

Material Science

Two Material will Combine together and form alloy Only when the Conditions of Hume-Rothery rule satisfied.

Before Condition of Hume-Rothery apply crystal structure of Both material should be same.

- (i) The difference in the atomic radius should be less than 50%.
- (ii) Valency of both the material should be same
- (iii) Electronegativity and electron affinity of both the material should be comparable.

Phase diagram:- Phase diagram is a plot on temp Composition space showing the stability of various phase

In other words phase diagram tells us what will be the melting point of alloy.

Phase:- Physically distinct chemically homogeneous and mechanically separable state of any matter is called ~~state~~ phase.

Component:- No. of chemical formulas in the mixture of p

Dof:- No. of independent Variable require to define the state of any matter is called dof.

Mixture of diff phase will be in equ^m only when it follows Gibbs phase rule

$$P + F = C + 2$$

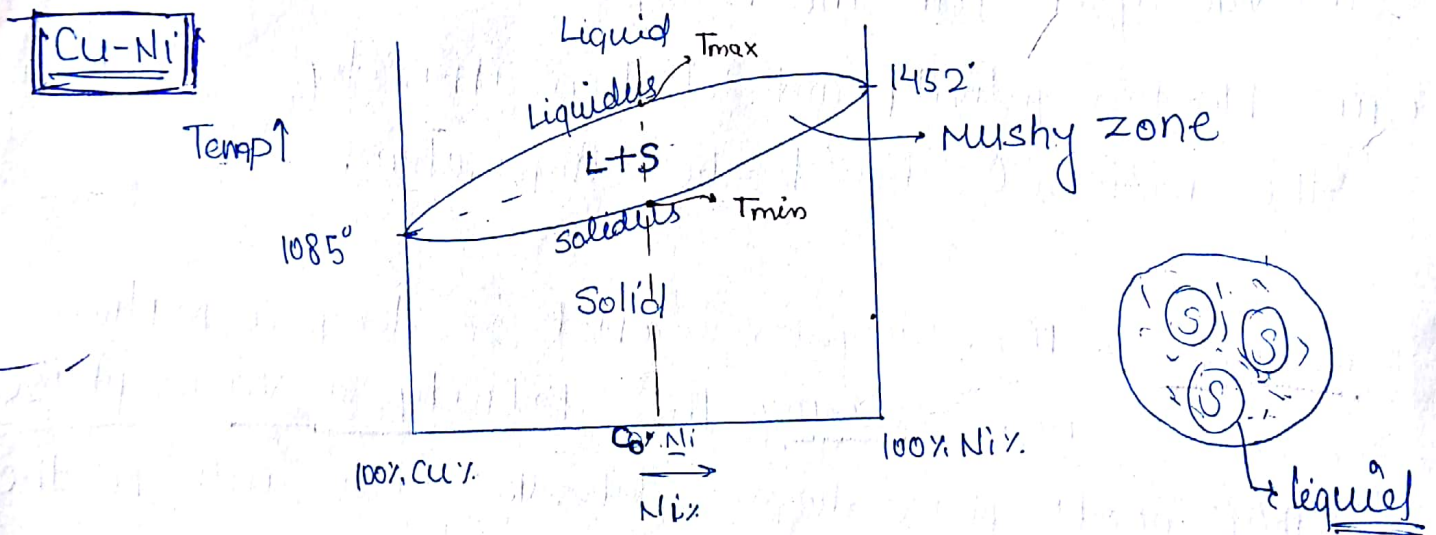
C = 1 unary phase diagram

C = 2 Binary phase diagram

C = 3 Ternary phase diagram

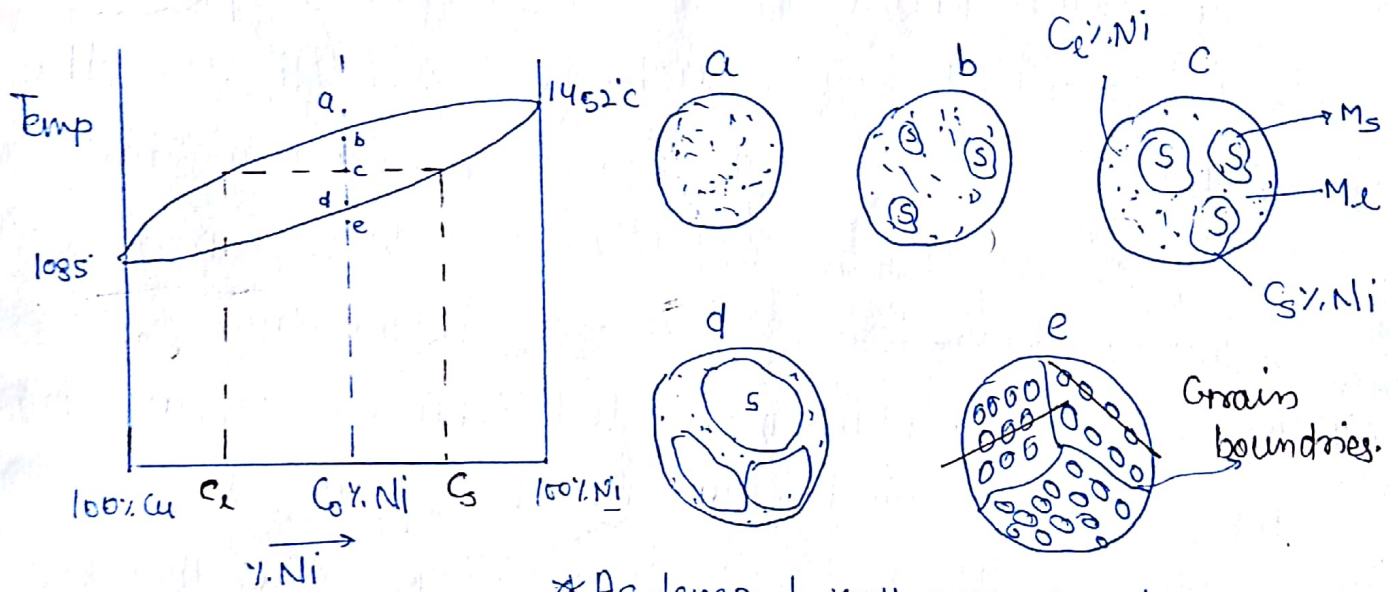
★ Binary phase diagram Type - 1 :- Materials which are completely soluble

both in the liquid and solid state.



Cu & Ni both combines together and produces a single phase in solid state it is called solid solubility. All the lines appearing on the phase diagram are the properties of alloy and can not be changed. There appears a region on such phase diagram where there is a mixture of liquid and solid called mushy zone.

larger is the extent of ushy zone more will be the variation in properties of that alloy. Any line on the phase diagram that separate the mushy zone with liquid phase is called liquidus. Any line on the phase diagram that separate mushy zone with solid phase is called solidus. as it can be seen in the diagram that ~~if~~ if mushy zone is appear in the alloy melting point will not be fixed there will a range of temp at which liquidification and solidification takes place.



* As temp. $\downarrow$ % Ni will also $\downarrow$

$$m_S C_S + m_L C_L = C_0$$

$$m_S + m_L = 1 \quad (\text{mass fraction})$$

$$m_S = \frac{C_0 - C_L}{C_S - C_L} \quad \text{lever rule}$$

$$m_L = \frac{C_S - C_0}{C_S - C_L}$$

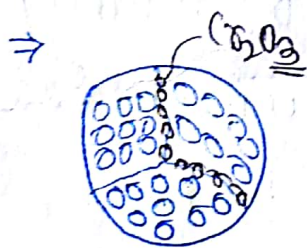
$$\begin{aligned} C_0 \% &\rightarrow \text{Ni} \\ (1 - C_0) \% &\rightarrow \text{Cu} \end{aligned}$$

★ lever rule can only be apply in a two phase region.

⇒ A sample of Cu-Ni with $C_0\%$ Ni is cooled along line a-e slowly. Point 'a' is above the liquids line so entire microstructure in the liquid phase. The ~~moment~~ temp. of sample slowly decreases to point 'b' solid start nucleating in microstructure at thousands of places. Up on the decreasing the temp from point 'b' to 'd' following conclusion can be drawn by using lever rule

- ① As the temp. decreases mass fraction of solid phase keeps on increasing
- (ii) The moment solid nucleated $\%$ of Ni in the solid is quite high upon decreasing the temp $\%$ of Ni in solid keeps on decreasing at approach towards the overall composition C_0 .
- (iii) At high temp. phenomena called diffusion appear in the solid which tries to homogenise the composition. It is said the every 20°C increase in temp. diffusion multiply by 2 ($2\times$ diffusion) so Ni will diffusion from ~~to~~ center to outward direction and make composition uniform through. so within the solid phase composition of Cu & Ni will uniform.

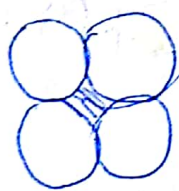
Each and every solidification form will have a particular arrangement of atom. The moment temp. of the sample slightly decreases below the solidus line different solidification fronts will fuse together and entire microstructure will convert into solid phase. The regions where different solidification front are meeting there will be mismatch in the orientation of atom. These region of orientation mismatch are called grain boundaries.



Fe 18-8 SS

18% Cr when it come in contact with $O_2 \rightarrow Cr_2O_3$
8% Ni

works phase stabilizer



Interstitial voids

18% Ni - Austenite phase stabilizer
8% Cr - Ferrite phase

Super Alloy - material which only single grain boundary.

Whiskers:-

At the grain boundary since bond length is large so easily bond can break so atmospheric oxygen first attach the grain boundary and Corros it. That's why it is said that grain boundaries are at high energy level. π

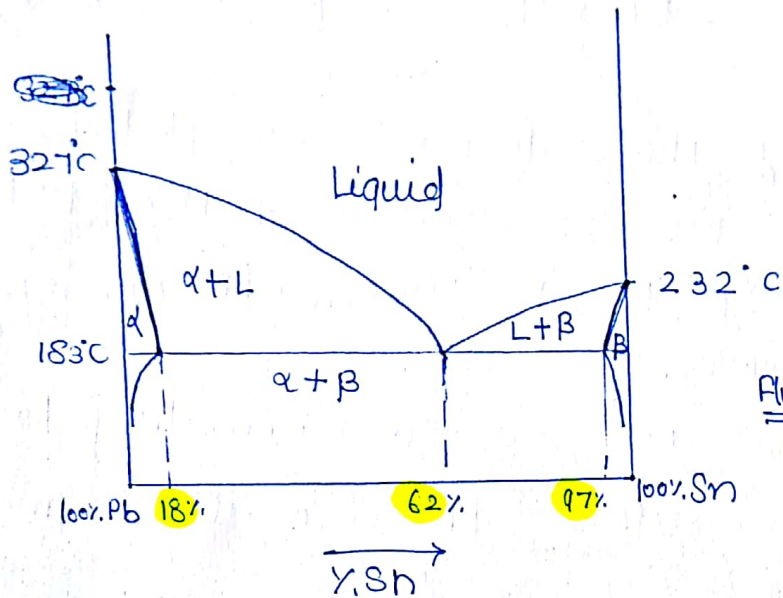
To increase Corrosion resistance of any material ~~corrosion~~ is added in it. α after reacting with oxygen produces ~~cor~~ Cr_2O_3 (Chromium oxide) and it get accumulate grain boundary, protecting the grain boundary from the attack of other gases.

- Ni is a phase stabilizer. In case of iron Ni is Austenite phase stabilizer and α is Ferrite phase stabilizer.
- To protect any material from grain boundary corrosion either foreign phase accumulate at grain boundary or the grain boundaries should completely remove from material.
- The material where there is no grain boundaries are called super alloy. ~~super~~
- Super alloys in thin section are called whiskers.

Binary phase diagram of Type-2 :-

Materials that are completely soluble in the liquid state but partially soluble in the solid state

Pb-Sn



- ⇒ α phase is solid solution of Sn in Pb and max. 18% tin (Sn) can be dissolve in lead (Pb) at 183°C. This solid solubility decreases by decreasing the temp.
- ⇒ β phase is solid solution of Pb in Sn and max. 3% lead (Pb) can be dissolve in tin at 183°C. This solid solubility decrease by decreasing the temp.

⇒ $183^\circ\text{C}, 62\% \text{ Sn}$
 $L \rightleftharpoons \alpha + \beta$ Eutectic point (No mushy zone)

for Pb-Sn 183°C eutectic temp.

62% Sn ~~the~~ eutectic composition

* Eutectic reaction
nice melting

it called invariant $F = 0$

$$C + 2 = F + P$$

⇒ at P_{atm}

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

$$\Rightarrow C + 1 = F + P$$

These reaction done on P_{atm} and P_{atm} have 1 Dof

modify Gibbs rule for ^{binary} Eutectic system

$$C+1 = F^* + P$$

at eutectic point $F^* = 0$

$$2+1 = P \Rightarrow P = 3 \text{ (phase)}$$

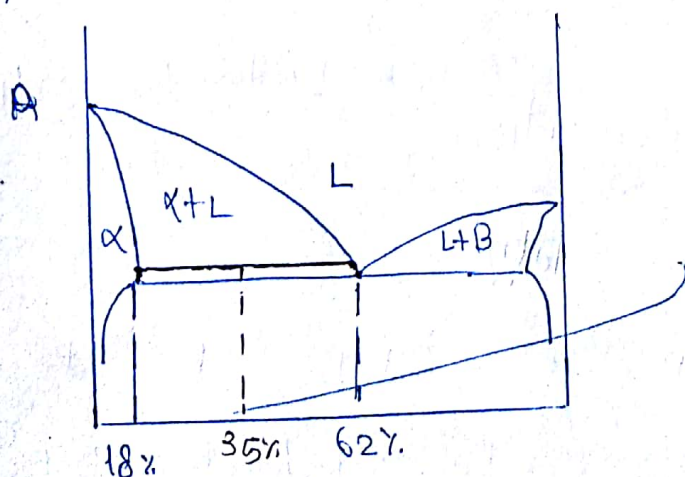
⇒ All the binary phase diagrams are plotted at atmospheric pressure but pressure is one of the DOF. So we have restricting 1 DOF this will change the Gibbs equation.

⇒ Invariant means DOF = 0 so according to modify Gibbs phase rule 3 phase will be in equilibrium at eutectic point. Φ

⇒ The temp. at which Eutectic reaction appear is called eutectic temp. and composition at which eutectic reaction appear called eutectic composition.

Problem:- Calculate the mass fraction of phases present in a Pb-Sn alloy with 35% Sn and at 184°C

Solⁿ

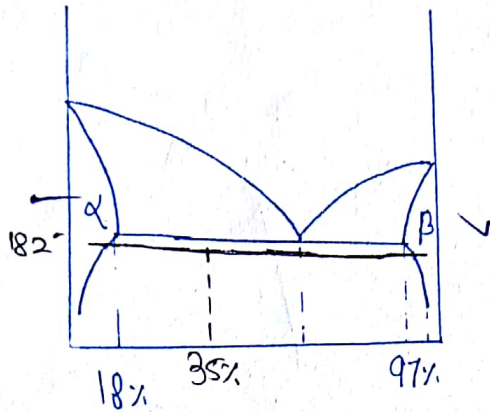


$$m_g = \frac{62-35}{62-18} = 0.61$$

$$m_l = \frac{35-18}{62-18} = 0.39$$

Problem:- Calculate the mass fraction of the phase present in a Pb-Sn alloy 35% Tins(Sn) and at 182°C

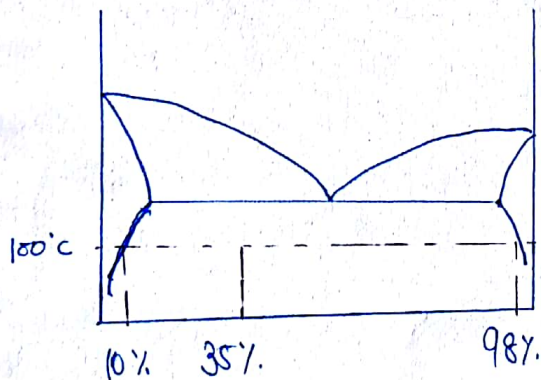
Solⁿ



$$m_{\alpha} = \frac{97-35}{97-18} = 0.72$$

$$m_{\beta} = \frac{35-18}{97-18} = 0.22$$

Problem:- Calculate the mass and volume fraction of the phase present in Pb-Sn alloy with 35% Sn at 100°C . at this temp 10% Sn can desolve Pb completely and 2% Pb desolve in Sn ~~desolve~~ completely
density of Pb = 10.96 gm/cc & Sn = 13.28 g/cc



$$m_{\alpha} = \frac{98-35}{98-10} = 0.715$$

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

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

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

$\rho_{\text{Pb}} = 10.96 \text{ g/cc}$

$\rho_{\text{Sn}} = 13.28 \text{ g/cc}$

i.F $A \rightarrow S_A \rightarrow 20\%$

$B \rightarrow S_B \rightarrow 80\%$

$$\frac{1}{S} = \sum_{i=1}^n \frac{x_i}{S_A}$$

$$\frac{1}{S} = \frac{0.2}{S_A} + \frac{0.8}{S_B}$$

So

$$\frac{1}{S_{\alpha}} = \frac{0.1}{S_{sn}} + \frac{0.9}{S_{pb}} \quad - (1)$$

$$\frac{1}{S_{\beta}} = \frac{0.02}{S_{pb}} + \frac{0.98}{S_{sn}} \quad - (2)$$

$$V_{\alpha} = \frac{\frac{m_{\alpha}}{S_{\alpha}}}{\frac{m_{\alpha}}{S_{\alpha}} + \frac{m_{\beta}}{S_{\beta}}}$$

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

from eq (1)

$$\frac{1}{S_{\alpha}} = \frac{0.1}{13.98} + \frac{0.9}{10.96}$$

$$S_{\alpha} = 11.15$$

$$\frac{1}{S_{\beta}} = \frac{0.02}{10.96} + \frac{0.98}{13.28}$$

$$S_{\beta} = 13.22$$

$$V_{\alpha} = \frac{\frac{0.715}{11.15}}{\frac{0.715}{11.15} + \frac{0.285}{13.22}}$$

$$V_{\alpha} = 0.748 \quad V_{\beta} = 0.252$$

Phase change

1. Crystal structure change & ~~crystal structure~~
2. Size of unit cell change.

These are detected by

1. XRD machines
2. Electron microscope

SEM
(Scanning)

- Surface topography
- type of fracture

Transmission EM
(TEM)

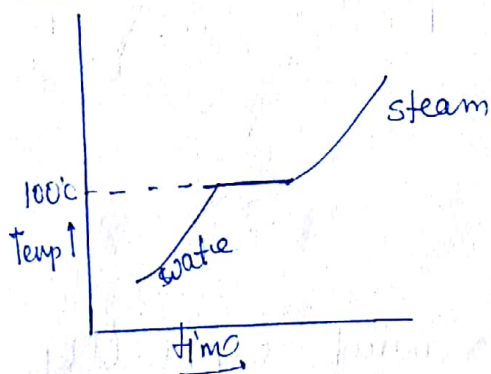
②
Cleavages - Brittle

③ Dimple - cups & cone

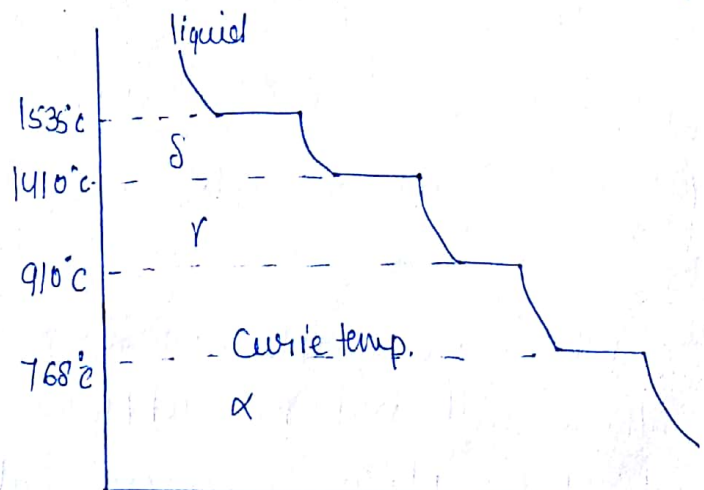
Earlier when SEM & TEM not develop ~~state~~

Horizontal line detected the phase change (in temp vs time graph)

For water



For Iron

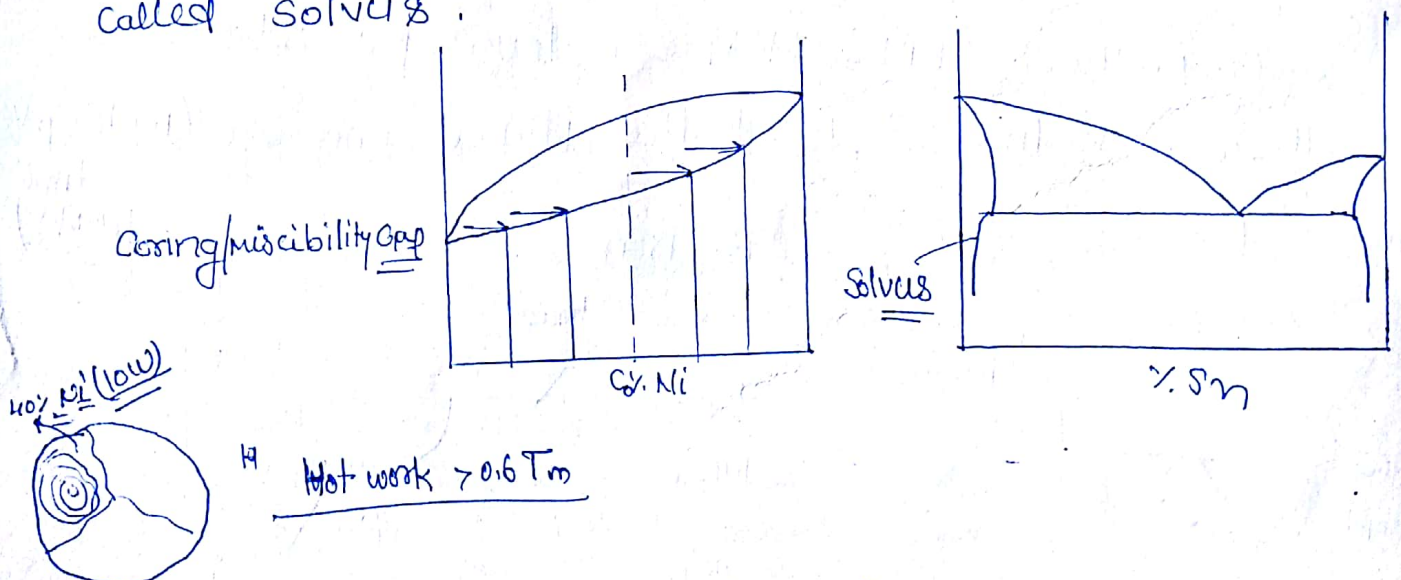


at 768°C no change in phase it change magnetic property

Whenever there is phase change in material either the crystal structure change or there is change in size of unit cell. Generally latent heat transaction indicate the phase change. But in case of iron at 768°C there is no change in the phase only magnetic properties of material disappear this temp is called Curie temp. The characteristic of iron due to it which it exist in diff phase at diff temp is called Allotropy.

05/08/16

⇒ Any line on the phase diagram that separates a single solid phase with a mixture of solid phase is called solvus.



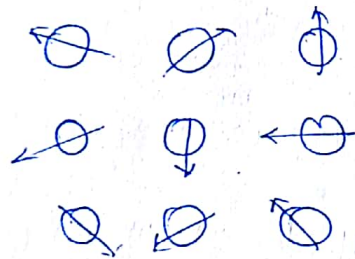
When the sample of Cu & Ni is cooled rapidly, there will not be sufficient time for the diffusion to take place so upon solidification of material there will be composition gradient within the

grain and at the grain boundary % Ni will be very low.

It can be seen in the Cu-Ni phase diagram that lower is the % of Ni, lower will be its melting point. So upon hot working the material grain boundary material will melt out producing cracks this leads to brittle fracture and this phenomena is called coring / miscibility gap.

Materials

① Paramagnetic :-



Brass $\Rightarrow$ Cu-Zn

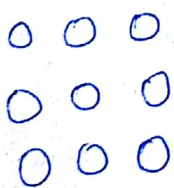
Bronze $\Rightarrow$ Cu + ()
↳ other alloy

Paramagnetic are in

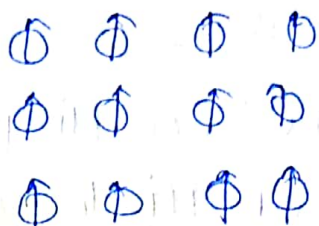
random orientation

left hand side of the periodic table material are in paramagnetic in nature and there is no pairing of atoms and there magnetic dipole are randomly oriented. Such material exhibits colour like alloy of copper. (C)

② Diamagnetic :- ~~the~~ These material are present are on the RHS of periodic table and there is pairing of atom. There will no magnetic dipole.



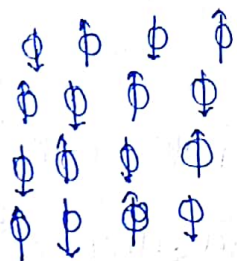
③ Ferromagnetic! — Iron, Co, Ni are ferromagnetic at room temp.



At room temp these material will have magnetic dipole only in one direction. These material are magnetic in nature.

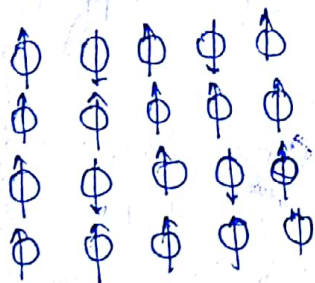
⇒ Iron is a such material which some_{time} behave ~~ferromagnetic~~ paramagnetic and some time diamagnetic depending upon the temperature

④ Antiferro! — only chromium is antiferro material.

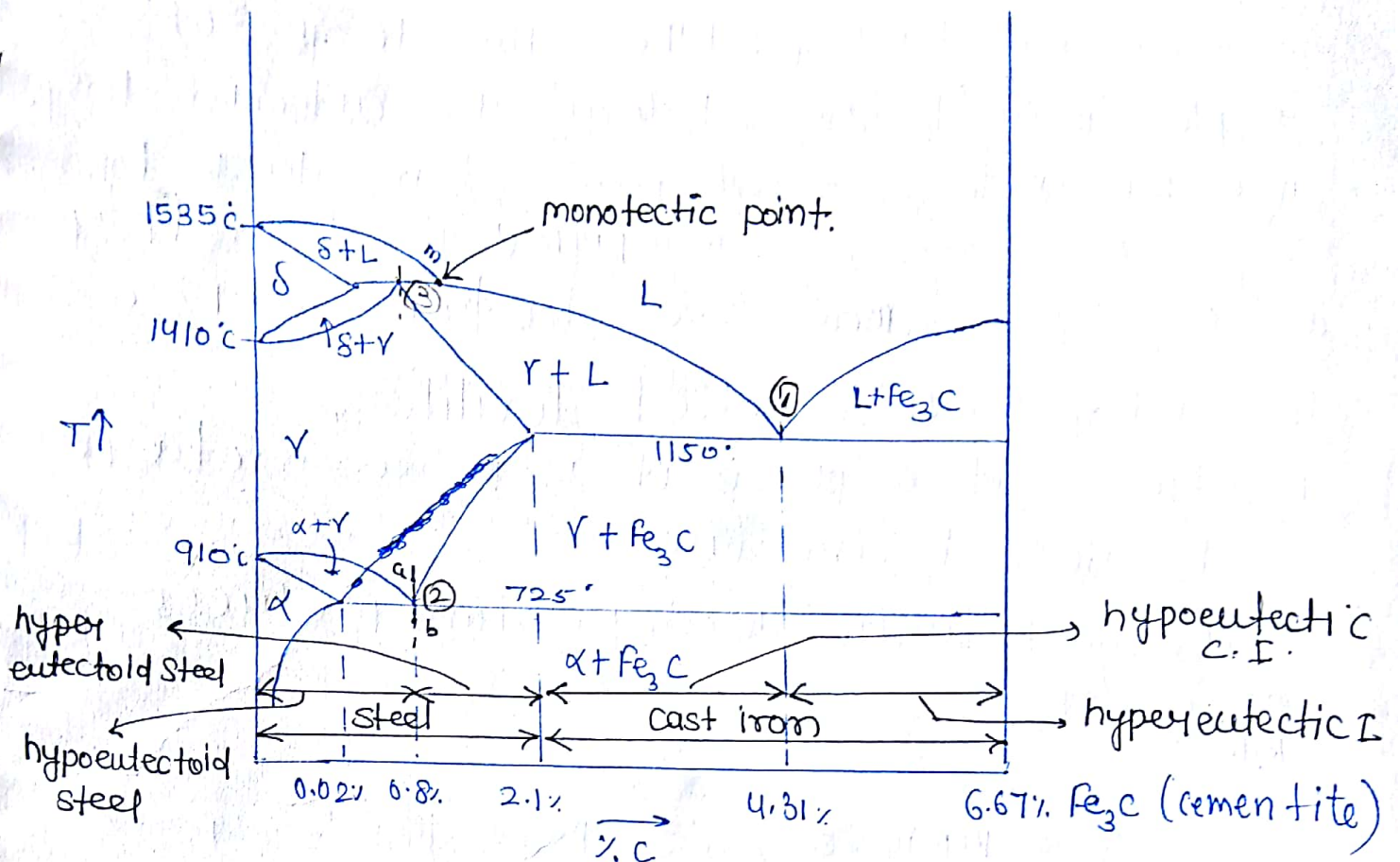


⇒ All the magnetic dipole moment are parallel but are in opposite direction eg. Cr

⑤ Ferrimagnetic! — Combination of ferromagnetic & antiferromagnetic. No material behave like this only compounds follow this characteristic, or this type of behaviour.



Fe-C phase diagram / Iron-cementite (Fe_3C) diagram.



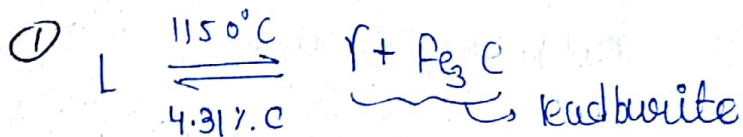
α - Ferrite bcc

γ - Austenite fcc

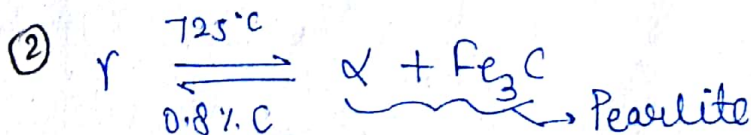
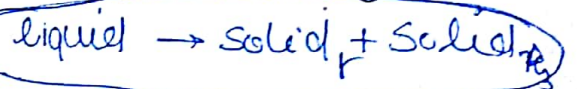
δ - Ferrite bcc

Fe_3C - Orthorhombic

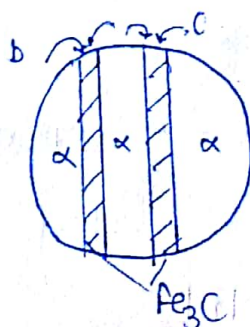
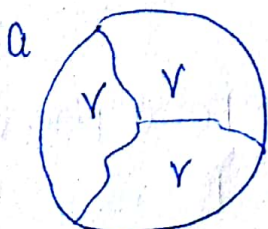
* max. solubility of Carbon in Fe is 6.67%



Eutectic Reaction



Eutectoid Reaction

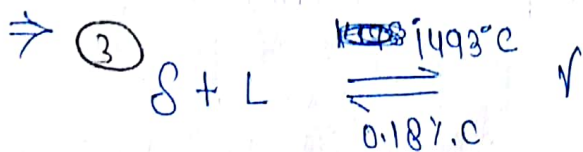


At 0.8% C at 726°C carbon is uniformly distributed in the microstructure. When the temp. of sample slowly decreases below the eutectoid temp. since Austenite can not present in stable form. so carbon form one interstitial site to another and produce alternate like structure ' $\alpha + \text{Fe}_3\text{C}$ '

→ this microstructure called 'Pearlite'.

pearlite is not a phase it is phase mixture of Ferrite and cementite.

similarly Eutectic decomposition produces ~~lede~~ lede bursite.



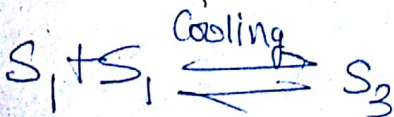
Peritectic Reaction
Solid + liquid $\rightarrow$ Solid

* When there is a large difference in the melting point of two material, the phase diagram of such alloy peritectic reaction appear.

$\Rightarrow$ Fe-C diagram is such a ~~diagram~~ diagram where three invariant reaction appears simultaneously.

* Point m is a monotectic point but it is not a invariant point. $\text{Dof} = \underline{2}$

Peritectoid Reaction: - it doesn't appear on Fe-C phase diagram when two solid convert into one solid



carbon %

0 - 2.1%

2.1 - 6.67%

steel

cast iron

hypo eutectoid (0 - 0.8)

hyper eutectoid (0.8 - 2.1)

hypo eutectic (2.1 - 4.3)

hyper eutectic
(4.3 - 6.67)

Steels

0 - 0.3% C, low carbon steel (mild steel)

0.3 - 0.7% C, Medium carbon steel

> 0.7% C, High carbon steel

① Gray Cast iron! — In pure iron carbon system when more than 6.67% C is added, a portion of C come out on the microstructure and appear in free or flake form. Such cast irons are called Gray Cast iron. These material are used to manufacture machine bed. because Graphite pockets act like vibration damper and hence absorbs vibration.

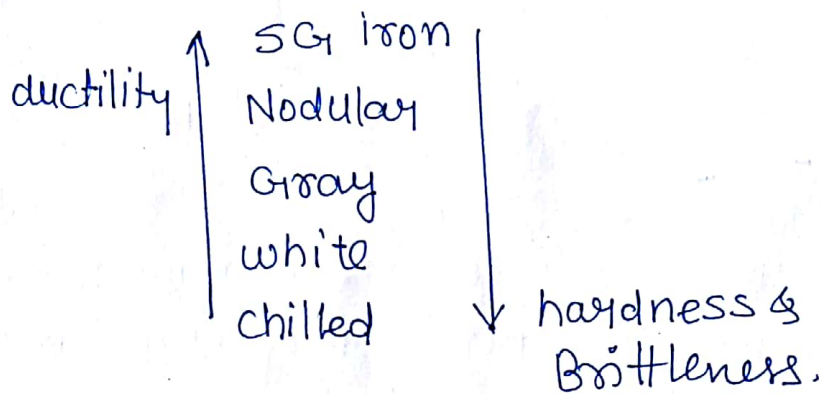
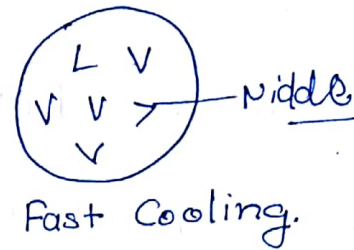
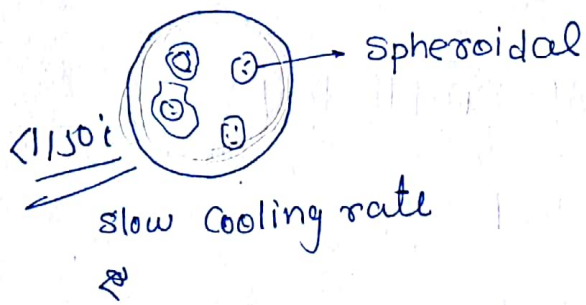
② White Cast iron! — very hard and brittle.

When a % of C is less than 6.67% entire amount of carbon will appear in combined form and these material are called white cast iron.

③ Chilled Cast iron! — Cast iron of such composition in which normally it will fringe as gray but forced to appear as void by rapid cooling is called chilled C.I.

both white and chilled cast iron are brittle in nature so these material are not use directly in any engineering application. These material are used to make ductile Cast iron.

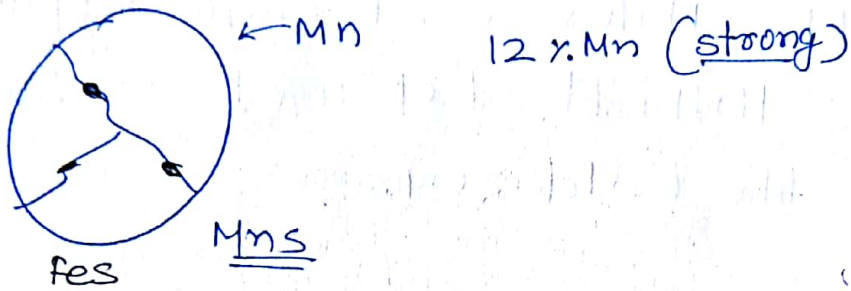
④ Spheroidal Gray C.I (SG iron) ⑤ Nodular C.I.



If the objective to produce ductile cast iron small amount of Mg, Ce (Cerium) is added in the material. These material act like catalyst in the diffusion process of carbon. After producing chilled cast iron the material again heat to a temp $< 1150^{\circ}\text{C}$ and then cooled extremely slowly in the Furnace at thousand of places carbon will diffuse at the centre and produces spheroidal. This increase the overall ductility of material.

if the cooling rate ~~of~~ are slightly faster combined form of carbon appears in the ~~in~~ middle like form is called Nodular Cast iron.

Effect of sulphur (S) and manganese (Mn)



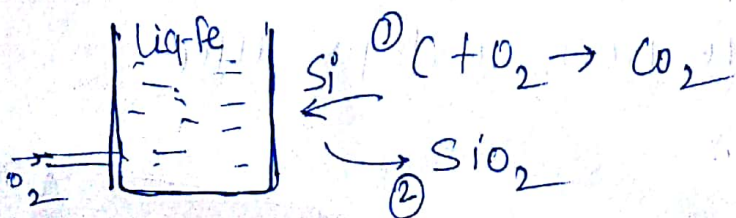
Whatever liquid & solid present in nature impurity of S sulphur cannot be avoided so sulphur will present in iron also. Impurity of sulphur in iron is very dangerous because after reacting with iron it produces iron sulphide (fes) and it gets accumulated at grain boundaries.

Melting point of fes is very low so upon ~~when~~ warm forming of the material, fes will melt out producing cracks at grain boundaries that lead to brittle fracture. This phenomenon is called hot shortness or sulphur-embrittlement.

To avoid the ill effect of sulphur small amount of ^{manganese} ~~manganese~~ (Mn) is added in material. Mn captures sulphur before sulphur captures iron, and produces ~~manganese~~ sulphide (MnS), ^{manganese} ~~manganese~~.

Melting point of Mns is quite high so hot-shortness phenomena will be gone. Shear strength of Mns is low and this increases the machinability of material. Further addition of Mn increase strength of material and with 12%, Mn Material become exceptionally strong Hadfield steel used in heavy duty applications like bulldozer.

To produce steel carbon has to be removed from material, so O_2 is injected in liquid iron pond. O_2 after reacting with carbon present in liquid iron produces CO_2 . So carbon is removed from material by converting into gas. Since it is exothermic reaction liquid iron pond appears to boil and this phenomena is called steel ~~boil~~ boil. When we stop the flow of O_2 there will be a tendency in steel to capture ~~o~~ a portion of oxygen (O_2). Silicon (Si) is added in the liquid metal to remove this trapped oxygen (O_2) when O_2 is completely removed from material it is called skilled steel and when removal of O_2 is partial it is called semiskilled steel.



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

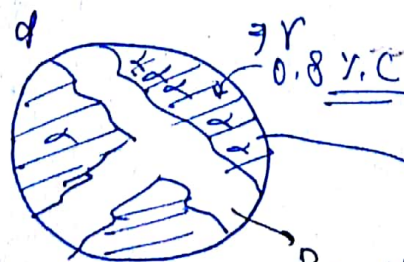
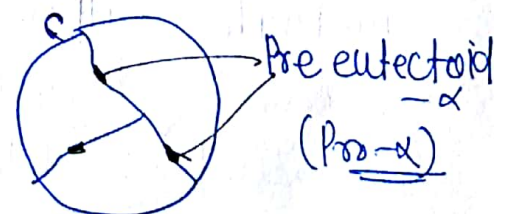
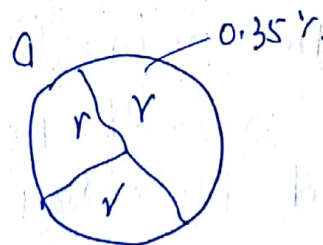
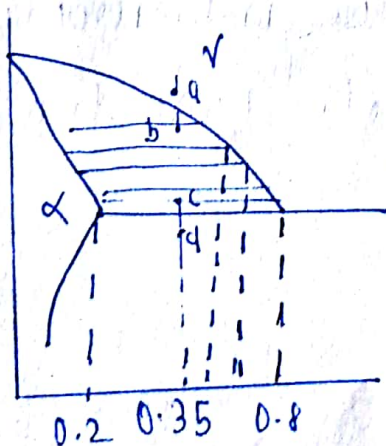
eg:- ~~ex~~ to produce 4.3 %

$$\begin{aligned} \%C &= 3.3\% > \text{So } C\text{-equivalent} \\ \%Si &= 3\% \\ &= 3.3 + \frac{1}{3}(3) \\ &= 4.3\% C \end{aligned}$$

{ Gray Cast iron }
2.4 - 4 %

By the addition of Si in liquid iron entire ~~iron~~ Fe-C diagram shift towards left and Graphite formation appears at much lower % of C. So when Si is added in liquid iron Graphite will be discharge and since it is having lower density, due to buoyancy force it come over the surface of liquid metal and sparkles. this phenomena called Kish.

Development of micro-structure in iron-carbon system:-



From pt b to c
%C in γ increase

Pro- γ + eutectoid- α
= total - α

A sample of hypoeutectoid steel is cooled along line a-d and its changes in microstructure are observed. At point a entire microstructure is Austenite with carbon uniformly distributed in it. To moment temp slightly decreases to point b, Ferrite start appearing in the microstructure. This Ferrite that appear before the eutectoid temp is called Pro-eutectoid Ferrite and it get accumulate at grain boundaries. Upon slowly decreasing the temp. from point b to c Following Conclusion can be drawn by using lever rule.

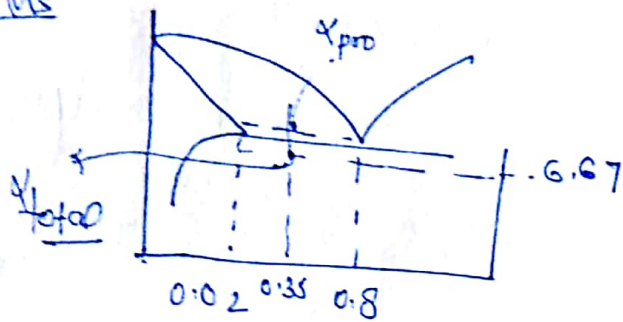
(i) upon decreasing the temp, mass fraction of pro-eutectoid Ferrite (x) increases -

(ii) % of carbon in austenite keeps on increasing and at point 'c' % of carbon will be exactly equil to eutectoid composition.

iii) The moment temp. slightly decrease to point d austenite within the grain converse into Ferrite. Amount of Ferrite present Ferrite microstructure is called eutectoid-Ferrite (

Problem:- What is the % of proeutectoid Ferrite, eutectoid Ferrite and total Ferrite in steel having 0.35 % carbon.

Ans



$$\alpha_{pro} = \frac{0.8 - 0.35}{0.8 - 0.02} = 0.577$$

$$\alpha_{total} = \frac{6.67 - 0.35}{6.67 - 0.02} = 0.95$$

So $Fe_3C = 1 - 0.95 = 0.5$

~~$\alpha_{eutectoid}$~~

eutectoid $\alpha \rightarrow 0.95 - 0.57 = 0.38$