

LECTURE NOTES
ON
Heat Treatment Technology



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METALLURGICAL ENGINEERING

GOVT. POLYTECHNIC SONEPUR

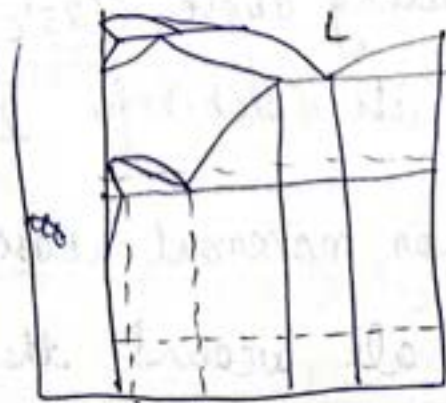
Principle of heat treatment of Steel

Introduction :-

- The different properties of the steel related to the structure of the material.
- The desired mechanical properties can be obtained by different process of heat treatment.
- The process consist of formation of austenite and obtained transform products i.e. perlite, Bainite, Martensite.

Formation of Austenite :-

- This is the preliminary step of heat treatment
- ⇒ Austenite is form on heating of hypoeutectoid, eutectoid, hypereutectoid steel above A_3 , A_1 , & A_{cm} respectively.
- Eutectoid steel formed at particular temperature but other steels are formed over the range temperature.



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✓ Mechanism of Austenitic Transformation

- Consider a steel of which is mixture of ferrite and cementite (pearlite).
- It is in the lamellar form i.e., alternating layer betⁿ ferrite and cementite.
- These layers are direct contact to each other.
- The cementite has 6.67% C & α has 0.02% C.
- The pearlite is stable ^{at room temp}, even there is a ^{carbon} concentration gradient betⁿ ferrite & cementite.
- It is ^{not} possible because below 200°C carbon movement is not able to take place.
- But when the temp. increases carbon get the ability to diffuse into ferrite.
- But the diffusivity is extremely slow because ferrite has the max^m solubility of carbon max^m upto 0.025%.
- ⇒ So, on heating above 723°C BCC iron changes to FCC and its solubility limit increases to 2.11%.
- Hence carbon movement easily takes place to distribute all around the matrix of the iron.
within

- is slow transformation starts at low temp.
- At any type of heating austenetic transformation takes place in the range of temp not at constant temp.
 - In this curve the end of transformation curve will not give any idea for homogeneous austenite.
 - So it is concluded that ^{homogeneous} austenite will obtain only when some time is given at the transformation temp.
 - This time for ^{getting} homogeneous austenite is called holding time.

Austenitic grain size :-

Nuclei of austenite is form as soon as steel is heated to at A₁ temp.

- Then these nuclei are grow till completion of ferrite and cementite transformation to austenite.

At the transformation a particular austenitic grain size is obtain. i.e. original grain size.

- But when the temp and time is given after homogeneous austenite formation then further growth takes place of this original grain.
- The grain size of austenite is very important because many mechanical properties depends on it such as tensile, compressive, impact, yield strength.
- Acc. to the grain growth grain size is ~~depen~~ classified into 2 types : i) Inherently fine grain steel
ii) Inherently coarse grain steel.

i) Inherently ~~fine~~ coarse grain steel :-

- If the steel has coarser grain then the austenitic grain size also coarser in size because coarse grain provide less nucleation site for the austenitic transformation.
- If less nuclei is formed at high temperature it grows easily to form coarser grain in austenite.

ii) Inherently fine grain steel :

- If the steel has fine grain then the nucleation site is more and the no of austenetic nuclei will form at the grain boundary.
 - Hence, due to the higher nucleation its growth is restricted due to the impingement of and fine grain is obtained in the austenite.
 - It is also found that if the steel contain carbide, nitride, oxide then it restrict the growth of austenetic grain because these are refractory materials and they are not moved with the iron and carbon but deposited at the grain boundary and restrict the growth of austenite.
- So these kind of steel form fine grain steel.

Determination of austenetic Grain size :-

The most popular method for designating the austenite grain size has been developed by ASTM (American society of testing materials) where, i.e

$$n = 2^{N-21}$$

where n = average of grain per square inch at
 N = grain size index

Methods of determination of Austenitic Grain Size

HEYN'S INTERCEPT METHOD:-



- This method is applied when the grains are not in equi-axed.
- Here count the numbers of grain intercept by a line of known length.
- The length of the line is 0.005 inch and the grain is counted at (1000 $\times$) magnification.
- This number of grain is called mean intercept.
- Similarly 10 numbers of measurement at 10 different places & the avg. is taken.
- Then according to ASTM grain size number n

$$n = \frac{2 \log I}{\log 2} + 3$$

MC Quaid Method :-

- This principle involve carbonising the steel at 925°C for 8 hours followed by slow cooling in the furnace.
- Longer carbonising period and slow cooling upto room temp. resulting ^{precipitation} of carbide at grain boundary.
- This precipitation of carbide at grain boundary facilitate the estimation of grain size.

Etching Constant Method :-

- This method is generally employed for harden steel in which the structure should be completely martensitic.
- This method consist of etching the specimen, which is prepare for the metallography.
- In general, the solⁿ contain 5 ml HCl, 1 gm picric acid and 100 ml ethyl or methyl alcohol.
- This etching operation developed an excellent contrast betⁿ two grain which can be easily counted by using metallurgical microscope.

Importance of Austenitic Grain Size :-

- There is various effect of grain size in the properties of the steel.
- The yield strength of the material is depend on the grain size which is expressed by "Hall-petch equation".

$$\sigma_0 = \sigma_i + k_y D^{-1/2}$$

where σ_0 = yield stress/strength

σ_i = frictional stress opposing the motion of dislocation.

k_y = amount of dislocation piled up at the grain boundary.

D = Avg. grain diameter.

- Grain size also influence the impact strength increase of low carbon steel if the grain size is increase its transition temp also increases, which make the steel highly prone to brittle failure.
- Coarse grain steel ^{has} better creep resistance than fine grain steel above the equi-cohesion temp & vice versa.

Decomposition Of Austenite :-

Austenite is a solid solⁿ of carbon in γ iron.

→ Acc. to iron carbon equilibrium diagram decomposition takes place at A_1 , A_3 & A_{cm} temperatures. per eutectoid, hypoeutectoid & hypereutectoid respectively.

→ During decomposition carbon movement takes place.

→ Some carbon move from their original position to the other position to combine and form Fe_3C .

→ The place where the carbon leave decreases the carbon concentration and form α -iron.

→ Similarly in hypo & hyper case pro-eutectoid α and pro-eutectoid ^{Fe}cementite form respectively from the austenite.

→ The process of decomposition of austenite to form ferrite and cementite is a diffusion process. i.e both carbon & iron atom move ~~to~~ each other for peritectic transformation.

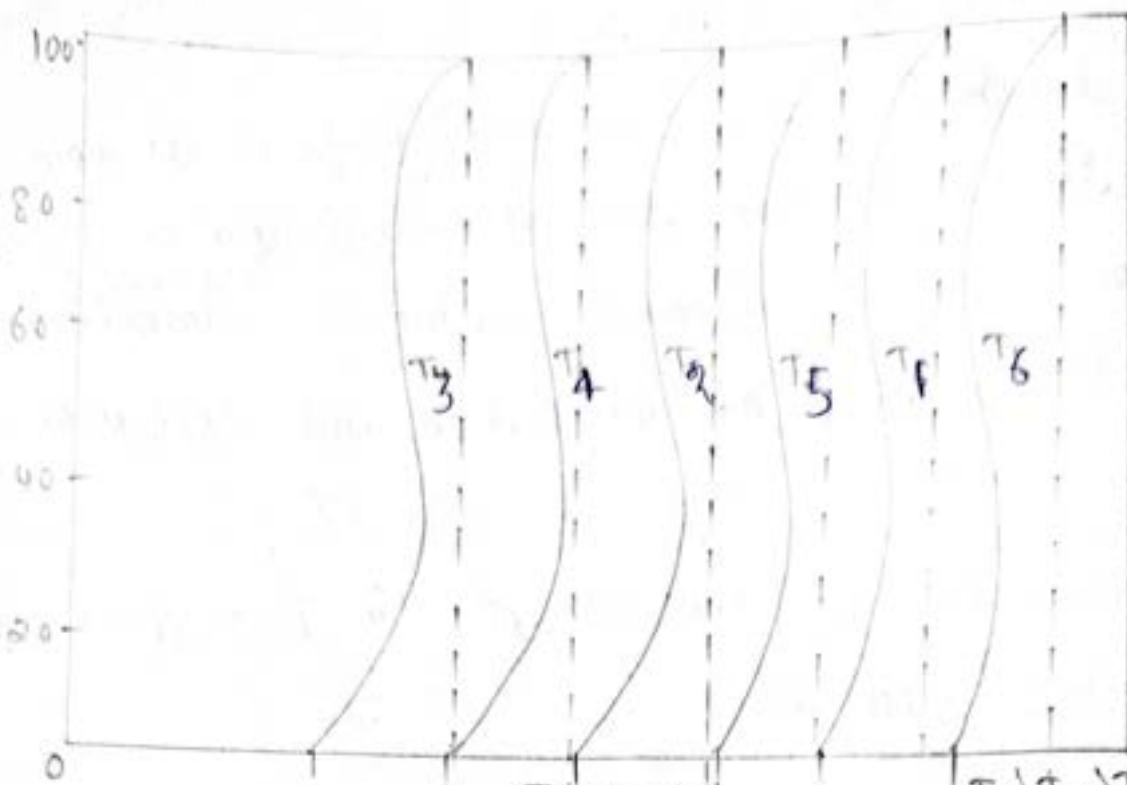
- The process of decomposition of austenite takes place in such a way that when pearlite will form automatically ferrite and cementite is in lamellar form.
- The diffusion takes place at higher temperatures so pearlitic transformation required higher temp.
- When the transformation temp. further decreases the rate of diffusion decreases and only carbon movement takes place to form Bainite.
- Further decrease in transformation temp. completely stops the diffusion and a diffusion less product is obtained i.e. martensite, which has B.C.C B.C.T crystal structure.

Time, temperature - Transformation Curve :-

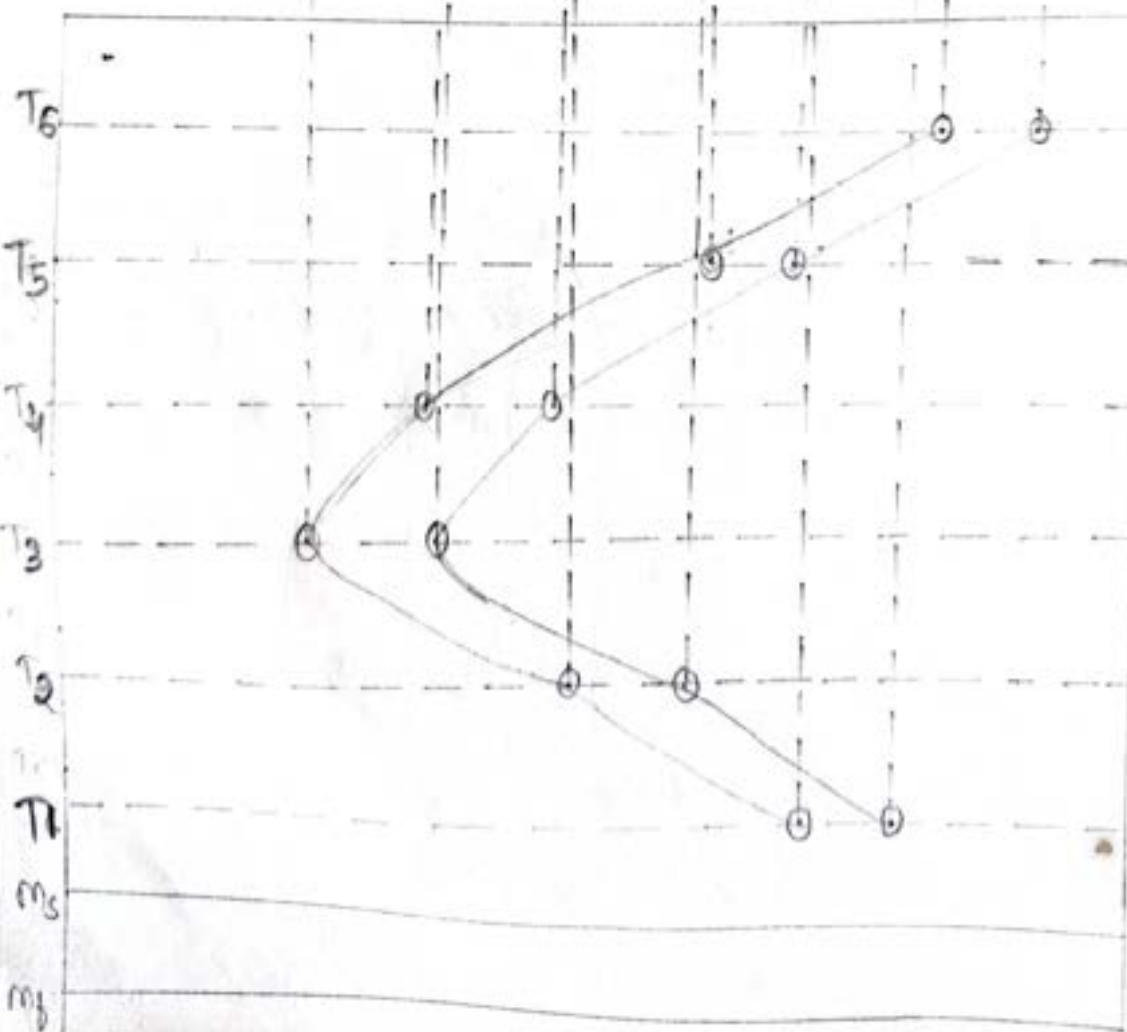
- The decomposition of austenite is very important because the product which obtained has special mechanical properties.
- The kinetics of transformation is better studied in transformation at a constant temperature rather than ~~rather~~ continuous cooling.
- It is also called iso-thermal transformation.
- A no. of small samples are taken from the same steel with equal size.
- All the steels are heated to its ^{ising} austenite temp and holding at this temp to get homogeneous austenite.
- Then all the samples are quickly transfer to the another bath maintained at a constant temp. below the A_1 temp.
- Then all the samples are taken one by one after definite interval of time and quenched.
- The % age of martensite depends on the determine % age of transformation of austenite into martensite

T.T.T Curve

% of austenite transformation →



Temperature →



Effect of Alloying element in TTT diagram :-

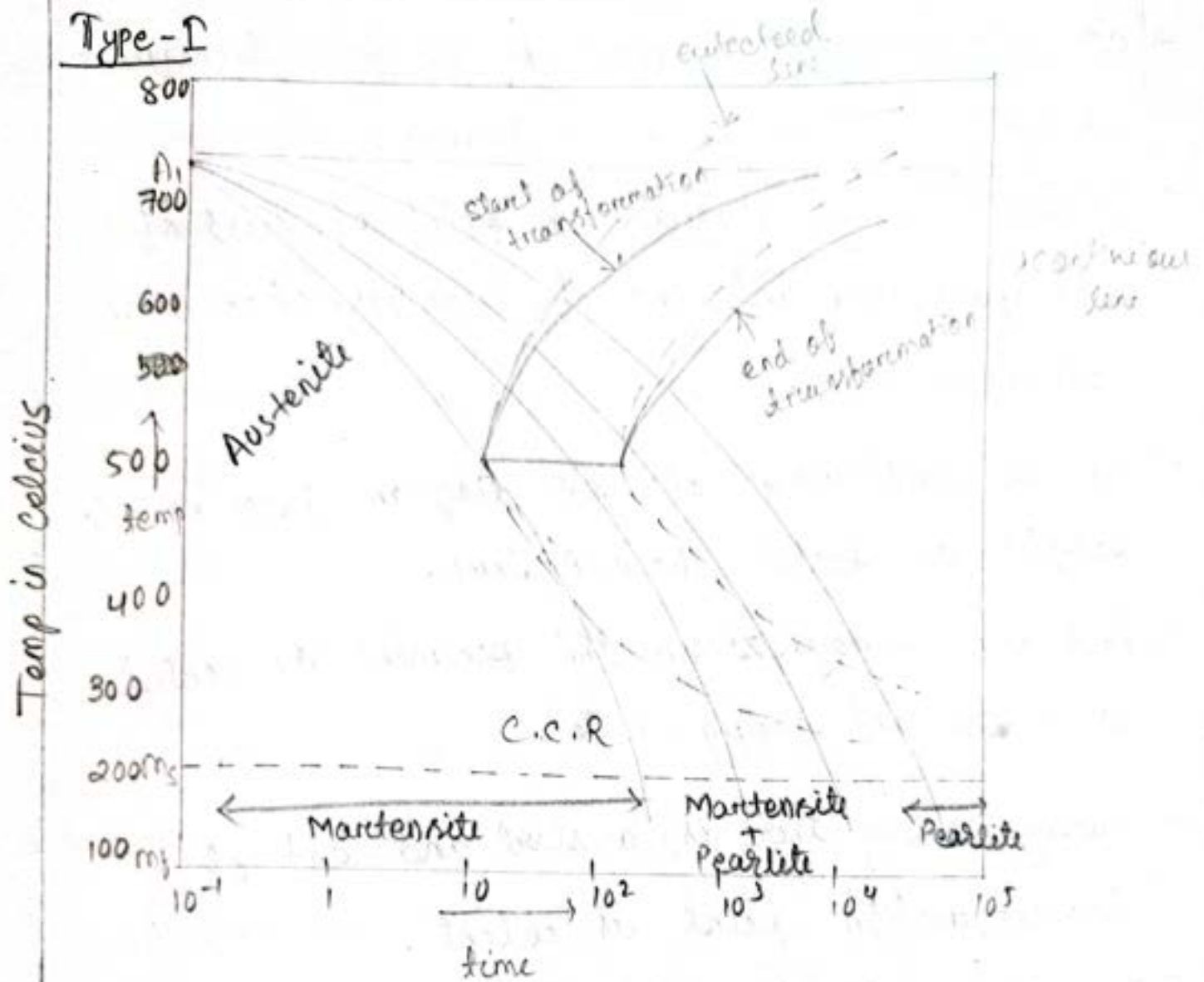
- Almost all alloying element ~~except~~ ^{except} cobalt decreases the rate of decomposition of austenite because all carbides are more stable than the cementite.
- So it restricts the diffusion of carbon and formation of cementite. Hence, the decomposition of austenite takes so much time for the transformation.
- Alloy affects mainly on the formation of pearlite ~~iron~~ because it involves both iron and carbon diffusion.
- But the effect is very less in Bainitic transformation because only carbon atom diffusion takes place.

Classification of TTT diagram for alloy steel :-

- It is classified into 4 types

C.C.T

c.c.r = Critical cooling rate



→ This diagram is develop because all the industries practices are follow the continuous cooling ^{mode} rather than iso-thermal cooling to decrease the productivity as well as availability.

→ This diagram co-relate the transformation, time and continuous cool, which is most useful for diffⁿ heat treatment process.

- CCT diagram can be obtained by the same technique at which T.T.T diagram is drawn.
- In case of C.C.T diagram the point of start of transformation and end of transformation is in continuous form.
- For the construction of C.C.T diagram large no. of samples are heated above A_1 temp.
- And after homogenization the specimens are cooled at a constant cooling rate.
- During cooling there is a start and end of transformation point is obtained.
- By joining all the points C.C.T curve can be drawn. plotted.
- This curve gives the idea about C.C.R (critical cooling rate) (e.g. open eutectoid steel)
- If the cooling rate is greater than C.C.R then martensite will obtain.
- If the cooling rate is slower than C.C.R then pearlite will form.
- There is no isothermal transformation takes place during the continuous cooling.

Pearlitic Transformation

- It is a eutectoid mixture of 2 phases mainly ferrite and cementite.
- It consists of alternating layers of ferrite and cementite.
- It is formed when the sample is slowly cooled.
- Pearlite content 88% α (ferrite) and 12% Fe_3C (cementite)
- One of the important aspects in pearlitic transformation is the formation of 2 entirely different phases:
 α (0.025% C, BCC) and Fe_3C (6.67% C, Orthorhombic)
- This is possible only due to the diffusion of Carbon and iron atoms.

Mechanism of Transformation

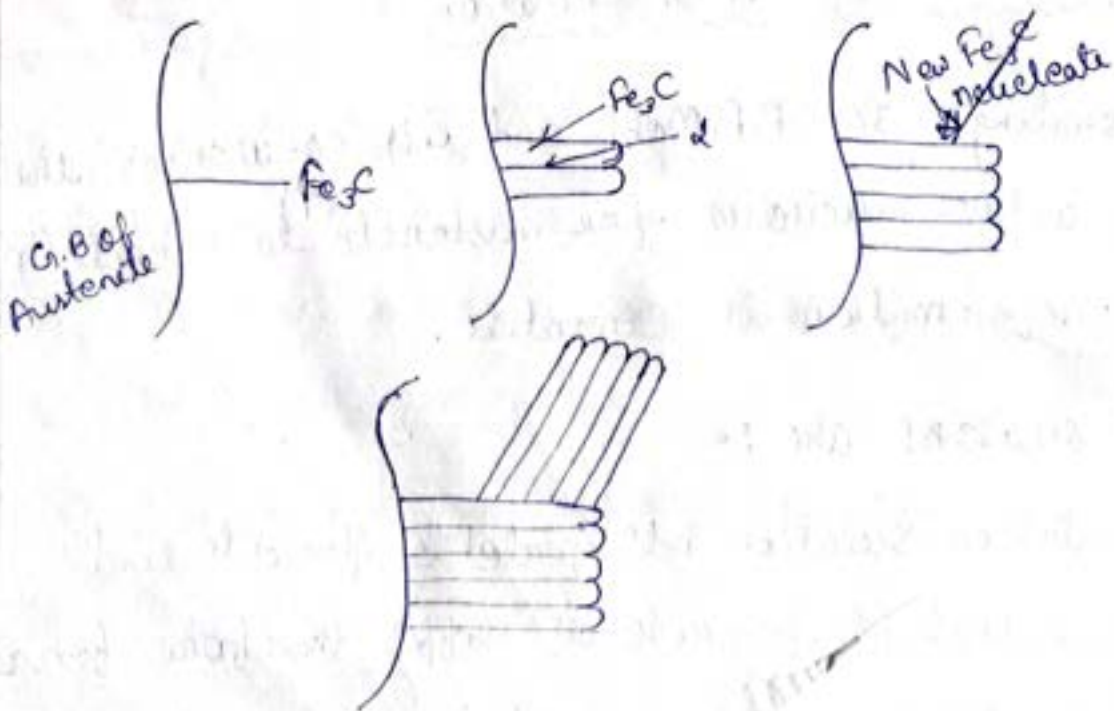
- According to R.F. Mehl and his co-workers that the active nucleus for austenite (A) to pearlite (P) transformation is cementite.
- The reasons are :-
 - Orientation relation between pearlitic ferrite and pro-eutectoid ferrite is different therefore ferrite can't be an active nucleus.

ii → Formation of pearlite is affected by the presence of cementite but there is no effect with the ferrite - of the existence of ferrite.

iii → Pro-eutectoid cementite and eutectoid cementite platelets are generally parallel in nature to cementite spherul nucleate.

→ But acc. to Smith for the pearlitic ~~both~~ transformation both ferrite and cementite can be the active nucleous.

→ The most popular model proposed combinely by F.C. Hall and R.F. mehl that is



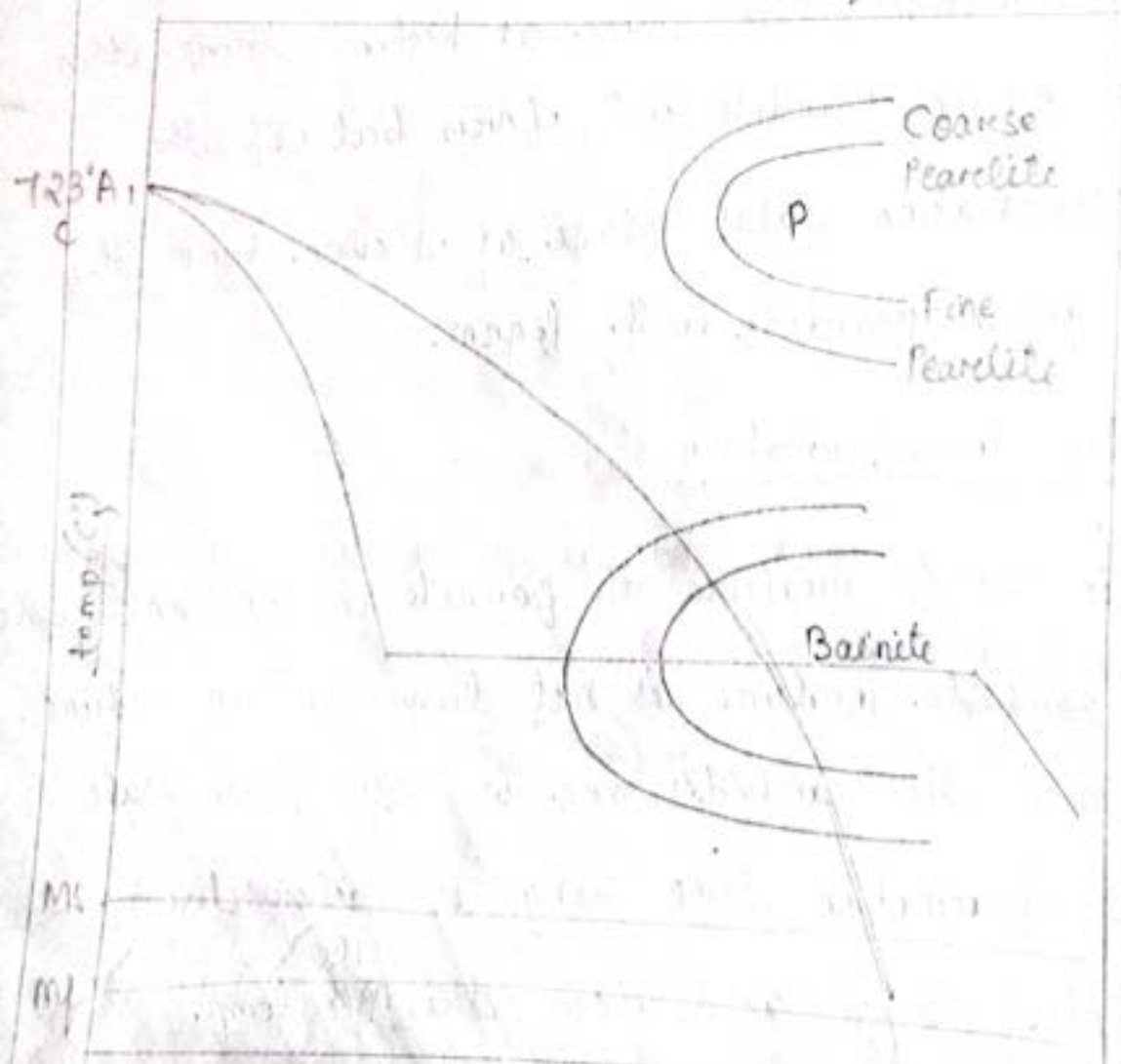
- The formation of pearlite is a diffusion controlled process.
- Initially the rate of decomposition is slow but it increases upto some temp. and again decreases to become zero.
- With this respect pearlite transformation rate increases upto a certain temp and again decreases.
- The curves 'a' & 'b' give the information that if the transformation takes place at higher temp. then coarse grain pearlite will form but if the transformation takes place at lower temp then fine grain pearlite will form.

Bainitic Transformation :-

- Bainite is a mixture of ferrite and epsilon carbide.
- This carbide mixture is not lamellar in nature and also the carbides are in very finer scale.
- Bainite formation temp range is below the M_s pearlitic range and above the M_f temp.

- For a eutectoid steel the ~~bainite~~^{bainite} range is 200°C - 500°C.
- The temp where transformation start is ~~Bs~~ B_s and the end of transformation temp is B_f .
- The bainitic transformation takes place either isothermally or by continuous cooling. ~~but is special~~
- ~~Q&Q~~
- In general eutectoid steel bainite will be form only by iso-thermally.

Mechanism:-

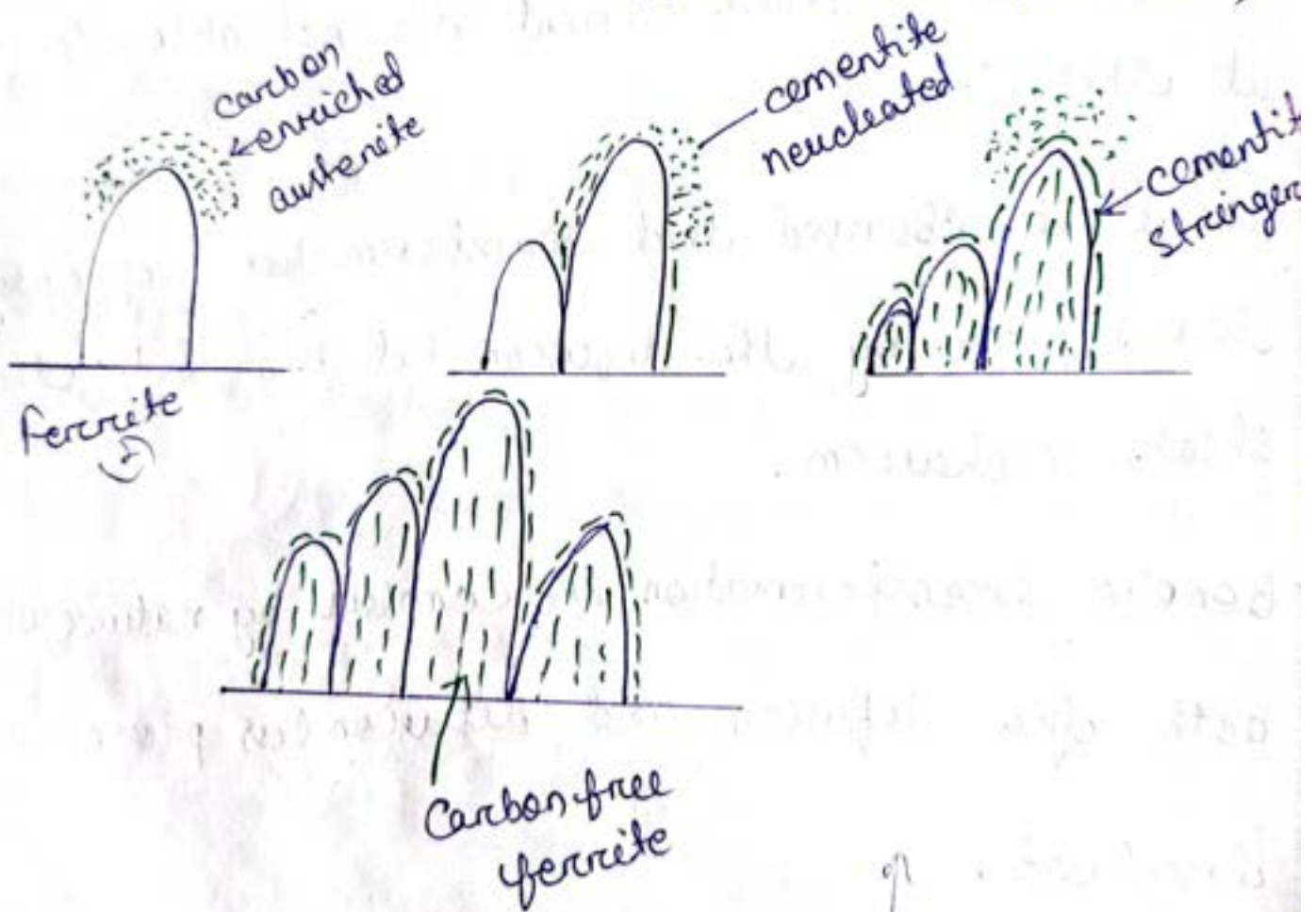


- It is also a diffusion controlled process but the formation of bainite starts at a temp. where the diffusion of iron atom very slow or zero.
- So, for this transformation carbon diffusion is very important.
- ~~except~~ ^{except} carbon other element also not able to move at this temp.
- So, it is observed that transformation not only takes place by the diffusion but also with the shear mechanism.
- Bainitic transformation is complex by nature where both the diffusion and diffusionless process are involved.
- The shearing is due to formation of carbon concentration gradient in the austenite matrix. i.e due to the carbon diffusion some places are enriched with carbon and some are depleted to the carbon.

→ This gradient creates internal stress which is responsible for shear of the iron atom.

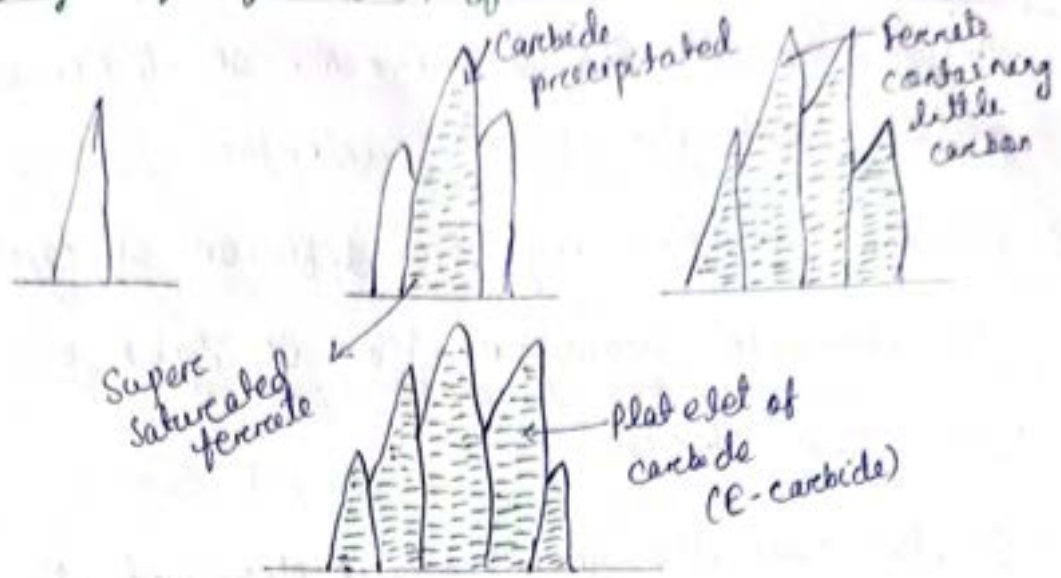
Q-6: Bainitic structure :-

There are 2 type of structure are obtent during bainitic transformation → Upper bainite (Feathery)
→ Lower bainite (Acicular)



Stages of formation of upper bainite :-

Stages of formation of lower bainite:-



- The micro structure of upper bainite consist of ^{lath}~~large~~ shaped ferrite with precipitated carbide parallel to the ^{needle}~~middle~~ axis.
- But the lower bainite consist of ferrite plates within which carbide precipitated at some angles.
- Both upper and lower bainite nucleated by ferrite.
- Ferrite is form when low carbon austenitic region is found.
- The ferrite is initially nucleated and grow into bainitic plane when the holding temp is at bainetic range.
- At the sides of the ferrite carbon is enriched in austenite.

- And finally it leads to formation of cementite at the austenite - bainite interface.
- Stringer is form by the diffusion of carbon but the ferrite transformation is takes place by the shear forces.
- In this way the growth takes place and the upper bainite is form in the ^{feathery} fibrous nature.
- The lower bainite is differ from upper bainite with respect to the transformation temp.
- In the lower bainite super saturated ferrite is nucleated by shear mechanism. ~~due~~ ^{Due} to the low temp carbon diffusion is slow, so its depletion process is also slow resulting formed of super saturated ferrite.
- At the interfaces of ferrite and austenite carbides are precipitated and an intermetallic compound is form i.e; iron carbide or ~~epitaxial~~ ^{Fe}-carbide which is nucleated from super saturated ferrite.
- So its growth creat some angle to the ferrite nuclei and form a ~~with~~ needle like structure in

BCC - " = 1.08

soft metal - f.c.c
(lead, copper, zinc, gold)

the matrix is called acicular.

Martensite Transformation :-

- The transformation of martensite is completely diff" from pearlite and bainite transformation.
- Martensite Transformation takes below 200°C , at this temp the carbon and iron atom diffusion is completely negligible.
- So a diffusion less transformation takes place.
- During transformation γ iron changes to α iron as no diffusion of carbon or iron atom at this low temp.
- So the α -iron form which has the same chemical composition with the γ iron.
- That is carbon is present in ferrite iron in super saturated state.
- Accordingly martensite can be defined as a super saturated interstitial solid solⁿ of carbon in α iron.
- So martensite acquires BCT crystal structure.
- The tetragonality is due to presence of higher

amount of carbon and has the C/a ratio ≈ 0.8 ~~100~~ ^{0.8, 33}.

Q.32

Mechanism :-

(rapid cooling)

- Martensite is formed by quenching of austenite.
- On quenching the rate of diffusion of both the atom decreases and transformation doesn't take place by diffusion, so it may be called a ^adisplacible transformation that takes place by co-operative movement of a large no. of ~~near~~ neighbouring atom.
- But each atom moves a distance which is less than the one atomic distance.
- When the temperature decreases to room temp. from A_1 , then the driving force for the transformation is max^m.
- Hence, the transformation takes place by the movement of individual atoms.

Retained Austenite

- If the austenite present at room temp due to faster cooling then that is called retained austenite.
- In simple word retained austenite is the untransformed austenite.

- Austenite transform to martensite on rapid cooling, below M_s temp and above M_f temp.
- Both M_s and M_f temp. decreases with increasing in carbon content.
- So amount of retained austenite increases with increasing the carbon %age.
- All alloying element except Al & Co decreases the M_s temp..
- Hence the ~~sub~~ formation of retained austenite increases.
- Retained austenite is diff^r than the parent austenite that it has higher amount of dislocation and many other imperfection.
- It decreases the strength of the material.
- When retained austenite is undesirable then 2 treatments are adopted for removal of retained austenite, those are :- tempering and subzero treatment.

Heat Treatment Of Steel

→ Introduction :-

- Metals and alloys are used in diffⁿ places due to diffⁿ property.
- These mechanical property are controlled in the metal by alloying element, grain size and heat treatment.
- (Out of this all factor heat treatment mostly affect the mechanical properties.)

→ The diffⁿ heat treatment processes are

i) Annealing

ii) Normalizing

iii) Hardening

iv) Tempering

v) Marit Tempering

vi) Aus Tempering

vii) Sub-zero Treatment

Stress Relieving :-

→ This process is employed to ~~release~~ relieve internal stresses, no microstructural changes occur during this process.

→ (Internal stresses are developed in the body due to application of diffⁿ processes i.e.

casting, welding, machining, grinding, hammering, case hardening and phase transformation.

- These internal stress affect the property of the steel. so it should be removed before use in the process.
- The process consist of. heating the steel to a temp. below the A₁ temp, holding at this temp for sufficient time followed by uniform cooling.
- Cooling is the most important factor because if the cooling rate is fast then internal stress again produce in the body material.
- (Alloy steels has the higher austenitic range so, these steel can heated at higher temp for the stress relieving).

i) Annealing -:

- It is a process where steel is heated to a pre-determined temp. holding at this temp. followed by cooling at a very slow rate.
- The temp to which steel is heated and holding time are determined by various factors.

Various factors such as

- i) Chemical composition
- ii) Size, shape and desired property of the steel

Objective of Annealing

The purpose of annealing

- i) Relieve internal stresses develop during solidification
- ii) machining, rolling and welding
- iii) Improve or restore the ductility and toughness
- iv) Enhance machinability
- v) Eliminate chemical non-uniformity
- vi) Refine grain size
- vii) Reduce the gaseous content in steel

Classification of Annealing

A) Annealing treatment can be classified on the basis of i) Temp of treatment.

ii) Phase transformation

iii) Purpose of treatment

i) Temp. of treatment $\rightarrow$ Acc. to the heat treatment temp. it is classified into 3 category

i $\rightarrow$ full annealing

ii $\rightarrow$ Partial annealing

iii) Subcritical annealing

ii) Phase Transformation $\rightarrow$ First order annealing
Second order annealing

iii) Purpose of treatment $\rightarrow$

i) Diffusion annealing

ii) Spheroidizing annealing

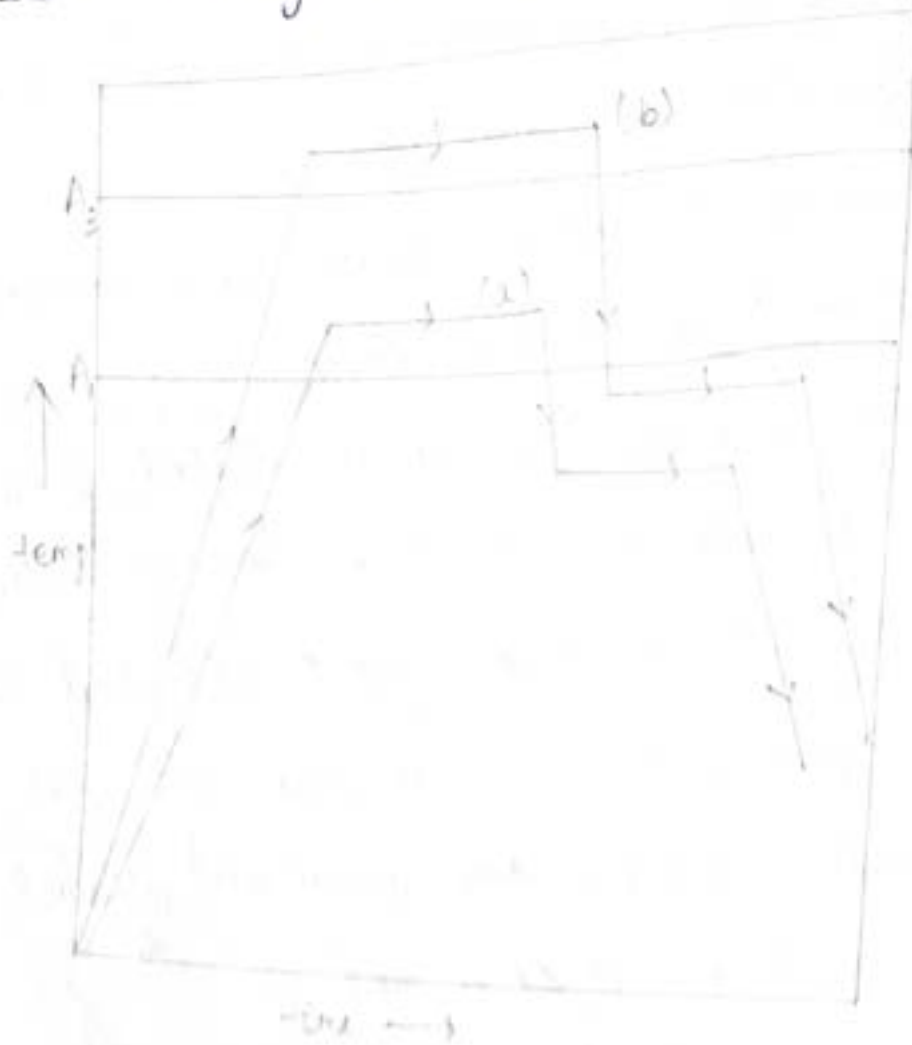
iii) Re-crystallization annealing

iv) Process annealing

1) Full annealing $\rightarrow$ It consist of heating the steel to austenitic region, holding at this temp followed by slow cooling. such as cooling in the furnace.

$\rightarrow$ Steel is heated to above $30-50^{\circ}\text{C}$ above the critical temp and hold at this temp for homogeneous austenite.

→ It is restricted to larger component because sudden cooling to ^{below} A_1 temp is not possible.



(a) = eutectoid steel

(b) = hypo-eutectoid steel

Diffusion Annealing

- This is also called homogenizing annealing.
- It is employed to eliminate chemical non-uniformities, columnar grains, dendrites.
- These defects are observed mostly in high carbon and high alloy steels.

- All these defects promote the brittleness property and ^{decrease the ductility} and toughness.
- In this annealing steel is heated about 1000 to 1200°C and held at this temp for longer time i.e. about $10-20$ hour followed by slow cooling.
- If the steel containing segregated zone that can be completely eliminated by this process.
- Due to higher temp. heating and max^m holding time grain coarsening takes place.
- During ~~slow~~ cooling it gives coarse pearlite, which is not desirable, but it is only carried out to eliminate above defects.
- At high Temp scaling takes place which increase the metal loss.
- Due to grain coarsening a secondary heat treatment needed for getting required property.

Partial Annealing:-

Partial annealing is also called inter critical anneal or incomplete annealing.

- In this process steel is heated ⁱⁿ betⁿ the lower A_1 & A_{cm} followed by slow cooling.
- This is mainly carried out for hypereutectoid steel.
- The microstructure consist of pearlite & cementite.
- The pearlite is fine in nature, and cementite present in the grain instead of grainboundary which gives better mechanical property.
- It is a less expensive due to low temp involvement.
- This steel has higher machinability.
- Hypo-eutectoid steels are not subjected to this treatment because α & pearlite combination decreases the mechanical property.

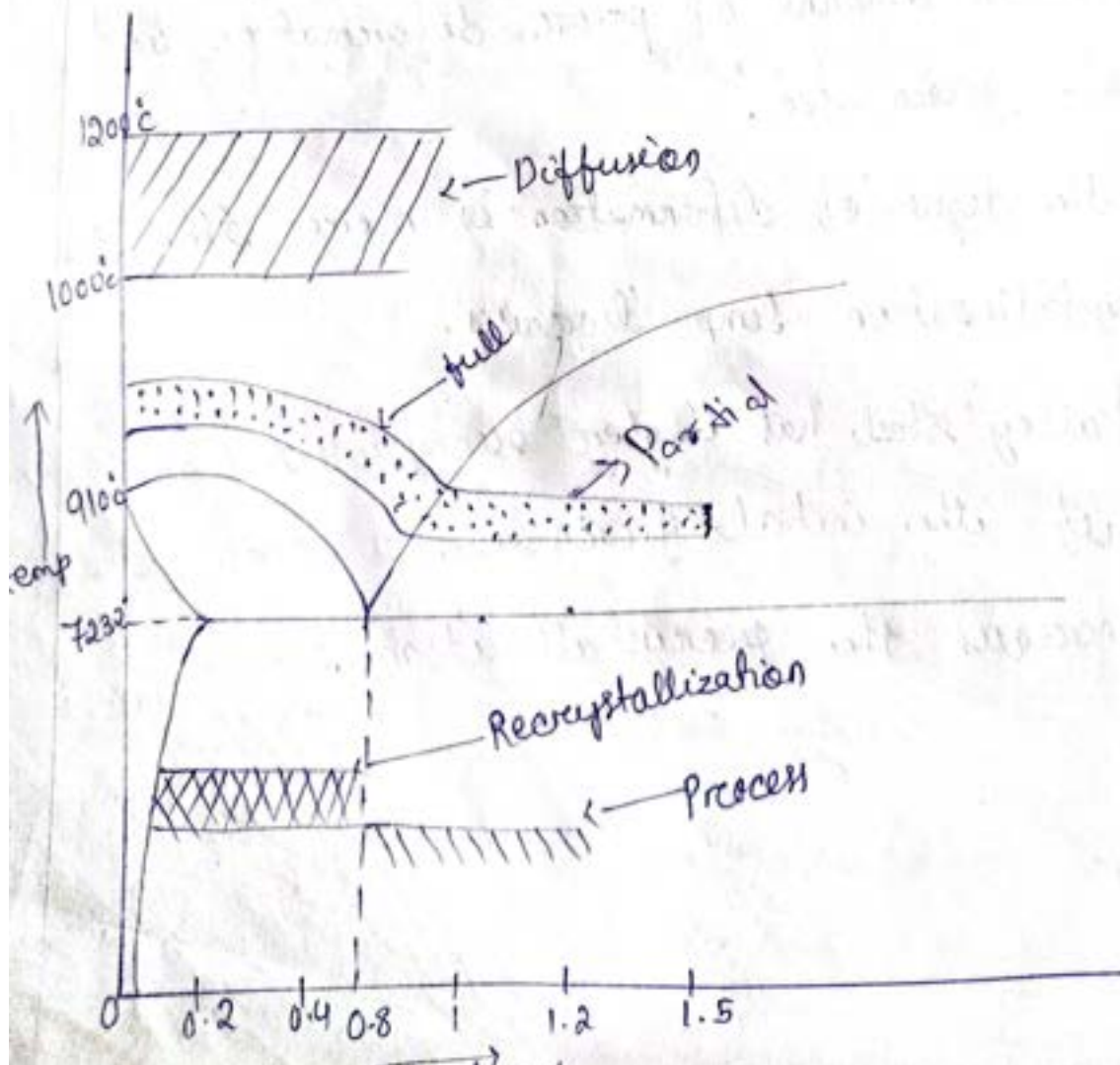
Recrystallization Annealing :-

- The process consist of heating the steel above the recrystallization temp, holding at this temp followed by slow cooling.

- It results decrease in hardness and strength and increase in ductility.
- This treatment may be the final treatment in the industrial manufacturing process, because due to the recrystallization all the internal stress are removed which is born during the working operation.
- The temp of recrystallization annealing is not fixed, it is completely depends on chemical composition amount of prior-deformation and initial grain size.
- If the degree of deformation is more then the recrystallization temp decreases.
- High alloy steel has higher recrystallization temp and if the initial grain size is coarse then as increases the recrystallization temp.

Process Annealing : (Sub critical annealing)

- In this process steel is heated to a temp. below the lower critical temp (A_1) temp, held at this temp for sufficient time followed by slow cooling.
- The purpose of this treatment is to reduce hardness but increases ductility.
- The process is less expensive compare to other.
- It is differ from recrystallization annealing because recrystallization may or maynot take place in this annealing.



Spheroidizing Annealing :-

- It is a heat treatment process which results consist of globules or spheroids of carbide in the matrix of ferrite.
- This is possible when ~~coagulation~~^{coagulation} of cementite takes place.
- This process consist of heating steel to a temp just below the lower critical temp. holding at this temp for long period followed by slow cooling.
- Another method involve heating the steel just above the A_1 , followed by cooling to a temp just below the A_1 temp & held at this temp and ^{till} all the carbide changes to spheroids.
- Eutectoid steel and hypereutectoid steel both are heat 20-30°C and 30-50°C respectively above the A_1 .
- It improves machinability as well as ductility.
- Hypoeutectoid steels are not subjected to this process because ~~high duct.~~ softness & increases the sticky or gumming nature in the metal.

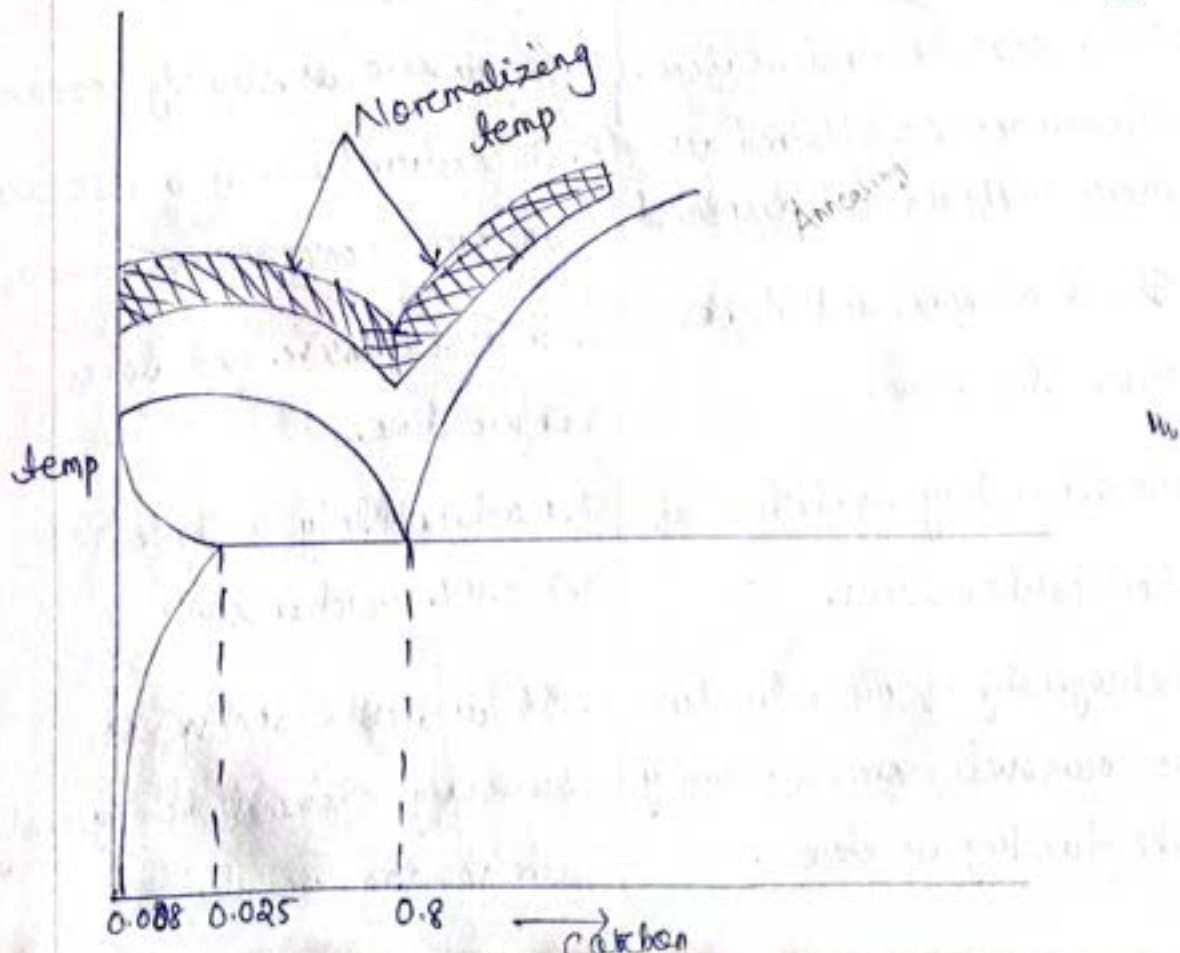
Normalizing :-

- Normalizing is a process of heating steel to about 40-50°C above the upper critical temp. and the holding for proper time followed by cooling in still air or slightly agitated air.
- All the steels are heated above A_3 and A_{cm} for hypo and hypereutectoid steel.
- After normalizing the resultant microstructure is fine pearlite.
- The cooling rate is slightly faster than the annealing.
- Due to the presence of fine pearlite, it has better mechanical property than the annealed structure.
- The structure depends on the thickness of the material.
- If higher thickness materials are subjected to this process, then the grain size is finer to coarser from surface to centre.
- This process is generally employed for eliminating chemical inhomogeneous and increase the

mechanical property.

- By normalizing and optimum combination of strength and ductility is obtent which is specially required for high level of mechinability.
- Normalizing is a very effective process to eliminate the carbide network, which is not able to be eliminated during annealing, but due to shorter cooling time carbide network doesnot able to appear in the structure.

Differentiate both Annealing and Normalizing:-



Differentiate betⁿ Annealing and Normalizing :

Normalizing

1. Higher hardness, strength (with low ductility) which increase with the increase of carbon of the steel.
2. Internal stresses are more due to faster air-cooling used.
3. As the temperature of transformation lowers, fine pearlite is obtained.
4. Grain size obtained is fine.
5. Microstructure obtained is more uniform and dispersed.
6. It is cheaper and takes much less time.
7. Machinability is better of low carbon steels.
8. Heterogeneity of microstructure is removed more efficiently like banding in steel.

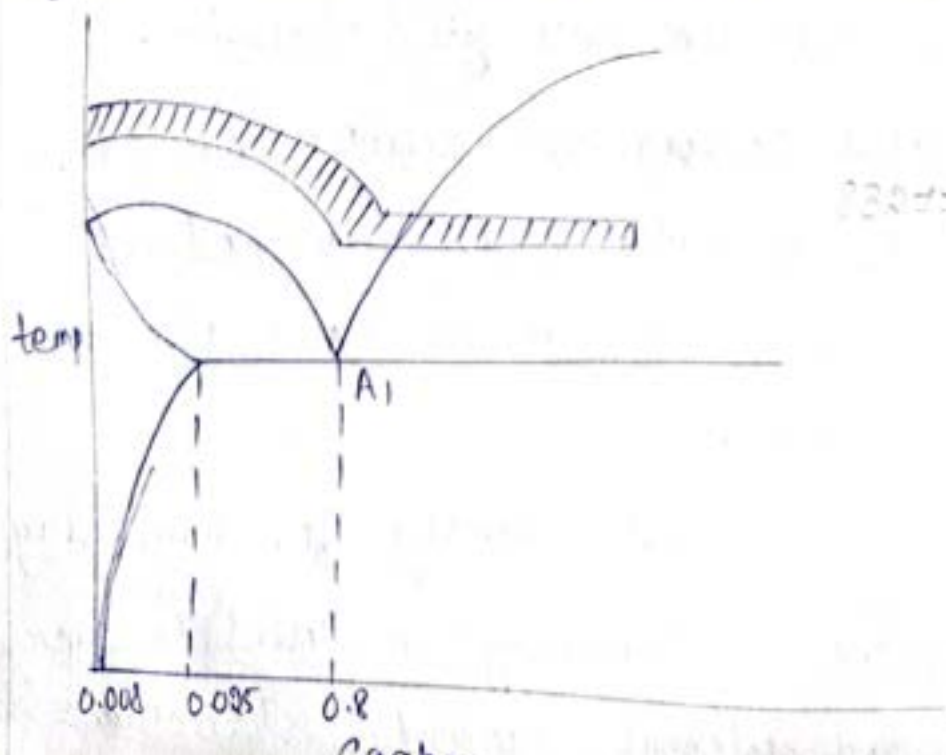
Full-annealing

1. Lower hardness, strength & with high ductility.
2. Internal stresses are minimal.
3. Temp of transformation is at or close to A_1 producing coarse lamellar pearlite.
4. Grain size is slightly coarser.
5. Microstructure is a bit less uniform (compare 10.55 0_2 and 0_1).
6. It is expensive and takes longer time.
7. Machinability is better of 0.3-0.4% carbon steels.
8. It is less effective in removing chemical heterogeneity like banding in steel.

Hardening :-

Hardening treatment consist of heating the steel to austenizing temp / hardening temp, holding at that temp followed by rapid cooling / quenching in water, oil or salt bath.

- The high hardness develop by the process due to phase transformation from austenite to martensite
- For hardening the cooling rate should be equal to or more than the C.C.R
- For hypoeutectoid steel, it should be heated above $50-50^{\circ}\text{C}$ above the A_3 , whereas eutectoid and hypereutectoid steels are heated $30-50^{\circ}\text{C}$ above A_1



as well as increases mechanical property.

Factors affecting hardening method :-

The different factors which affect the hardening treatment are :-

- i) ~~Chemical~~ composition (ex-Carbon (hardener))
- ii) Size and shape
- iii) hardening cycle (heating rate, holding time, cooling rate)
- iv) homogeneity and grain size of austenite (γ)
- v) quenching media
- vi) Surface condition

i) Chemical Composition :-

- It is largely determines the hardening temp. because some elements are changes the critical temp.
- Some element also increases the formation of retained austenite. and retards ~~more~~ martensitic transformation.
- Carbide forming element decreases the martensitic temp.

ii) Size and shape :-

→ Larger parts are difficult to complete transformation to martensite because a thermal gradient occurs betⁿ the surface and the centre.

→ Larger parts heat removal from the centre is slow, which promote to pearlitic transformation rather than martensitic transformation.

→ ^{For the} Integrated shapes the corners and then the transform to martensite much rapidly which causes ~~the~~ developing of highly internal stress resulting ~~peeping~~ cracking.

iii) Hardening cycle :-

→ For complete hardening the austenite should be homogeneous, which ~~obtain~~ ^{obtain} by heating of hypo-eutectoid steel 30-50°C above A_3 .

→ And heating of eutectoid and hypereutectoid steel 30-50° above A_1 .

→ For better martensitic transformation the cooling rate should be just above C.C.R to avoid formation of internal stress.

iv) Homogeneity and grain size of Austenite :-

- martensitic transformation largely depends on the grain size of austenite.
- If coarser austenite will form then it converted to coarser martensite and doesn't give sufficient amount of required hardness.
- And also if in-homogeneous austenite transform to martensite then anisotropic characteristics will found in the martensite.

v) Quenching media :-

- Quenching medium is the important consideration which provide cooling rate of specimen.
- The medium characteristics such as temp, specific heat, boiling point, thermal conductivity should be large enough to provide required cooling rate.

vi) Surface Condition :-

- The surface should be free of iron dust, oil, oxides, because all act as a insulation for heat conduction to the quenching medium and decrea

the cooling rate.

Hardening Methods :-

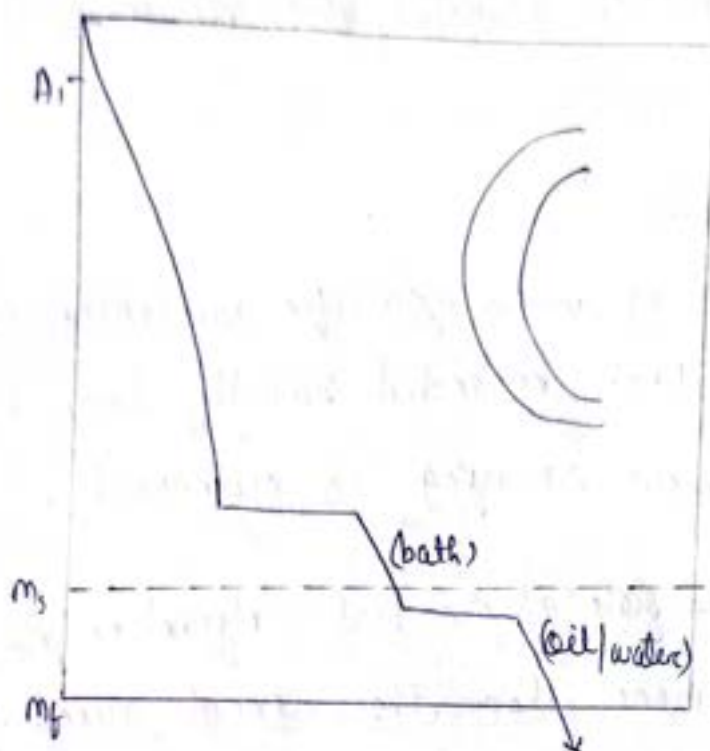
- Hardening can be employed in steel components in several ways depending upon the quenching procedure.
- The diffⁿ methods are:
 - i) direct quenching (simplest)
 - ii) quenching in stages in diffⁿ (less stress than direct) media
 - iii) spray quenching
 - iv) self tempering
 - v) Aus II are iso-thermal quenching
 - vi) mar tempering / stepped quench

i) Direct quenching :-

It is the conventional and ~~the~~ simplest quenching method which consist of heating the steel component to hardening temp, holding at this temp followed by direct quenching. This is the cooling process where highly internal stress develop resulting cracking, which is not desirable.

→ It is carried out only for smaller components.

ii) Quenching in stages in diffⁿ media :-



Date :-

- It consists of quenching steel part from hardening temp to a bath maintained at a temp above M_s .
- In the bath the sample is ^{held} for some time followed by cooling in water or oil.
- The care should be taken that the holding time shouldn't touch the bainitic transformation starting time.
- In this process internal stress developed is less than the direct quenching method.

- This is because of 2 reasons. firstly → reduce severity of quenching.
→ due to stages of quenching less internal stress develop.

iii) Spray quenching :-

Spray quenching is a specific hardening method in which steel part is cooled rapidly from hardening temp by continuous spraying of quenchant.

- In this case the rate of ~~ex~~ heat extraction from steel part is more than the direct quenching method.
- Water is commonly used as a spraying quenching media.

iv) ~~Soft~~ Tempering :-

- Hardening treatment develop maximum hardness and strength of the material but it has an adverse effect to the other mechanical properties such as ductility, toughness and impact strength.
- It also increases brittleness property.
- The degree of brittleness depends on the severity of quenching and carbon content in the steel.

→ The brittleness and internal stress should be decreased before application hence, a process is developed which consist of heating hardened steel below the lower critical temp, holding at this temp followed by slow cooling.

→ This process is called Tempering.

→ Tempering treatment result optimum ^{combination} ~~condition~~ of mechanical property.

→ Hardening followed by tempering is the only conventional heat treatment method to achieve optimum mechanical property.

Stages of Tempering :-

→ A no. of structural changes takes place because due tempering treatment.

→ This changes is due to iso-thermal transformation of retained austenite and ejection of carbon from BCC crystal structure.

1st stage of Tempering; (upto 200°C)

At this temp. tetragonality of martensite decreases. Steel having more than 0.2% C has supersaturated

Carbon when hardened.

- At this temp martensite decomposes to low tetragonality martensite having the C/a ratio 1.014.
- Whereas the martensite has C/a ratio 1.08.
- Due to smaller diffusion of C., (Fe_{2.4}) C-carbide will form.
- At this stage the hardness is decreases due to loss of tetragonality, but it is slightly increases due to formation of C-carbide.
- These 2 factors will control the hardness value at this stage.

2nd stage of Tempering (200-300°C)

- Decomposition of retained austenite → The amount of retained austenite depends on chemical composition of the steel as well as the temp of quenching.
- In this stage retained austenite decomposes to lower bainite.
- So at this stage due to formation of C-carbide hardness of retained austenite increases, and transfers to lower bainite.

3rd stage of Tempering :- (400-350°C)

- At this temp the tetragonality martensite is completely lost and dissolution of C-carbide also takes place.
- Due to the dissolution of $\text{Fe}_2.4\text{C}$ small nod like structure will form and the structure contains α & Fe_3C .
- ~~At~~ At this stage sharp decrease of hardness is observed.

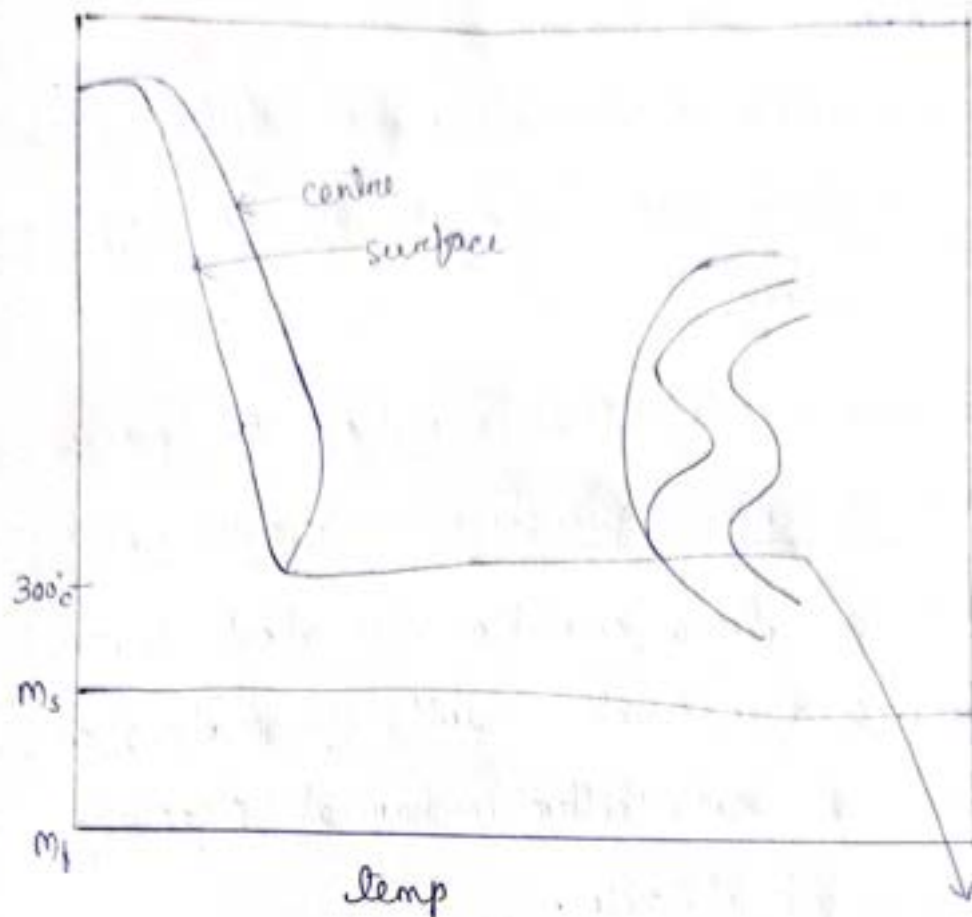
→ 4th stage of Tempering (350-700°C)

- At this stage growth of cementite takes place.
- Growth of cementite starts at about 300°C, but finally it is in the spheroidised nature i.e. α containing spheroids of cementite in the ferrite structure.
- The hardness is completely decreases and ductility increases and also improve machinability.

Temper Brittleness / Temper embrittlement :-

- The objective of tempering of steel is to reduce hardness, brittleness and restore ductility, and machinability, but it has been found that for certain steel either on cooling slowly or for holding longer period in a temp range of 400-660, so a marked decrease of toughness.
- This phenomenon is called temper embrittlement or temper brittleness.
- Temper brittleness doesn't occur in plain carbon steel but widely observed in alloy steels.
- P, As, Sb as a alloying element increases the tendency of temper brittleness.
- But the presence of embrittlement can be decreased by addition of Mo, Ti and Zr in the steel.

Aus Tempering :-



- This is a special type of heat treatment process in which austenite is only transformed to only bain.
- In general in continuous cooling austenite transformation to either martensite or pearlite depends on cooling rate.
 - Aus tempering consist of heating the steel to its austenising temp, holding at this temp to get homogeneous austenite, followed rapid cooling to above M_s temp (200–450°C)

- And held at this temp till all the austenite transform to bainite.
- After completion of Transformation steel is taken out from the bath and cooled in air or any desired rate of cooling.
- Due to iso-thermal transformation the process is called iso-thermal quenching or iso-thermal hardening.
- The rate of transformation is about lower bainitic range which result formation of lower bainite and has better mechanical property than the tempered bainite.
- For this transformation the steel should be cooled from austenitic temp in such a way that the surface and centre part of the specimen cooling rate should be more than the CCR.
- Due to restriction in size it is not suitable for larger objects.
- This process is better suitable for alloy steel because alloying element increases the critical cooling rate by shifting the TTT curve towards right and hence

steel gets sufficient time for the transformation.

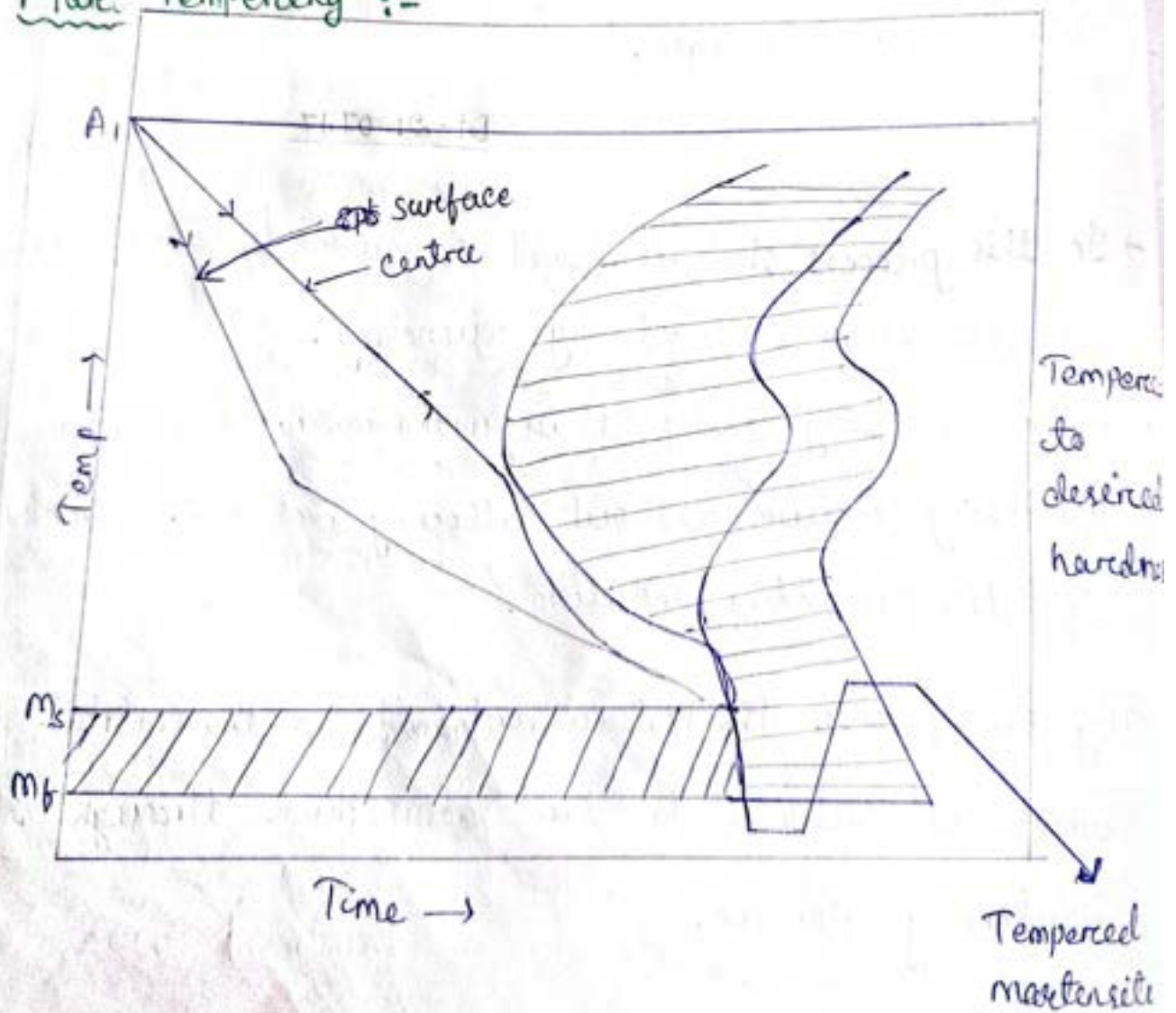
Self Tempering :-

Hardening is always followed by tempering is carried out to obtain optimum combinations of mechanical properties.

- Sometime oil is not needed mandrinete through out the cross secⁿ.
- For example in some type of application soft core and hard case is required to get better hardness and impact strength.
- In this process steel is heated to austenitic temp, holding at this temp followed by quenching.
- After quenching the part is withdrawn from the quenching medium without allowing to cool completely in the quenching medium.
- By this process the heat is retained in the central part which is release to the atmosphere through the hardening portion.

- Due to this temp the hardest portion get temper.
- The tempering takes place by its own heat. So this type of tempering is called self tempering.
- In this process both martensite at the surface and pearlite at the core.
- The portion of pearlite at the core depends on the time of quenching, material retained inside it, quenching medium.
- This process result soft core and hard case.

Max Tempering :-



- mart tempering involve heating the steel to the austenizing temp. held at this temp for sufficient time for followed by quenching into a bath which have the temp above 150 to 300°C.
- Steel is held at this temp to equalize the temp betⁿ surface and the centre.
- After equalizing the sample is cold in quenching medium to get martensite.
- The holding time should be very short and only achieve to equalise the temp betⁿ surface to & the centre.
- The holding time shouldn't be touch with the bainitic transformation point.
- Martensite is formed by two stages of cooling which help to decrease in the internal stress, distortion and cracking but it improves mechanical property.
- Mart tempered steels are generally tempered to desired temp to achieve improved ^{mechanical} ~~mod~~ property. (strength, toughness & wear resistance property).

Sub-zero Treatment :-

- When the steel is hardened, it is very difficult to achieve martensitic structure through out its cross section.
- If the cooling is so fast, then the retained austenite will be present in the steel.
- Presence of retained austenite greatly reduces all the mechanical properties.
- High carbon & high alloy steel promote the formation of retained austenite.
- So for improving the mechanical properties with the retained austenite, treatment is carried out i.e. called subzero treatment or cold treatment.
- This process consists of cooling the steel below subzero temp. i.e. temp. lies betⁿ -30 to -70°C .
- At this temp retained austenite converted to martensite but the process develops higher amount of internal stresses, so tempering is carried out to remove internal stresses.
- Sub-zero treatment increases the strength & hardness.

✓ Mechanism of quenching :-

The removal of heat during quenching takes place in 3 stages.

- i) Vapour blanket stage
- ii) Liquid boiling stage
- iii) Liquid cooling stage

i) Vapour blanket stage :- As the workpiece comes in contact with the quenchant the surrounding of the specimen heated up to the boiling point of the quenchant and get vapourised.

→ This vapour creates an envelope around the workpiece and obstructs further cooling. Because vapour film is a poor conductor of heat.

→ The workpiece is cooled at this stage by conduction and radiation.

ii) Liquid boiling stage :-

In the 1st stage the vapour film is no longer stable below a particular temp.

→ As soon as the vapour film is broken the quencher comes in contact with the workpiece.

- Now the fresh coolant comes in contact with the workpiece and the process is repeated.
- This is continuous till the temp of the surface comes down to below the boiling point of the liquid.
- Very rapid cooling takes place^{at} in this stage.

iii) Liquid cooling stage :-

- It starts when the temp of the surface of the workpiece become equal to the boiling point of the quenchant.
- Cooling at this stage takes place by conduction and convection.



Diffⁿ type of quenchant

Water :-

Water is the most popular quenching medium due to low cost, availability and easy handling.

- Now pollution problem is associated with the use of water.
- Water has max^m cooling rate among all quenchants except aqueous solⁿ.
- It is restricted only to plain carbon steel & low alloy carbon steel.
- The steel develop excessive internal stress due to faster cooling also development of distortion & crack.
- Complicated shapes can't be water quenched due to the above.
- Another ~~major~~ ^{major} disadvantage associated with water quenching is that vapour blanket stage stable for longer period.
- This problem can be ~~more~~ ^{minim} eliminated by agitating the quenching bath.

→ Water quenched object get rusted.

Aqueous solⁿ :-

If highly ionised salt added to the water decreases the viscosity of water as well as reduces the duration of vapour blanked stage.

→ Both this parameters help in improving the cooling power of water.

→ In this way the vapour formation decreases rapidly.

→ Aqueous solⁿ such as Sodium chloride (NaCl), calcium chloride (CaCl_2) added with the water.
(brine solution)

→ If NaOH is added with the water called ~~caustic~~ caustic solution.

→ If the solⁿ maintained at 20°C then the solⁿ has max^m cooling power.

→ This is very colder than water.

→ High ~~corrosive~~ ^{corrosive} nature, handling equipment are corroded rapidly.

→ Production of corrosive fume is harmful to human skin.

Oil :-

- Most of the oils used as quenchants are mineral oil.
- These are generally paraffin based oil.
- Quenching in oil provide slower cooling as compare to water.
- Oils are graded according to their viscosity.
Commonly used oil has viscosity value 100 SUS at 40°C
(Saybolt Universal sec)
- For obtaining faster cooling rate oil with viscosity 50 SUS at 40°C is maintained.
These oils are called ^{fast} ~~first~~ quenching oil.

Hot quenching oil :-

- ~~Hot~~ Hot quenching oil has the viscosity 250-300 SUS at 40°C.
- Use of oil medium resulting low distortion and cracks.
- These oils are well suited for intricate integrate shape object.
- ^{Presence} ~~Presence~~ of water in oil is undesirable because it may result non-uniform cooling also distortion and crack.

Air :-

Most of the alloy steel hardened by air these are called air hardening steel.

→ These steels are always almost free from distortion and crack.

Gases :-

→ Gases are used to quenching faster than the air and slower than the oil.

→ A moving stream of gas remove the heat from the workpiece faster than the air.

→ The common used gases are H, He, N₂, Ar.

→ H has the max^m cooling efficiency but it is not used for the safety.

→ He is quite expensive.

→ Ar has very low cooling efficiency, so N₂ is widely used as a quenching gas.

Salt bath :-

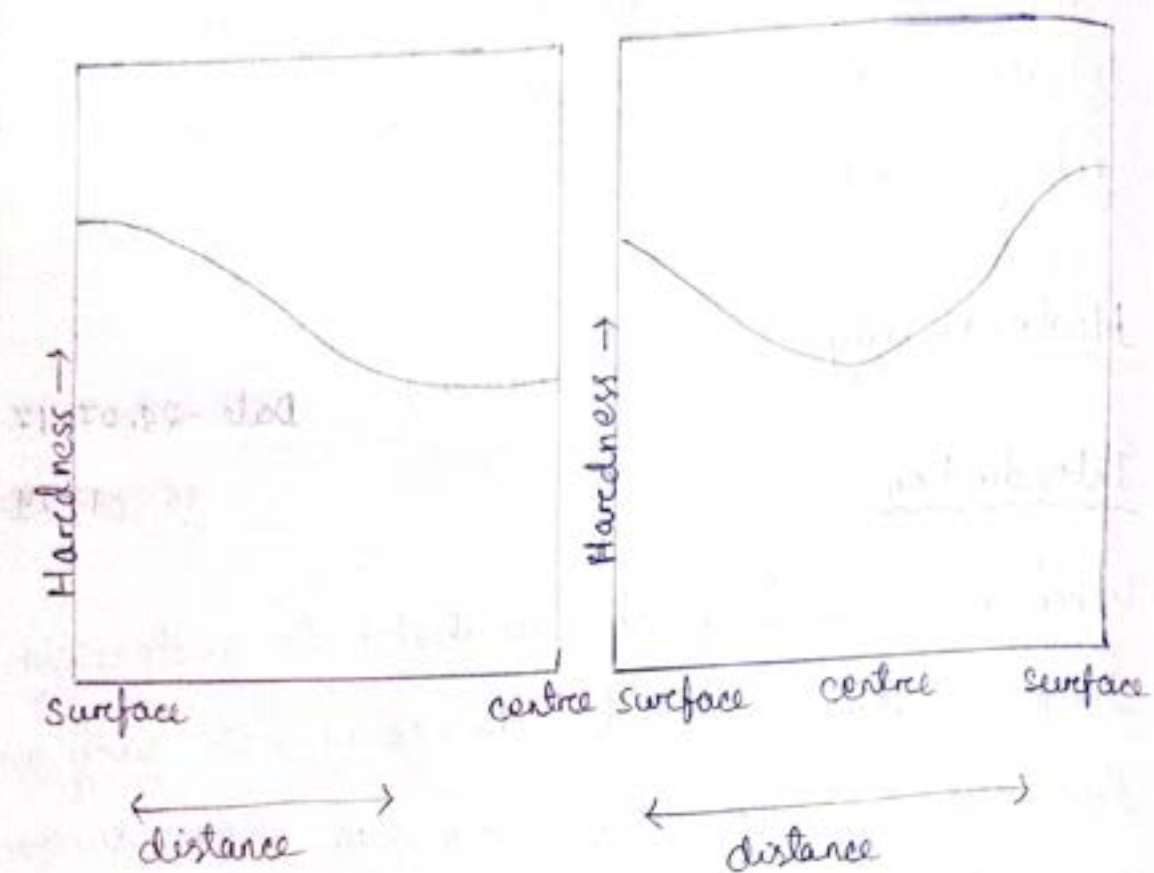
→ It is the salt suited quenching medium for steel with good hardenability and thin secⁿ.

Hardenability :- (3rd Chapter)

Introduction :-

- When a pear piece of steel is heated to austenising temp and then quenched, the cooling rate vary across the cross secⁿ i.e., the cooling rate from surface to centre is not same.
- At the centre the cooling rate is slow as compared to surface.
- Hence, due to this thermal gradient surface became martensite and centre will transform to pearlite.
- The depth of hardness is a measure of hardenability and it depends on depth of martensite from surface to centre.
- It may be defined as the susceptibility of steel to harden when it quenched and is related to the depth and distribution of hardness across the cross section.

Distribution of hardness across the cross section



- The max^m hardness depends on the carbon content of the steel and also critical cooling rate, retained austenite and self tempering.
- Hardenability depends on addition of alloying elements, grain size of austenite, quenching media and size of the specimen.
- On the basis of hardenability, steel can be divided into two types :-
 - i) Shallow hardening
 - ii) Deep hardening

- In shallow hardening steel depth of hardness is limited to a small distance from surface to the center of the specimen.
- Carbon steels are shallow hardening type.
- In deep hardening steel, hardening is uniform through out the cross secⁿ or depth of martensitic structure is max^m.
- DBTT also found in single specimen whereas 50% martensite and 50% pearlite found in a particular zone of the specimen.

Determination of Hardenability :-

Hardenability can be determined by 4 diffⁿ methods.

- i) Jominy's critical diameter method
- ii) Jominy ^{end} quenched test
- iii) Estimation of hardenability from chemical composition
- iv) Fracture test

1) Grossman's critical diameter method :-

M.A. Grossman gave a direct method for measuring the hardenability in terms of critical diameter.

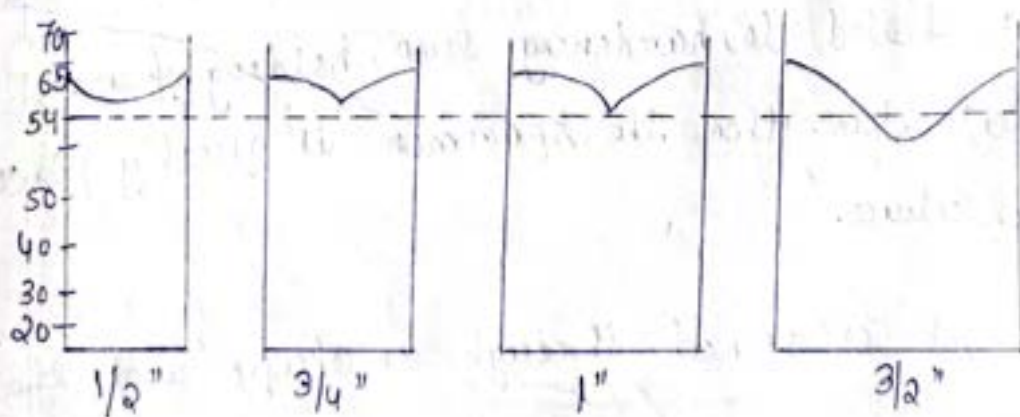
- In this method no. of steel bars of different diameters are quenched from austenitic temp.
- The different diameters of the samples are $\frac{1}{2}$ inch, $\frac{3}{4}$ inch, 1 inch, $\frac{3}{2}$ inch.
- The length of each bar must be at least 5 times the diameter to avoid end effect.
- If the carbon content is greater than equal to 0.6%, then the martensite has the hardness Rc 65.
- If the diameter of the rod increases then the cooling rate decreases and gives rise to ^{softer} pearlite.
- The portion of the rod which contains more than 50% martensite is considered as a hardened region and if its content is less than 50% then called unhardened region.
- The 50% martensitic zone can be easily distinguished by etching method.

→ Also the hardness value changes rapidly from Rc 50 to lower value.

→ This zone is also taken as a transition zone for the hardened and unhardened zone part.

→ Acc. to the Grossman's, sample the bar having 1 inch diameter shows 50% martensite and 50% pearlite at the centre. i.e. this sample is completely hardened.

✓ This 1 inch diameter is taken as a critical diameter below which part is completely hardened and above which soft core will be found at the centre.

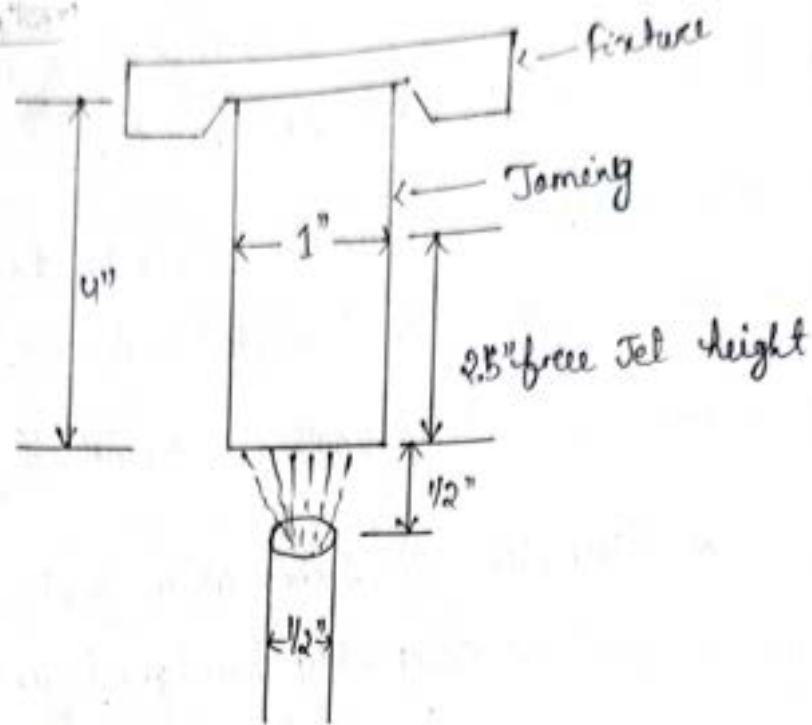


ii) Jominy End Quenched Method :-

→ In the grossman method the test is carried out according to the critical diameter in which large samples are needed as well as it is a time consuming process.

→ So a convenient & common method is developed called "End Quenched, 1st".

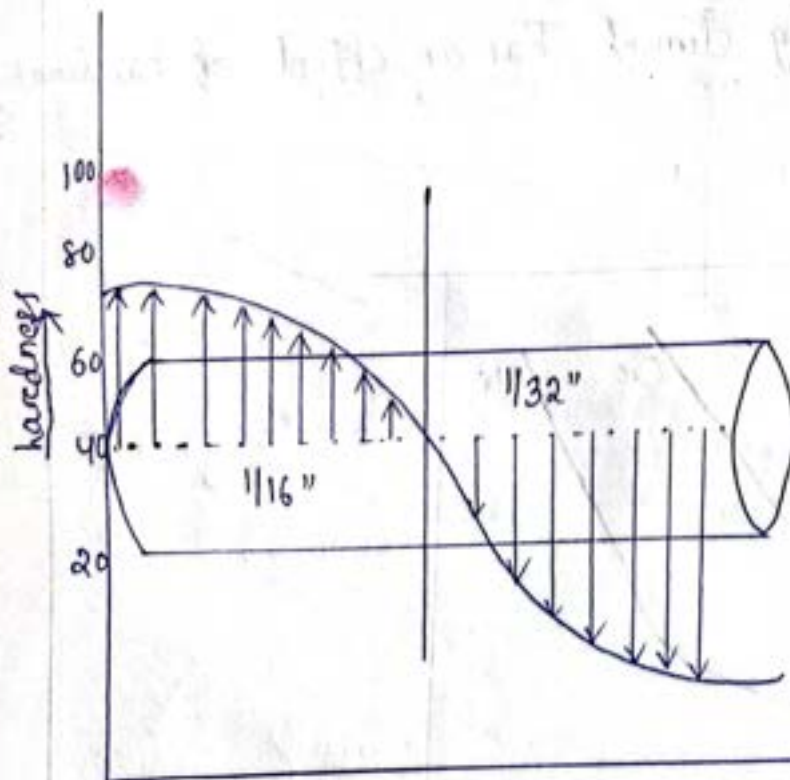
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- In this test a steel bar of 1" diameter and 4" in long is heated to hardening temp, holding for sufficient time then the specimen is quickly placed in a fixture.
- A water jet is opened through an orifice with the diameter $\frac{1}{2}$ ".
- The distance betⁿ the orifice and lower end of the bar is also $\frac{1}{2}$ ".
- The temp of the water is 24°C and the free jet height is 2.5".

- Water strokes continuously for 30 min and then cooled to room temp.
- The cooling rate is very rapid at the lower end and it gradually decreases from lower end to top end.
- After quenching 2 shallow flat surface of 0.02" deep are ground 180° apart on the test bar.
- The hardness is determined at interval of $\frac{1}{16}$ ", near the quench end and this is reduced to $\frac{1}{32}$ " with the increasing of distance from the quench end.

Hardness Test :-



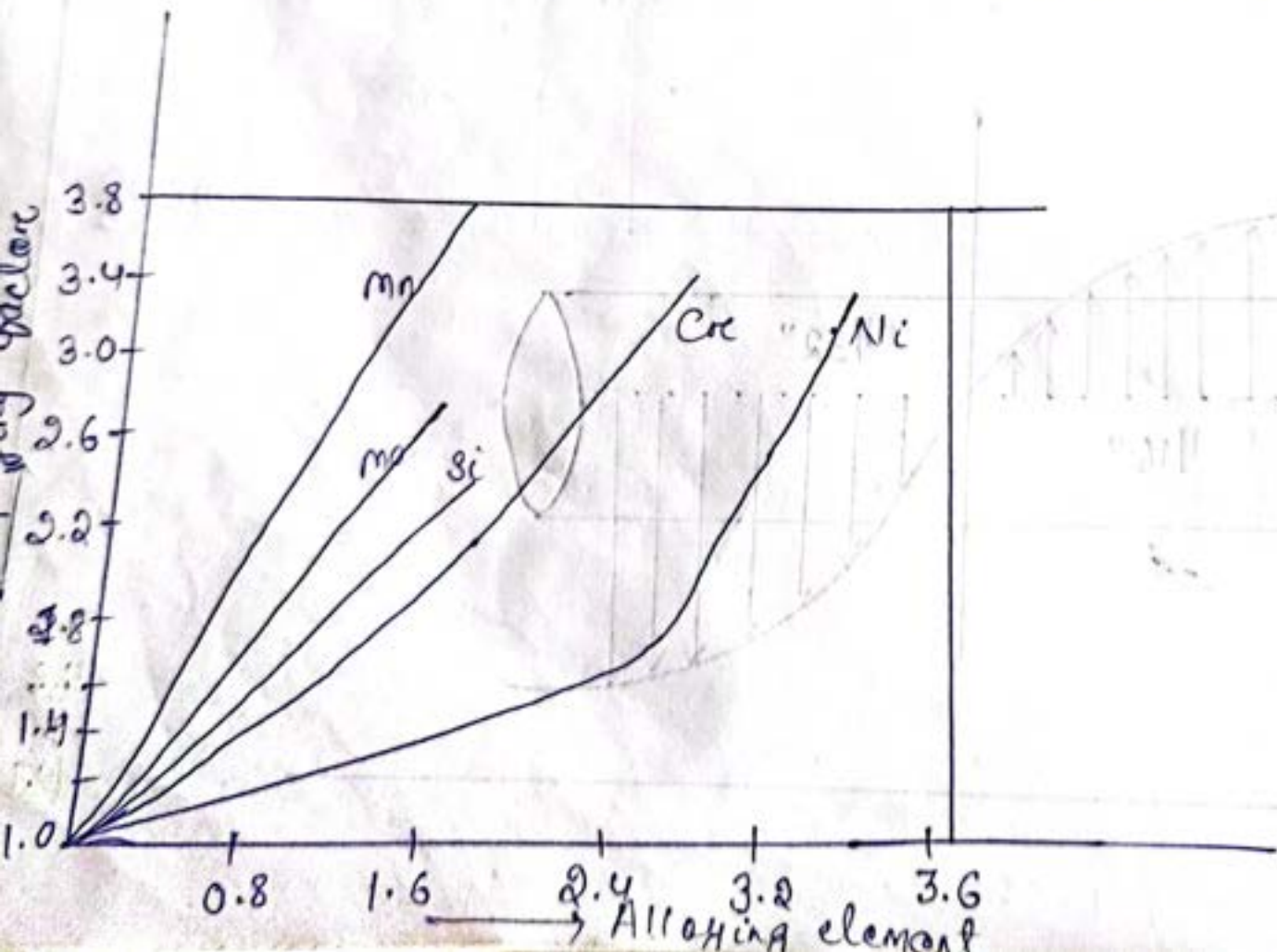
Jominy distance.

Estimation of hardenability from chemical composition

→ It is also possible to estimate the hardenability from chemical composition and grain size of steel.

→ Every steel hardenability depends on the carbon content and grain size.

→ But some alloying element has an effect of hardenability.



The effect of alloying hardenability is shown in the figure. i.e. Mo, Mn, Cr, Ni, are very effective. The base diameter is multiplied by the multiplying factor F for each of the alloying element is

$$D = D_c \times F_{Cr} \times F_{Mn} \times F_{Ni}$$

Fracture Test :-

If the material is consist of both martensite and pearlite then the fracture takes place and exhibit both ~~pearlite~~ brittle and ductile fracture.

- The area under goes with the martensite prevail brittle fracture and the area under goes with the ~~pearlite~~ ^{brittle} prevail.
- The change over from brittle to ductile fracture give the region, where ~~mart~~ the changeover takes place from martensite to pearlite.
- This method is based on the nature of fracture seen.

Factor Influencing Hardening

→ Basically hardenability of steel depends on

1) Austenitic grain size

2) Carbon content

3) Alloying element

Austenitic Grain Size :-

→ Many heat treatment process the first step is heating the steel to the austenizing temp.

→ Austenite starts above A_1 , A_3 , A_{cm} depends upon the diff. type of steel.

→ Austenite formation start by nucleation and grain growth

→ In the begning the no. of austenitic grains is large but later on due to high mobility at high temp the growth of austenitic grain takes place and the no. of grain is decreases.

→ Fine grain steel shows lower hardenability because during quenching due to fine grain austenite more no. of sides are available for pearlitic transformation.

→ So martensite formed at the surface and core area transform to pearlite which decrease the hardenability of steel. but coarse grain steel provide less

new nucleation site before pearlitic transformation and increases hardenability.

Effect of Carbon :-

- Hardenability of steel is greatly influenced by the carbon content.
- It increases with respect to carbon content but after eutectoid composition hardenability decreases with the increase in carbon content.

Effect of alloying element :-

- Except cobalt all the alloying element shift the TTT curve downwards ~~right~~ right. i.e. even at slower cooling rate martensite will form at the centre.
- So alloying element increases the hardenability of steel.
- Alloying element should be homogeneously distributed.
- Presence of carbon, nitride, inclusion decreases the hardenability.

ch-9

SURFACE HARDENING METHOD

It is a different type of heat treatment method in which surface is made hard as compare to core.

→ Because in some application hardness and impact strength both are simultaneously needed so both for obtaining this two property in a single mass, surface is made hard and core is made soft.

→ This is achieved by 2 types of method.

i) Chemical heat treatment method

ii) Phase transformation method

Chemical heat treatment method :-

It is of 14 type :-

- i) Carburising
- ii) Pack carburising
- iii) Liquid "
- iv) Gas "
- v) Vacuum "
- vi) Post "
- vii) Nitriding
- viii) Cyaniding
- ix) Carbo-nitriding
- x) Plasma nitriding
- xi) Salt bath nitro-carburising

xiii) Boronizing

xiv) Chromizing

xv) Toyota diffusion process

Phase Transformation method :-

It is of 4 types

i) Flame hardening

ii) Induction hardening

iii) Electron beam hardening

iv) Laser Laser hardening

* Carburising :-

- This is the most widely surface hardening method.
- It is carried out in low carbon steel which contain 0.10 - 0.25% of carbon.
- It is carried out in the temp range of 900-930°C and the surface is enriched with carbon upto 0.7-0.9.

② In this process carbon is diffuse into steel by heating above transformation temp and holding the steel in contact with carbonaceous material, which may be a solid, liquid & gas.

① At this temp austenite picked up carbon from the carbonaceous material due to higher solubility limit.

→ The depth of carbon diffusion is directly proportional to the length of holding time.

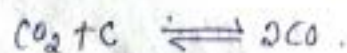
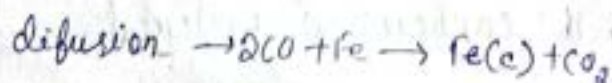
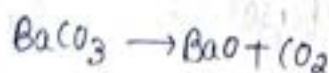
→ As t increases the hardness of the steel, increases the hardness of the ^{steel} surface and the core is in soft state.

✓ Pack Carburising :-

→ This method is also called solid carburising.

→ This is the oldest method in which steel components are packed with 80% granular coal and 20% barium carbonate (BaCO_3) as energizer in heat resistant boxes as heated at 933°C in the furnace.

→ The following reactions take place



- The case depth depends on the specific period of time.
- Generally carburizing time varies from 6 to 8 hours and case depth about 1mm to 2mm.

Liquid Carburizing :- / Cyaniding

- It is also known as salt bath carburizing.
- In this process carburizing occurs through molten cyanide (or oil or gas).
- It is carried out in a pot type furnace heated by oil or gas.
- Bath temp is maintained about $815-900^{\circ}\text{C}$.
- This process can be made continuous.
- The bath top is covered by graphite or coal to reduce heat losses and excessive decomposition of cyanide.
- With the sodium cyanide (NaCN) energizer are added that is Barium chloride (BaCl_2)
- $$\text{BaCl}_2 + 2\text{NaCN} \rightarrow \text{Ba}(\text{CN})_2 + 2\text{NaCl}$$

$$\text{Ba}(\text{CN})_2 + \text{Fe} \rightarrow \text{Fe}(\text{C}) + \text{BaCN}_2$$
- Sometimes Nitrogen also diffused with the iron which is beneficial for increasing hardness of

Surface.

- This process gives a thin and clean hardened i.e. 0.08 mm thick.

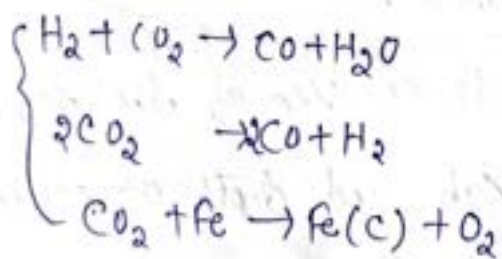
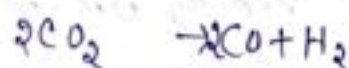
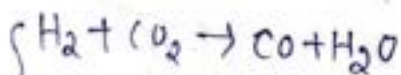
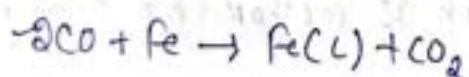
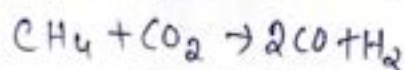
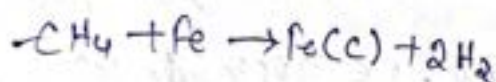
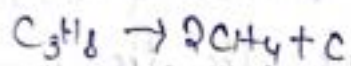
Gas Carburising :-

- This is most widely used method for carburising.
- It is carried out in a retort type, sealed quench type, continuous pushed type furnace.
- All these furnaces are heated by gas firing or electrically heated.
- Gas carburising temp is about 870°C - 950°C .
- The carburising gas produced from liquid methanol, liquid iso-propanol or gaseous hydrocarbon such as propane and methane.
- Before introducing carburising gas carrier gas is given to the furnace.
- This is a mixture of propane or methane with air is cracked in hot retort at an endothermic gas generator to form carrier gas.
- Generally carrier gas contain nitrogen 40%, Hydrogen 40%, CO (20%), CO_2 (0.3%), CH_4 (0.5%), H_2O (0.5%)

and oxygen in furnace.

- This gas is purged into the atmosphere furnace atmosphere with slightly positive pressure.
- This prevent air into the furnace and oxidation of the component.
- When the material reaches to carburizing temp propane and methane is introduced into the furnace.

→ During Carburisation



- mainly carburising occurs by CO_2 conversion of CO_2 to CO .
- In the recent development N_2 is used as a carrier gas so N_2 also diffuses into the surface of the iron and increase hardness.

Vacuum carburising :-

It is a process of carburising carried out either in vacuum or in reduced pressure.

- It takes place in 2 stages.
- In the 1st stage carbon is made available to the steel for absorption.
- And in the 2nd stage diffusion of carbon into the steel.
- Initially the job is introduced into the furnace and then evacuated (to make vacuum) the furnace is heated upto austenising temp, i.e. 925°C to 1050°C .
- The gaseous hydrocarbon such as methane or propane is introduced into the furnace.
- The quantity of gas depends on size of the job, surface area of the job and depth of carbon introduction of the job.

At this temp, when the gas comes in contact with the surface of the job then it cracks, and carbon deposited on the surface.

Diffusion is continuous till the required depth of required % of carbon is attained.

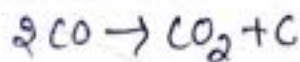
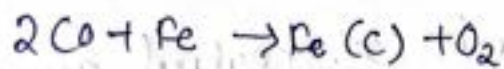
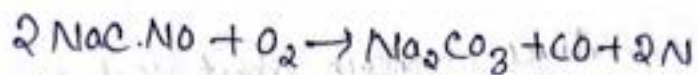
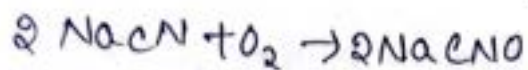
Cyaniding :-

→ Cyaniding is carried out in a liquid bath of sodium cyanide.

→ In this process the job or the parts are immersed in a liquid bath of NaCN, with the concentration of 80% to 90%, and at a temp of 800 to 960°C.

→ When the sodium cyanide bath react with the oxygen in the air which is pass through the bath.

→ ~~that is~~ following reaction takes place, i.e



→ Carbon & Ni both are diffuse into the steel and give thin layer of Carbonytride E-phase.

→ This process required 30 to 90 min.

→ For obtaining 0.5-2 mm depth process take 1.5 to 6 at a temp of 950°C.

→ Higher temp high carbon diffusion take place upto 0.8-1.2% and Ni 0.2-0.3%.

✓ Nitriding :-

- Nitriding process for those alloys steel which contain stable nitriding forming element such as Al, Cr, Mo, V, W.
- Nitriding is carried out in the ferritic region i.e. below 590°C .
- So there is no phase change occurs during nitriding.
- Before nitriding hardening is carried out by heating to 930°C and quenching in oil followed by tempering at 650°C to develop bainitic structure at the centre.
- To develop bc.
- All machining and grinding operation should be completed before nitriding.
- The portion which is not to be nitrided are covered by thin coating of tin by electrolysis.
- Then ammonia gas is passed into the furnace where it dissociate into nascent nitrogen and hydrogen by the rxn $2\text{NH}_3 = 2[\text{N}]_{\text{Fe}} + 3\text{H}_2$
- The treatment takes about ~~20 hrs~~ 21 to 100 hrs depend on the case depth.

- After nitriding the steel part is allowed to cool slowly in the furnace in the presence of ammonia.
- The time required to obtaining case depth of 0.5 mm is about 100 hr.
- It gives the case hardness about 900-1100 VHN.
- This layer has better wear resistance and better corrosion resistance.

Demerits

- During nitriding process a white layer of Fe_4N (X-nitride) and Fe_3N (E-nitriding) form on the outer layer.
- This layer is very brittle and tends to crack with application of force.
- This white layer shouldn't be formed during the nitriding process.
- There are 2 process by which white layer can be suppressed. i.e. i) flame process
ii) Gas nitriding or plasma nitriding process.

i) Flame process (Double stage Nitriding)

- The first stage carried out at a temp of 445-525°C for 15-20 hr. with around 20% dissociate ammonia

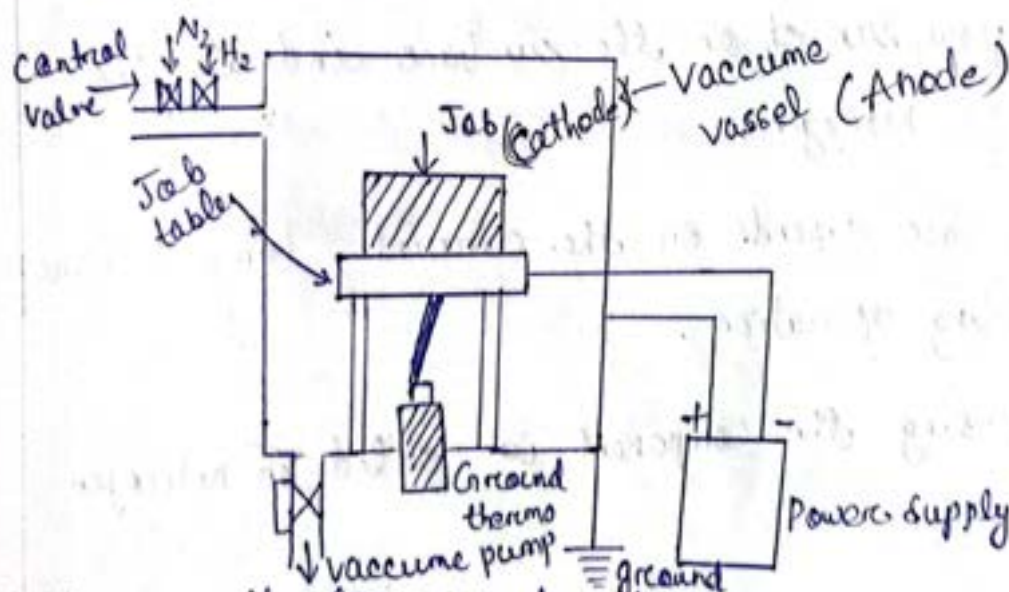
to achieve faster growth of nitrided case.

→ In the 2nd stage at a temp of $550-565^{\circ}\text{C}$ with 75-80% dissociated ammonia.

→ The iron nitride form in 1st stage dissociates so, white layer reduces to $0.05-0.01\text{ mm}$. are even gets eliminated.

→ Elimination of white layer ~~decreases the~~ decreases the hardness.

ii) Plasma Nitriding :-



→ Plasma nitriding is also known as ion nitriding process.

→ In this process the steel component to be nitrided act as a cathode.

→ The component is heated by electrical heaters to $370-650^{\circ}\text{C}$.

→ After obtaining temp gas mixture of N_2 & H_2 supply to the chamber at $.1-10\text{ torr}$.

- A DC voltage of 500-1000 volt is applied betⁿ the cathode & anode. to form plasma.
- Current At this plasma H_2 & N_2 gas gets ionised.
- The ionised gas those are bombarded the surface of the component then a part of the energy heat the surface and alloy. the diffusion of nitrogen and the remaining part is utilised for displacing the secondary electron.
- When a glow seen on the surface indicate the diffusion of nitrogen.
- Nitriding case depends on the current, temp & time of nitriding operation.
- After nitriding the component is cooled in nitrogen atmosphere.
- This process of nitrogen diffusion is very controlled and avoid the formation of white layer.
- Plasma nitriding is mainly used for various components such as valve, piston rod and cast iron parts such as pump, gear houses.

Salt bath Nitro Carburizing :-

- In this process nitrogen & carbon both are diffused in to the steel surface at $570-580^{\circ}\text{C}$ in salt bath.
- Salt bath are 2 types i.e. those containing ~~steel~~ cyanide and those not containing cyanide.
- Cyanide free baths are more popular because these are not hazardous.
- Generally the salt contain mixture of sodium and Potassium cyanides ^(KCN) and carbonates.
- The time for obtaining a case depth of 10-15 micro m is about 1.5 hour.
- This process is used for ferrous material because time taken is very short, it is not suitable for large object odd shaped component.
- It is carried out for gear and pinion shaft piston rings, extrusion die, forging die spindle of grinding machine, gun barrels, crank shaft and other wear component.
- ~~It is the~~

Boronizing :-

- It is one of the recent method of hardening, which is applied for ferrous material such as carbon steel and tool steel.
- Both packed and gaseous lecture are used for boronizing.

Pack process

In this process the components are packed in heat resistance boxes with the mixture of granules or paste of boron carbide and other boron compound at a temp $900-1000^{\circ}\text{C}$.

- Boron diffusion take place and form Fe_2B at the outer surface & Fe_3B at the interior.
- Fe_2B is more brittle and not desirable.
- It is decreased by lowering treatment temp, treatment time and the alloy steel, which are not contain any element higher affinity towards boron.
- The boride layer has the hardness $1500-2100 \text{ VHN}$.
- It has the depth $0.012 \text{ mm} - 0.127 \text{ mm}$.

- The treatment time for obtaining case depth of 0.15 mm is 6 hr at about 900°C .

Application

It is used generally for high wear resistance material such as hot forging die, wear ~~die~~ drawing die, extrusion die. and other component such as nozzles, plungers, gears, shaft and rollers.

Cromizing :-

- It is a surface hardening method carried out in 2 ways such as :-
- i) Pack cromizing
 - ii) Gasous cromizing
- The components to be cromized are packed with chromium powder and additives.
- Chromium powder is a mixture of 60% chromium ore fume powder, 0.2% ammonium ~~id~~ iodide and 39% krollin.
- Process takes place at a temp $900 - 1020^{\circ}\text{C}$.
- At this temp chromium carbide is form on the surface of the steel.
- For obtaining case depth of 0.02-0.04 mm time necc is about 12 hours.

- The hardness of Chromium carbide (CrC_2) is about 1500HV.
- There are 2 type of chromizing operation takes place.
 - i) Hard chromizing
 - ii) Soft chromizing

Hard chromizing :-

- If the steel contain enough carbon more than 0.35% C and the steel is chromized then it is called hard chromizing.
 - It gives better corrosion and wear resistance ^{layer} at the surface.
 - Chromium carbide is formed on the surface.
- ### Soft Chromizing :-

If the steel having the carbon content less than 0.35% and to be chromized then it is called soft chromizing. This steel has high ductility.

Chromizing layer provide excellent corrosion resistance and carbon oxidation.

Toyota Diffusion Process :-

- This process is initially developed by Toyota Diffusion Process research centre and laboratory, which provide a maximum hard & wear resistance surface.
- It is mainly used for automotive press tools.
- In this process carbide forming element such as vanadium and Niobium are diffused into the steel in a salt bath.
- The temp of the process is 1000°C .
- The carbide layer of 5-12 micrometers is formed on the surface.
- The hardness of the carbide layer is 3000 VBN.
- The salt bath which is used for the process having the composition based on borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$).
- The carbide forming element added in the salt bath in ferroform, i.e. ferro vanadium & ferro niobium.
- After the treatment the component are quenched and tempered.
- This method is very appropriate for edge of tool steel.
- The process takes about 10-12 hours.
- This is very widely used in Japan.

wear resistance, seizure.

Post Carburizing :-

- The carburizing takes place at $900-930^{\circ}\text{C}$.
- At this temp the steel is over heated and the process time is very prolonged.
- This may cause grain coarsening through out the cross secⁿ and decreases all the mechanical properties.
- So post carburizing treatment is developed with the objectives:
 - a) Improve the microstructure and refine the coarse grains of core & case.
 - b) Achieve high hardness at the surface.
 - c) Break the carbide network.

Process

- If the steel is fine grain steel, then the work piece is heated above A_1 temp and directly quenched.
- If the steel is coarse grain through out the cross secⁿ then double heat treatment is required to improve the property of case and core.
- In such cases steel is first heated above A_3 temp (900°C) and normalized to refine the grain size of

→ In the second step heating of work piece above A_1 to $(760-780)$ followed by quenching.

→ In the 2nd heat treatment austenite transform to martensite and the case hardness will increase.

→ In the 1st treatment at high temp carbide network dissolve and due to air cooling further carbide network not able to form, and restrict the carbide formation.

→ Flame Hardening is the simplest method of surface hardening

→ In this process workpiece is heated up by ~~oxy-acetylene~~ ^{oxy-acetylene} or ~~acetylene~~ ^{oxy-acetylene} or orifuel blowpipe followed by spraying the Jet of water as ~~coolant~~ coolant.

→ After hardening treatment stress relieving annealing is carried out in the oil bath at $180-200^{\circ}\text{C}$.

→ The hardness increases due to formation of martensite on lower bainite at the surface.

- The carbon content in the steel required for flame hardening is varies from 0.3-0.6%.
- High carbon steel also flame hardened but it must proper care on stress relieving annealing after treatment otherwise crack will developed at the surface.
- Temp of flame hardening ($240-3300^{\circ}\text{C}$).
- There are 4 different types of flame hardening

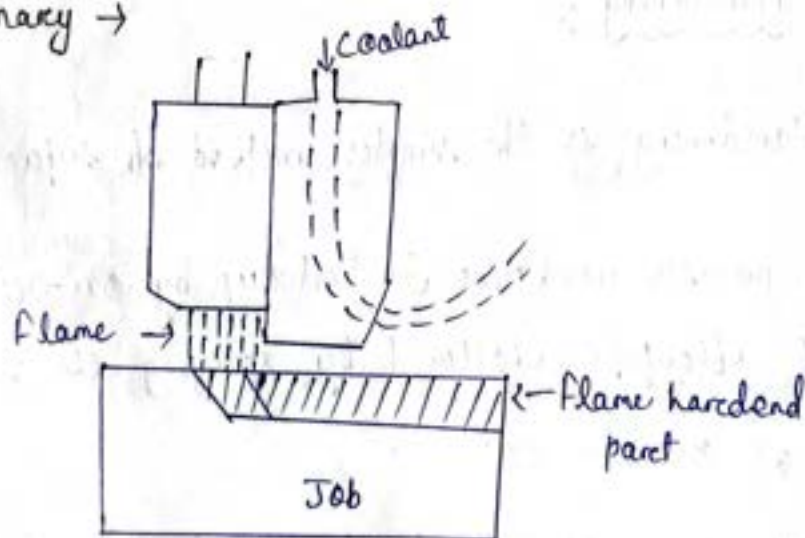
i) Stationary

ii) Progressive

iii) Spinning

iv) Progressive - spinning

i) Stationary →

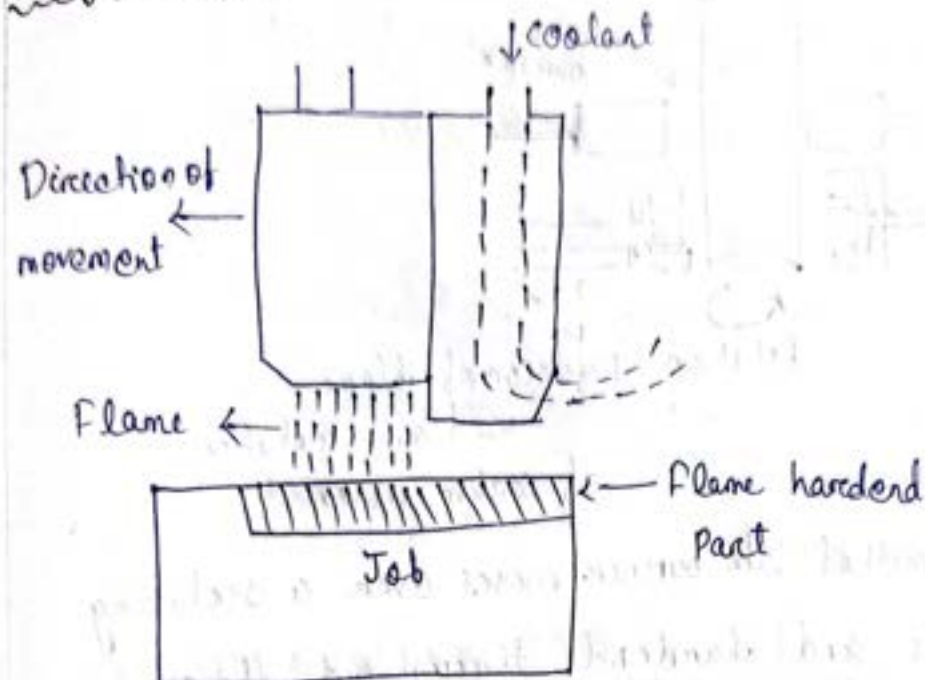


- In this method both burner and workpiece are stationary
- After heating the surface of the job, flame is removed and immediately coolant is applied on the

surface to achieve martensite at the surface.

→ The depth of hardness is depend on the time of heating.

Progressive :-

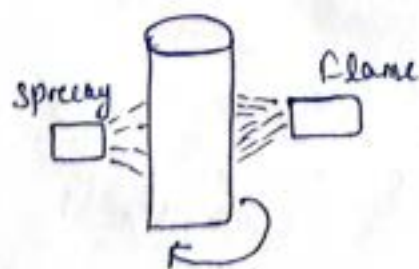


→ In this case flame & cooling arrangement is moveable.

→ Job is stationary.

→ Flame is move over the surface of the job in a particular direction.

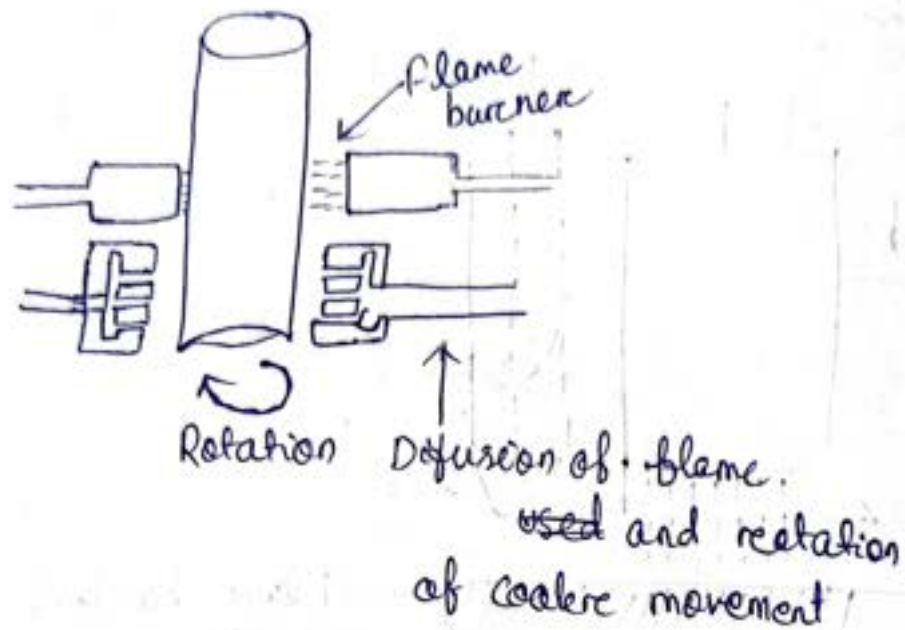
Spinning :-



→ In this method cylindrical objects are surface hardened where the burner and water jet arranged opposit

to each other and in both them the part is heated

iv) Progressive spinning :-



- In this method the burners moves over a rotating work piece and hardened through out the surface area.
- All the process form martensite at the surface to achieve required degree of hardness.

Electron beam :-

- * This process is used for those component which can't induction harden because of distortion.
- * In this process work piece is kept in vacuum at 0.06 m pressure.
- * Electron beam is focus on the work piece to heat the surface.
- * In beginning energy input is high, but it is reduced with time as the component gets heated up.
- * This is carried out to avoid melting up the surface.
- * All the process is computer control and upto 0.57 m case depth can be achieved.

Laser hardening :- (Self hardening)

- * Laser beam is used for surface hardening treatment.
- * There are very high intensity so it melt the work piece in a shorter time.
- * So, a lens is used to reduced the intensity of the laser on the surface of workpiece by decreasing the spot.
- * The defocused spot can be scan upto $1-25 \text{ mm}$.

→ In the earlier stage 1kg/watt are available which diameter very from 5 to 10mm but now a days 20kg watt ~~laser~~ also available.

→ Case depth of hardening is depends on both time and the distance.

→ It is a very fast process than induction and flame hardening process.

→ No, separate quenching media are required, since quenching is effected by mass of the surrounding unheated portion.

→ The microstructure of laser heated steel consist of bainite & ferrite and rarely martensite.

Case Depth Measurement :-

→ Case depth is defined as the perpendicular distance from the surface of the steel to the point at which changes in hardness, microstructure, chemical composition of the case and core can be distinguished.

→ The case depth can be measured by 4 methods

i) Hardness method

ii) Chemical

iii) micro-structure method

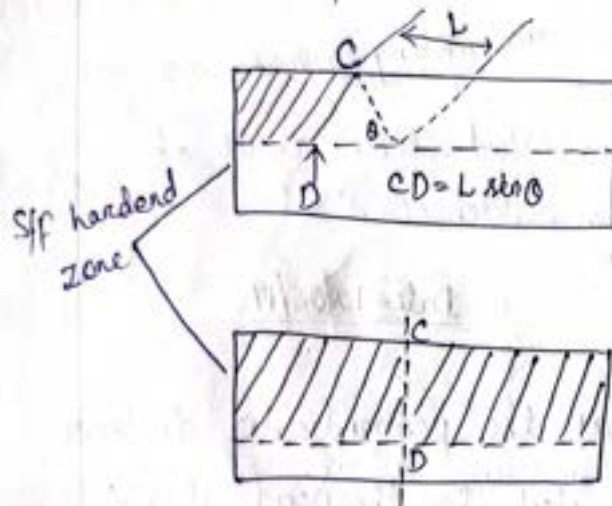
iv) micro-scopie method

Flordness Method

- In this method hardness value taken along case and core.
- It is a very accurate method.
- Specimen for this method are prepared by 5 method procedure.

- i) Cross secⁿ
- ii) Taper grinded
- iii) Slope grinded

i) Cross secⁿ procedure $\rightarrow$

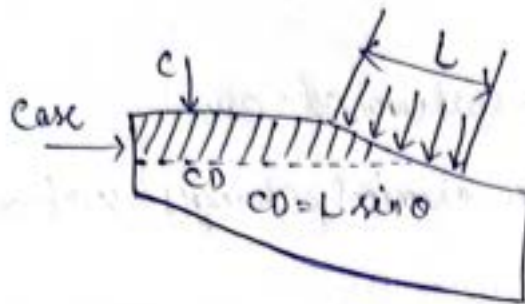


- The specimen is ~~not~~ ^{cut} caught + on to the hardness surface.
- Care should be taken there is no change in hardness during cutting.
- The surface area should be polished w/ fine emery paper.
- For the light and medium case hardness is taken at a particular angle.
- And in the heavy case the hardness is measured

perpendicular to the surface.

→ the change in hardness at a depth from surface is calibrated and measure the depth of hardness.

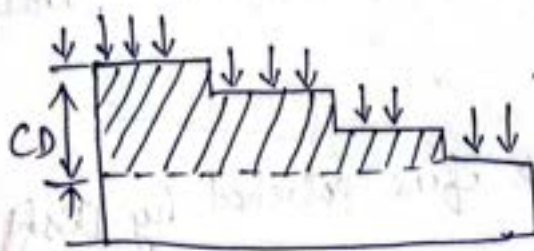
ii) Tappor Grinde procedure :-



→ This method is best suitable for light & medium case in which ~~shallow~~ ^{shallow} taper is ground from the case of the steel. and the hardness is measure along the tappere surface.

→ Case should be taken, there is no change in hardness

iii) Step grinde procedure :-



For medium and heavy case step grinde procedure is suitable.

→ In this case the hardness value are measured along, step of known distances from the surface.

All the 3 procedures use the rockwell hardness to measure the hardness.

→ A care should be taken the indentation shouldn't be deep impression.

ii) Chemical Method :-

→ It is mainly used for carburised cases.

→ It also used for other chemical changes surface hardened sample.

→ Presence of carbides, nitrides contain is estimated from the surface towards depth of the sample.

iii) Macro structure method :-

In this technique the test specimen is cut perpendicular to the hardened surface.

→ Then the surface is ground and polished through 00/40 emmory paper.

→ After polishing it is fine polished by Disk polisher.

→ Then the sample is etching with suitable reagent and then washed and dried.

→ The polish surface is examine under microscope at 20x.

Microscopic Method :-

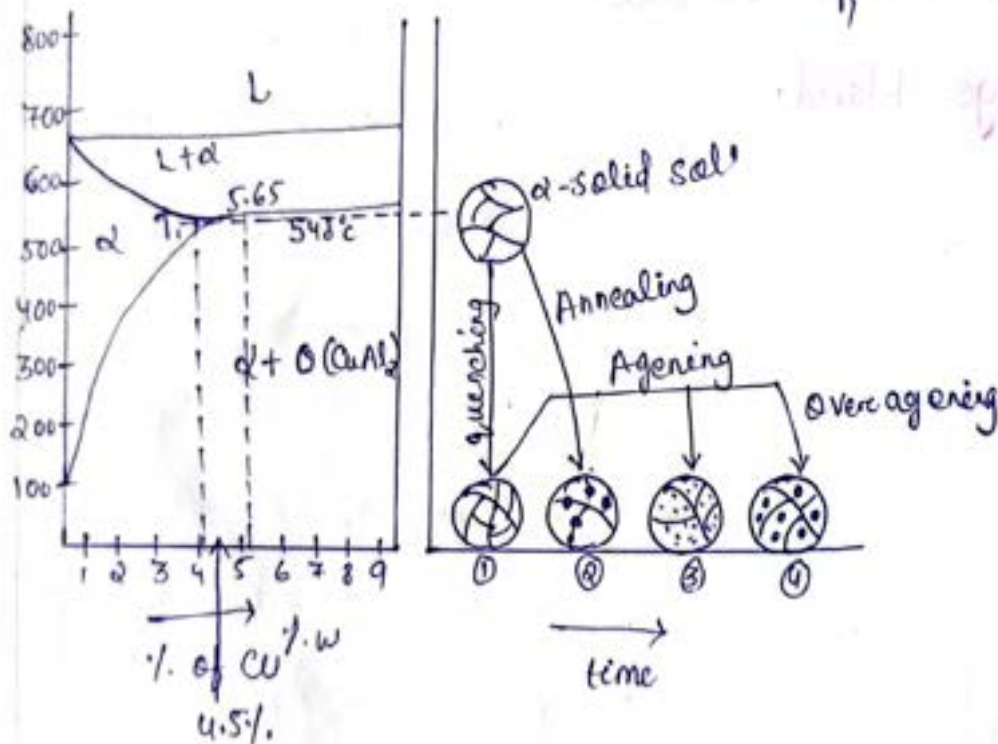
→ In this method the specimen is cut perpendicular to the hardened surface.

→ Then the cut surface is polished and etched.

→ Then the sample is examine under microscope with calibrated eyepiece to measure the depth of hardened microstructure.

Edge Hardening Method

- In 1906 Alfred Willis a German scientist discovered the edge hardening process.
- He found that quenched alloy of Al with copper and magnesium called duralumin increases its hardness with the time, this is called edge hardening or precipitation hardening.



Basic Requirement of Age hardening :-

The main basic requirement of the precipitation hardening is that the solid solubility limit should decrease with the decreasing temp.

- At this diagram aluminium-copper is mixed at a temp (Al-4.5%Cu)

of T_1 .

- If this alloy cooled slowly to room temp then the duralumin^(Q) ~~can~~ coarse precipitates form at the grain boundary. (Fig. 2)
- This doesn't cause any improvement in mechanical properties
- If this alloy quenched from T_1 , high temp phase α retained at the room temp.
- Because of rapid cooling no time is available for the diffusion and the alloy is in SSSS (super saturated solid solⁿ) state. (Fig. 1)
- This super saturation creates a force for the reject of excess solute atom in the form of precipitates (Q).
- Due to the limited diffusion at room temp the solute atom and solvent atom move & form ~~fine~~ extremely fine precipitates (CuAl_2), this is called ageing. (Fig. 3)
- If further time is available then the precipitates growth takes place by addition of fine precipit and decrease hardness of the solⁿ. (i.e. overage (Fig. 4.))

Steps of Age hardening :-

Age hardening treatment can be expressed in 3 steps

- i) Solutionizing
- ii) Quenching
- iii) Ageing

i) Solutionizing :- It is the process of heating the alloy just above the solvus temp (T_1) to obtain a single phase solid solⁿ. (α).

The temp should not be max^m otherwise oxidation or melting may occur.

ii) Quenching :- The solutionized alloy is cooled fast and retains the high temp single phase at room temp. as SSSS.

iii) Ageing :- It is the process of decomposition of SSSS to finely fine precipitates.

This precipitation distributed along the grain boundaries of the grain and restrict the movement of dislocation, which increases the strength and hardness of the ~~and~~ alloy.

→ Ageing can be carried out by 2 way

- i) Natural ageing
- ii) Artificial ageing

i) Natural Ageing $\rightarrow$ It is the process of age hardening by holding the quenched alloy for longer time at ^{sc.} room temp.

ii) Artificial Ageing $\rightarrow$ It is the process of age hardening by holding the quenched alloy for slightly above room temp.

Over ageing :- If at any given temp ageing is allowed to take place for much longer time than coarsening of precipitate occurs by the dissolution of smaller precipitates which are quite widely spaced. and the alloy becomes soft. This is called overageing.

TMT (Thermo Mechanical Treatment)

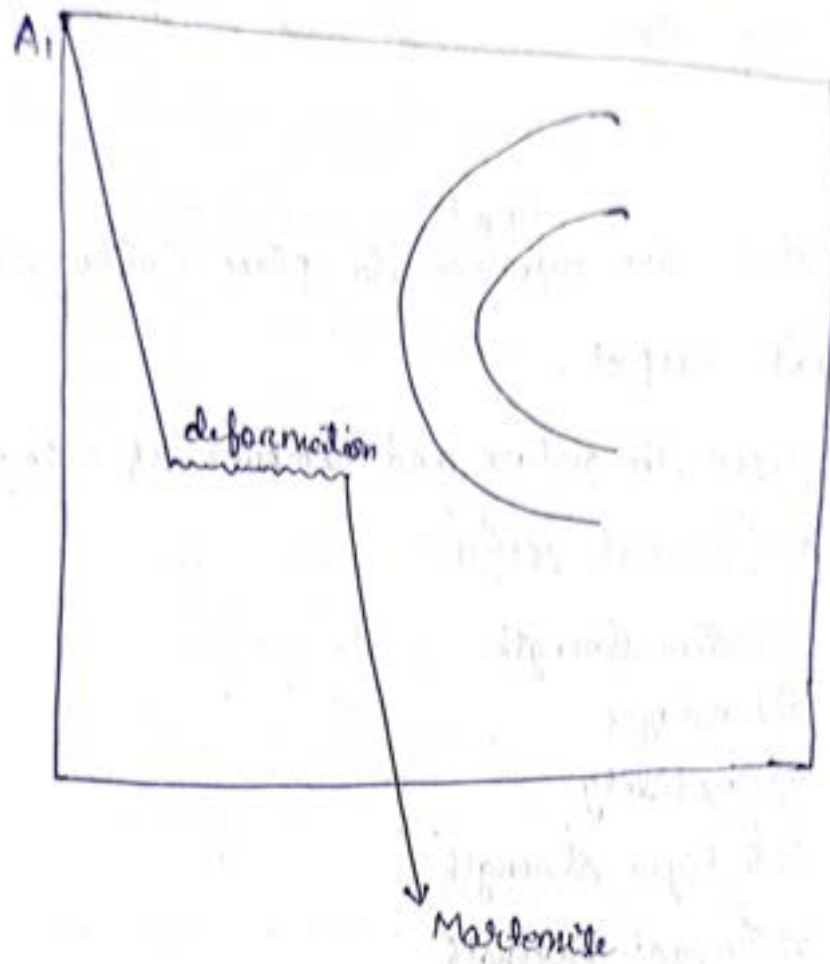
- Thermo Mechanical Treatment is the combination process of Heat treatment and mechanical working.
- It is of 2 types → HTMT & LTMT (Low temp)
(High temp. thermo mechanical treatment)
- High temp is carried out above the recrystallisation temp.
- And the low temp is carried out below recrystallisation temp.
- There are different types of treatments are aus forming, Hot churning, cryoforming.

Aus forming :-

It consist of heating steel above upper critical temp to get austenite.

- This austenite super cooled to a temp below recrystallisation temp, then it is deformed by any mechanical operation to get desired shape.
- After deformation it is quenched to get completely martensitic structure.
- No transformation should take place during the deformation.

mechanical deformation/treatment should be carried out at a const. temp to avoid phase transformation.



- Tensile strength, yield strength, ductility of austempered steel are higher than the hardened and tempered steel
- All the steel are not subjected to this process due to very ^{less} short incubation period.
- So the steel has higher incubation period, or alloy steel are subjected to this process.

Alloy Steel

→ Generally steel is divide into 2 category

- i) Plain carbon steel
- ii) Alloy steel

Alloy steel :-

(good)
Alloy steels are superior to plain Carbon steel in different respect.

→ Depending upon the nature and amount of alloying element alloy steel ⁱⁿ general possess

- i) Better strength
- ii) hardness
- iii) Ductility
- iv) Fatigue strength..
- v) Impact strength
- vi) Excellent high & low temp property
- vii) Enhance corrosion and wear resistance
- viii) " electrical and magnetic property.

Classification of alloy steels :-

Low alloy steel → upto 5%.

Medium " " → 5 to 10%.

High alloy steel → more than 10%.

Classification of alloying element :-

It is divided into 3 category such as -

- i) Austenite stabilizer
- ii) Ferrite stabilizer
- iii) Carbide forming element

i) Austenite stabilizer $\rightarrow$ Mn, Ni, Cu, Co, Zn increases the range of austenite.

These elements have FCC crystal structure or similar to γ phase.

$\rightarrow$ These elements are more soluble than ferrite.

$\rightarrow$ Element like C, H called as an austenitic stabilizer.

ii) Ferrite stabilizer $\rightarrow$ Cr, W, Mo, V, Si, Al, Be, Nb, P, Ti, Zr increases the range of α phase.

$\rightarrow$ Most of these elements have BCC crystal structure and these are more soluble in ferrite than austenite.

$\rightarrow$ These elements decrease the ferrite formation and increase the A_1 & A_3 temp, which results in an increase in ferritic region also increases its stability.

ii) Carbide forming element :-

These element form carbides in the presence of C is called carbide forming element. But the strength of carbide formation depends on the affinity towards Carbon.

* Arrangement of diffⁿ carbide forming element with the increase of affinity for C :-

Iron (Fe) $\rightarrow$ Mn $\rightarrow$ Cr $\rightarrow$ W $\rightarrow$ Mo $\rightarrow$ V $\rightarrow$ Ti $\rightarrow$ Nb $\rightarrow$ Ta $\rightarrow$ Zr
(Tantalum)

Graphitizing element :- Si, Ni, Cu, Al are common graphitizing because it prevent the common formation of Fe₃C.

Neutral element $\rightarrow$ Co is the only element which neither form carbide nor graphitization.

Characteristic effect of alloying element in steel:

Mn $\rightarrow$ Mn is used as a deoxidiser as well as reducer of S.

Mn is least expensive among all the alloying elements.
 $\rightarrow$ It increases yield strength, tensile strength and hardness and toughness of steel.

→ It increases hardenability of the steel.
→ Upto 12-14% Mn helps in manufacturing of hard feed Mn steel.

* Ni → It is austenitic stabilizer.

Ni increases the strength of pearlite because it dissolves with the ferrite of pearlite and increases the strength of pearlite ferrite.

→ It increases toughness and ductility of plain C steel.

→ It is used for manufacturing of corrosion and oxidation resistance of steel.

→ Ni alloys with the iron to form alloy such as Invar, Elanvar.

15.11.17

* Chromium → It is less expensive than Ni, and it is a strong carbide forming element.

→ It is added to ~~make~~ alloy steel to make stainless and high speed steel.

→ Also increases hardness and wear resistance.

→ Cr also helps for age hardening.

→ Cr mostly added in low C steel is about 12-25%.

increase the corrosion resistance by making a passive film of Cr_2O_3 on the surface of the steel.

→ It is used to manufacture cutlery steel and surgeon blades.

★ Mo → Mo is a ferrite stabilizer and strong carbide forming element.

It is used in manufacturing of ^{high} speed steel and added to instead of W.

→ It increases hardenability of the steel.

→ It increases creep resistance.

→ It decreases the resistance to softening in tempering.

→ No carbide increases wear resistance.

★ W → It is a highly expensive metal.

→ It is also a strong deoxidizer but generally not added to high cast.

→ It is completely dissolved in α & γ .

→ It forms a carbide such as W_4C , W_6C .

→ It increases wear & abrasion resistance of steel.

→ It is used to manufacturing HSS.

→ It is also high heat & corrosion resistance as NiCrMo.

* V → It is a ferrite stabiliser and strong carbide forming element.

→ It forms the carbide like V_4C_3 & VC.

→ It is also expensive deoxidiser.

→ It is about 1-2% is enough for steel to harden.

→ It's carbide doesn't dissolve at high temp because it forms highly stable carbide.

→ It enhances hardenability & hardness of the steel.

SS (Stainless Steel) :-

→ SS are stainless in nature because it contains about 12-18% Cr.

→ This steel possesses excellent corrosion & oxidation resistance.

→ The Cr is used because it has more affinity for O_2 than Fe. So it forms ^a thin film of Cr_2O_3 on the surface of the steel.

→ The film is continuous and passive in nature.

→ So there is no further reaction. Takes place both Fe & O for the corrosion.

→ SS has different type of properties such as :-

i) Good corrosion & oxidation resistance.

ii) Good creep strength.

iii) High strength & hardness.

iv) High ductility & formability.

v) Excellent pleasing appearance.

vi) Good machinability.

★ Acc to the composition SS are of 5 types:-

i) Ferritic SS

ii) Martensitic SS

iii) Austenitic SS

iv) Duplex SS

v) Precipitation hardenable SS