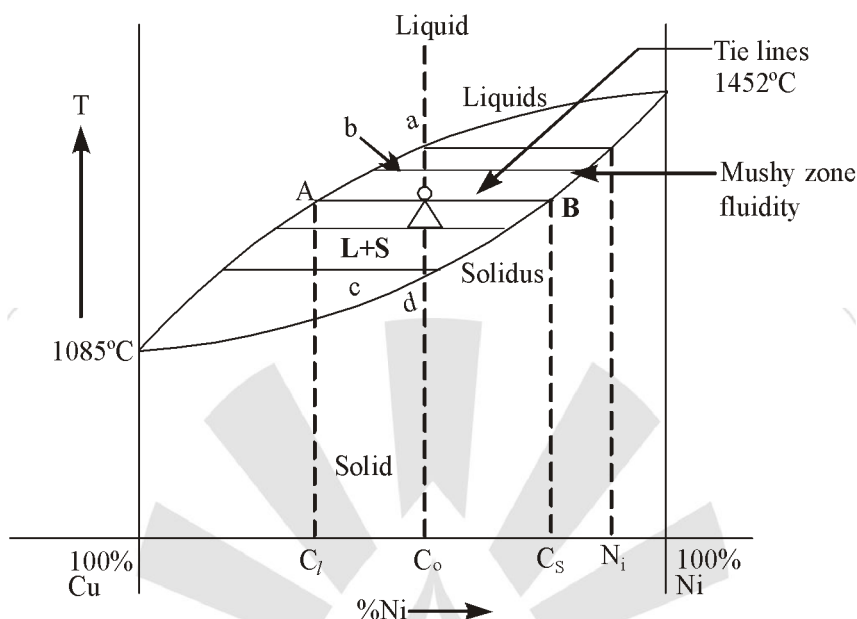
(a) Cu-Ni Phase Diagram:

Materials which are completely soluble in the liquid state as well as solid state.

The line which separates the Mushy zone with the liquid phase is called liquidus and the line which separates the Mushy zone with the solid phase is called Solidus.

Larger is the mushy zone of material, lesser will be its fluidity and hence large variation will be there in the properties of alloys. Fluidity also increases by increasing the temperature but there is a limit in casting practice beyond which we cannot increase the temperature.

Higher the temperature rise, design becomes very complex, also at high temperature moisture disintegrate in H_2 and O_2 and as hydrogen gas is coming out, it creates large. Number of pin holes on the surface of casted part. These defect is called Pin Hole Porosity.



Cu-Ni Phase Diagram

m_l = liquid

m_s = solid

$$m_s + m_l = 1$$

$$m_s c_s + m_l c_l = c_0$$

$$(1 - m_l) c_s + m_l c_l = c_0$$

$$\therefore c_s - c_s m_l + c_l m_l = c_0$$

$$\therefore m_l (c_l - c_s) = c_0 - c_s$$

$$\therefore m_l = \frac{c_0 - c_s}{c_l - c_s} \text{ (lever Rule)}$$

$$m_s = 1 - \frac{c_0 - c_s}{c_l - c_s} = \frac{c_l - c_s - c_0 + c_s}{c_l - c_s}$$

$$\therefore m_l = \frac{c_l - c_0}{c_l - c_s} \text{ (lever Rule)}$$

Upon slowly cooling the sample of copper and nickel along line "a-d", following microstructures changes will be occurred.

At point "a" entire microstructure will be in the liquid phase. As soon as the temperature decreases slightly below the liquids line, solid particle at the liquid region upon decreasing nucleate.

For the temperature from point b to c, following conclusions can be drawn by drawing a no. of tie lines

(i) Mass fractions of solid phase increases.

- (ii) The moment solid nucleates, percentage of nickel in solid phase is very high and by decreasing the temperature, percentage of Nickel in solid phase is decreasing and approaching towards over all composition c_0 .

At high temperature, phenomenon called diffusion appears in the material in which the atoms diffuses from higher to lower concentrations. It is solid so that at every 20°C increase in temperature, diffusion get doubles.

So nickel diffuses from centre to outward direction, making the entire composition homogeneous.

The moment temperature decreases slightly below the solidus line, entire sample converts into the solid phase. Each solidification front will have a particular arrangement of atoms and the region where two solidification front meets, there will be orientation mismatch of atoms called Grain Boundaries.

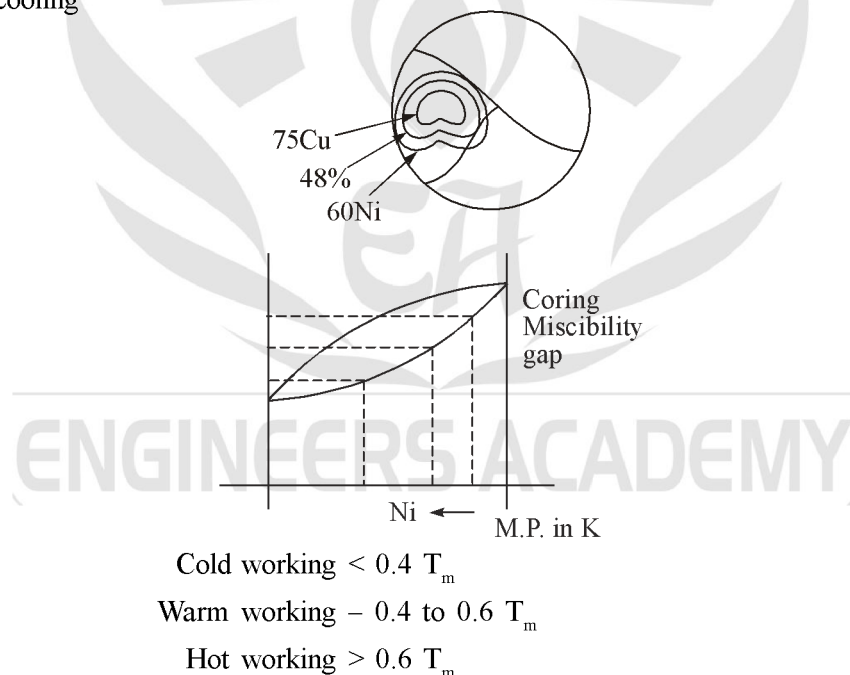
Bond length at the grain boundaries will be higher, larger the bond length, easily bond can break. That is why it is said that grain boundaries are at the high energy level. So atmospheric oxygen first attacks the grain boundaries atom and corrodes the materials. Finer is the grain structure, lesser will be the corrosion resistance of materials.

Generally to improve the corrosion resistance, chromium is added in the material, which after reacting with oxygen produces Chromium oxide which gets settle down at the grain boundaries, protecting the atoms from further oxidation.

- (i) Generally in iron nickel is called austenite phase stabilizer.

- (ii) Chromium is called ferrite phase stabilizer.

For Rapidly cooling



If the sample of copper and nickel is cooled rapidly. Since there is no sufficient time for diffusion to take place. There will be concentration gradient within the grain. At the grain boundaries, percentage of Nickel will be very low.

It can be observed in the phase diagram that lower is the percentage of Nickel, lower will be melting point of material. So upon hot working, the grain boundary material will melt out producing cracks, these leads to Brittle Fractures and the phenomenon is called Coring or Miscibility Gaps.

Note: All the binary phase diagram are plotted at a particular pressure which is one of the degree's of freedom. So the modified gibb's phase rule can be written as:

$$C + 2 - 1 = F - 1 + P$$

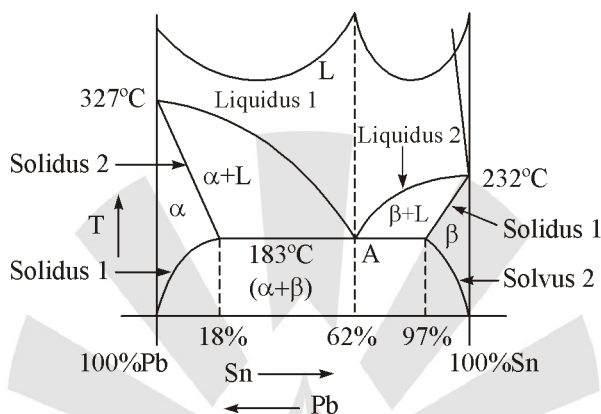
$\Rightarrow$

$$C + 1 = F + P$$

(b) Pb-Sn Phase Diagram:

Materials which are completely soluble in the liquid state but partially soluble in the solid state.

Phase Diagram of Pb-Sn (Lead Tin) (Soldering Alloy)



Pb-Sn Phase Diagram

$$0.5 T_m = 0.5 (327 + 273) - 273$$

$$= 27^\circ\text{C} \text{ (Melting point of lead)}$$

α = Phase is solid solubility of Sn (Tin) in Pb (lead) and

β = Phase is solid solubility of Pb in Sn.

Maximum solid solubility appears at 183°C and it decreases by decreasing the temperature. Any line on the phase diagram which separates a single solid phase with a mixture of solid phases. is called solidus

At point-A



$$C + 1 = F + P$$

$$2 + 1 = 0 + P$$

$\therefore$

$$P = 3$$

On such phase diagrams, there appears a point at which there is no Mushy zone and liquid directly converts into two different solids. It is called Eutectic Reaction. At Eutectic point three phases exist in equilibrium simultaneously.

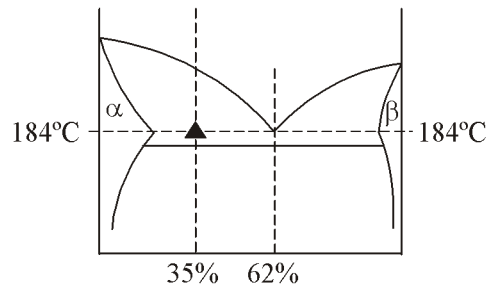
Example: Calculate the mass-fractions of phases present in an alloy of lead-Tin with 35% Sn and 62% Pb and at 184°C .

Solution: We know,

$$m_\alpha = \frac{62 - 35}{62 - 18} = \frac{27}{44} = 0.613$$

And

$$m_\beta = \frac{35 - 18}{62 - 18} = \frac{17}{44} = 0.386$$



Example: Calculate the mass and volume fraction of lead and Sn alloy with 35% Sn and 100°C. At this temperature, 10% Sn can be dissolved in Pb and 2% Pb can dissolve in Sn. Take density of Pb and Sn to be 10.25 g/cc. and 13.38 g/cc

Solution: 35% Sn at 100°C

$$m_{\alpha} = \frac{98.35}{98 - 10} = 0.715$$

And

$$m_{\beta} = \frac{35 - 10}{98 - 10} = 0.285$$

$$\alpha = 10\% \text{ Sn} + 90\% \text{ Pb}$$

And

$$\beta = 98\% \text{ Sn} + 2\% \text{ Pb}$$

∴

$$\frac{1}{\rho_{\alpha}} = \frac{0.1}{\rho_{\text{Sn}}} + \frac{0.9}{\rho_{\text{Pb}}}$$

And

$$\frac{1}{\rho_{\beta}} = \frac{0.98}{\rho_{\text{Sn}}} + \frac{0.02}{\rho_{\text{Pb}}}$$

$$\rho_{\alpha} = 10.49 \text{ gm/cc}$$

And

$$\rho_{\beta} = 13.29 \text{ gm/cc}$$

∴ Volume fraction

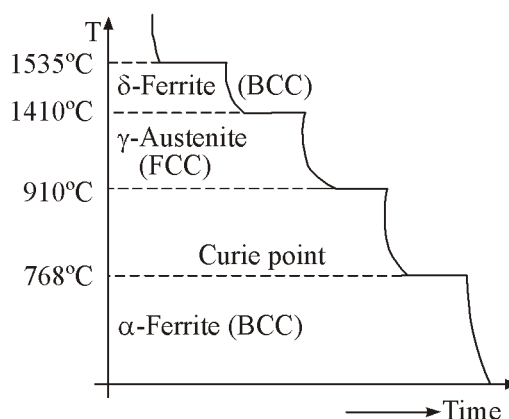
$$V_{\alpha} = \frac{\frac{m_{\alpha}}{\rho_{\alpha}}}{\frac{m_{\alpha}}{\rho_{\alpha}} + \frac{m_{\beta}}{\rho_{\beta}}} = 0.76$$

And

$$V_{\beta} = 1 - V_{\alpha} = 0.24$$

1.3 IRON CARBON PHASE DIAGRAM

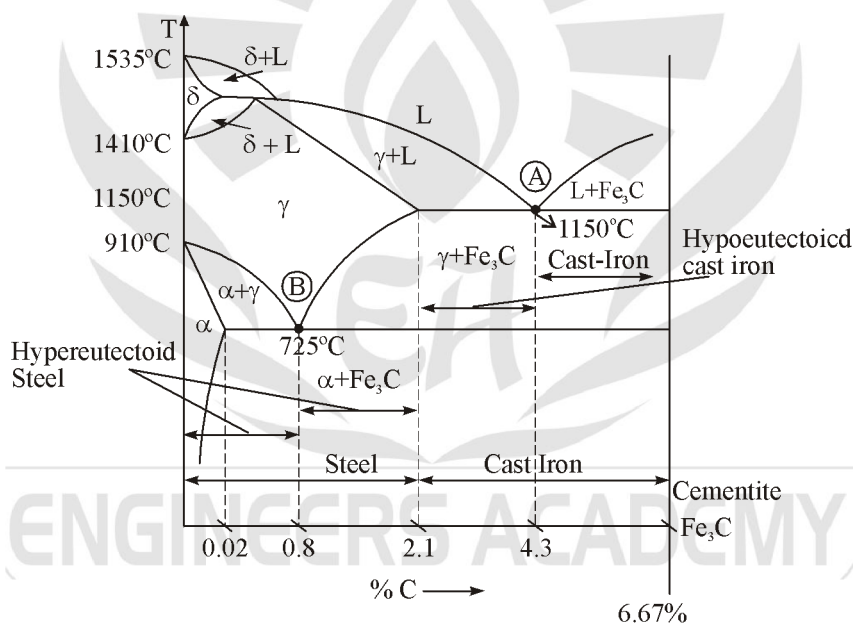
Generally latent heat transactions indicates the change of phase and it can be represented by a horizontal line on temperature time graph. But in case of iron at 768°C, there is no change of phase and only magnetic properties are disappearing. These temperature is called *Curie Point*.



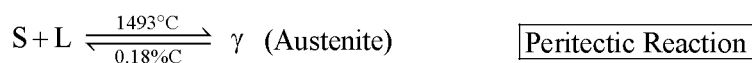
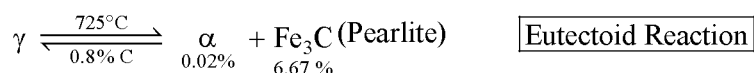
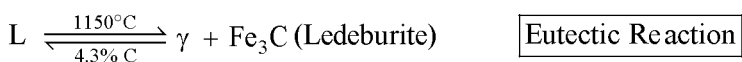
These characteristic of Iron due to which it exist in different phases at different temperature is called Allotropy.

1.3.1 Paramagnetic Materials

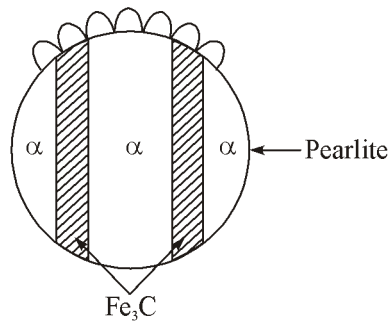
Are those in which electron are unpaired and such materials exhibit colour like alloys of copper. Di-Magnetic materials are those in which electrons are paired and such materials are colourless. But some materials such as iron which sometimes behave as paramagnetic and sometimes as Di-Magnetic, depending upon temperature, due to its unique characteristic are called as *Ferro-Magnetic*.



Fe-C Phase Diagram



Both are not phase of iron these are phase mixture of iron.



When one solid upon cooling converts into two different solids, this reaction is called Eutectoid reaction. Austenite is not stable below 725°C. So carbon diffuses from one interstitial site to another and forms an alternate plate-like structure of α and Fe_3C called pearlite. It all takes place by a diffusion process.

Similarly, eutectoid decomposition produces alternate plates of austenite and cementite, and their microstructure is ledeburite. Pearlite and Ledeburite are not phases, these are phase mixtures.

Note: Five phases of Iron:

α - Ferrite, γ - Austenite, δ - Ferrite, Cementite, Martensite

When there is a large difference in the melting point of two materials, peritectic reactions appear on such phase diagrams and these diagrams are called "**Peritectic Phase Diagrams**".

Peritectoid Reaction : When two solids combine together to form a single solid (one component) is called peritectoid reaction



1.3.2 Classification of Steel

(a) **Low Carbon Steel/Mild Steel :**

Percentage of Carbon : 0 – 0.3%

(b) **Medium Carbon Steel :**

Percentage of Carbon : 0.3 – 0.7%

(c) **High Carbon Steel :**

Percentage of Carbon : > 0.7%

(d) **Gray Cast Iron :**

Cast iron of such composition in which carbon appears in free or flake form is called Gray Cast Iron. These materials are used in making machine beds, piston rings etc.

(e) **White Cast Irons :**

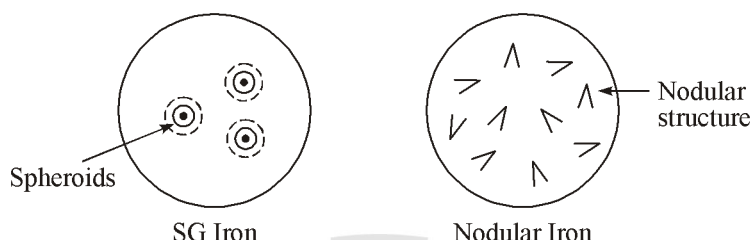
Cast iron of such composition in which entire carbon appears in the combined form is called white cast iron.

(f) **Chilled Cast Iron :**

Cast iron of such composition in which it will normally freeze as Gray but forced to appear as white are called chilled cast Iron (Sudden cooling). White and chilled cast irons are extremely brittle, and these materials are used to produce **Ductile Cast Iron**.

(g) Ductile Cast Iron :

Chilled Cast Iron is heated to a temperature below 1150°C and then cooled slowly in the present of Magnesium or Cerium (Ce). Carbon diffuses towards the centre and produce spheroidal structure which are Ductile. Slightly higher cooling rates produces Nodular structure.



Note: We cannot avoid sulphur in Iron, it is from nature.

1.3.3 Effect of Sulphur and Mangnese in Iron

Whatever liquid and solid present in the nature impurity of sulphur cannot be avoided.

Sulphur in iron is a very dangerous impurity because after reacting with iron, it produces iron sulphide (FeS) which is having very low melting point.

So upon heating FeS melts out producing cracks at grain boundaries which leads to Brittle fracture. These phenomenon is called Hot shortness. To eliminate the ill effect of sulphur, Mangnese is added in the material. Mangnese capture sulphur, before sulphur captures iron and produces MnS (Mangnese Sulphide).

MnS is not only having high melting point but also it is having low shear strength, which increases the machinability of material. Further addition of mangnese, increases the strength of materials and with 12% Mn materials becomes exceptionally strong called Hadfield steel, used in haecavy duty applications like Bulldozers etc.

1.3.4 Effect of Silicon on Steel

Steels are very difficult to cast because it undergoes excessive shrinkages during solidification. So steel is having a tendency to capture oxygen from surroundings. Addition of silicon and, absorbs these Oxygen and produces SiO_2 which settles down as sludge.

Note: When deoxidization process of steel is complete it is called Killed Steel, but when the deoxydization is partial, it is called semi-killed steel.

Effect of Silicon in Cast Iron

$$C\text{-equivalent} = \%C + \frac{1}{3} \%C \%Si + \%P = 4.3 \%$$

$$3.3 \% C + 3\% Si$$

1.3.5 Effect of Silicon and Phosphorous

Addition of silicon and phosphorus in iron, shifts the iron -carbon diagram towards left. So, graphite flakes in cast-iron appears at much lower percentage of carbon. Addition of silicon in liquid iron, discharges graphite in red hot condition, & since graphite is having lower density, it jumps over the surface of liquid iron and sparkles. These phenomenon is called KISH.

Elements	Gray C.I.	White C.I.
C	2.5 – 4	1.8 – 3.6
Si	1 – 3	0.5 – 1.9
Mn	0.4 – 1.0	0.25 – 0.8
S	0.05 – 0.25	0.06 – 0.2
P	0.05 – 1.0	0.06 – 0.18

1.3.6 Development of Micro-structure In Fe-C System

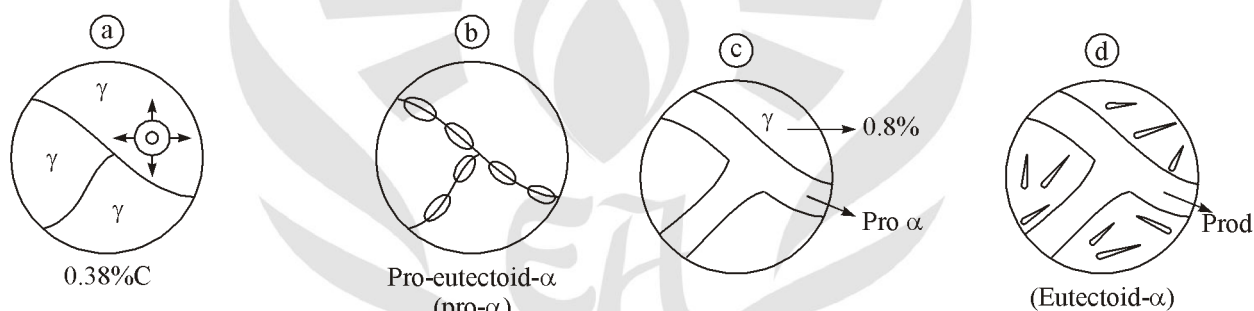
Upon cooling the sample of hypoeutectoid steel, with 0.35% C along line "a-d", following microstructural changes can be observed. At point "a", it is all austenite within the grain with 0.35% C. When the temperature decreases slightly below to point "b", Ferrite phase starts appearing in microstructure.

These ferrite which appears before eutectoid temperature is called hypereutectoid ferrite. Upon decreasing the temperature slowly from point "b-c" following conclusions can be made using lever rule.

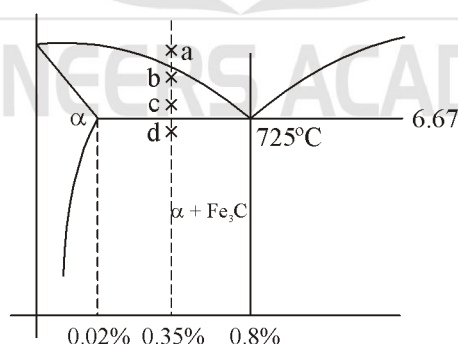
Mass fraction of pro-eutectoid ferrite increases.

Percentage of carbon in austenite within the grain increases and approaches towards the eutectoid composition.

Upon decreasing the temperature slightly below the eutectoid temperature, austenite within the grain converts into pearlite. Ferrite within the microstructure of pearlite is called Eutectoid Ferrite.



Development Of Micro-Structure



$$M_{\alpha} = \frac{6.67 - 0.8}{6.67 - 0.02} = 0.88$$

Example: Determine the mass fraction of pro-eutectoid ferrite, Eutectoid ferrite, total ferrite in steel sample having 0.35% C.

Solution: "b" Pro-eutectoid,

⇒

$$m_{\text{Pro-}\alpha} = 0.576$$

$$H_{\text{Fe}_3\text{C}} = 0.423$$

$$m_{\text{Pro-}\alpha} = \frac{0.8 - 0.35}{0.8 - 0.02} = 0.576$$

"d"

$$m_{\text{Total-}\alpha} = \frac{6.67 - 0.35}{6.67 - 0.02} = 0.95$$

"c"

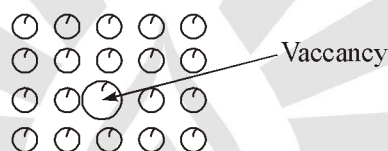
$$m_{\text{eutectoid-}\alpha} = 0.95 - 0.57 = 0.38$$

1.4 TYPES OF DEFECTS

1.4.1 Point Defect

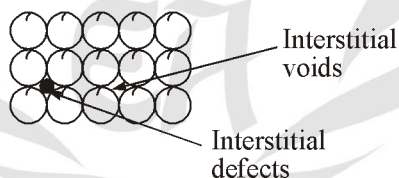
(a) *Vaccancy Defects*

When one atom from the crystal structure is escaped this type of defect is called as vaccancy defect.



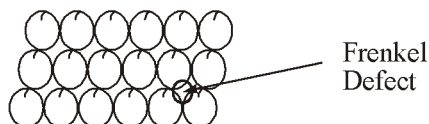
(b) *Interstitial Defects*

When one extra atom occupied the interstitial voids in crystal structure this type of defect is called as interstitial defect.



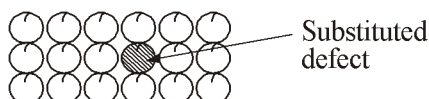
(c) *Frenkel Defects*

When one cation or anion is found extra in crystal structure this type of defect is called as frenkel defect.



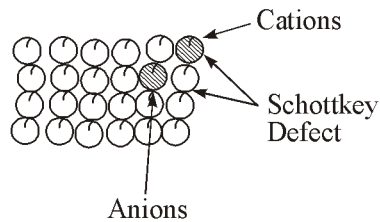
(d) *Substituted Defects*

When one extra atom replaced the previous crystal structures atom this type of defect is called as substituted defect.



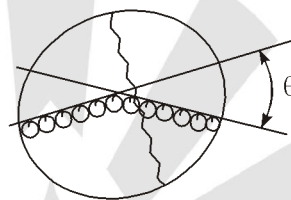
(e) Schottky Defects

When one cation and anion pair is found extra in crystal structure this type of defect is called as schottky defect.



1.4.2 Surface Defect

(a) Grain Boundary Defect



(b) Tilt Boundary Defect

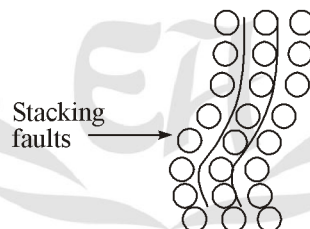
If $\theta = \frac{1}{2} \text{ to } 2^\circ$

Then it is called as tilt boundary defect.

(c) Twin Boundary Defect

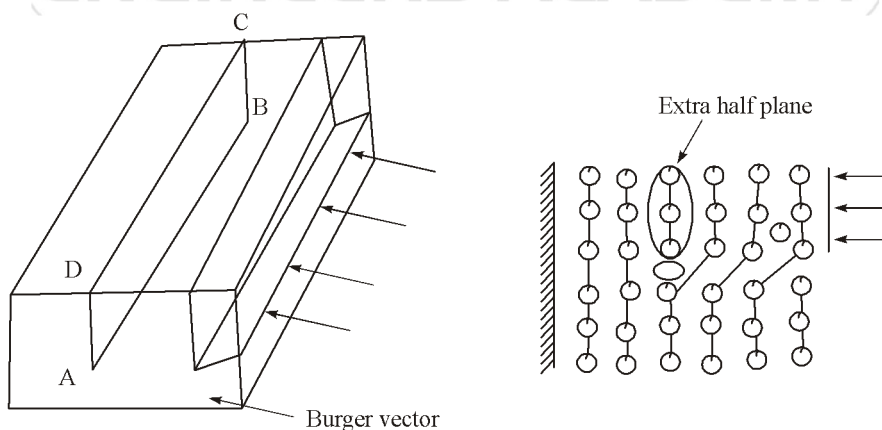
When the orientations across the grains boundaries are such, that it is the mirror image of each other it is called twin boundary defect.

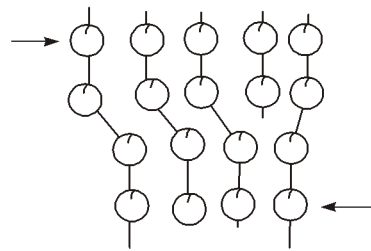
(d) Staking Faults



1.4.3 Line Defects

(a) Edge Dislocation



**AB (Edge) Dislocation**

Edge dislocation cannot be removed from material.

Although millions of edge dislocations are already there in the real material, but to understand the concept let us take an ideal material free from any defect. Once surface of these materials is restricted to deform and on the opposite face's 50% area a uniform pressure is applied, once this pressure exceeds beyond certain value, there will be slipping of atoms.

Slip is unit plastic deformation and it always appears in direction of applied load.

The direction of the slip is called Burger vector.

It can be observed in the diagram, that there will be a boundary AB between slipped and unslipped regions called Edge Dislocation.

It can be observed that at the edge dislocation line :

- (i) There appears an extra half plane.
- (ii) Interstitial void at the dislocation site will be slightly larger in size.

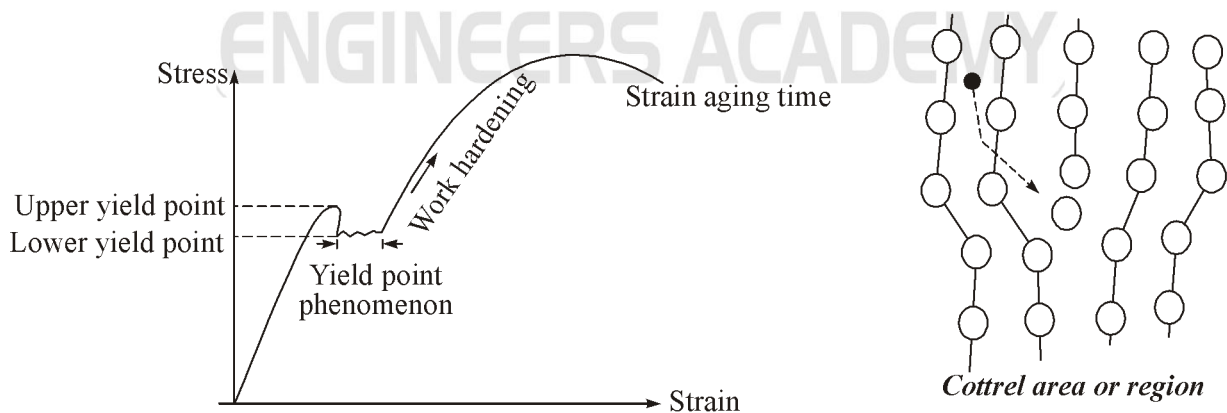
(b) Screw Dislocation :

In case of Edge dislocation, dislocation line is perpendicular to Burger vector. In screw dislocation, dislocation line is parallel to Burger vector.

Since millions of dislocations are already there within the grain, oriented in all the possible directions, when a load is applied on the materials, dislocations in that direction, starts moving within the materials. When the dislocation comes out it is said that plastic deformation has begin.

Any obstacle created in the movement dislocation, increase the strength of material.

1.5 YIELD POINT PHENOMENON



Carbon and nitrogen are interstitial impurity in iron. But the size of interstitial void is much smaller than size of carbon atom. So carbon diffuses through atomic structure and get accumulated to dislocation site and produces a carbon rich atmosphere called cottrel atmosphere.

These Cottrell atmosphere produces atomic strains in the host iron atoms, so when external load is applied on the material, slightly larger stresses are required to break the Cottrell atmosphere and jump the dislocation to new site. That is why upper yield point appears in materials.

Once the dislocation jumps the new site, relatively lower stresses are required to keep the dislocation moving. That is why lower yield point and yield point phenomenon appears in the material.

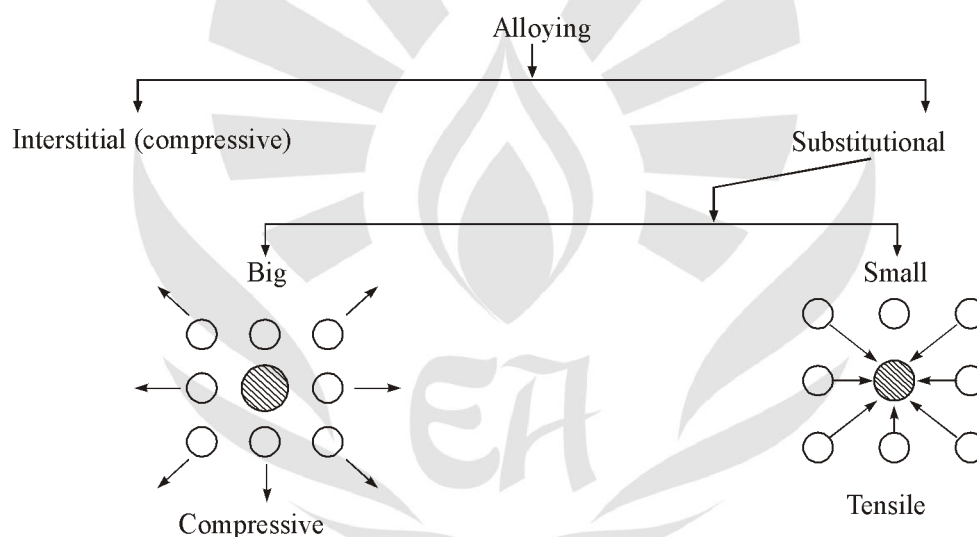
Upon unloading the material from the region of work hardening and unloading again, yield point phenomenon will not appear. But after waiting for some time (Around 2 years) carbon Nitrogen will again diffuse to dislocation site and again Cottrell Atmosphere will be produced. Hence yield point phenomenon will reappear in material.

The period after which yield point phenomenon reappears in material is called strain Aging Time.

This phenomenon doesn't appear in medium and high carbon steels because carbon is not only present at dislocation site but on the other interstitial sites as well. So once dislocation jumps into new position, carbon is already there to diffuse.

1.6 STRENGTHENING MECHANISM

1.6.1 Alloying



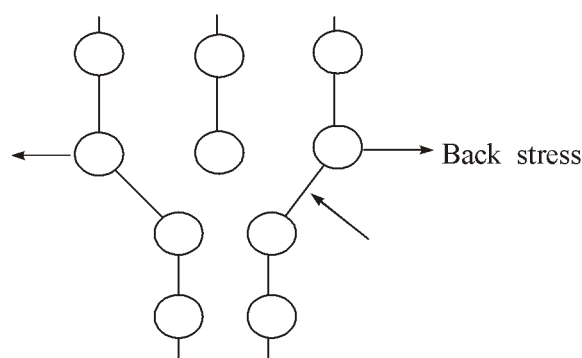
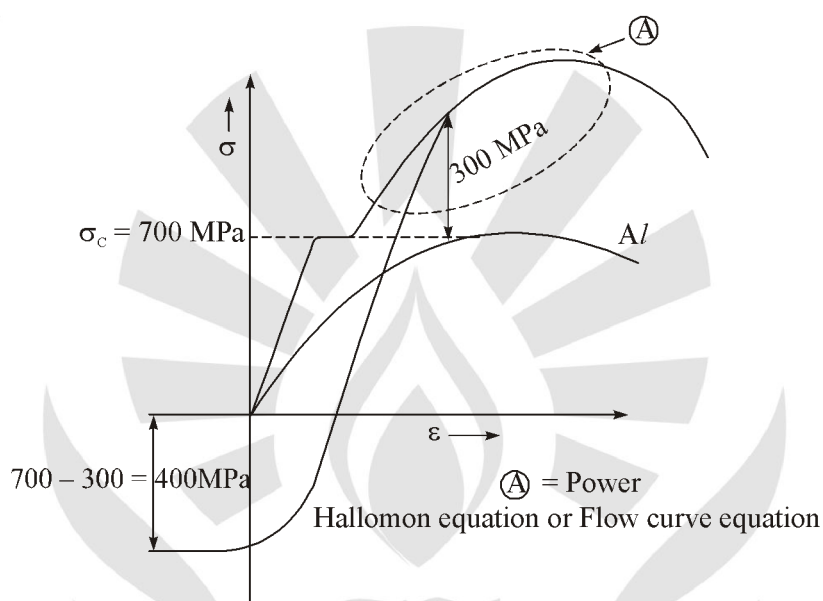
If impurity atoms occupy the interstitial site, it produces compressive strain field. A smaller size substitutional impurity produces tensile strain field and large size substitutional impurity produces compressive strain field. These strain fields create an obstacle to the movement of dislocation, which increases the strength of material. Larger the strain field created by impurity atom, more increase in strength will take place.

1.6.2 Grain Refinement

As soon as a dislocation reaches the grain boundaries, it has to change its direction and also due to larger bond length larger stresses are required by dislocation to cross through grain boundaries. Hence finer is the grain structure, stronger the material will be.

1.6.3 Work Hardening or Strain Hardening

Upon cold working any material, no. of dislocation increases. How much dislocation multiplication, material will undergo is the property and cannot be changed. These new dislocations which have been formed accumulate at the grain boundaries and produce a dislocation forest. The interaction between two dislocations is repulsive in nature.

*Bauschinger Effect*

So these dislocation forest creates a back stress in the movement of dislocation within the grain. These increases the strength of material.

Upon unloading the material from the region of work hardening and the reloading in the opposite direction, back stresses now support the movement of dislocation and as a result of that yield point in compression appears prematurely. These phenomenon is called Bauschinger Effect.

Note: Power law or Hollomon equation = Flow curve Equation"

$$\sigma_f = K \epsilon^n$$

σ_f = True stress

K = Strength coefficient

ϵ = True strain

n = 0.3 → Standard working exponent

Engineering Stress (Nominal Stress) $\sigma_0 = \frac{P}{A_0}$

True stress, $\sigma_f = \frac{P}{A} \times \frac{A_0}{A_0} = \sigma_0 \left(\frac{A_0}{A} \right)$

Now, $V = A_0 l_0 = A.l.$

$$\Rightarrow \frac{A_0}{A} = \frac{l}{l_0} = \frac{l}{l_0} - 1 + 1 = \frac{l - l_0}{l_0} + 1$$

$$\Rightarrow \frac{A_0}{A} = \epsilon + 1$$

$$\therefore \sigma_f = \sigma_0 (\epsilon + 1)$$

True Strain :

$$\int_0^\epsilon d\epsilon = \int_{l_0}^l \frac{dl}{l}$$

$$\Rightarrow \epsilon = \ln \left(\frac{l}{l_0} \right) = \ln(\epsilon + 1)$$

True Stress:

$$\sigma_f = \frac{P}{A}$$

$$\therefore \frac{d}{d\epsilon} [P = \sigma_f \cdot A]$$

$$\Rightarrow \frac{dP}{d\epsilon} = \sigma_f \cdot \frac{dA}{d\epsilon} + A \cdot \frac{d\sigma_f}{d\epsilon} \quad \dots(1)$$

And

$$V = Al$$

$$\therefore \frac{dV}{d\epsilon} = A \cdot \frac{dl}{d\epsilon} + l \cdot \frac{dA}{d\epsilon} \quad (V = \text{constant}) \quad \dots(2)$$

$$\Rightarrow 0 = \frac{A}{l} \frac{dl}{d\epsilon} + \frac{dA}{d\epsilon}$$

$$\Rightarrow \frac{dA}{d\epsilon} = -A \quad \dots(3)$$

$$\therefore \frac{dP}{d\epsilon} = -\sigma_f A + A \cdot \frac{d\sigma_f}{d\epsilon}$$

At UTS (Ultimate Tensile Stress)

$$\frac{dP}{d\epsilon} = 0$$

$$\therefore \frac{d\sigma_f}{d\epsilon} = \sigma_f \quad \dots(4)$$

$$\therefore \frac{d}{d\epsilon} [\sigma_f = K \cdot \epsilon^n]$$

$$\Rightarrow \frac{d\sigma_f}{d\epsilon} = K n \cdot \epsilon^{n-1} \cdot \frac{\epsilon}{\epsilon}$$

$$\therefore \frac{d\sigma_f}{d\epsilon} = \frac{n}{\epsilon} \cdot \sigma_f \quad \dots(5)$$

At UTS by, (4) and (5)

$$n = \epsilon$$