

Materials Science and Engineering (BMEE209L)

by

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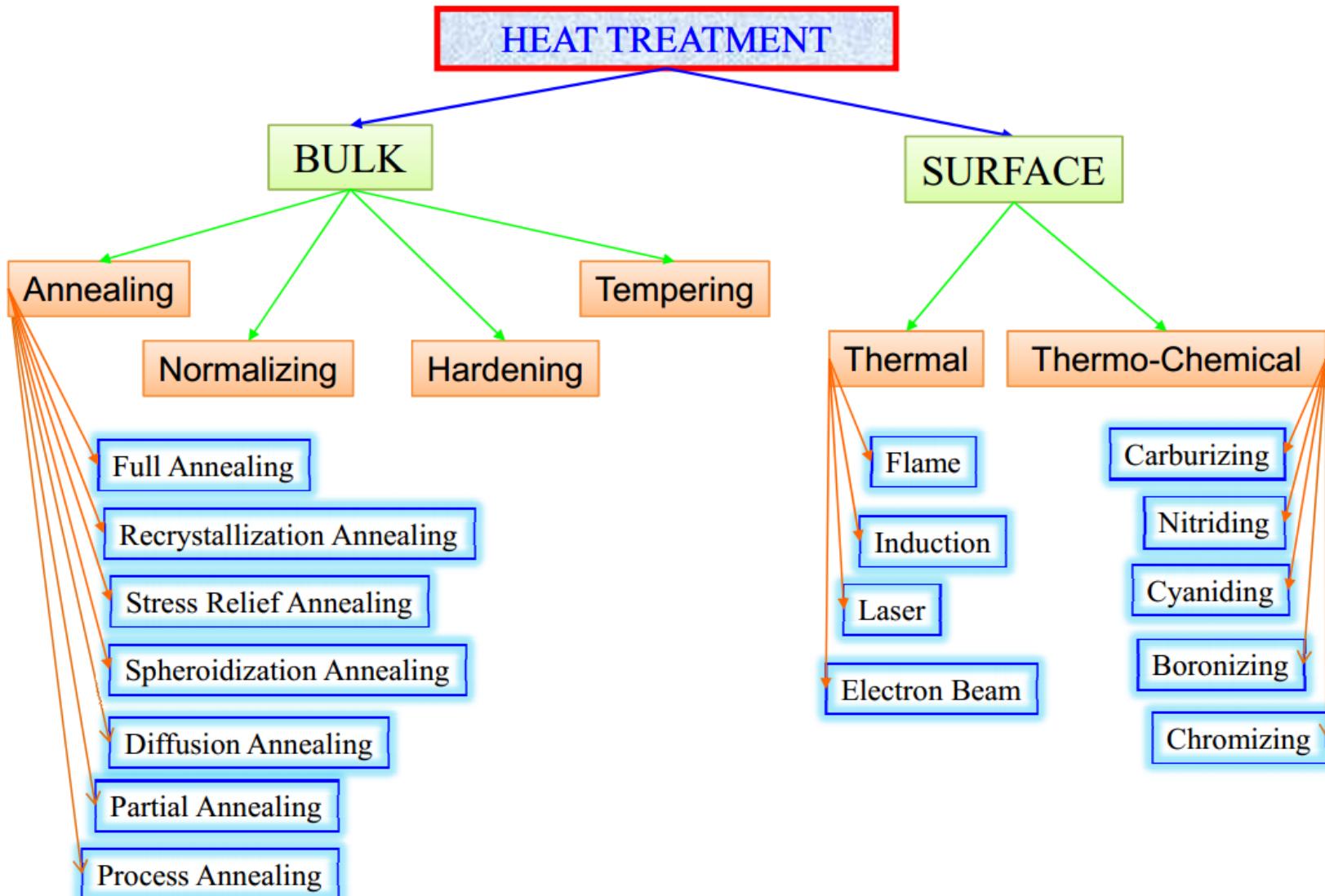


Content

□ **Module: 5 Heat Treatment** covers the following:

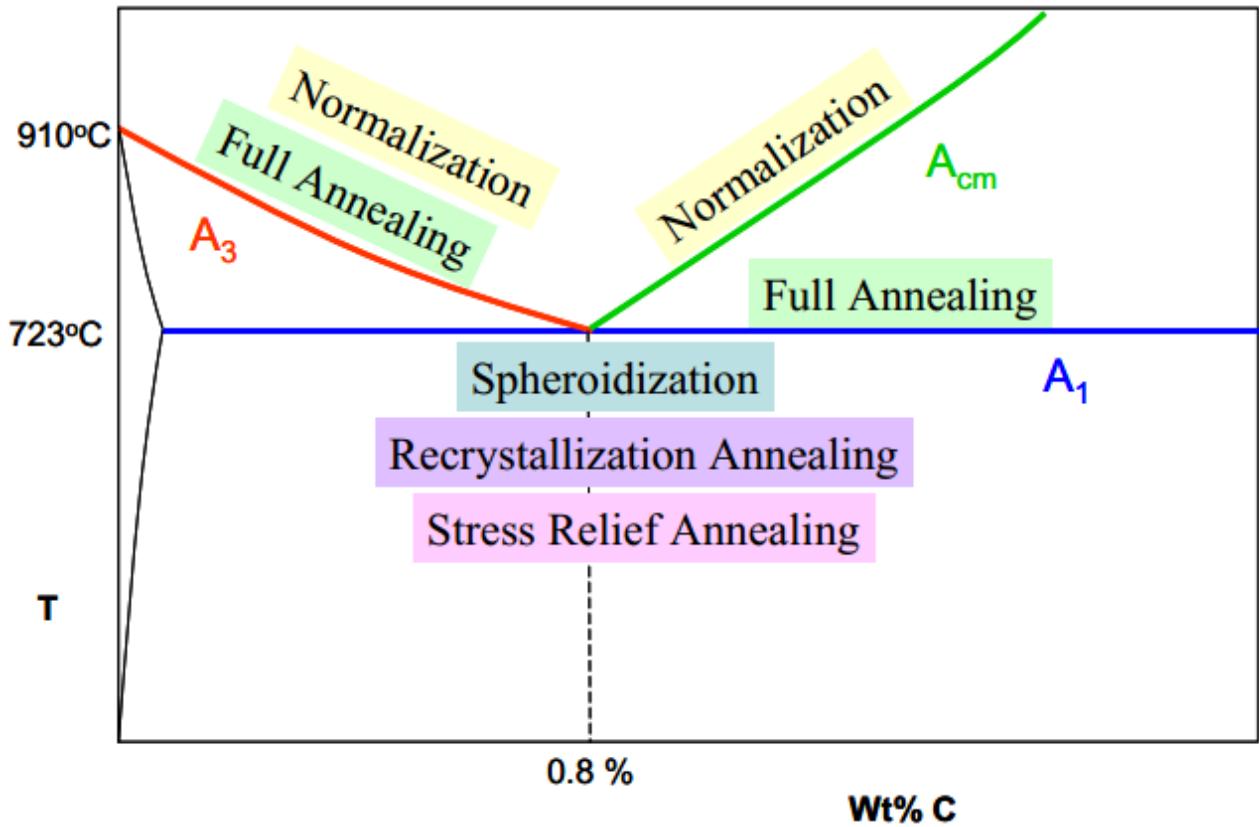
- Heat Treatment Processes for Steels (classification)
 - Annealing
 - Normalizing
 - Hardening
 - Sub-Zero treatment
 - Tempering
 - Tempering of Plain Carbon Steels
 - Tempering of Alloy Steels
 - Embrittlement During Tempering
 - Heat Treatment Defects
 - Hardenability – Introduction
 - Hardness and hardenability
 - Determination of hardenability
 - Factors affecting hardenability
 - Precipitation Hardening
 - Surface Hardening Treatment of Steels
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Classification



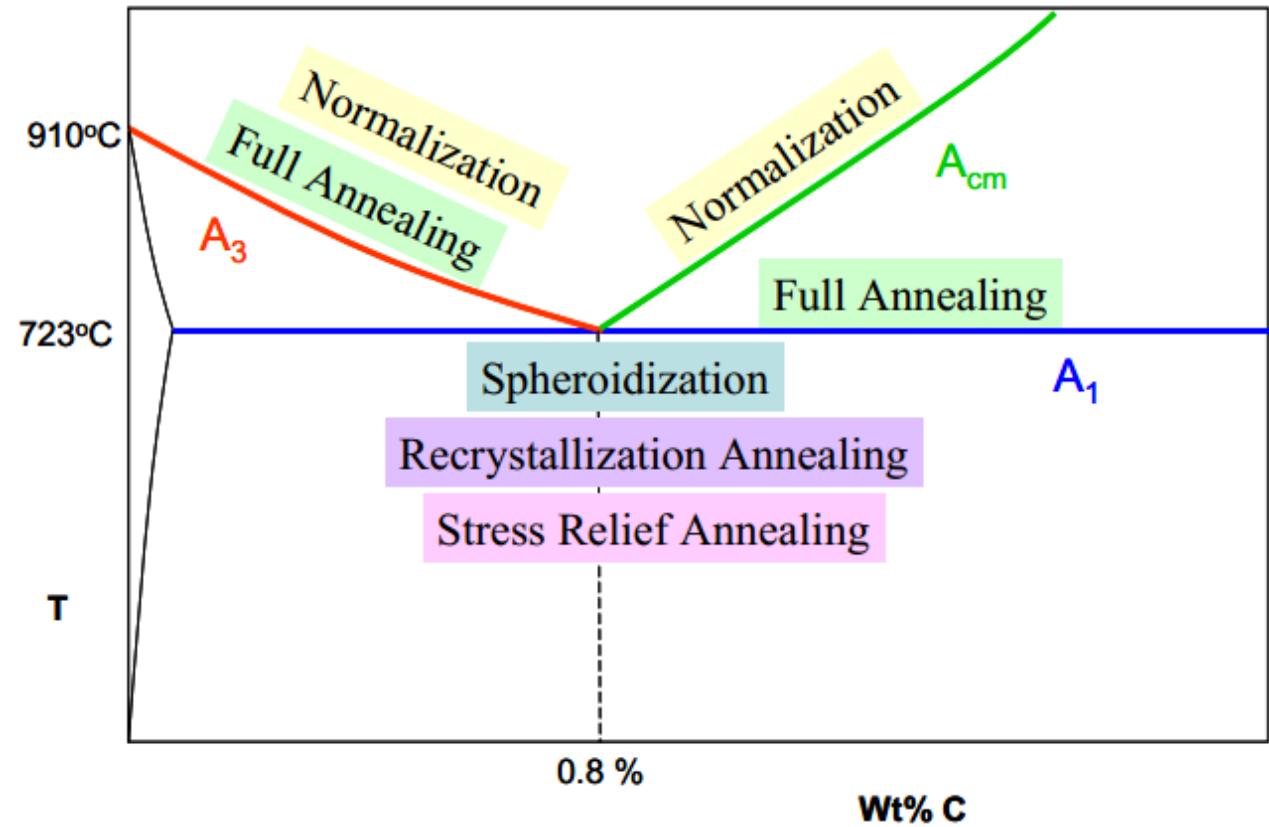
Annealing

- Full Annealing
- The steel is heated above A_3 (for hypo-eutectoid steels) | A_1 (for hyper-eutectoid steels) →(hold) →then the steel is furnace cooled to obtain Coarse Pearlite
- Coarse Pearlite has ↓ Hardness, ↑ Ductility



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- Recrystallization Annealing**
- The Heat below A_1 → Sufficient time → Recrystallization**
 - Cold worked grains → New stress free grains
- Used in between processing steps (e.g. Sheet Rolling)



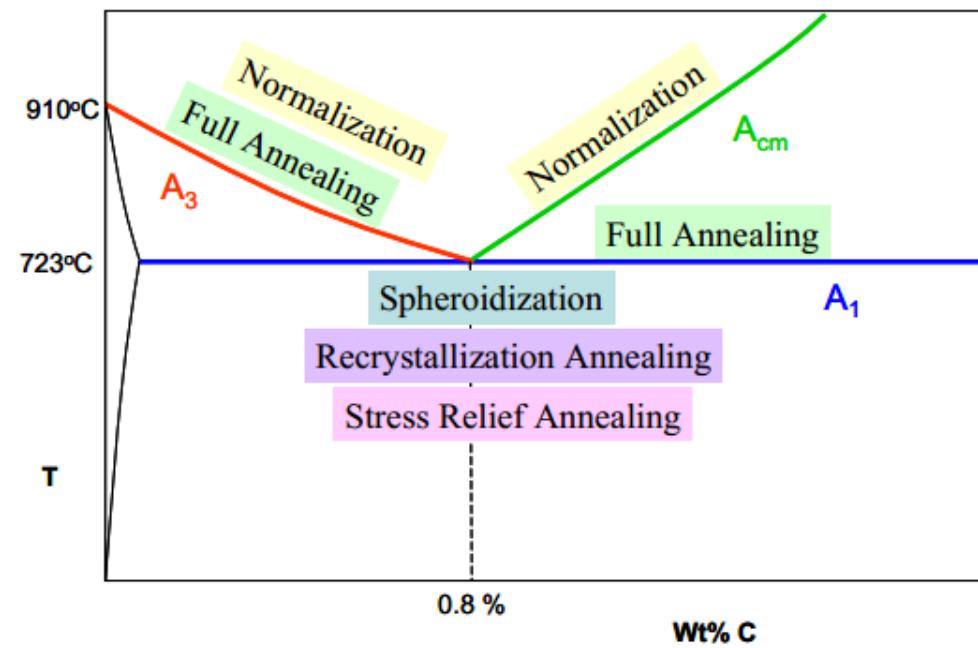
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□ Stress Relief Annealing

Residual stresses → Heat below A_1 → **Recovery**

- Differential cooling
- Martensite formation
- Machining and cold working
- Welding

Annihilation of dislocations,
polygonization



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Spheroidization Annealing

Heat below/above A_1 (Prolonged holding*)

Cementite plates → Cementite spheroids → ↑ Ductility

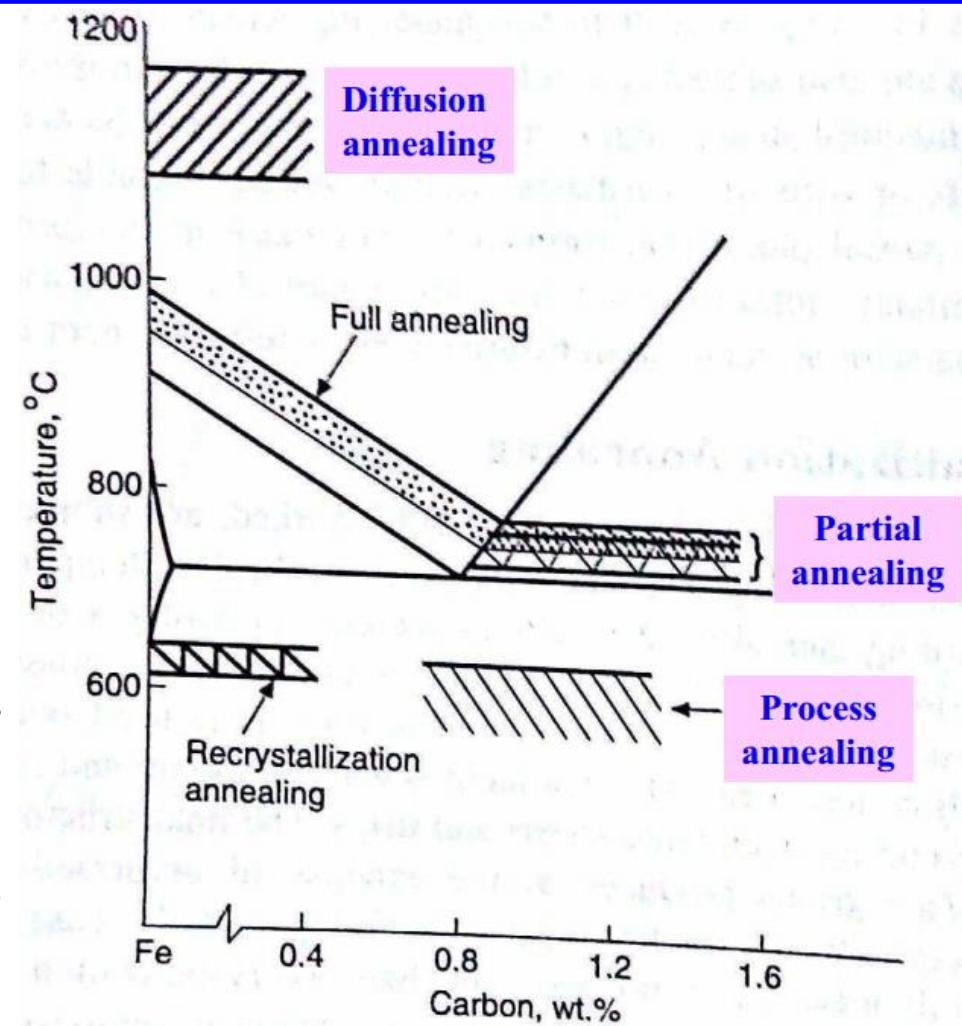
- Used in high carbon steel requiring extensive machining prior to final hardening and tempering
- Driving force is the reduction in interfacial energy
- The spheroidized structure is desirable when minimum hardness, maximum ductility, or (in high-carbon steels) maximum machinability is important.
- Low-carbon steels are seldom spheroidized for machining, because in the spheroidized condition they are excessively soft and “gummy”.
- Medium-carbon steels are sometimes spheroidization annealed to obtain maximum ductility.

*If the steel is kept too long at the spheroidized-annealing temperature, the cementite particles will coalesce and become elongated thus reducing machinability.



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- Diffusion Annealing
- This process also known as **homogenizing annealing**, is employed to remove any structural non-uniformity.
- Dendrites, columnar grains and chemical in-homogeneities are generally observed in the case of ingots, heavy plain carbon steel casting, and high alloy steel castings. These defects promote brittleness and reduce ductility and toughness of steel.
- In diffusion annealing treatment, steel is heated sufficiently above the upper critical temperature (say, 1000-1200°C), and is held at this temperature for prolonged periods, usually 10-20 hours, followed by slow cooling.
- Segregated zones are eliminated and a chemically homogeneous coarse grain steel is obtained by this treatment as a result of diffusion.
- The coarse grained structure can be refined either by plastic working for ingots or by employing a second heat treatment for castings.
- Hypo-eutectoid and eutectoid steel castings are given full annealing treatment, whereas hypereutectoid steel castings are either normalized or partially annealed for this purpose.



Temperature ranges for various types of annealing processes



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- Partial Annealing**
- Partial annealing is also referred to as **inter-critical annealing** or **incomplete annealing**. In this process, steel is heated between the A_1 and the A_3 or A_{cm} . It is followed by slow cooling.
- Generally, hypereutectoid steels are subjected to this treatment. Resultant microstructure consists of fine pearlite and cementite. The reason for this is that grain refinement takes place at a temperature of about 10 to 30 °C above A_{c1} for hyper-eutectoid steels.
- As low temperature are involved in this process, so it is cost effective than full annealing.

- Process Annealing**
- In this treatment steel is heated to a temperature below the lower critical temperature, and is held at this temperature for sufficient time and then cooled. Since it is a **subcritical annealing**, cooling rate is of little importance.
- The purpose of this treatment is to reduce hardness and to increase ductility of cold-worked steel so that further working may be carried out easily. It is an Intermediate operation and is sometimes referred to as in process annealing.
- The process is less expensive than Recrystallization annealing.

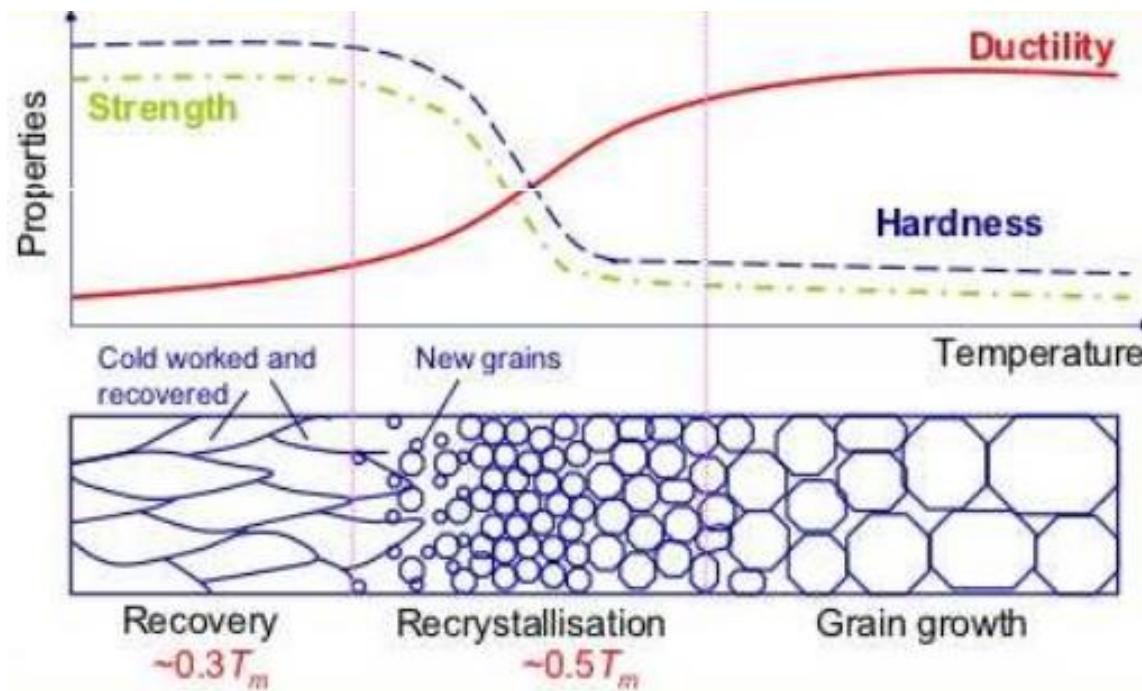


Concept of Recovery, Recrystallization, and Grain Growth

- Recovery, Recrystallization, and Grain growth are microstructural changes that occur during annealing after cold plastic deformation and/or during hot working.

- Three annealing stages:

- Recovery
- Recrystallization
- Grain Growth



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

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

- When a metal is hot worked. The conditions of deformation are such that the sample is soft and ductile. The effects of strain hardening are negated by dynamic and static processes (which keep the sample ductile)
- The lower limit of temperature for hot working is taken as $0.6 T_m$

Recrystallization temperature ($\sim 0.4 T_m$)

- The effects of strain hardening is not negated. Recovery mechanisms involve mainly motion of point defects.
- Upper limit $\blacktriangleright 0.3 T_m$



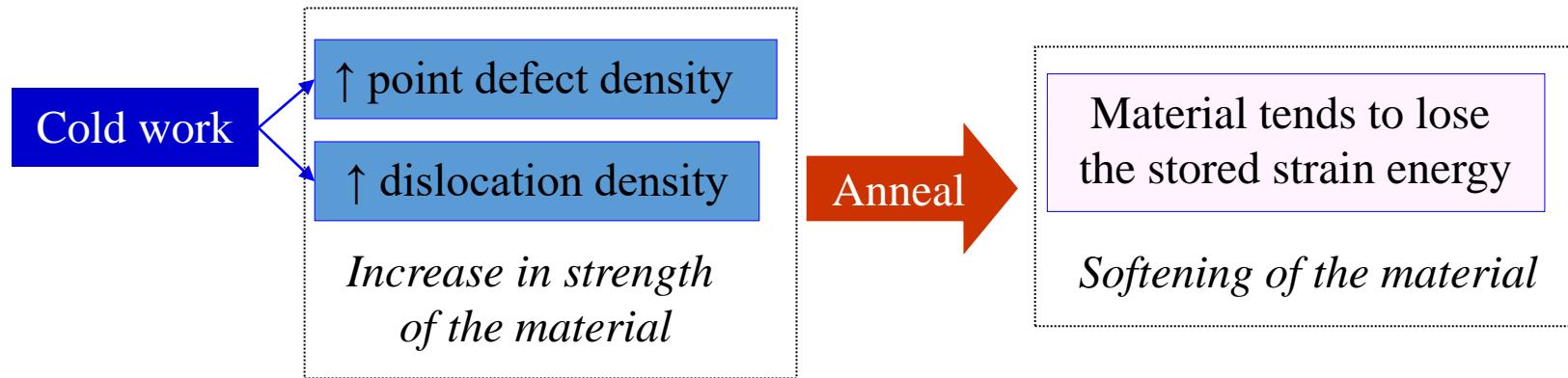
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- Plastic deformation in the temperature range $(0.3\text{--}0.5) T_m$ → **COLD WORK**
- Point defects and dislocations have strain energy associated with them.
- $(1\text{--}10)\%$ of the energy expended in plastic deformation is stored in the form of strain energy (in these defects) → The material becomes **battery of energy..!**
- The cold worked material is in a micro structurally metastable state.
- Depending on the severity of the cold work the **dislocation density** can increase 4–6 orders of magnitude more. The material becomes stronger, but less ductile.
- The cold worked material is stronger (harder), but is brittle.
- Heating the material (typically below $0.5 T_m$) is and holding for sufficient time is a heat treatment process called **annealing**.
- Depending on the temperature of annealing processes like **recovery** (at lower temperatures) or **recrystallization** (at higher temperatures) may take place.
- During these processes the material tends to go from a **micro-structurally metastable state** to a lower energy state (towards a **stable state**).
- Further **annealing** of the recrystallized material can lead to **grain growth**.

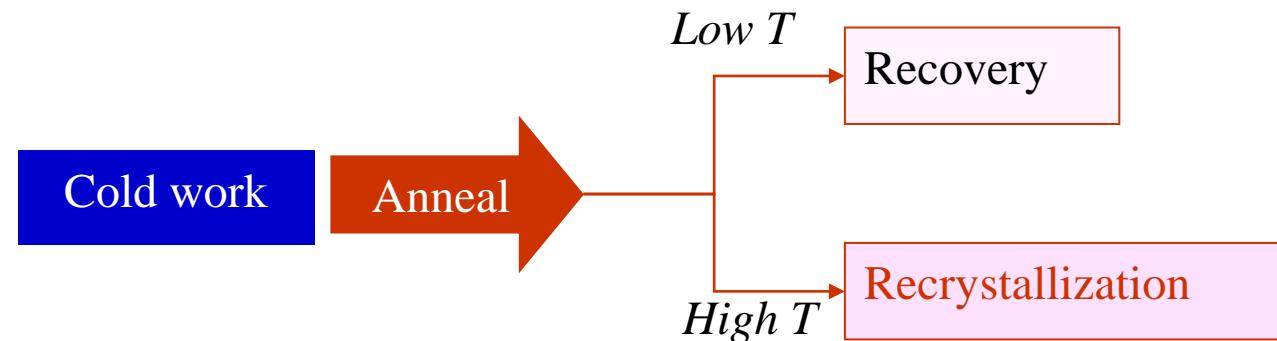
$$\begin{array}{ccc} \textit{Annealed material} & \xrightarrow{\textit{Cold work}} & \textit{Stronger material} \\ \rho_{\text{dislocation}} \sim (10^6 - 10^9) & & \rho_{\text{dislocation}} \sim (10^{12} - 10^{14}) \end{array}$$



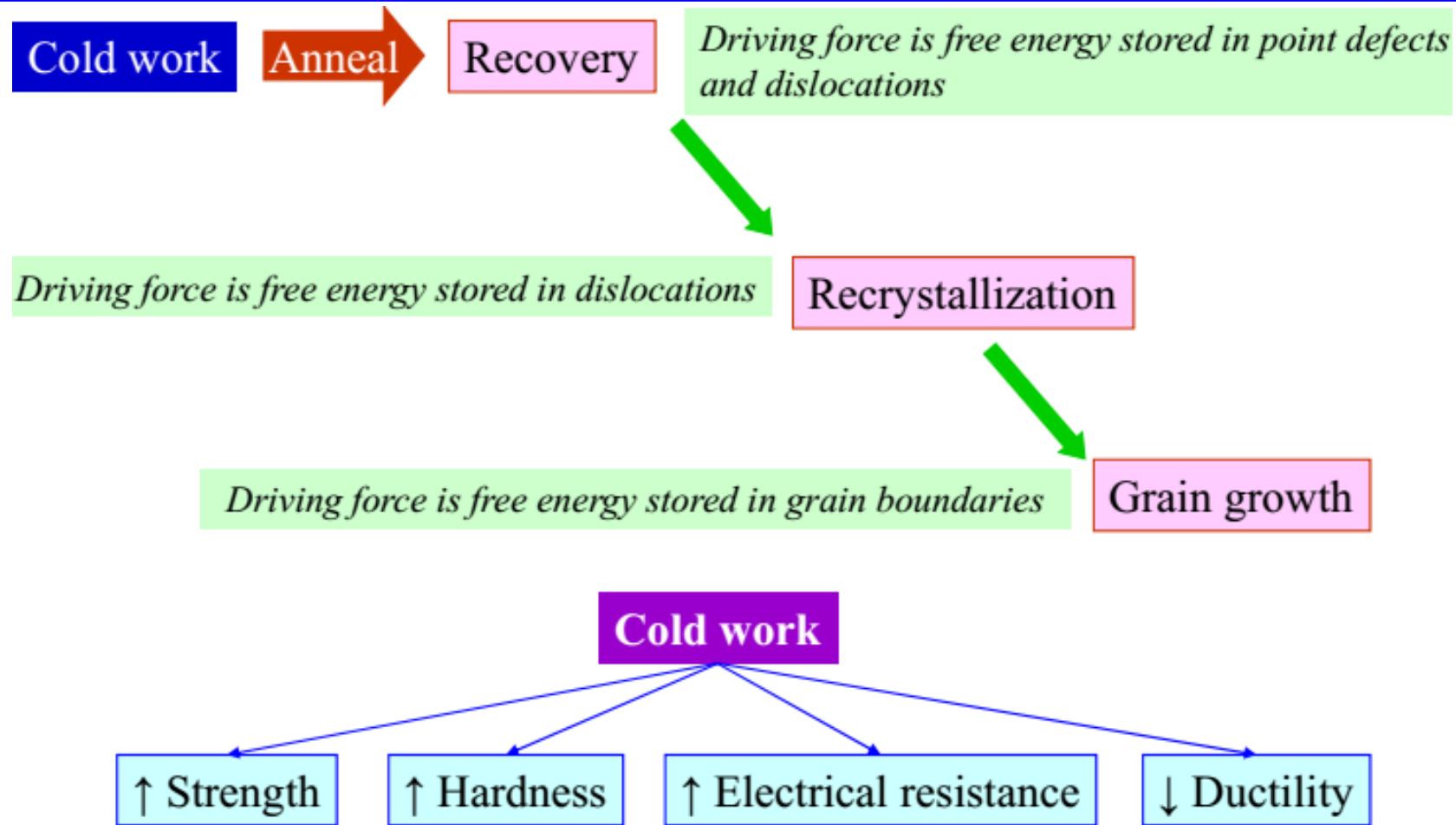
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- During cold work the point defect density (vacancies, self interstitials...) and dislocation density increase.
- Typical cold working techniques are rolling, forging, extrusion etc.
- Cold working is typically done on ductile metals (e.g., Al, Cu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



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

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



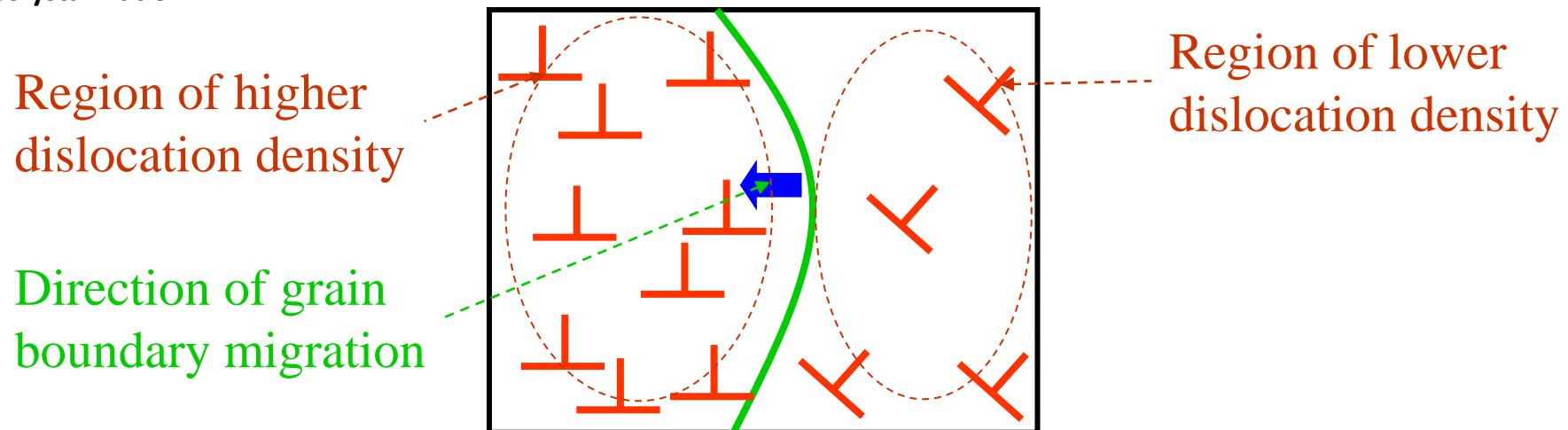
Recovery

- Recovery takes place at low temperatures of annealing.
- Apparently no change in microstructure.
- Excess point defects created during cold work are absorbed:-
 - at surface or grain boundaries
 - by dislocation climb
- Random dislocations of opposite sign come together and annihilate (destroy) each other.
- Dislocations of same sign arrange into low energy configurations:-
 - Edge dislocations 'rearrange' to form Tilt boundaries
 - Screw dislocations 'rearrange' to form Twist boundaries
- The formation of low angle tilt and twist boundaries is termed as Polygonization.
- Overall reduction in dislocation density is small.
- At the early stage of annealing of cold formed metals, external thermal energy permits the dislocations to move and form the boundaries of a polygonised sub-grain structure while the dislocation density stays almost unchanged.
- This process also removes the residual stresses formed due to cold working significant.
- The recovering of physical and mechanical properties varies with the temperature and time.



Recrystallization

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



Contd...

- Deformation $\uparrow \Rightarrow$ recrystallization temperature ($T_{\text{Recrystallization}}$) \downarrow
- Initial grain size $\downarrow \Rightarrow$ recrystallization temperature \downarrow
- High cold work + low initial grain size \Rightarrow finer recrystallized grains
- \uparrow cold work temperature \Rightarrow lower strain energy stored $\Rightarrow \uparrow$ recrystallization temperature
- Rate of recrystallization = exponential function of temperature

- The $T_{\text{Recrystallization}}$ = strong function of the purity of the material
- $T_{\text{Recrystallization}}$ (very pure materials) $\sim 0.3 T_m$
- $T_{\text{Recrystallization}}$ (99.999 % pure Al) $\sim 75^\circ\text{C}$

- $T_{\text{Recrystallization}}$ (impure) $\sim (0.5 - 0.6) T_m$
- $T_{\text{Recrystallization}}$ (commercial purity) $\sim 275^\circ\text{C}$

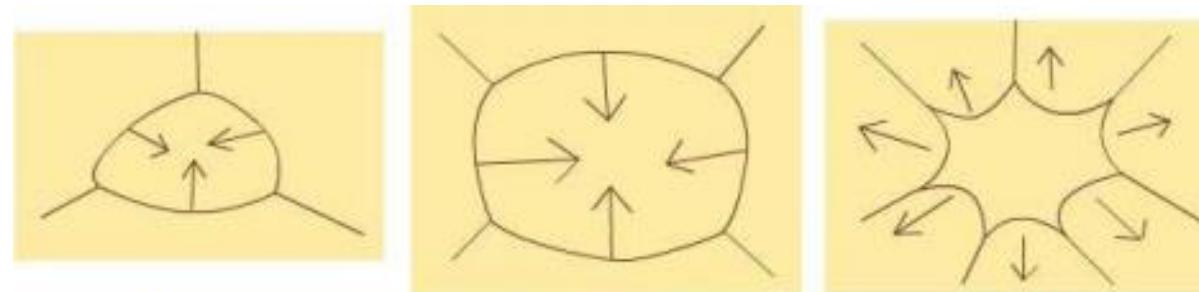
- The impurity atoms segregate to the grain boundary and retard their motion \rightarrow Solute drag (can be used to retain strength of materials at high temperatures).

- Second phase particles also pin down the grain boundary during its migration.



Grain Growth

- The interfaces in a material cost the **system energy**. The excess free energy associated with the interfaces is the **interfacial free energy**.
- Grain boundaries are the interfaces between two crystallites which are differently oriented in space; the excess free energy associated with the grain boundary is the **grain boundary energy**.
- The grain boundary energy acts as the driving force for the movement of grain boundaries. Hence, if a recrystallized material is further annealed, then grains growth takes place; bigger grains grow at the cost of smaller ones. This process is known as **grain growth**.
- Since the driving force for grain growth is the interfacial energy, and since the excess energy associated with a system due to interfaces is related to the curvature of the interface, the grain growth is curvature driven. In Figure we show the direction of movement of grain boundaries and their relationship to curvature (in 2D systems).

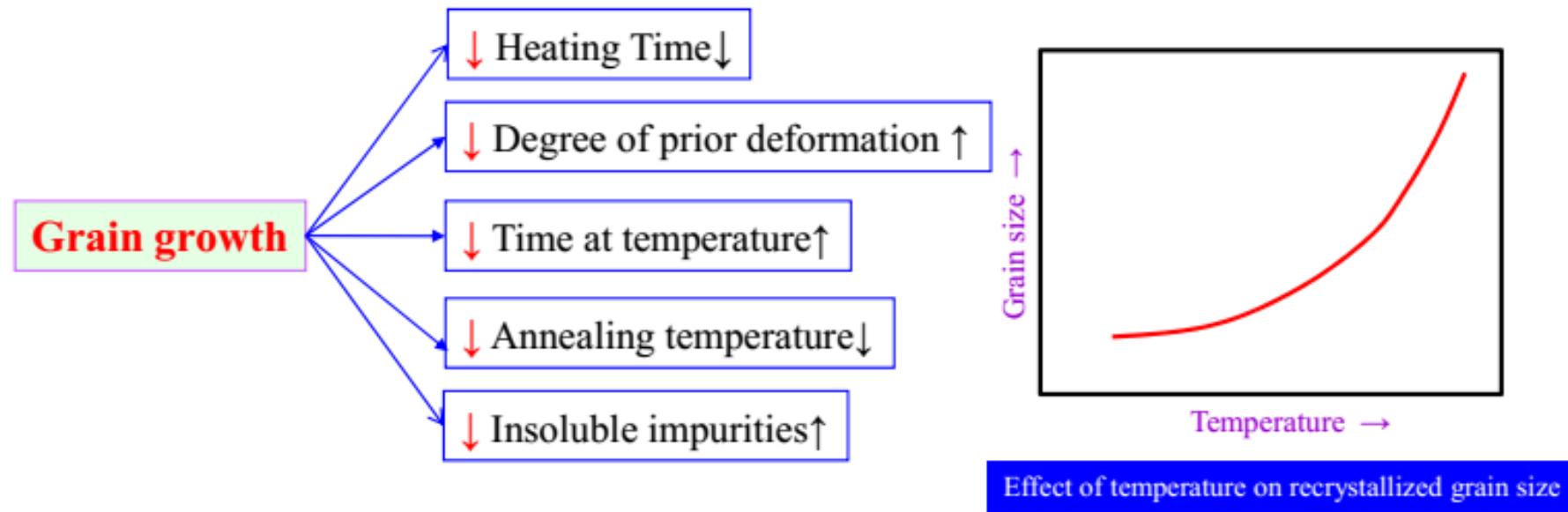


Curvature driven growth of grains (in 2D)

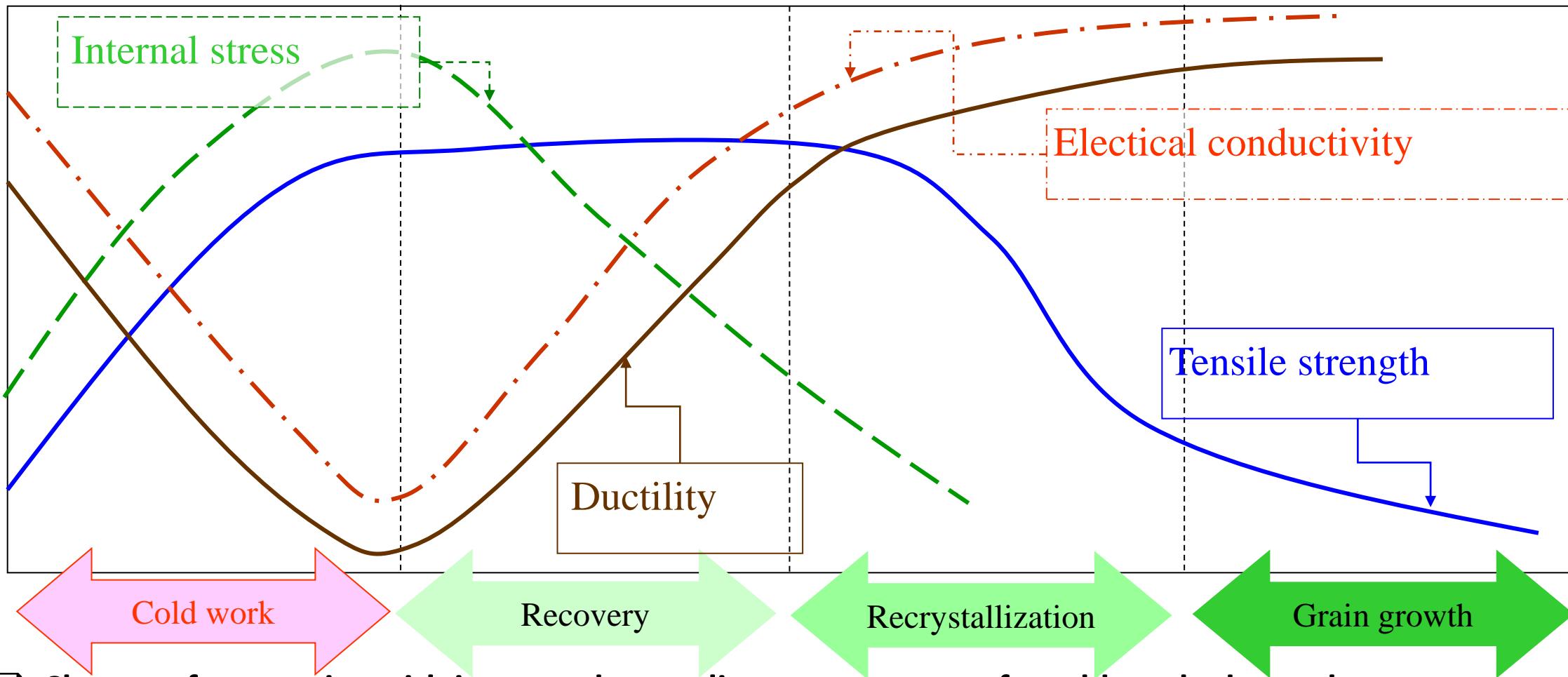


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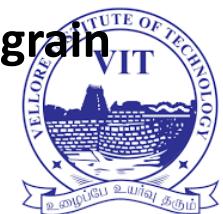
- Large grains have lower free energy than small grains. This is associated with the reduction of the amount of grain boundary.
- Therefore, under ideal conditions, the lower energy state for a metal would be as a single crystal. This is **driving force** for grain growth.
- Opposing this force is the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



Summary

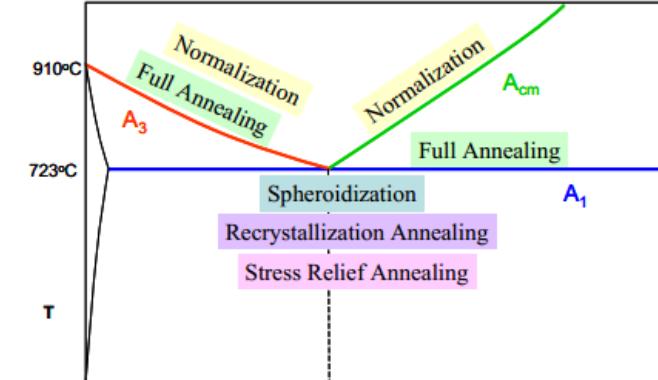
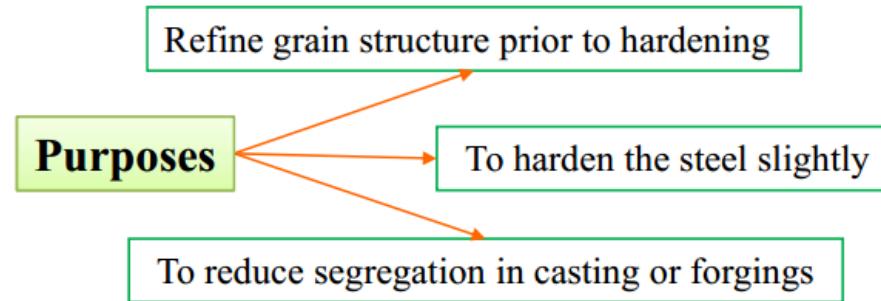


- Change of properties with increased annealing temperature of a cold worked sample.
- Note that there are changes in properties beyond recrystallization temperatures too due to grain growth.



Normalizing

Heat above A_3 | A_{cm} → Austenization → Air cooling → Fine Pearlite (Higher hardness)



- In hypo-eutectoid steels normalizing is done 50°C above the annealing temperature
- In hyper-eutectoid steels normalizing done above A_{cm} → due to faster cooling cementite does not form a continuous film along GB

Annealed Vs Normalized

Annealed	Normalized
Less hardness, tensile strength and toughness	Slightly more hardness, tensile strength and toughness
Pearlite is coarse and usually gets resolved by the optical microscope	Pearlite is fine and usually appears unresolved with optical microscope
Grain size distribution is more uniform	Grain size distribution is slightly less uniform
Internal stresses are least	Internal stresses are slightly more



Hardening

Heat above A_3 | A_{cm} → Austenization → Quench (higher than critical cooling rate)

- Certain applications demand high tensile strength and hardness values so that the components may be successfully used for heavy duty purposes. High tensile strength and hardness values can be obtained by a processes known as Hardening.
- Hardening process consists of four steps. The first step involves heating the steel to above A_3 temperature for hypo-eutectoid steels and above A_1 temperature for hyper-eutectoid steels by $50^{\circ}C$.
- The second step involves holding the steel components for sufficient soaking time for homogeneous austenization.
- The third step involves cooling of hot steel components at a rate just exceeding the critical cooling rate of the steel to room temperature or below room temperature.
- The final step involves the tempering of the martensite to achieve the desired hardness. Detailed explanation about tempering is given in the subsequent sections. In this hardening process, the austenite transforms to martensite. This martensite structure improves the hardness.
- In the hardening process, which involves quenching and tempering. During quenching outer surface is cooled quicker than the center. In other words the transformation of the austenite is proceeding at different rates. Hence there is a limit to the overall size of the part in this hardening process.



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- A few salient features in hardening of steel

- Proper quenching medium should be used such that the component gets cooled at a rate just exceeding the critical cooling rate of that steel.

- Alloy steels have less critical cooling rate and hence some of the alloy steels can be hardened by simple air cooling.

- High carbon steels have slightly more critical cooling rate and has to be hardened by oil quenching.

- Medium carbon steels have still higher critical cooling rates and hence water or brine quenching is necessary.

Factors affecting Hardening Processes

- Chemical composition of steel
- Size and shape of the steel part
- Hardening cycle (heating/cooling rate, temp, soak time)
- Homogeneity and grain size of austenite
- Quenching media
- Surface condition of steel part

Hardening Methods

- Conventional or direct quenching
- Quenching in stages in sequence in different media
- Spray Quenching
- Quenching with self tempering
- Austempering or Isothermal Quenching
- Martempering



Retained Austenite

- Austenite that is present in in the ferrous alloys even after the completion of the heat treatment process is referred to as **retained austenite**. In simple words, retained austenite is the **untransformed austenite**.
- Austenite transforms to martensite between M_s and M_f temperatures as it is essentially an athermal transformation. However, this transformation never goes to completion, i.e., 100% martensite (M_f temperature line is illustrated as dotted line in TTT diagrams).
- This is because at M_f , a small amount of (~1%) of austenite is present in highly stressed state along with ~99% martensite, and can not transform to martensite because unfavourable stress conditions.
- Both M_s and M_f temperatures decrease with increase in carbon content. Therefore amount of retained austenite in hardened steels increase with increase in carbon content.

- All alloying elements, except Al and Co, lower the M_s temperature and hence enhance the amount of retained austenite. Therefore, both high carbon steels and high alloy steels are more prone to the presence of retained austenite.
- The substructure of retained austenite differs from that of the original austenite as it has as a higher density of imperfections like dislocations, stacking faults, etc. which are created by local plastic deformation of the austenite by martensite crystals.
- Tool steels may have retained austenite in the range of 5-35%. At the surface of a quenched steel, that restraints are minimum. **R.A is less at surface than center of the part**.



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- Advantages**
- Ductility of austenite can help to relieve some internal stresses developed due to hardening, to reduce danger of distortion and cracks. 10% retained austenite along with martensite is desirable.
- The presence of 30-40% retained austenite makes straightening operation of the components possible after hardening. Straightening increases the hardness slightly.
- Non-distorting steels owe their existence to retained austenite. Here enough austenite is retained to balance the transformational contracting during heating, on the formation of austenite from ferrite carbide aggregate on the one hand, and the expansion corresponding to the formation of martensite during cooling, on the other, Here, the basis of dimensional stability of non-distorting steels is the presence of retained austenite.

- Disadvantages**
- The soft austenite if present, in large amounts, decreases the hardness of hardened steels.
- As retained austenite may transform to lower bainite, or to martensite, there takes place increase in dimensions of the part. Not only it creates problems in precision gauges, or dies, the neighboring parts may be put under stress by it. In the component itself, stresses may be created to cause distortion or cracking.
- Retained austenite decreases the magnetic properties of the steel.



Sub-Zero Treatment

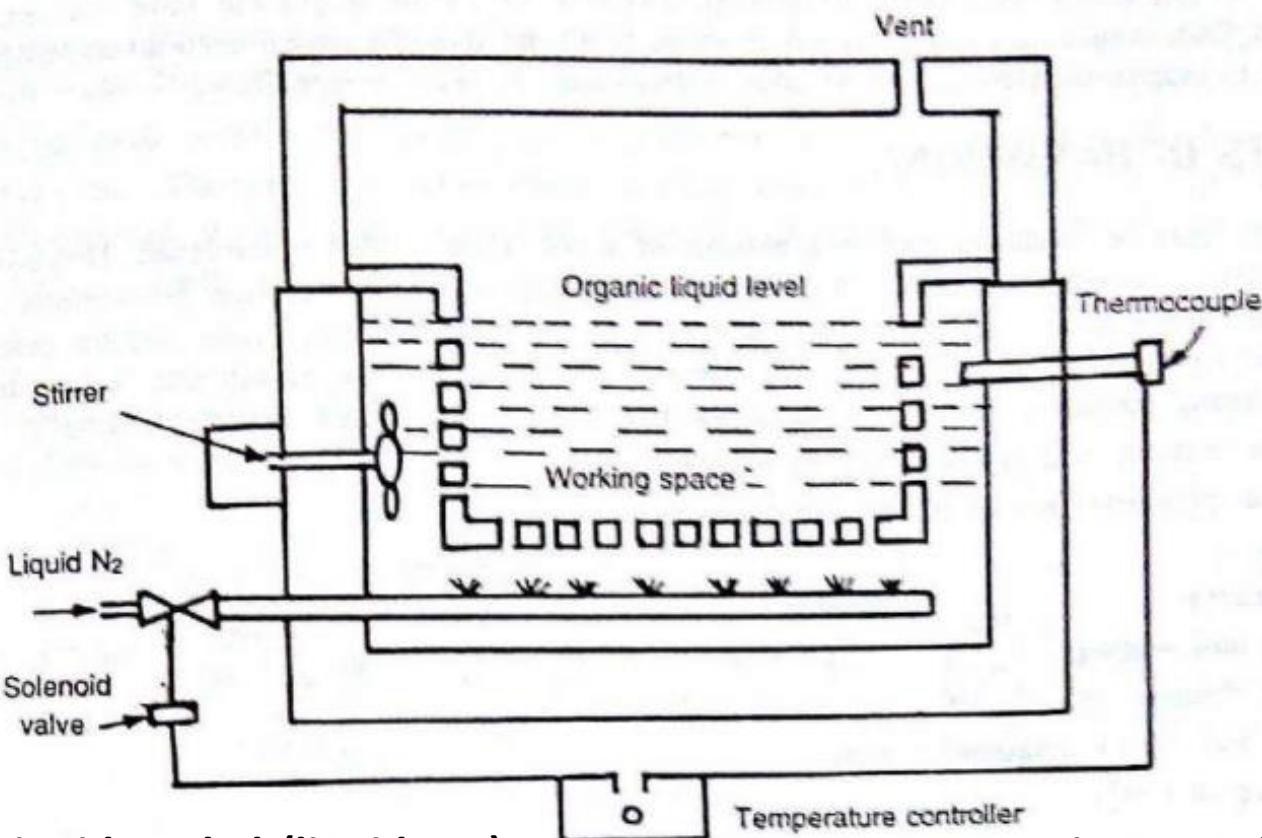
- The retained austenite is generally undesirable, sub-zero treatment is one of the method to eliminate retained austenite.
- As the room temperature lies between M_s and M_f temperatures of steel, quenching to room temperature results in retained austenite.
- Sub-zero treatment consists in cooling the hardened steel to a temperature below 0 °C. The temperature of the sub zero treatment depends on the position of M_f temperature of the steel.
- A steel can be cooled much below the M_f temperature, but it, evidently achieves nothing, because it cannot bring about any additional increase of hardness, or any additional increase of martensite, because the martensitic transformation ends at M_f temperature.
- Sub-zero treatment is more effective, if it is carried out immediately after quenching operation. Any lapse of time between hardening and the cold treatment causes the stabilization of austenite, makes the retained austenite resistant to further transformation.
- Most steels can be cooled by sub-zero treatment in a low cooling unit with one of the mediums as given in table (next page) .
- The low-cooling unit consists of two vessels, the interior one of copper, where the parts or tools to be deep frozen, are placed and the exterior one of steel provided with a good heat insulation.



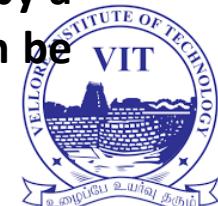
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Table : Subzero Coolants with Temperature of Application

Coolant	Minimum temperature °C
Dry ice (solid CO_2) + Acetone	-78
Ice + Salt (NaCl)	-23
Ice + Salt (CaCl_2)	-55
Liquid air	-183
Liquid Nitrogen	-196
Liquid Pentane	-129
Freon	-111



Liquid cooled (liquid N_2) system. Components are immersed in a bath of alcohol, or trichloro ethylene, which is cooled by a submerged liquid nitrogen spray (-150°C), cooling rates can be controlled.



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- The space in between the vessels is filled with one of the chosen medium, or a system (figure in previous page) which is inexpensive and can be used.
- Usually the temperature range used is in range of -30°C to -150°C , and total time of cooling and holding at that temperature (M_f) varies from $\frac{1}{2}$ –1 hour. The hardness increased by 2–4 HRc.
- As the amount of martensite increases by sub-zero treatment, it increases hardness, abrasion resistance, fatigue resistance and eliminates the danger of developing grinding cracks.
- As the newly formed martensite may add further to unfavorable stresses to cause distortion and cracks, the complicated, or intricate shaped components may be first tempered at 150 – 160 $^{\circ}\text{C}$ immediately after first quenching and then given the sub-zero treatment.
- **Sub-Zero treatment has been most extensively used for...!**
 - Alloyed tool steels - like high speed steel, which now shall need only single stage tempering.
 - Tools and components which need exact dimensions – gauges.
 - Carburized steels, especially alloy steels (having elements like Ni in it) to increase their hardness and wear resistance.
 - Steels having 0.8–1.1% C as hardness increases by 1–3 HRc.

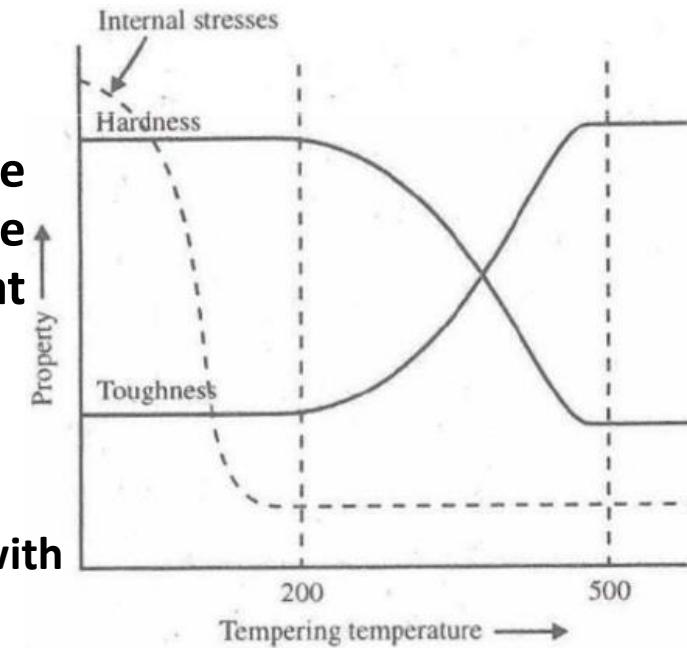


Tempering

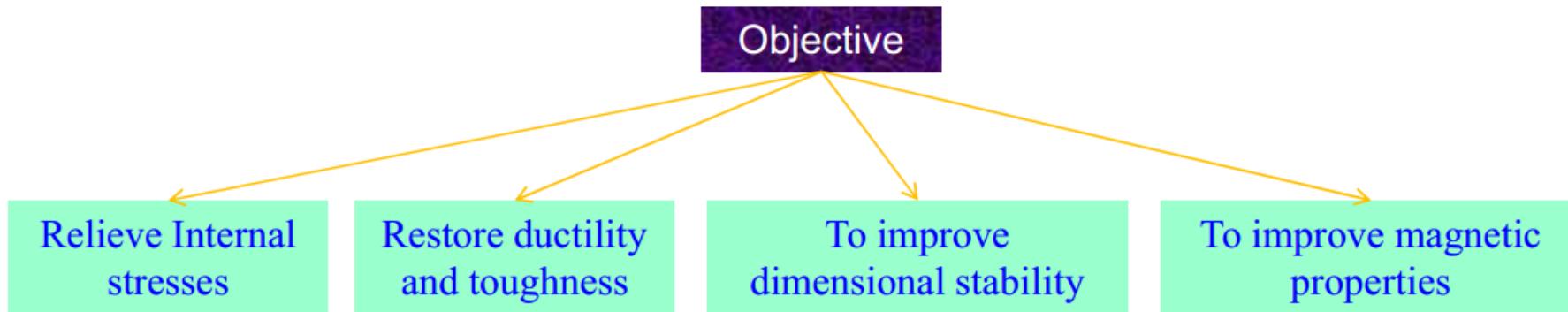
- The hardened steel is not readily suitable for engineering applications. It possesses following three drawbacks.
 - Martensite obtained after hardening is extremely brittle and will result in failure of engineering components by cracking.
 - Formation of martensite from austenite by quenching produces high internal stresses in the hardened steel.
 - Structures obtained after hardening consists of martensite and retained austenite. Both these phases are metastable and will change to stable phases with time which subsequently results in change in dimensions and properties of the steel in service.

- Tempering helps in reduce these problems. Tempering is the process of heating the hardened steel to a temperature maximum up to lower critical temperature (A_1), soaking at this temperature, and then cooling, normally very slowly.

Variation in properties with tempering temperature



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Structure in as Quenched state

- Highly supersaturated martensite
- Retained austenite
- Undissolved carbides
- Rods, or plates of carbide particles produced during ‘auto-tempering’
- Segregation of carbon



Tempering of Plain Carbon Steels

- First Stage of Tempering
- First stage of tempering temperature extends from room temperature to 200 °C. The tempering reactions in steels, containing carbon less than 0.2%, differ somewhat from the steels containing more than 0.2% carbon.
- In the former, if carbon atoms have not yet segregated (during quenching) to dislocations, these diffuse and segregate around the dislocations and lath boundaries in the first stage of tempering. No ϵ -carbide forms as all the carbon gets locked up to the dislocations (defects).
- Martensite in steels with more than 0.2% carbon is highly unstable because of super saturation, and interstitial diffusion of carbon in BCT martensite can occur. Thus in the first stage of tempering, the decomposition of martensite into low-tetragonality martensite (containing ~0.2%C, c/a ~ 1.014) and ϵ -carbide, $Fe_{2.4}C$ occurs. (There are reports of precipitation of eta-carbide, Fe_2C and Haggs carbide, $Fe_{2.2}C$).
- ϵ -carbide is a separate phase and is not a preliminary step in the formation of cementite, but it nucleates and grows more rapidly than cementite. It has HCP structure with $c = 4.33A^\circ$, $a = 2.73A^\circ$, $c/a = 1.58A^\circ$ and forms as small (0.015-0.02 μm) platelets, or needles observed under electron microscope.
- The structure at this stage referred to as tempered martensite, which is double phase mixture of low tetragonal martensite and ϵ -carbide.
- In this stage volume \downarrow because specific volume of martensite \downarrow due to rejecting of C atoms.



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- **Second Stage of Tempering**
- Second stage of tempering temperature lies **between 200-300 °C**. The amount of retained austenite in the as-quenched steel depends mainly on the composition of the steel, and the temperature to which steel is quenched.
- In the second stage of tempering **retained austenite transforms to lower bainite** (the carbide in bainite is ϵ -carbide). The matrix in lower bainite is cubic ferrite ($c/a = 1$), whereas in tempered martensite, the low tetragonal martensite has $c/a \sim 1.014$.
- When retained austenite changes to lower bainite, there takes place increase in volume.

- **Third Stage of Tempering**
- Third stage of tempering temperature lies **between 200-350 °C**. In this stage of tempering, **ϵ -carbide dissolves in matrix**, and low tetragonal martensite loses its completely its carbon and thus, the tetragonality to become ferrite .
- Cementite forms as rods at interfaces of ϵ -carbide and matrix, twin boundaries, interlath boundaries, or original austenite grain boundaries.
- During this stage, volume decreases just as in stage one, due to complete loss of tetragonality. In a 1% carbon steel, the total decrease in length in the first and third stages is around 0.25%.

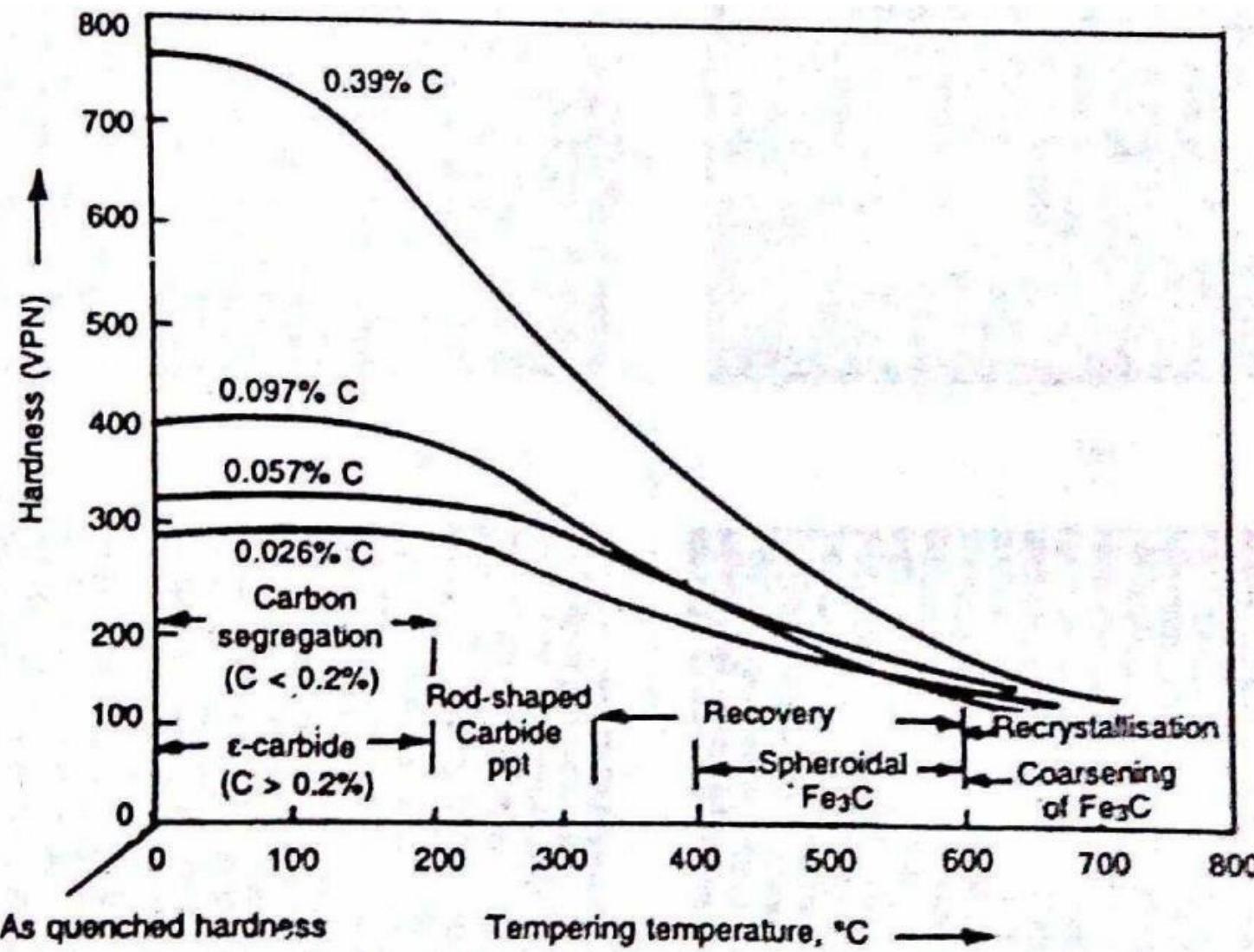


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- **Fourth Stage of tempering**
- **Fourth Stage of tempering temperature lies between 350-700 °C.**
- **Growth and spheroidisation of cementite, as well as recovery and Recrystallization of ferrite occur.** Though the growth of cementite starts above 300 °C, its spheroidisation starts above 400-700 °C.
- Spheroidisation takes place due to reduction in interfacial energy of ferrite-cementite interfaces. As quenched martensite has high concentration of lattice defects. Though their annealing out starts in the third stage of tempering, but the cementite precipitates retard the recovery processes.
- Substantial recovery processes starts occurring only above 400 °C. original lathe boundaries are stable up to 600 °C, but above this, these are replaced by equiaxed-ferrite grain boundaries - the process, which is best described as 'Recrystallization'.
- In the end, the optical microstructure consists of equiaxed ferrite grains with coarse spheroidal particles of cementite, and then the structure is called globular pearlite, or spheroidized cementite.
- The structure perhaps is the most stable of all ferrite - cementite aggregates, and is the softest with highest ductility with best machinability.



Effect of Carbon on Tempering



Effect of tempering temperature (1 hour at each temperature) on hardness and reactions



Tempering of Alloy Steels

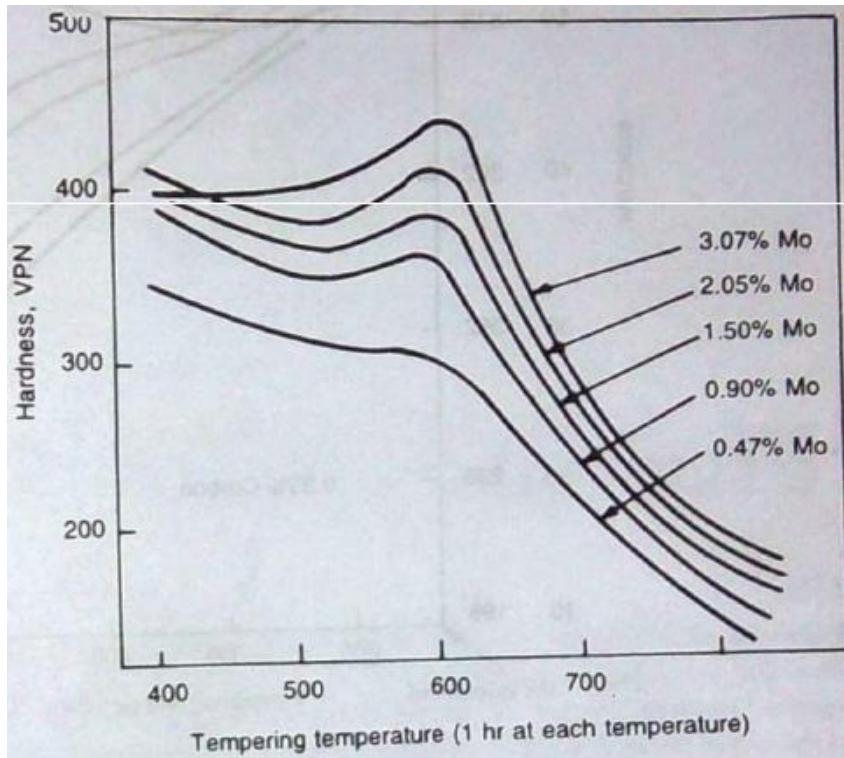
- The presence of alloying elements, steels can change their nature and properties effectively.
- Most common elements (except Co) shift the CCT curve to longer times, which essentially result in the increase of hardenability of the steels, so that pearlitic transformation can be avoided easily to obtain martensitic structure, even at a slower rate of cooling and in thicker parts.
- Alloying elements also lower M_s and M_f temperatures, increasing further the amount of retained austenite. The decomposition of retained austenite on tempering, plays quite a significant role on the properties of tempered steels, specially having high carbon and high alloying elements.

- Some elements, that are not found in carbides, but are present as solid solution in ferrite, are Al, Cu, Si, P, Ni, and Zr. Some elements arranged in order of increasing tendency to form carbides are Mn, Cr, W, Mo, V and Ti. These carbide forming elements retard most effectively the rate of softening during tempering of the steel.
- The first stage of tempering does not appear to be effected by the presence of the alloying elements. However, most of the alloying elements in steels tends to increase the hardness after tempering than a plain carbon steel with the same carbon content.
- At smaller concentration, they merely retard the tempering processes hence the softening, particularly at higher temperature ($> 500^{\circ}\text{C}$), where these elements have good diffusivity to take part in tempering reactions.

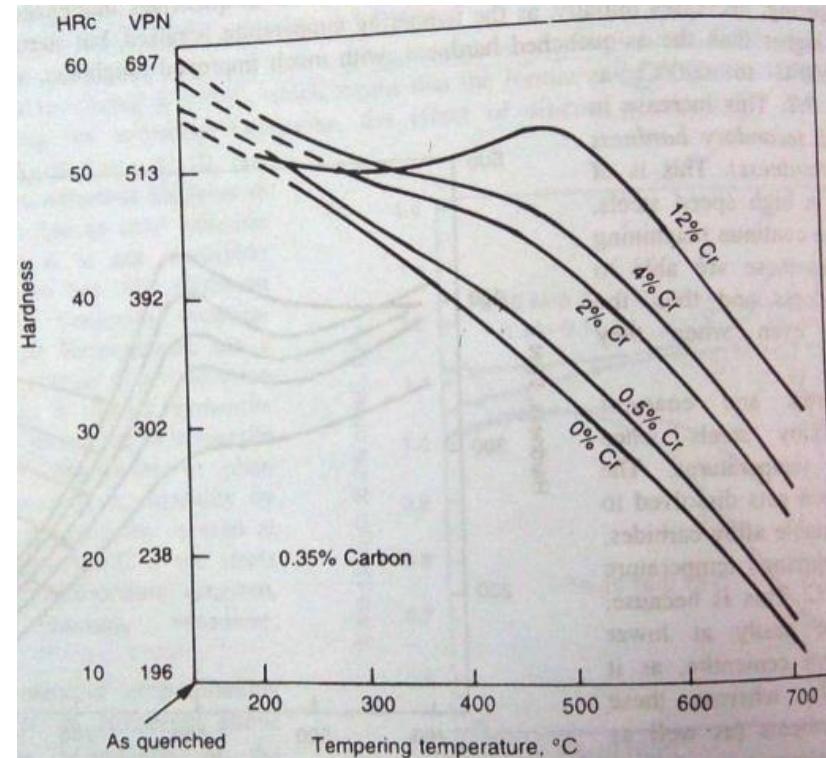


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- When alloy carbides are formed, the drop in hardness during tempering is not only retarded but is significantly increased. The steel is then said to **secondary hardening**.
- Thus, 0.5% chromium, or less than 0.5% Mo resists softening but secondary hardening is produced by either 12% chromium, or 2 % Mo. Stronger the carbide, the more potent is the secondary hardening.



Effect of increasing Mo on tempering of as quenched 0.1% C steel



Effect of increasing Cr in 0.35% C steel on tempering



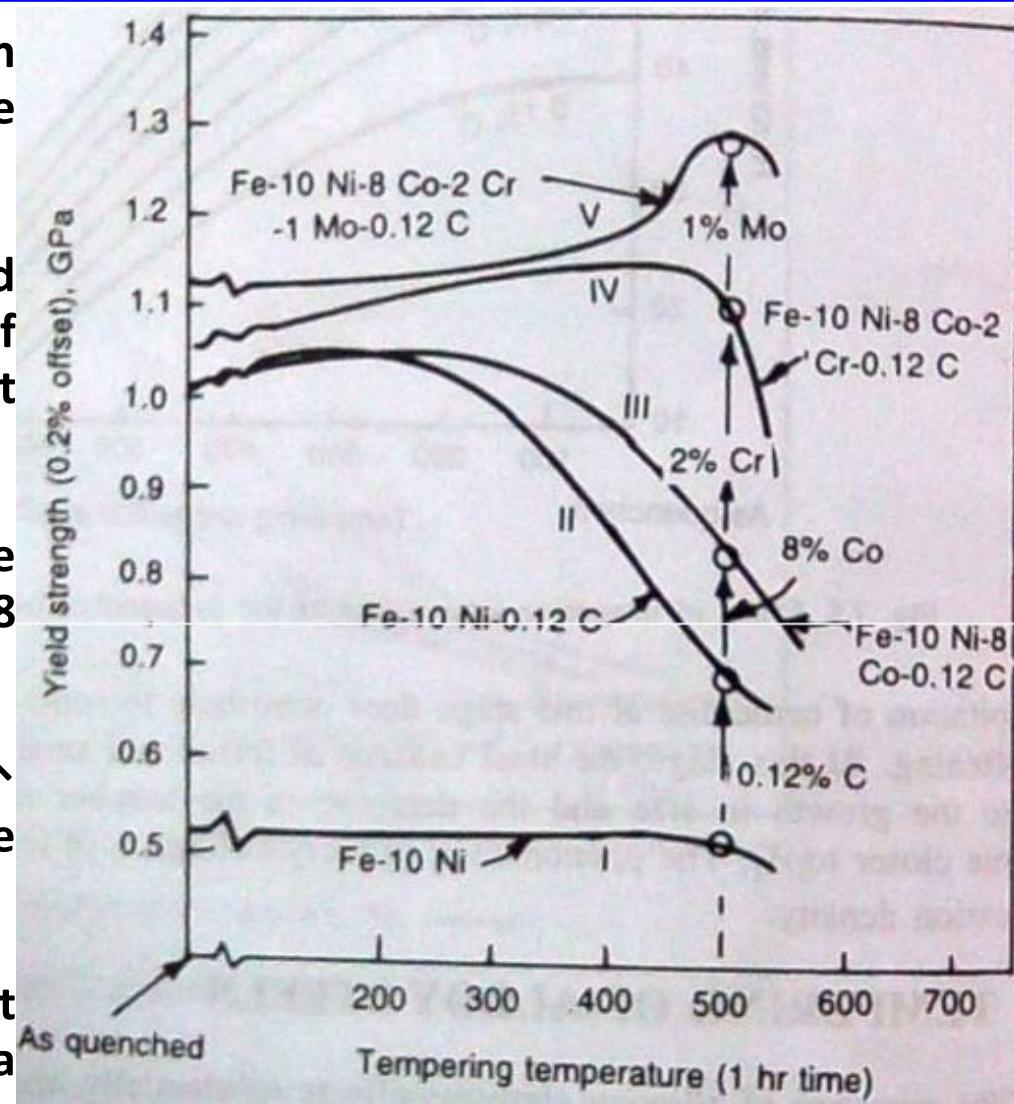
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- Element, such as, silicon dissolves in ϵ -carbide to stabilize it. Steels with 1-2% silicon have ϵ -carbide present even after tempering at 400 °C, which means that the formation of cementite is delayed considerably, and thus, resisting the softening. Otherwise, the **effect of silicon is essentially due to solid solution strengthening.**
- Nickel has a small, but constant effect on tempered hardness at all temperatures due to solid solution strengthening as it is not a carbide former.
- Manganese has little effect on softening at low tempering temperatures, but at high temperatures, has a strong effect on due to its faster diffusion then, and thus, it resists cementite coarsening as it is present in cementite as $(Fe, Mn)_3C$.
- Martensite in plain carbon steels losses its tetragonality by 300 °C, but the tetragonality is seen at 450 °C, or even at 500 °C if the steels have elements like Cr, W, Mo, Ti, V and Si.
- The basic cause of steep softening in carbon steels on tempering above 400 °C, is the coagulation of the cementite particles. Alloying elements notably Si, Cr, Mo, V, when present in steels, retard the coalescence and the coarsening of cementite particles., resulting in enhanced hardening over and above the solid solution hardening effect.
- Elements like Cr, Si, Mo, or W delay coarsening to temperature range of 500-550 °C. Up to tempering temperature 500 °C, the carbides formed are of iron with proportional alloying elements in it, but above 500 °C, alloying elements can form their own carbides and thus, coarse cementite particles are replaced by fine dispersion of more stable alloy carbides.



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- An Fe-10 Ni alloy shows constant hardness on tempering up to 450 °C and then, there takes place some decrease in strength (curve I).
- Addition of 0.12% carbon increases the as quenched strength to almost double, and slow decrease of hardness occurs on tempering to fall to 0.7 GPa at 500 °C.
- A 8% cobalt addition, which doesn't enter the carbide, delays the softening to have strength of 0.8 GPa at 500 °C.
- Addition of 2% Cr almost continuously but slowly ↑ hardness to start falling at above ~450 °C to become 1.1 GPa at 500 °C by fine dispersion of Cr carbide.
- Addition of Mo causes secondary hardening, as it is very strong carbide forming element, to attain a hardness of 1.3 Gpa at 500 °C.



Effect of C, Co, Cr, and Mo on tempering of Fe-10Ni steels



Tempering of Alloy Steels: Secondary Hardening

- In alloy steels, having larger amounts of strong carbide forming elements like Mo, Ti, V, Nb, W, Cr etc., and C, a peculiar phenomena occurs, the hardness of the as-quenched martensite (called primary hardness) on tempering, decreases initially, as the tempering temperatures is raised, but starts increasing again to often become higher than the as quenched hardness, with much improved toughness, when tempered in the range of 500-600 °C. This increase in hardness is called **secondary hardness** (also called **red hardness**).
 - This is great importance in high speed steels, as these are able to continue machining, at high speeds (as these are able to resist fall in hardness and thus, the cutting property) even when they become red hot.
 - Secondary hardening is a process, **similar to age hardening**, in which coarse cementite particles are replaced by a new and much finer alloy carbide dispersion of V_4C_3 , Mo_2C , W_2C (which normally form on dislocations). As in aging a critical dispersion causes a peak in the hardness and strength of the alloy, and as over aging takes place, i.e., carbide dispersion slowly coarsens, the hardness decreases.
 - **Secondary hardening is best shown in steels containing Mo, V, W, Ti and also in Cr steels at high chromium concentrations.**
 - The amount of secondary hardening in an alloy steel is directly proportional to the volume fraction of the alloy carbides, and thus is directly proportional to the concentration of strong carbide forming elements present in steels. The alloy carbides must precipitate as fine dispersion in ferrite matrix rather than massive carbide particles.
-



Time and Temperature Relationship in Tempering

- For a given steel, a heat treater might like to choose some convenient tempering time, say over night, otherwise different than 1 hour, and thus, wants to calculate the exact temperature required to achieve the constant hardness.
 - Hollomon and Jaffe's "tempering parameter" may be used for this purpose as it relates the hardness, tempering temperature and tempering time. For a thermally activated process, the usual rate equation is:

- Where, t is the time of tempering to develop a given hardness, R is the gas constant, A is the pre-exponential constant, and Q is the 'empirical activation energy'. 'Q' is not constant in the complex tempering processes but varies with hardness. Thus, hardness was assumed to be a function of time and temperature:

- Interestingly, $[te^{-Q/RT}]$ is a constant, and let it be t_0 . Equating activation energies of eq (1) and (2) gives,

$$Q = T[Int - Int_0] = f(H)$$

- As t_0 constant then,

$$H = f[T(C + Int)]$$

- ❑ Where, C is a constant, whose value depends on the composition of austenite. The single parameter which expresses two variables time and the temperature i.e., $T(C + \text{Int})$ is called the **Hollomon and Jaffe tempering parameter** (hardness in vickers is preferable).



Temperature and Colors for Heating and Tempering of Steel

Colours of Hot Solid metal	°C	Process of Heat treatment
White	1500	
Yellow white	1300	High speed steel hardening (1230-1300°C)
Yellow	1100	
Orange Red	1000	Alloy steel hardening (800-1100°C)
Light-Cherry-Red	900	
Cherry-red	800	Carbon steel hardening
Dark-red	700	
Vary dark-red	500	High speed steel tempering (500-600°C)
Black red in dull light, or darkness	400	
Steel gray	300	Carbon steel tempering (150-575°C)
Colour of Oxide film	°C	Parts Heat treated
Steel Gray	327	Cannot be used for cutting tools
Pale-light blue	310	For springs
Purple	282	Spring and screw drivers
Brown	270	Axes, wood cutting tools
Gold	258	Shear blades, hammer faces, cold chisels
Dark-straw-light-brown	240	Punches and Dies
Light-Straw-Yellow	220	Steel cutting tools, files, paper cutters

↑ HEAT COLOURS
↓ TEMPER COLOURS →



Heat Treatment Defects

- Heat treatment of steels or aluminum can lead to several defects. The principal types of defects found in quenching of steels are internal and external cracks in the work, distortion and warping.
- **CRACK:** When the internal tensile stresses exceed the resistance of the steel to separation the crack occurs. The insertion of the tools in the furnace without preheating for tempering is one of the main causes of crack propagation. The crack formation is reduced by preheating the tool between 200 °C to 300 °C.
- **DISTORTION:** Distortion occurs due to uneven heating, too fast cooling, part incorrectly supported in furnace, incorrect dipping in quenching and stresses present before preheating. Distortion can be prevented by preheating the tool or check furnace capacity, reduce the hardening temperature, and by reviewing the method of dipping.
- **WARPING:** Asymmetrical distortion of the work is often called warping in heat-treating practice. Warping is usually observed upon non-uniform heating or over heating for hardening. It also occurs when the work is quenched in the wrong position and when the cooling rate is too high in the temperature range of the martensite transformation. An elimination of these causes should subsequently reduce warping.
- The properties required in the heat treated part are obtained without the parts being distorted beyond the acceptable limits.
- The ideal design for a heat treatable part is the shape that when heated (or cooled) would have the same temperature at every point with in the part.



Hardenability – Introduction

- Hardenability is one of the most important properties of a steel because it describes the ease with which a given steel can be quenched to form martensite or the depth to which martensite is formed on a given quench.
- It is an important property for welding, since it is inversely proportional to weldability, that is, the ease of welding a material.
- The ability of steel to form martensite on quenching is referred to as the **hardenability**.
- **Hardenability** is a measure of the capacity of a steel to be hardened in depth when quenched from its austenitizing temperature.
- Steels with high hardenability form martensite even on slow cooling.
- High hardenability in a steel means that the steel forms martensite not only at surface but to a large degree throughout the interior.
- For the optimum development of strength, steel must be fully converted to martensite.
- To achieve this, the steel must be quenched at a rate sufficiently rapid to avoid the decomposition of austenite during cooling to such products as ferrite, pearlite and bainite.
- Hardenability of a steel should not be confused with the hardness of a steel.

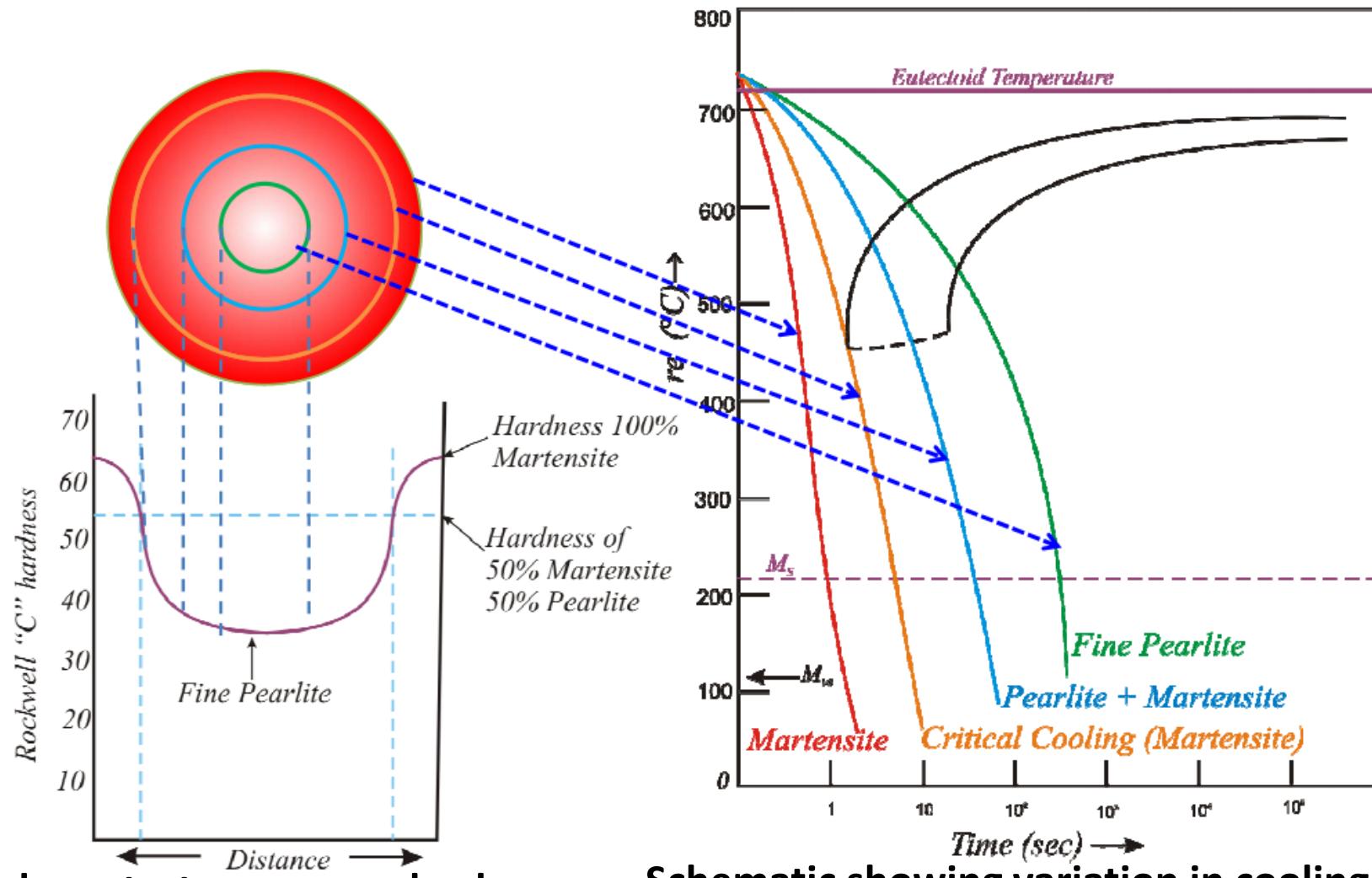
Hardness ≠ Hardenability

The **Hardness** of a steel is a measure of a sample's resistance to indentation or scratching

Hardenability refers to its ability to be hardened to a particular depth under a particular set of conditions.



Hardness Profile in a Cylinder from Case to Core



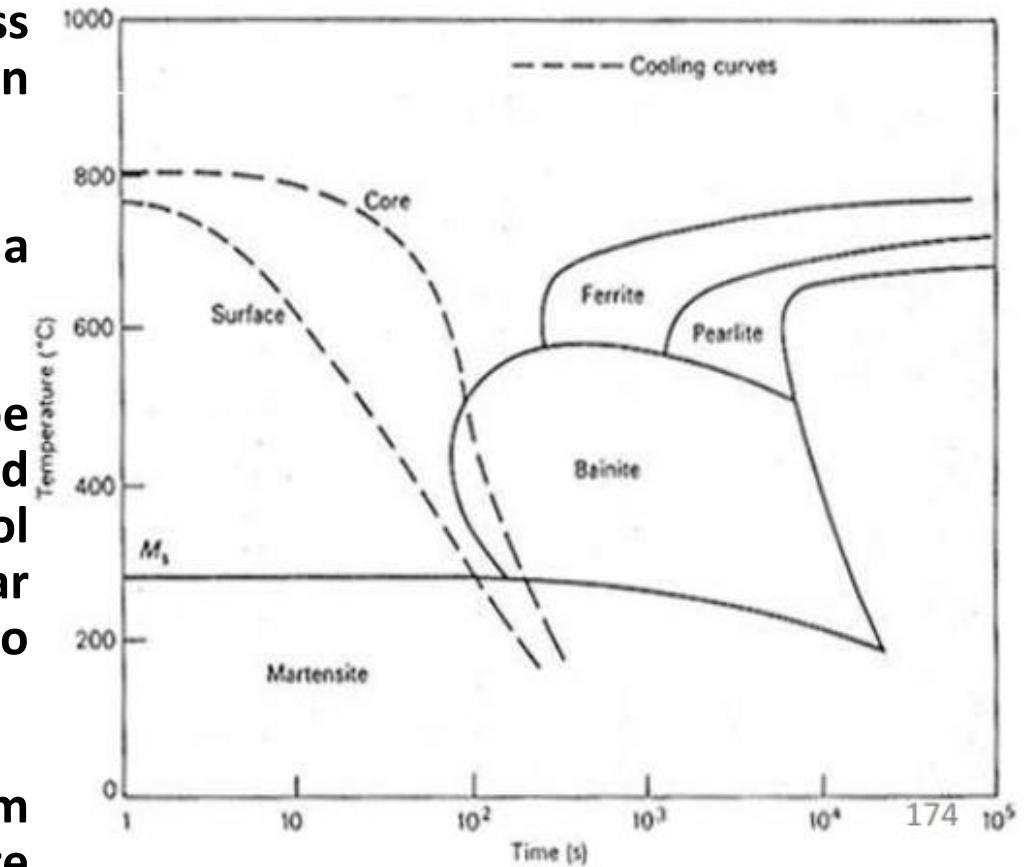
Typical hardness test survey made along a diameter of a quenched cylinder

Schematic showing variation in cooling rate from surface to interior leading to different microstructures



Hardenability

- It is a **qualitative measure** of the rate at which hardness drops off with distance into the interior of a specimen as a result of diminished martensite content.
- Hardenability is more related to **depth of hardening** of a steel upon heat treat.
- The depth of hardening in a plain carbon steel may be 2-3 mm vs 50 mm in an alloy steel. A large diameter rod quenched in a particular medium will obviously cool more slowly than a small diameter rod given a similar treatment. Therefore, the small rod is more likely to become fully martensitic.
- The **hardenability** of a steel is the maximum diameter of the rod which will have 50% martensite even in the core when quenched in an ideal quenchants. This diameter is known as D_i or ideal diameter.



Relation between cooling curves for the surface and core of an oil-quenched 95 mm diameter bar



Determination of Hardenability

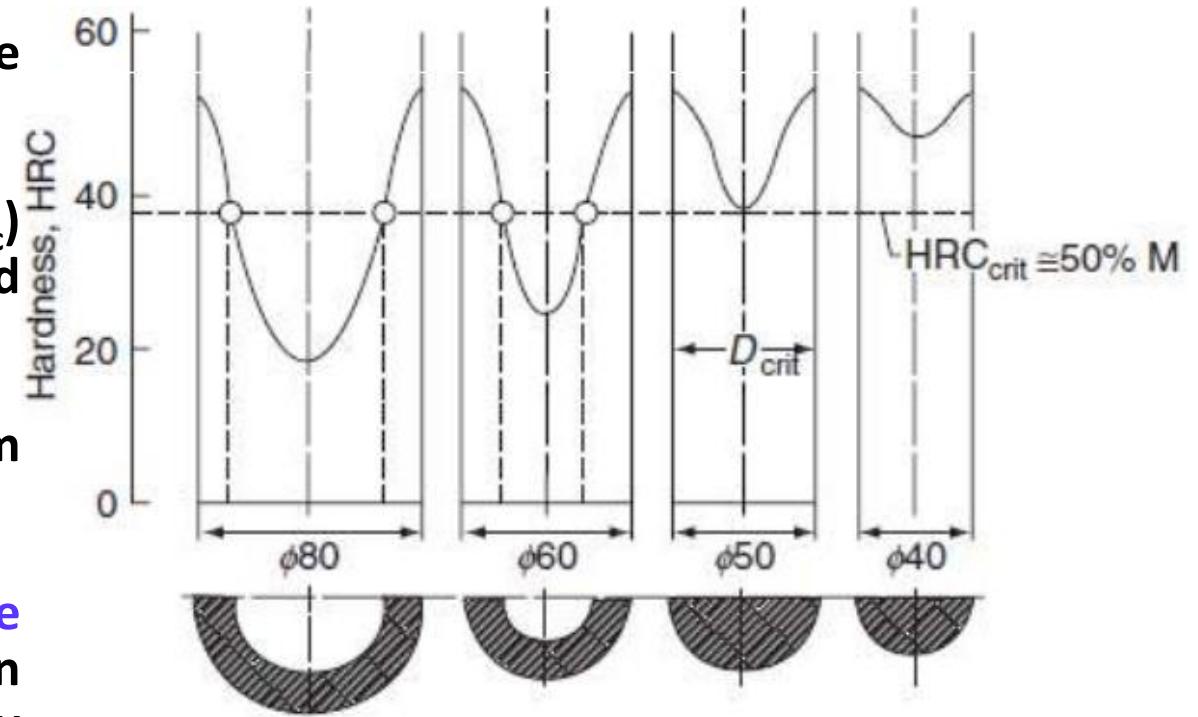
□ Hardenability of steel is determined by the following methods:

- Grossman's critical diameter method
- Jominy end quench test
- Estimation of hardenability from chemical composition
- Fracture test



Grossman's Critical Diameter Method

- In Grossman's method, we use round bars of different diameters.
- These bars are quenched in a suitable quenchants.
- Further, we determine the critical diameter (D_c) which is the maximum diameter of the rod which produced 50% martensite on quenching.
- The ideal diameter (D_i) is then determined from the curve.
- This type of experiment requires multiple austenitisation and quenching treatments on specimens of varying diameter just to quantify the hardenability of a single material.



Determination of the critical diameter
 D_{crit} according to Grossmann



Contd...

Process	Variable	H Value
Air	No agitation	0.02
Oil quench	No agitation	0.2
"	Slight agitation	0.35
"	Good agitation	0.5
"	Vigorous agitation	0.7
Water quench	No agitation	1.0
"	Vigorous agitation	1.5
Brine quench (saturated Salt water)	No agitation	2.0
"	Vigorous agitation	5.0
Ideal quench		∞

If the increase in rate of heat conduction is greater than the decrease due to persistence of the vapor film, the net result will be an increase in the actual cooling rate. However if the reverse is true, then the result will be decrease in cooling rate.

Severity of Quench as indicated by the heat transfer equivalent H

$$H = \frac{f}{K} \quad [m^{-1}]$$

f → heat transfer factor

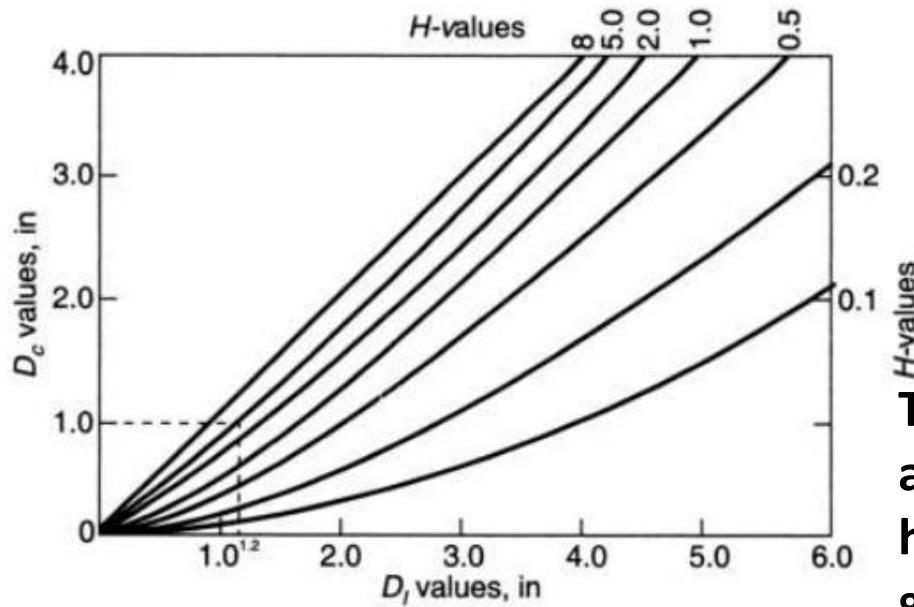
K → Thermal conductivity

Note that apart from the nature of the quenching medium, the vigorousness of the shake determines the severity of the quench. When a hot solid is put into a liquid medium, gas bubbles form on the surface of the solid (interface with medium). As gas has a poor conductivity the quenching rate is reduced. Providing agitation (shaking the solid in the liquid) helps in bringing the liquid medium in direct contact with the solid; thus improving the heat transfer (and the cooling rate). The H value/index compares the relative ability of various media (gases and liquids) to cool a hot solid. Ideal quench is a conceptual idea with a heat transfer factor of ∞ ($\Rightarrow H = \infty$).



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- The relation between ideal critical diameter D_I and critical diameter D_C and severity of quench (H) can be determined from thermodynamic considerations.
- These relations are shown in Grossman's master graph. In this figure the D_I is plotted as the abscissa, and the D_C is plotted as ordinate.
- A number curves are plotted in this graph and each belongs to different rates of cooling. In every case, the rate of cooling is measured by the H -value or the severity of quench.
- From this graph, by knowing the value of D_C , the corresponding value for D_I can be found out. For example, assuming $D_C = 1$ inch and $H = 5$ (for agitated brine quench), the critical diameter or hardenability works out to 1.2 inch with help of figure.



From figure it can be observed that

$$D_I = D_C \text{ for } H = \infty$$

$$D_I > D_C \text{ for } H < \infty$$

The relation between ideal critical diameter D_I and critical diameter D_C that can be fully hardened by using a quenching medium with a given cooling power H .



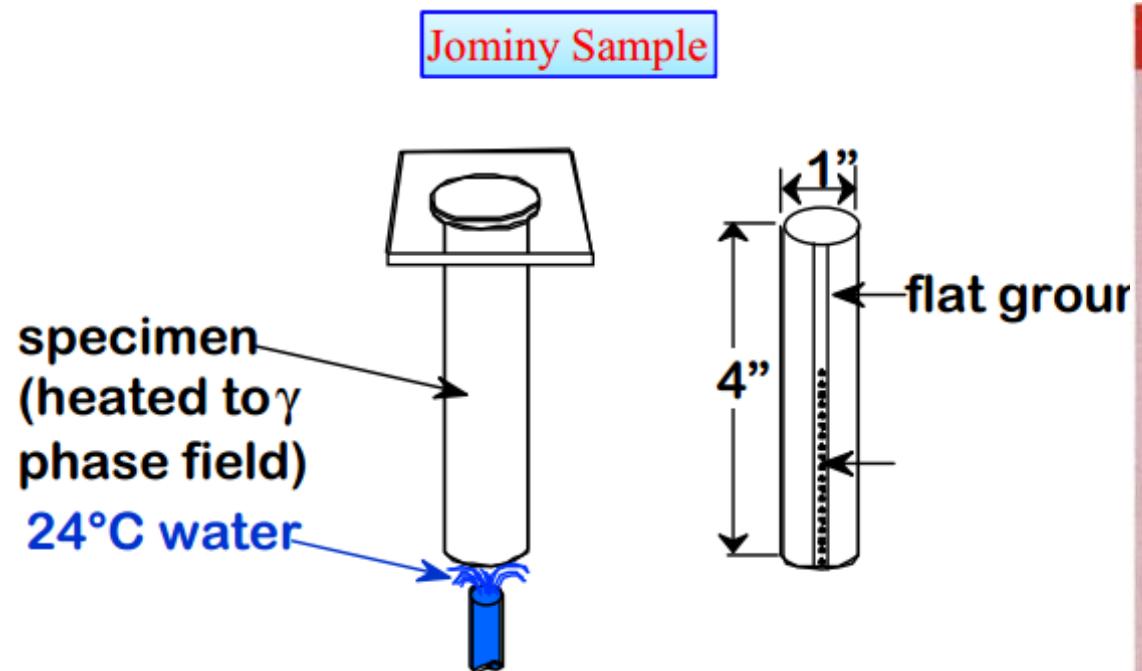
Jominy End-Quench Method

- The most commonly used method for determining hardenability is the end quench test developed by **Jominy** and **Boegehold**.
- Grossmans method requires multiple austenitisation and quenching treatments on specimens of varying diameter just to quantify the hardenability of a single material.
- An alternative approach is to develop a more convenient standard test method that can be used for relative comparison of hardenability. The Jominy end-quench test is one such approach.
- The Jominy end-quench test is specified in ASTM standard A255 and is a widely used method for quantifying hardenability. Its wide use adds to its value, since the utility of empirical relations and data comparison becomes more reliable as more data are accumulated.
- Moreover, Jominy data have been collected on a large enough scale to offer a high degree of statistical certainty for many steels.
- These data have been correlated with measurements and/or calculations of D_c .
- By using these correlations, a single Jominy test can be used to estimate D_c and D_I for a given steel (and austenite grain size).
- Information gained from this test is necessary in selecting the proper combination of alloy steel and heat treatment to minimize thermal stresses and distortion when manufacturing components of various sizes.



Jominy End-Quench Method—Principle

- The hardenability of a steel is measured by a Jominy test with following procedure.
- In conducting this test, a 1 inch round specimen 4 inch long is heated uniformly to the proper austenising temperature. It is then removed from the furnace and placed on a fixture where a jet of water impinges on the bottom face of the sample.
- After 10 min. on the fixture, the specimen is removed, and to cut along the longitudinal direction.
- And then Rockwell C scale hardness readings are taken at 1/16 inch, intervals from the quenched end. The results are expressed as a curve of hardness values vs distance from the quenched end. A typical hardenability curve shown below for eutectoid steel.



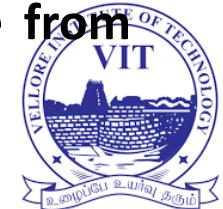
Jominy Distance (in.)	Cooling Rate ($^{\circ}\text{C/s}$)
$\frac{1}{16}$	315
$\frac{2}{16}$	110
$\frac{3}{16}$	50
$\frac{4}{16}$	36
$\frac{5}{16}$	28
$\frac{6}{16}$	22
$\frac{7}{16}$	17
$\frac{8}{16}$	15
$\frac{9}{16}$	10
$\frac{10}{16}$	8
$\frac{11}{16}$	5
$\frac{12}{16}$	3
$\frac{13}{16}$	2.8
$\frac{14}{16}$	2.5
$\frac{15}{16}$	2.2



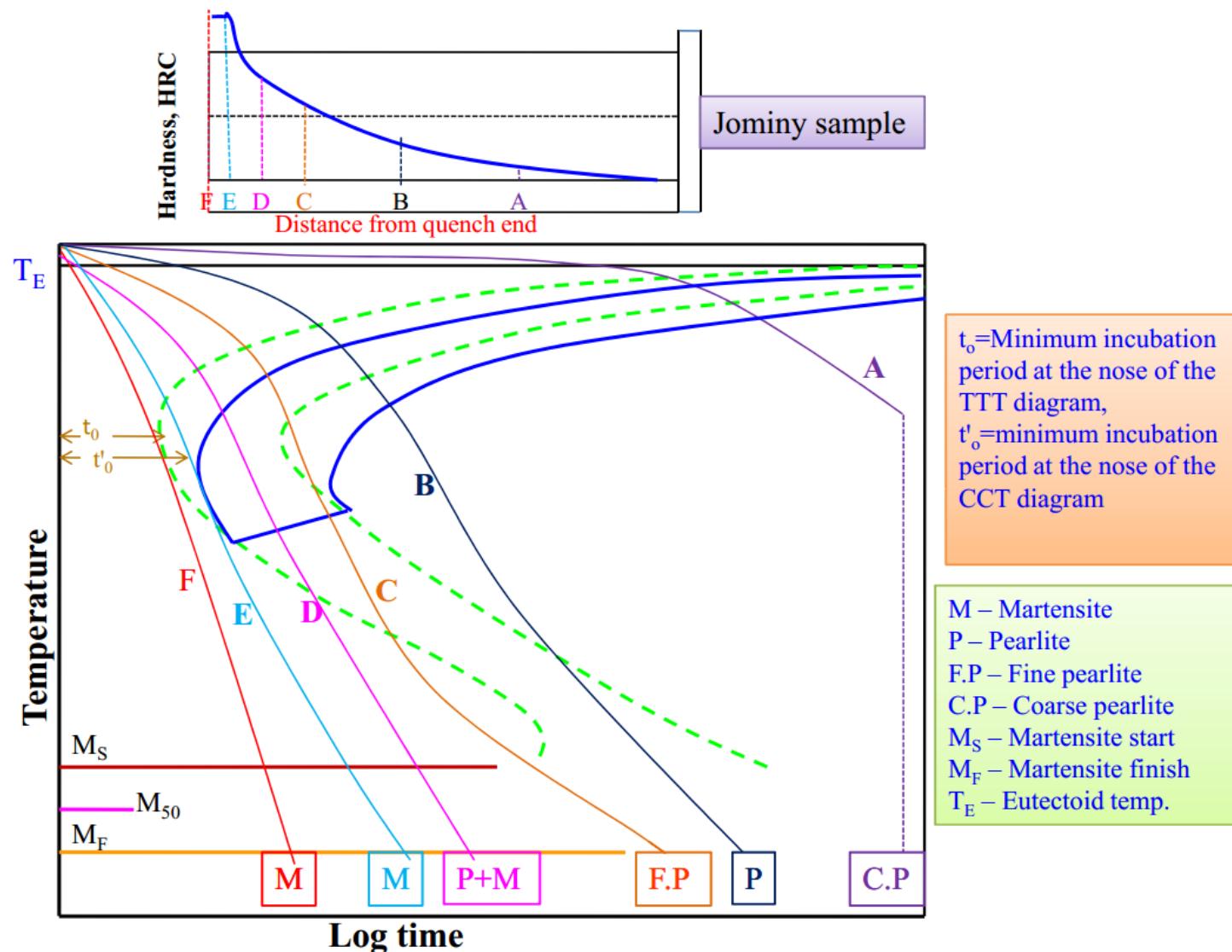
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- A number of Jominy end quench samples are first end-quenched for a series of different times and then each of them (whole sample) is quenched by complete immersion in water to freeze the already transformed structures.
- Cooling curves are generated putting thermocouple at different locations and recording temperature against cooling time during end quenching.
- Microstructures at the point where cooling curves are known, are subsequently examined and measured by quantitative metallography. Hardness measurement is done at each investigated point.
- Based on metallographic information on investigated point the transformation start and finish temperature and time are determined. The transformation temperature and time are also determined for specific amount of transformation.

- These are located on cooling curves plotted in a temperature versus time diagram. The locus of transformation start, finish or specific percentage of transformation generate CCT diagram (next slide).
- A, B, C, D, E, F are six different locations on the Jominy sample shown in Figure (before slide) that gives six different cooling rates. The cooling rates A, B, C, D, E, F are in increasing order.
- The corresponding cooling curves are shown on the temperature log time plot. At the end of the cooling curve phases are shown at room temperature. Variation in hardness with distance from Jominy end is also shown in the diagram.

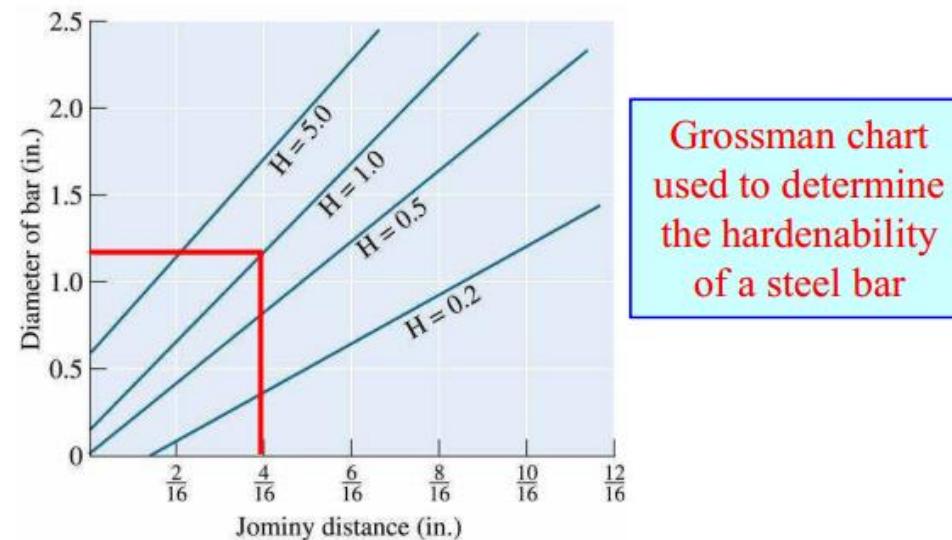
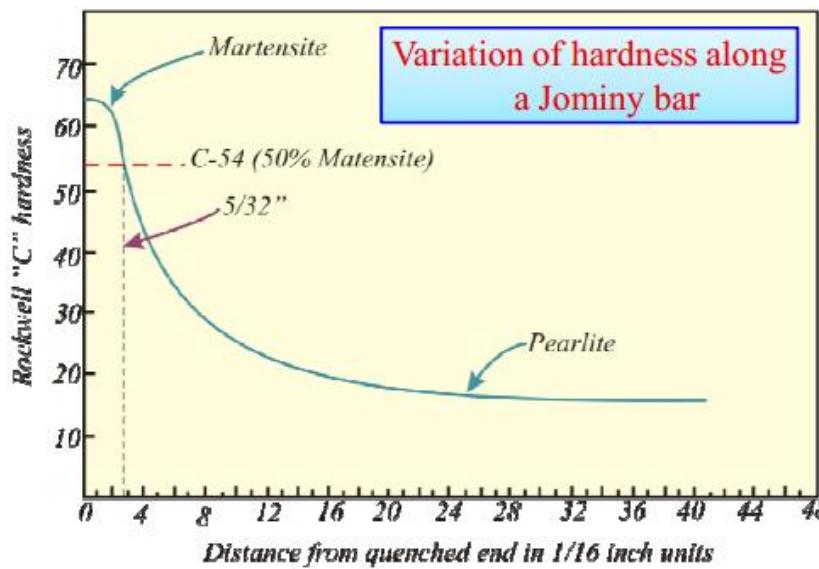


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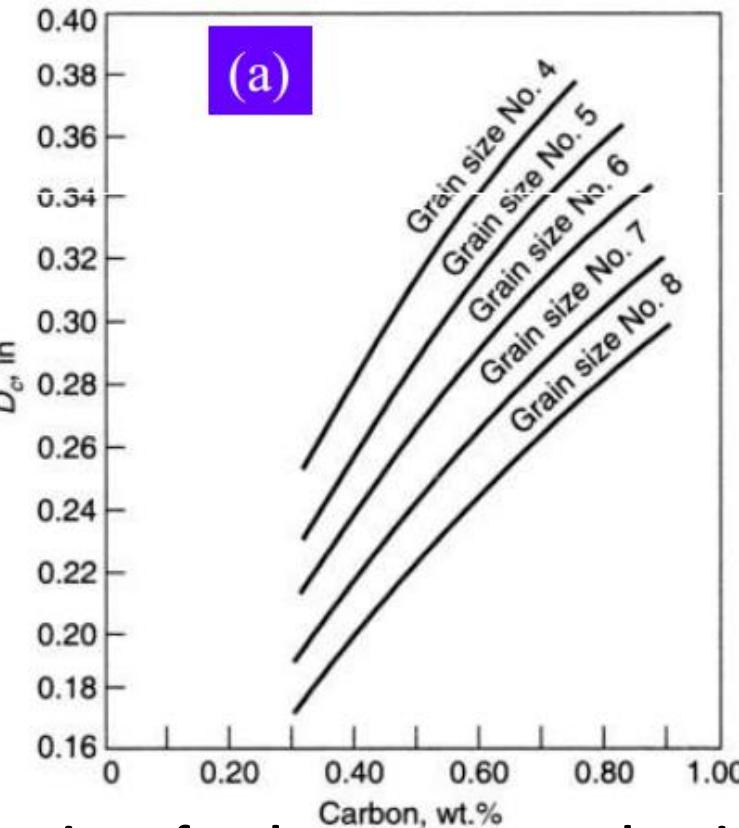
Determination of Hardenability from Jominy Curve

- After plotting the Jominy distance vs hardness curve, the Jominy distance having hardness equal to 50 % martensite is determined.
- Then the diameter of a rod having cooling rate similar to the cooling rate at the Jominy distance having 50 % martensite is determined from the graph correlating the Jominy distance with the diameter of the rod having similar cooling rate for water quenching.
- This diameter gives the hardenability of the steel in water quenching (having H value equal to 1).
- Hardenability in any other quenchants can be determined from the same graph.
- D_i (hardenability in ideal quenching medium) can also be determined in a similar manner.
- We can determine hardenability for any other amount of martensite in the core in any quenchants in a similar way.



Estimation of Hardenability from Chemical Composition

- Although the ideal critical diameter is generally determined experimentally, it is also possible to estimate it from **chemical composition** and the **grain size** of steel.
- This method is based on the fact that the hardening of steel is controlled basically by the carbon content.
- Every steel has a base hardenability which depends only on carbon content and grain size. Alloying additions change the rate of reaction.
- Furthermore, the effect of each alloying element is independent of other alloying elements. The effect is also independent of carbon content and grain size.
- Figure gives base hardenability in terms of ideal critical diameter. It is clear from the figure that, as the carbon content and grain size decreases, the base diameter value $D_{c,i}$ also declines.
- The effect of alloying elements in the hardenability is shown in Figure (b) (next slide).
- Mo, Mn and Cr are seen to very effective. The base diameter obtained from Figure(a) is multiplied by the multiplying factors F for each of the alloying elements given in figure (b).



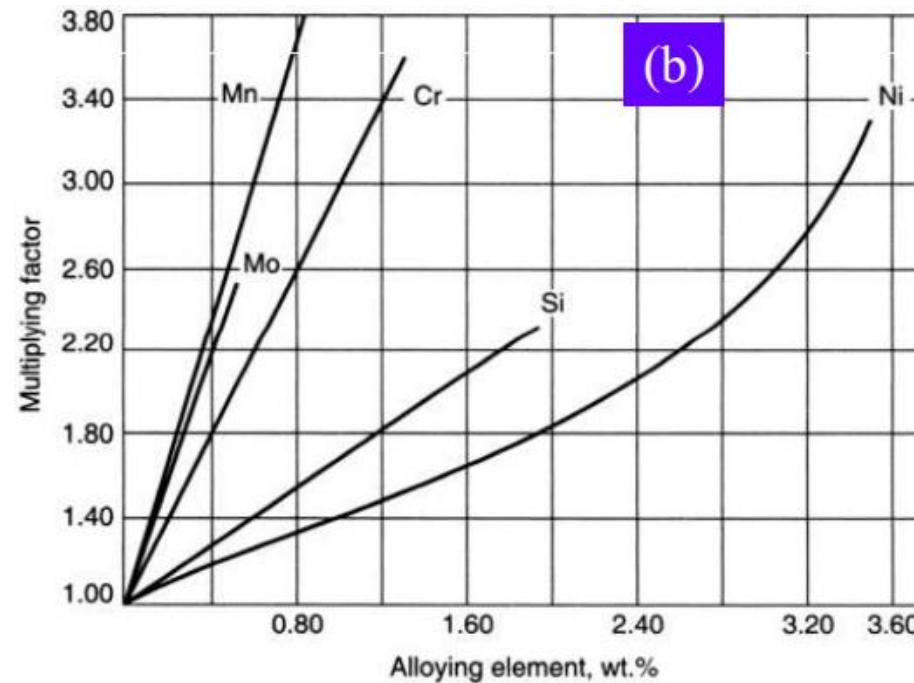
Base diameter as function of carbon content and grain size



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$$D = D_c \text{ (base diameter)} \times F_{Mn} \times F_{Cr} \times F_{Ni}$$

- For example, for a steel of grain size ASTM 8, with 0.5% carbon, 0.6% Mn, 1% Cr and 2%Ni, $D_i = 0.22$ (From figure a) $\times 3.00$ (Mn factor from figure b) $\times 3.17$ (Cr factor from figure b) $\times 1.77$ (Ni factor from figure b) = 3.70 inches
- Sulphur and phosphorous are present in low concentrations in steel as impurity. Their combined effect can be ignored in most of the cases. Multiplying factors for sulphur and phosphorus are unity



Multiplying factor F as a function of weight % for a set of alloying elements



Significance of Hardenability Multiplying Factor

- The Hardenability Multiplying Factor shows the rate at which the hardening depth is increased with the percentage of the alloying element
 - The ideal diameter (D_I) is calculated from: $D_I = D_{IC} \times F_{Mn} \times F_{Cr} \times F_{Ni} \times F_{Si} \times F_{Mo}$
- where, D_{IC} is the basic D_I factor for carbon and f_x is the multiplying factor for the alloying element x.

Carbon %	grain size			Alloying factor, f_x				
	No. 6	No. 7	No. 8	Mn	Si	Ni	Cr	Mo
0.05	0.0814	0.0750	0.0697	1.167	1.035	1.018	1.1080	1.15
0.10	0.1153	0.1065	0.0995	1.333	1.070	1.036	1.2160	1.30
0.15	0.1413	0.1315	0.1212	1.500	1.105	1.055	1.3240	1.45
0.20	0.1623	0.1509	0.1400	1.667	1.140	1.073	1.4320	1.60
0.25	0.1820	0.1678	0.1560	1.833	1.175	1.091	1.5400	1.75
0.30	0.1991	0.1849	0.1700	2.000	1.210	1.109	1.6480	1.90
0.35	0.2154	0.2000	0.1842	2.167	1.245	1.128	1.7560	2.05
0.40	0.2300	0.2130	0.1976	2.333	1.280	1.246	1.8640	2.20
0.45	0.2440	0.2259	0.2090	2.500	1.315	1.164	1.9720	2.35
0.50	0.2580	0.2380	0.2200	2.667	1.350	1.182	2.0800	2.50
0.55	0.2730	0.2510	0.2310	2.833	1.385	1.201	2.1880	2.65
0.60	0.284	0.262	0.2410	3.000	1.420	1.219	2.2960	2.80
0.65	0.295	0.273	0.2551	3.167	1.455	1.237	2.4040	2.95
0.70	0.306	0.283	0.260	3.333	1.490	1.255	2.5120	3.10
0.75	0.316	0.293	0.270	3.500	1.525	1.273	2.6200	3.25
0.80	0.326	0.303	0.278	3.667	1.560	1.291	2.7280	3.40
0.85	0.336	0.312	0.287	3.833	1.595	1.309	2.8360	3.55
0.90	0.346	0.321	0.296	4.000	1.630	1.321	2.9440	3.70
0.95	-	-	-	4.167	1.665	1.345	3.0520	-
1.00	-	-	-	4.333	1.700	1.364	3.1600	-



Fracture Test

- There is a contrast in the nature of fracture undergone by martensitic and pearlitic regions.
- Whereas martensite formed on the case exhibits brittle fracture, the pearlite formed in the core undergoes ductile fracture.
- Where there is changeover from martensitic to pearlitic structure, there is corresponding sharp change from brittle to ductile fracture.
- It is similar to a sudden change in hardness or microstructure as one passes from martensitic to pearlite region.
- This region of sudden change is the one that contains 50% pearlite and 50% martensite.
- The method based on the nature of fractured surface is successful when the transformation processes is quick and a sharp boundary is formed.
- When the transformation is sluggish, the method cannot be applied since the gradient in hardness is gradual, and it is not possible to get a clear demarcating boundary.



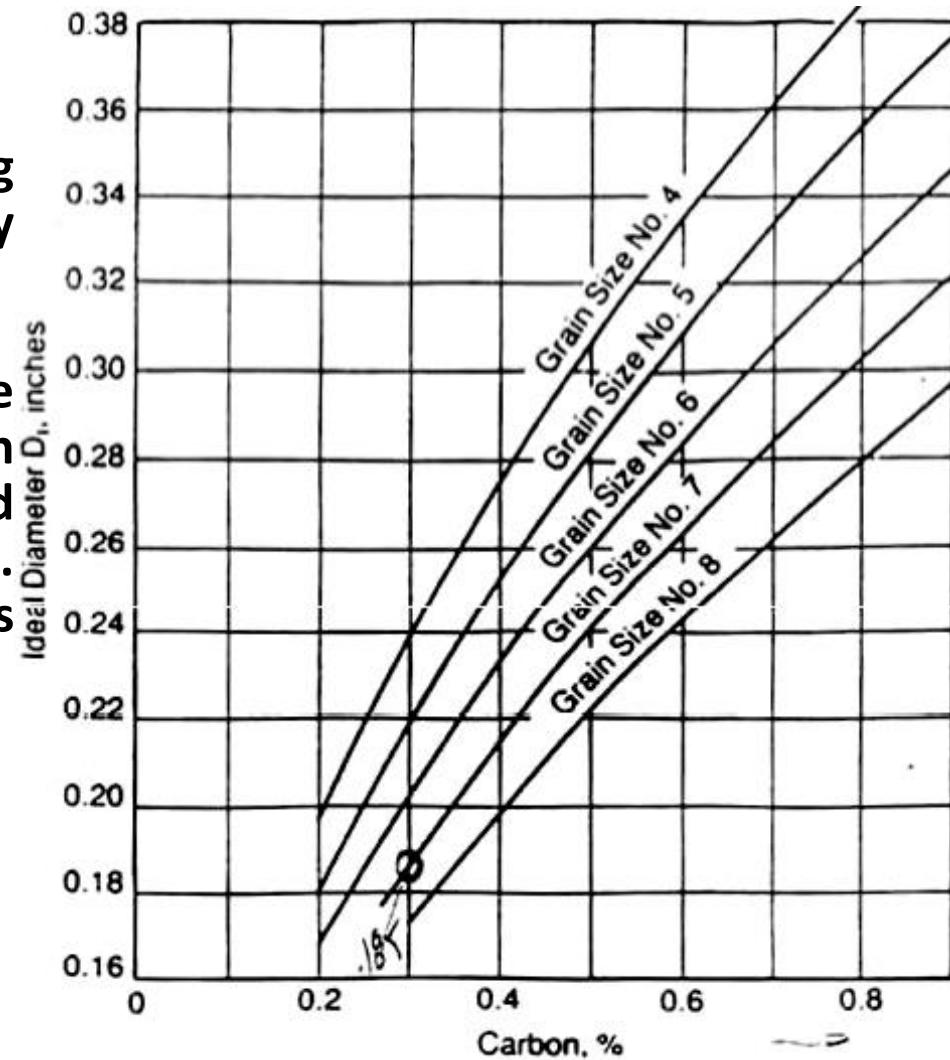
Factors Affecting Hardenability

- Slowing the phase transformation of austenite to ferrite and pearlite increases the hardenability of steels.
- The most important variables which influence hardenability are:
 - Quenching conditions
 - Austenitic grain size
 - Carbon content
 - Alloying elements
- Quenching conditions
- The fluid used for quenching the heated alloy affects the hardenability.
- Each fluid has its own thermal properties like:
 - Thermal conductivity
 - Specific heat
 - Heat of vaporization
- These cause rate of cooling differences.
- Ideal quenchant: It is one which brings down the surface temperature to room temperature instantaneously and keeps it at that temperature thereafter.



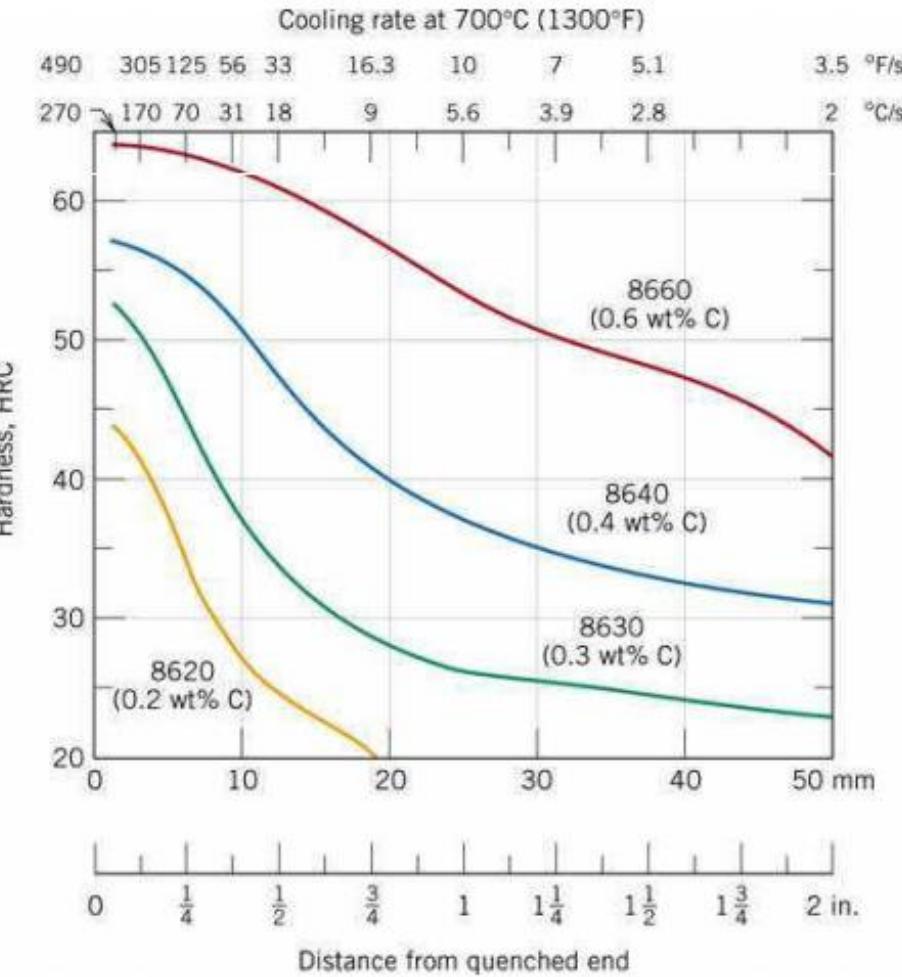
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- Austenitic grain size
- The hardenability increases with increasing austenite grain size, because the grain boundary area which act as nucleating site is decreasing.
- This means that the sites for the nucleation of ferrite and pearlite are being reduced in number, with the result that these transformations are slowed down, and the hardenability is therefore increased. The more γ -grain boundary surface the easier it is for pearlite to form rather than martensite.
- Smaller γ -grain size \rightarrow lower hardenability
- Larger γ -grain size \rightarrow higher hardenability



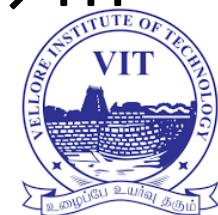
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- Percentage of carbon
- Carbon is primarily a hardening agent in steel.
- It also increases hardenability by slowing the formation of pearlite and ferrite.
- But its use at higher levels is limited, because of the lack of toughness which results in greater difficulties in fabrication and, most important, increased probability of distortion and cracking during heat treatment and welding.

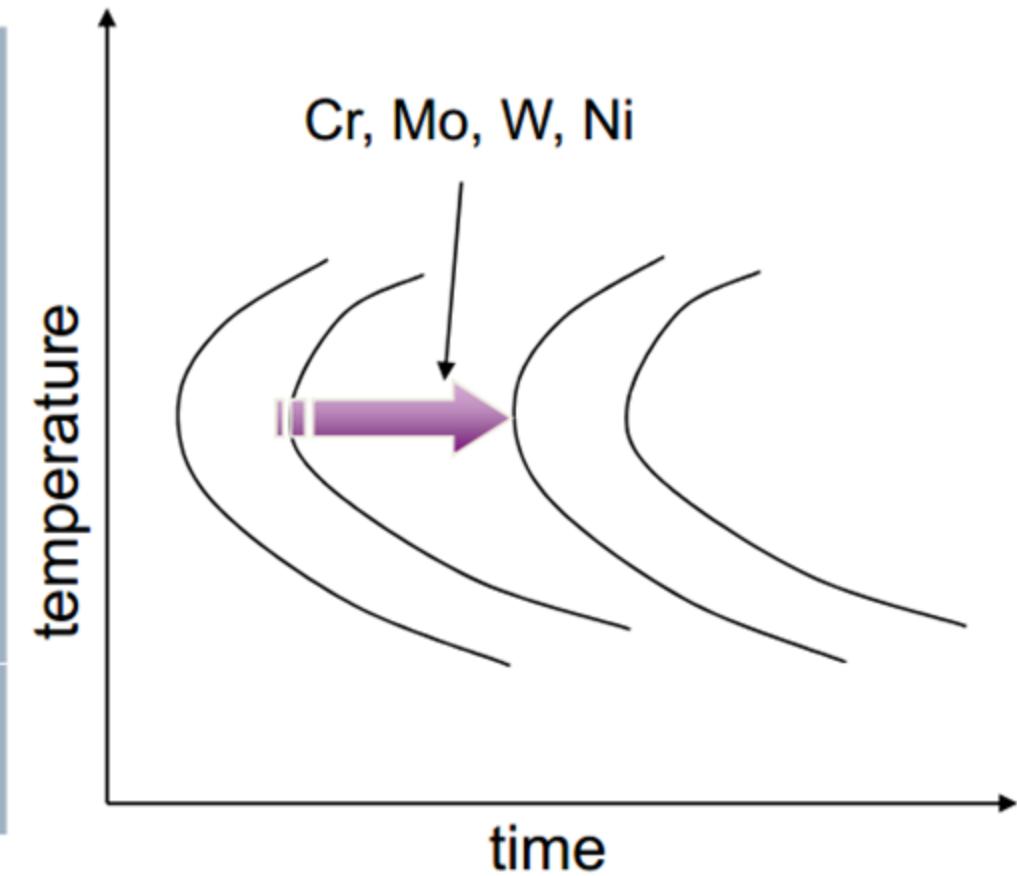
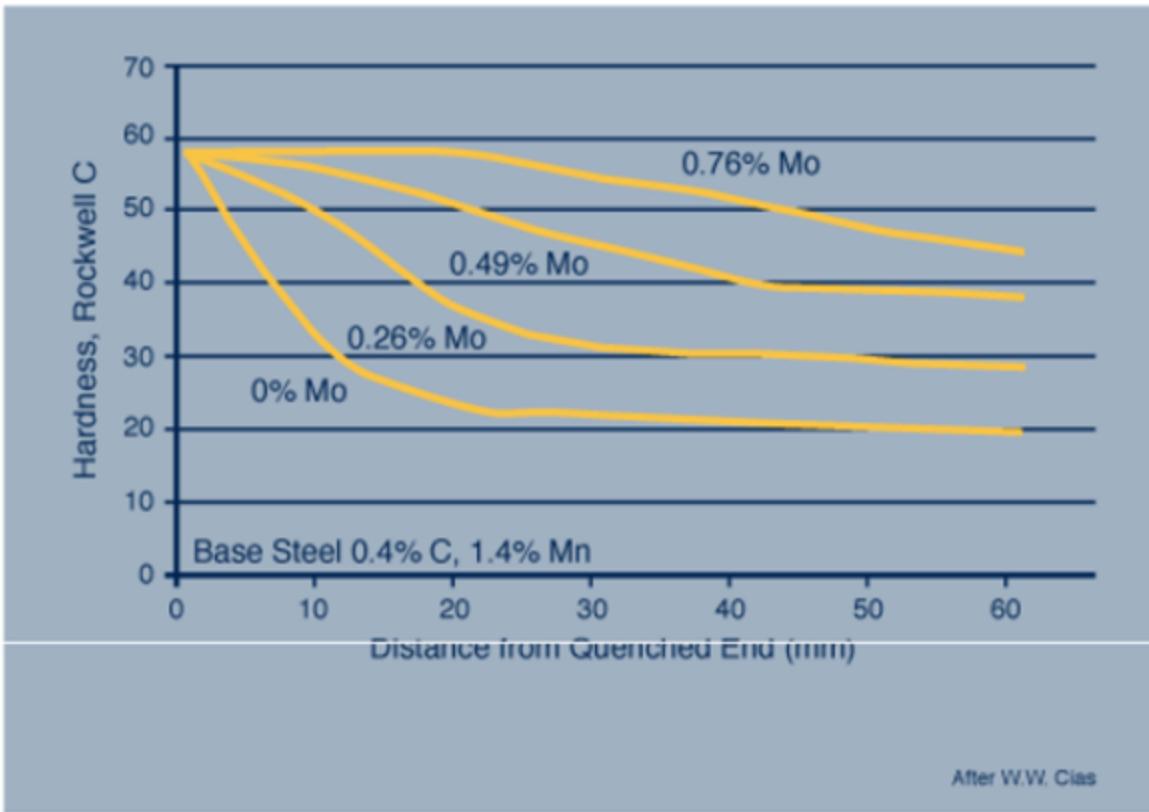


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- Effect of alloying elements
- Most metallic alloying elements slow down the ferrite and pearlite reactions, and so also increase hardenability. However, quantitative assessment of these effects is needed.
- Chromium, Molybdenum, Manganese, Silicon, Nickel and Vanadium all effect the hardenability of steels in this manner. Chromium, Molybdenum and Manganese being used most often.
- Boron can be an effective alloy for improving hardenability at levels as low as .0005%.
- Boron has a particularly large effect when it's added to fully deoxidized low carbon steel, even in concentrations of the order of 0.001%, and would be more widely used if its distribution in steel could be more easily controlled.
- The most economical way of increasing the hardenability of plain carbon steel is to increase the manganese content, from 0.60 wt% to 1.40 wt%, giving a substantial improvement in hardenability.
- Chromium and molybdenum are also very effective, and amongst the cheaper alloying additions per unit of increased hardenability.
- Hardenability of a steel increases with addition of alloying elements such as Cr, V, Mo, Ni, W → TTT diagram moves to the right.



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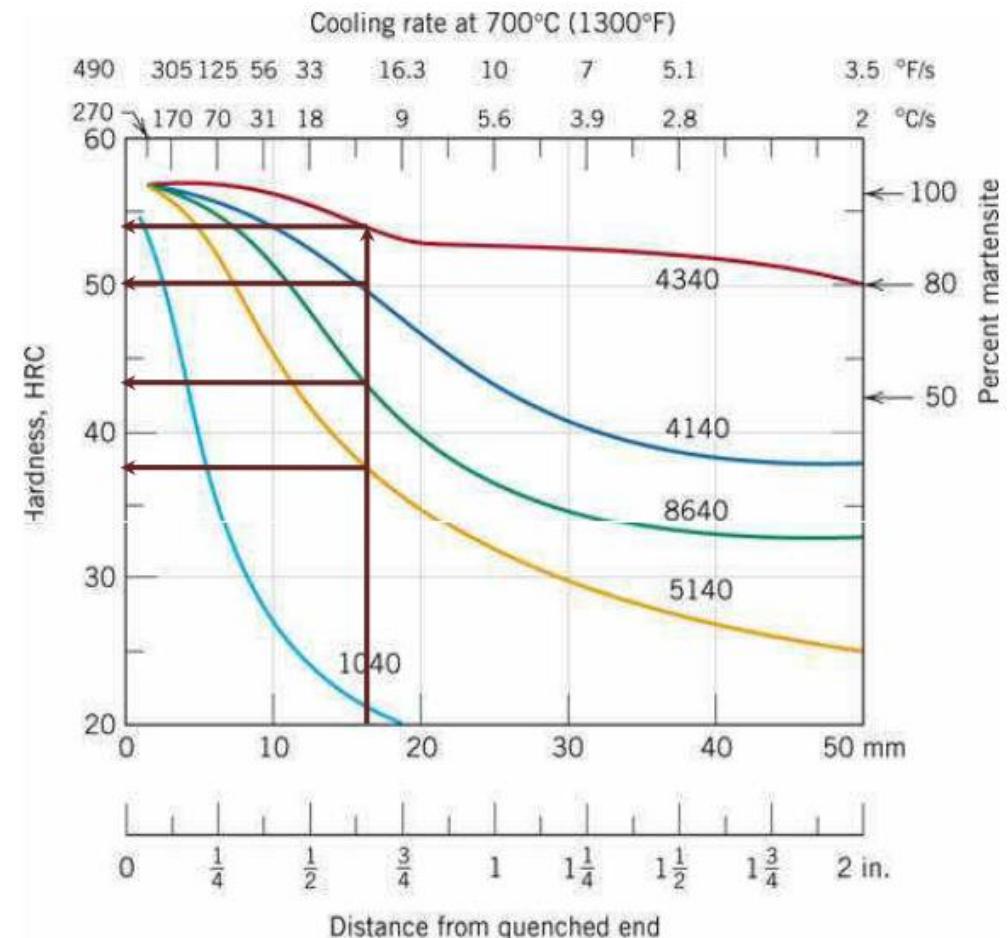
Exceptions:

- S – reduces hardenability because of formation of MnS and takes Mn out of solution as MnS.
- Ti – reduces hardenability because it reacts with C to form TiC and takes C out of solution; TiC is very stable and does not easily dissolve.
- Co – reduces hardenability because it increases the rate of nucleation and growth of pearlite.



Contd...

- All steels have 0.4 wt% C, but with different alloying elements. (in the figure shown)
- At the quenched end all alloys have the same hardness, which is a function of carbon content only.
- The hardenability of the 1040 is low because the hardness of the alloy drops rapidly with Jominy distance. The drop of hardness with Jominy distance for the other alloys is more gradual.
- The alloying elements delay the austenite-pearlite and/or bainite reactions, which permits more martensite to form for a particular cooling rate, yielding a greater hardness.



Hardness at center of a 3 inch bar is different for different steels indicating different amounts of martensite at the center



Effect of Boron on Hardenability

- Boron is added to steel for only one reason-to **increase hardenability**. Boron-treated steels have certain peculiar characteristics
 - Boron increases hardenability in hypo-eutectoid steel, has no effect on eutectoid steel, and decreases hardenability in hypereutectoid steel.
 - As the austenite grain size becomes finer, the hardenability effect of B increases.
 - Austenitizing at high temperature reduces the hardenability effect of B.
 - For the maximum B effect, the concentration should be in the range 0.0005-0.003 wt%.
-
- Increasing hardenability by adding B does not decrease the M_s temperature. These arise because of the manner in which B produces its effect and the interactions of B with other elements in steel.
 - To be effective, B must be in solid solution in austenite. The solubility of B in austenite is very low, for example, the solubility at 912 °C is about 0.001 wt%, increasing with temperature to a maximum value of about 0.005 wt.% at the eutectic.
 - In α -iron, the solubility is essentially zero, but is influenced by the impurities present. Because of its low solubility in austenite, B can be highly concentrated in grain boundaries.
 - When a boron steel is cooled from the hardening temperature the solubility of boron is reduced, which results in a still greater concentration of B at the grain boundaries.
 - Minute grains of boron carbide $Fe_{23}(BC)_6$ are formed there and to some extent they assume an orientation coherent with one of the two austenite grains between them which separate out.

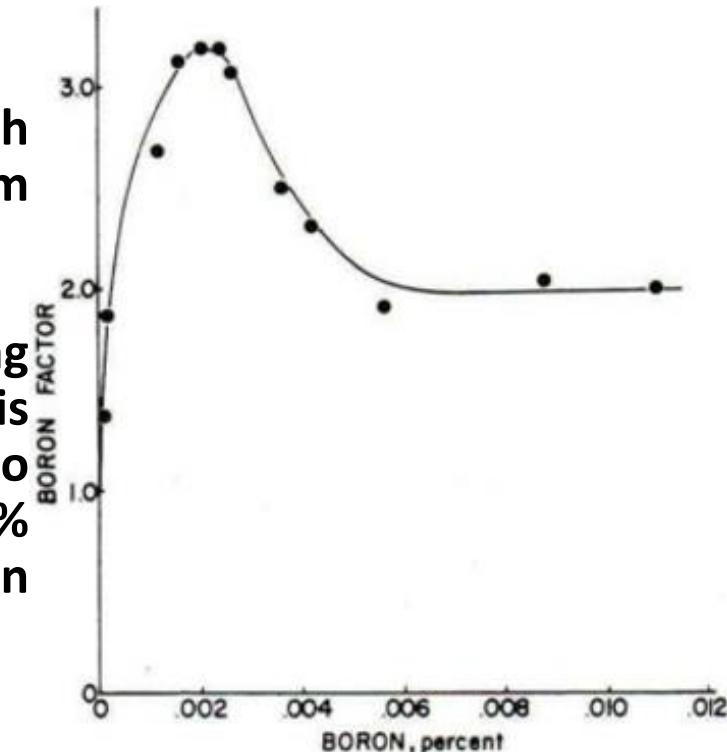


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- Atomic contact is thereby established between $\text{Fe}_{23}(\text{BC})_6$ and austenite, resulting in a reduction in the surface tension and grain-boundary energy.
- The presence of boron in solid solution and coherent boron carbide in the grain boundaries delays the formation of ferrite and pearlite and also to some extent, bainite; hence increasing the hardenability of the steel.
- The effect of B may be expressed quantitatively as the boron factor, which is the ratio of the ideal diameters, D_i , (according to Grossmann) for the steel with and without boron.

- D_i (with boron) is derived from the Jominy end- quench hardenability curve; D_i (without boron) is calculated from the chemical composition of the steel.

- The optimum B content, near 0.002 wt%, for increasing hardenability in 0.2% C, 0.65% Mn, 0.55% Mo (wt%) steel is shown in Fig. Boron contents above about 0.003 wt% lead to a loss in hardenability, and B in excess of about 0.004 wt% causes a loss in toughness through precipitation of Fe_2B in austenite grain boundaries.



Precipitation Hardening

- ❑ Precipitation hardening, also called Age hardening, is a heat treatment technique used to increase the yield strength of malleable materials (ability of a material to undergo large plastic deformations under compressive stress), including most structural alloys of Al, Mg, Ni, Ti, and some stainless steels.
- ❑ In superalloys, it is known for providing excellent high temperature strength.
- ❑ A process in which small particles of a new phase precipitate in matrix which harden material.
- ❑ Also known as Age Hardening because hardness often increases with time (even at room temperature)
- ❑ The precipitation hardening heat treatment involves the following three stages:
 - Solution treatment
 - Quenching
 - Aging



Solution Treatment and Quenching

Solution treatment:

- During solution treatment a part is heated to a temperature above the solvus temperature in order to dissolve the second phase in the solid solution.
- All the solute atoms dissolves to form a single phase solid solution.
- The part is held at this temperature for a time varying from 1–20 hrs until the dissolving has been accomplished.
- The temperature and the soaking time of solution treatment should not be too high to prevent excessive growth of the grains.

Quenching:

- Quenching is carried out in water, water-air mixture or sometimes in air.
- Object of the quenching operation is obtaining super saturation solid solution at room temperature.
- Since the second phase retains dissolved at this stage, hardness of the quenched alloy is lower than after age precipitation, however higher than hardness of the alloy in annealed state.

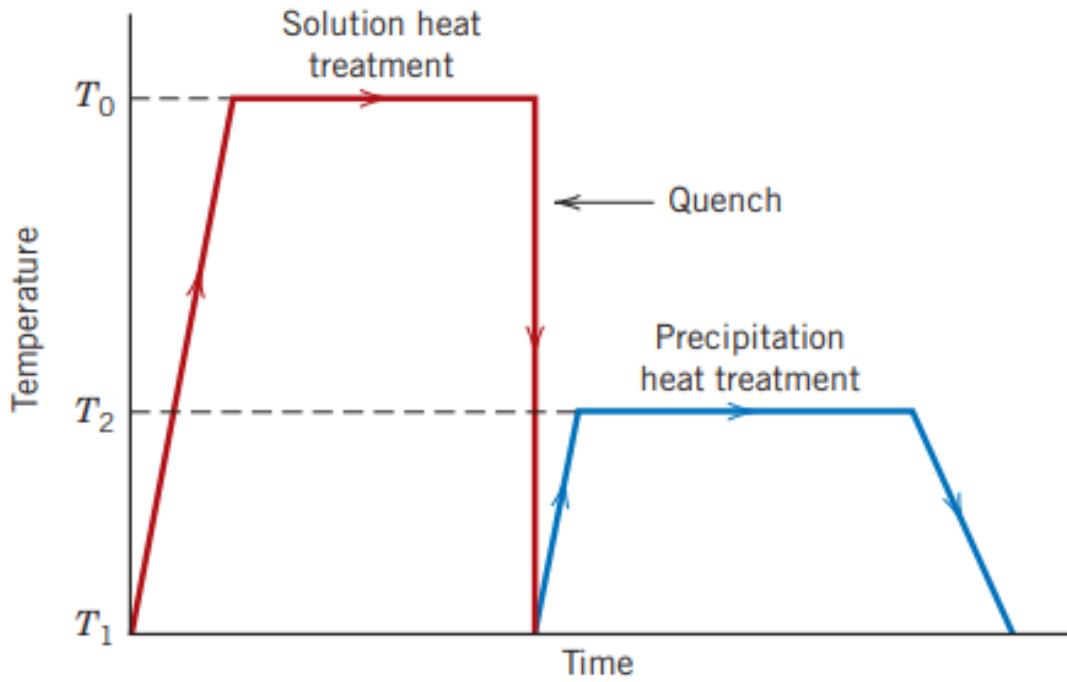


Precipitation Heat Treatment (Aging)

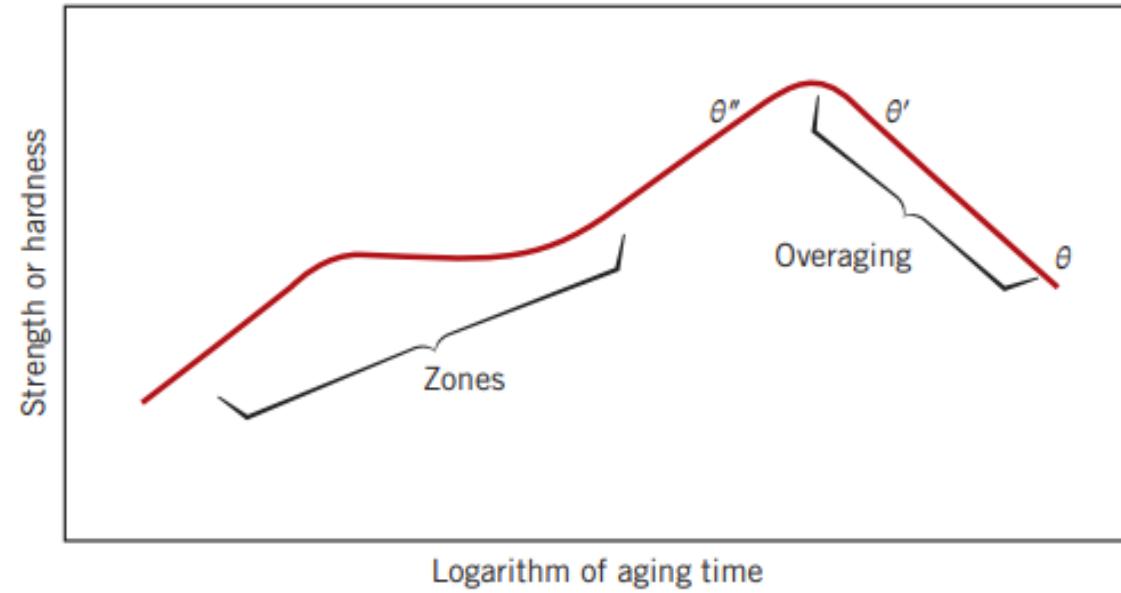
- Depending on the temperature at which this operation is carried out, aging may be **artificial** or **natural**.
- **Artificial aging:**
 - At this stage the part is heated up to a temperature **below the solvus temperature**, followed by soaking for a time varying between **2–20 hrs**.
 - The soaking time depends on the aging temperature (the higher the temperature, the lower the soaking time).
 - The aging temperature and the soaking time are also determined by the desired resulted combination of the strength and ductility of the alloy.
 - **Too high aging temperature** and **time** result in **overaging** – decrease of the strength and increase of ductility.
- **Overaging:**
 - The precipitates, however, continue to grow and the fine precipitates disappear. They have grown larger, and as a result the tensile strength of the material decreases.
- **Natural aging:**
 - Natural aging is conducted at room temperature and it takes a relatively long period of time (from several days to several weeks).



Contd...



Schematic temperature-versus-time plot showing both solution and precipitation heat treatments for precipitation hardening



Schematic diagram showing strength and hardness as a function of the logarithm of aging time at constant temperature during the precipitation heat treatment



Typical Precipitation Hardened Alloys

- **Al**

- 2014 Forged Aircraft Fittings, Al Structures
- 2024 High strength forgings, Rivets
- 7075 Aircraft Structures, Olympic Bikes

- **Cu**

Beryllium Bronze: Surgical Instruments, Non sparking tools, Gears

- **Mg**

- AM 100A Sand Castings
- AZ80A Extruded products

- **Ni**

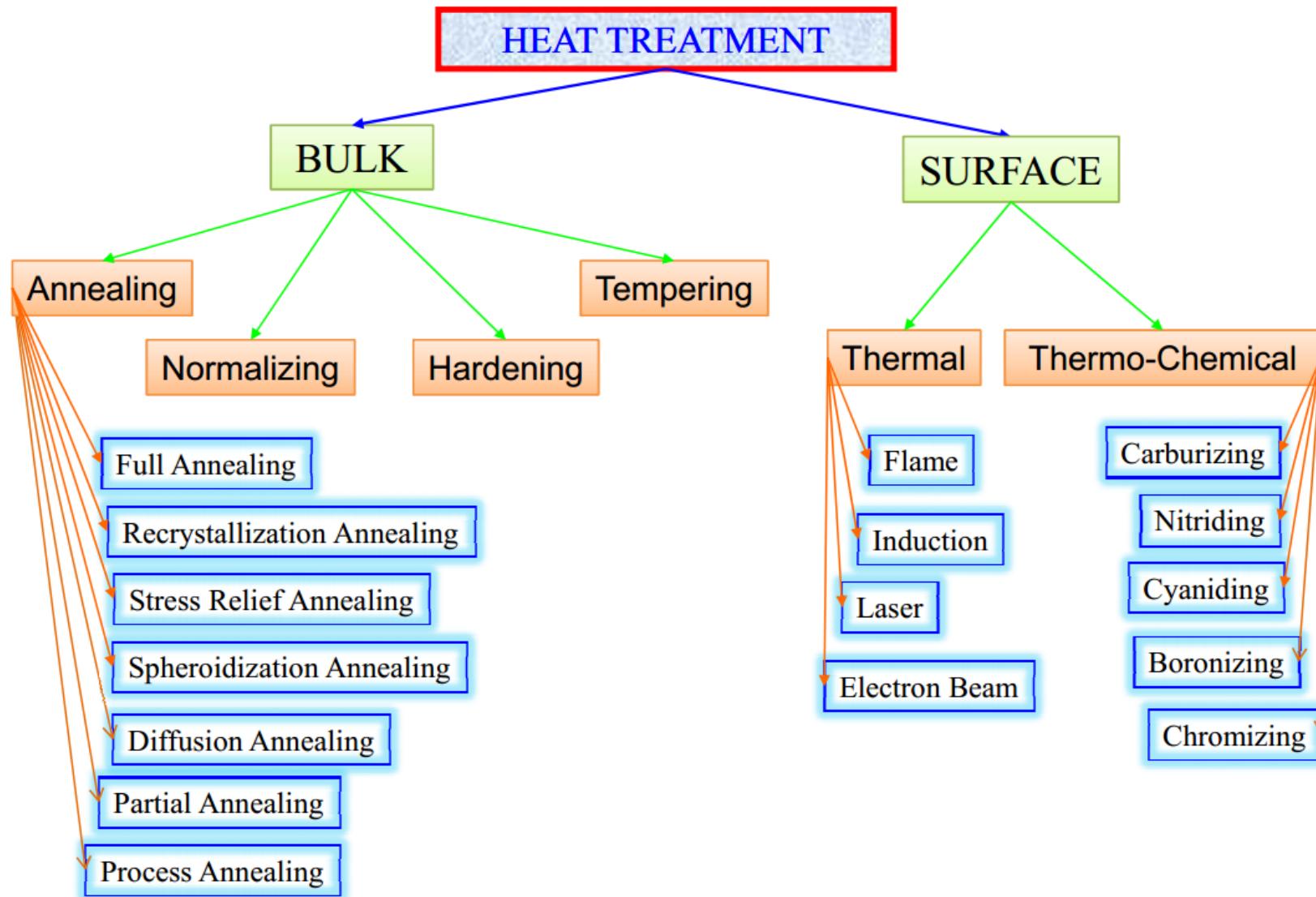
- Rene' 41 High Temperature
- Inconel 700 up to 1800F

- **Fe**

- A-286 High Strength Stainless
- 17-10P



Surface Hardening Treatment of Steels – Content

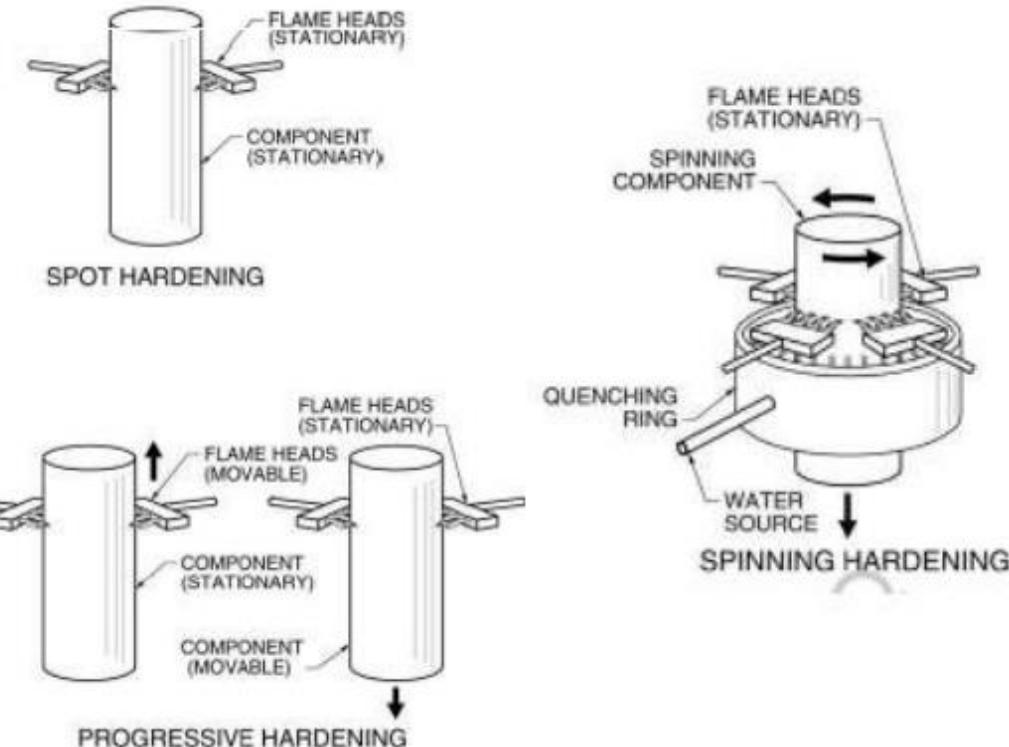


Flame Hardening

- Flame hardening is the simplest form of surface hardening heat treatment.
- This process consists of **heating the large work-piece**, such as crank shaft, axle, large gear, cam, bending roller, or any other complicated cross-section, by an **oxy-acetylene**, or **oxy- fuel blow pipe**, followed by **spraying of jet of water as coolant**.
- After hardening, **reheating of the parts** is carried out in furnace or oil bath at about 180-200 °C for stress relieving.
- Normally, case depth up to 3mm can be achieved.

- **Four methods** are generally use for flame hardening.

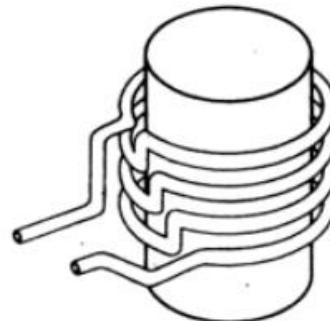
- **Stationary (Spot):** Torch and work is stationary.
- **Progressive:** Torch moves over a work piece.
- **Progressive-spinning:** Torch moves over a rotating work piece.
- **Spinning:** Torch is stationary while work piece rotates.



Induction Hardening

- Induction hardening may be used for **local surface heat treatment**. Generally, it is used to surface harden crank shafts, cam shafts, gears, crank pins and axles. In this process, **heating of the component is achieved by electromagnetic induction**.
- Here, an alternating current of high frequency passes through an induction coil enclosing the steel part to be heat treated. The induced emf heats the steel. the depth up to which the heat penetrates and rises the temperature above Ac_3 is inversely proportional to the square root of the AC frequency.
- Correspondingly, the hardened depth decreases with increasing frequency in induction hardening, the heating time is usually a few seconds. Immediately after heating water jets are activated to quench the surface. Martensite is produced at the surface, making it hard and wear resistant. The microstructure of the core remains unaltered. Induction hardening is suitable for mass production of articles of uniform cross section.

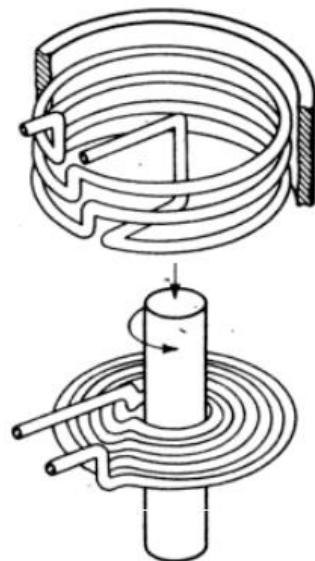
Five basic designs of work coils with the heat patterns developed by each are shown below



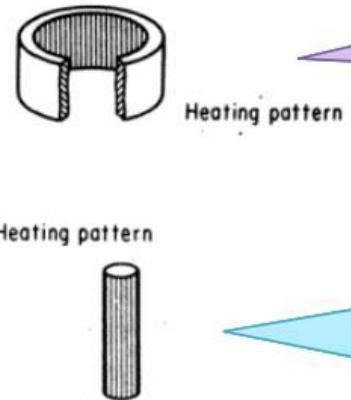
A Simple Solenoid for
external heating



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A Single turn coil for scanning a rotating surface, provided with a contoured half turn that will aid in heating the fillet

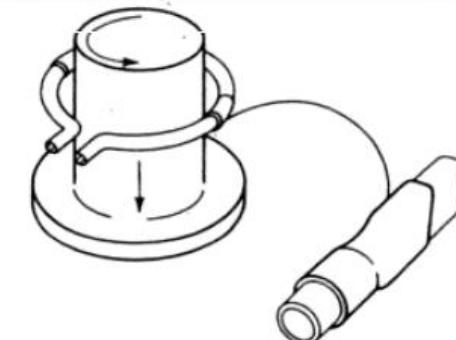


A 'Pancake' coil for spot heating.

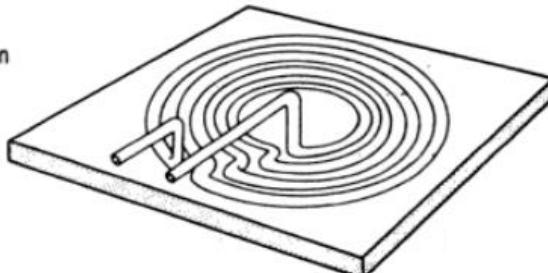
A coil to be used internally for heating bores

Heating pattern

A "pie-plate" type of coil designed to provide high current densities in a narrow band for scanning applications.



Heating pattern



Laser Hardening

- Laser hardening treatment is widely used to harden **localized areas of steel and cast iron** machine components. This process is sometimes referred to as laser transformation hardening to differentiate it from laser surface melting phenomena.
- There is no chemistry change produced by laser transformation hardening, and the process, like induction and flame hardening, provides an effective technique to harden ferrous materials selectively.
- As **laser beams** are of high intensity, a **lens is used to reduce the intensity** by producing a defocused spot of size ranging from 0.5-25 mm. proper control of energy input is necessary to **avoid melting**.
- Laser transformation hardening produces thin surface zones that are heated and cooled very rapidly, resulting in very fine martensitic microstructures, even in steels with relatively low hardenability.
- **High hardness and good wear resistance with less distortion** result from this process.
- Laser hardening has the advantage of **precise control** over the area to be hardened, an ability to harden re-entrant surfaces, very high speed of hardening and no separate quenching step (the quench is effected by the mass of the unheated material).
- The relationship between depth of hardening and power is as follows:

$$\text{casedepth(mm)} = -0.11 + \frac{3.02P}{(D_bV)^{1/2}} \quad P = \text{laser power; } D_b = \text{Incident beam diameter} \\ V = \text{traverse speed (mm/s)}$$

- The disadvantage is that the hardening is **shallower than in induction and flame hardening**.



Electron Beam (EB) Hardening

- This process is used for **hardening those components which cannot be induction hardened because of associated distortion**. Automatic transmission clutch cams (SAE 5060 steel) are hardened by this processes.
- Electron Beam (EB) hardening is **like laser treatment**, is used to harden the surfaces of steels. The EB heat treating process uses a concentrated beam of high-velocity electrons as an energy source to heat selected surface areas of ferrous parts. Electrons are accelerated and are formed into a directed beam by an EB gun.
- After exiting the gun, the beam **passes through a focus coil**, which precisely controls beam density levels (spot size) at the work piece surface and then passes through a deflection coil.
- To produce an electron beam, **a high vacuum of 10^{-5} torr** is needed in the region where the electrons are emitted and accelerated. This vacuum environment **protects the emitter from oxidizing and avoids scattering of the electrons** while they are still traveling at a relatively low velocity.
- Like laser beam hardening, the EB process **eliminates the need for quenchants** but requires a sufficient work piece mass to permit **self quenching**.
- A mass of up to eight times that of the volume to be EB hardened is required around and beneath the heated surfaces. Electron beam hardening does not require energy absorbing coatings, as does laser beam hardening.
- Normally, case depth up to 0.75 mm can be achieved by this method. **A minicomputer is used to control voltage, current, beam time and focus.**



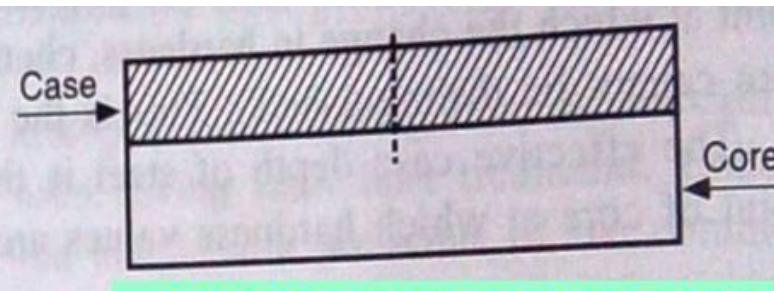
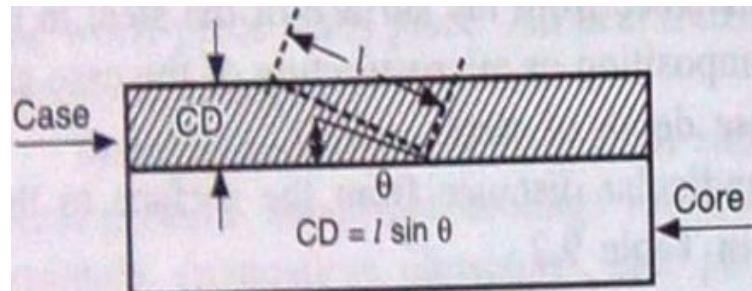
Case Depth Measurements in Steel

- Case depth (actual) is defined as “the perpendicular distance from the surface of the steel to the point at which the change in hardness, chemical composition or microstructure of the case and the core cannot be distinguished.
- Effective case depth is defined as the perpendicular distance from the surface of a hardened case to the farthest point at which a specified hardness value is obtained. This hardness criterion is HRC 50, except when otherwise specified. Effective case depth is always determined on representative samples, or the part itself but in the heat treated condition.
- On a broad basis, the methods used for measuring case depth can be classified as:
 - Chemical method
 - Hardness method
 - Macroscopic method
 - Microscopic method
- Chemical method
- It is a usual practice to apply this method only to carburized cases. It may also be applied to other case-hardening methods which involve change in chemical composition, viz. nitriding and carbonitriding. Carbon content is determined at various depths below the surface of case hardened specimen. Where hardening is due to formation of nitrides, nitrogen content is estimated. This is the most accurate method of determining case depth.



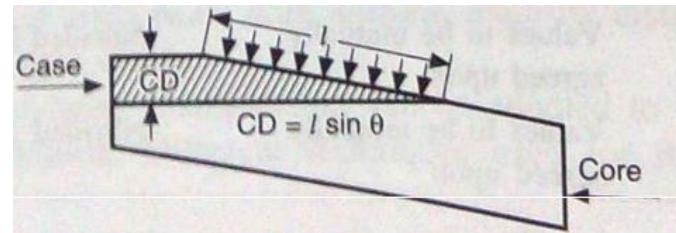
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- Hardness method**
- In this method, hardness values are taken along the case and core. It is a very accurate method since sharp change in hardness across case and core region can be measured.
- Specimens for this method are prepared by:
 - Cross section procedure
 - Taper-grind procedure
 - Step-grind procedure
- Cross section procedure**
- The specimen is cut perpendicular to the hardened surface at a pre-decided area. Care should be taken to ensure that no change in hardness takes place as a result of cutting. The surface area is polished up to 4/0 emery paper.



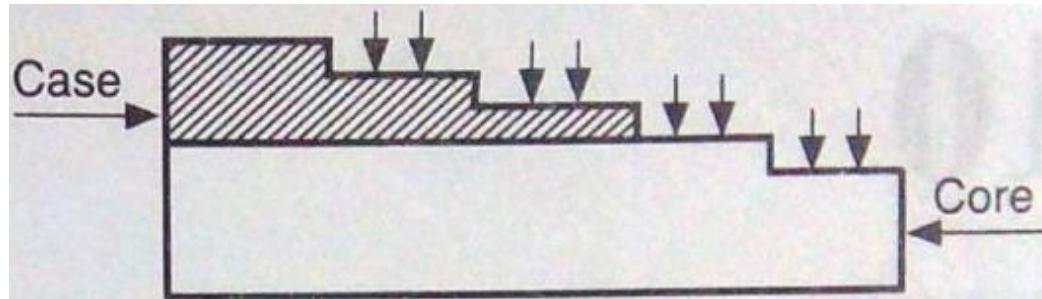
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- **Taper-grind procedure**
- This method is suitable for light and medium cases, and is illustrated in below figure. A shallow taper is ground through the case of steel, and the hardness values are found along the surface of the prepared taper.



Taper ground specimen for light and medium cases

- **Step-grind procedure**
- For medium and heavy cases, step-grind procedure is suitable. In this case, the hardness values are taken in steps of known distances below the surface. Here two predetermined depths are ground to ensure that the effective case depth is within specified limits.



Step ground specimen for medium and heavy cases



Contd...

- **Macroscopic method**
- In this technique, the test specimen is **cut perpendicular to the hardened surface**. The cut surface is ground and polished through 0/0 to 4/0 emery paper.
- After this, disc polishing is carried out, which is followed by etching with suitable etching reagent so that case and core regions can be distinguished.
- The etched specimen is washed in water or alcohol and dried, and is examined under a limited magnification of **20X**.

- **Microscopic method**
- In this method, the specimen is **cut perpendicular to the hardened surface** and the cut surface is ground, polished and etched.
- The specimen is examined under microscope with calibrated eye piece.
- The total case depth is the distance from the surface to the point up to which the modified microstructure is observed.



Thermo-Chemical Treatments of Steels

- Chemical heat treatment is the process used to achieve different properties in core and steel components. Numerous industrial applications require a hard wear resistant surface called the **case**, and a relatively soft, tough inside called the **core**. Example: Gears.
- They are **two different methods**. The first method is known as **thermo-chemical treatment** because the surface composition of steel **changes by diffusion of carbon and/or nitrogen and sometimes other elements**.
- The second method is known has **surface hardening**, it involves **phase transformation by rapid heating and cooling of the outer surface**. The **aim of both methods are same**.



Carburizing

- Carburizing is the most widely used method of **surface hardening**. Here, the surface layers of a low carbon steel (<0.25) is enriched with carbon up to 0.8-1.0 wt.%. The source of carbon may be a solid medium, a liquid or a gas.
- In all cases, the carbon enters the steel at the surface and diffuses into the steel as a function of time at an elevated temperature. Carburizing is done at 920-950 °C. At this temperature the following reaction takes place:



- Where $\text{Fe}_{(\text{c})}$ represents **carbon dissolved in austenite**. The rate of diffusion of carbon in austenite, at a given temperature is dependent upon the diffusion coefficient and the carbon concentration gradient.
- The carburizing equation given previously, $\text{Fe} + 2 \text{CO} \rightarrow \text{Fe}_{(\text{c})} + \text{CO}_2$ is reversible and **may proceed to the left**, removing carbon from the surface layer if the steel is heated in an atmosphere containing carbon dioxide (CO_2). This is called **decarburization**.
- Decarburization may be prevented by using an endothermic gas atmosphere in the furnace to protect the surface of the steel from oxygen, carbon dioxide and water vapor. An endothermic gas atmosphere is prepared by reacting relatively rich mixtures of air and hydrocarbon gas (usually natural gas) in an externally heated generator in the presence of a nickel catalyst.
- Carburizing can be done by pack carburizing, liquid carburizing, gas carburizing and vacuum carburizing.



Pack Carburizing

- This method of carburizing is also known as **solid carburizing**.
- In this process, steel components to be heat treated are packed with **80% granular coal and 20% BaCO₃** as energizer in heat resistant boxes and heated at 930 °C in furnace for a specific time which depends on the case depth required.
- Such a high temperature in furnace helps in absorption of carbon at the outer layer. The following reactions takes place:

(i) Energizer decomposes to give CO gas to the steel surface:



(ii) Carbon monoxide reacts with the surface of steel:



(iii) Diffusion of carbon into steel

(iv) CO₂ formed in step (ii) reacts with “C” in the coal:

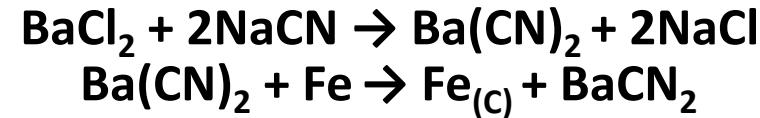


- For a given steel at a given temperature, the depth of penetration is dependent on diffusion and can be related to the time t by the equation:
case-depth = kv^t, where, k is a constant
- Generally, carburizing time varies from 6–8 hours, and case depth obtained varies from 1–2 mm.



Liquid Carburizing

- It is also popularly known as salt bath carburizing. In this process, carburizing occurs through molten cyanide (CN) in low carbon steel cast pot type furnace heated by oil or gas. Bath temperature is maintained between $815^{\circ}C$ and $900^{\circ}C$.
- The life of pot depends on quality of material, operating temperature and mode of operation, viz. whether it is continuous or intermittent. Continuous and automatic processes give good end results.
- The bath surface is covered with graphite or coal to reduce radiation losses and excessive decomposition of cyanide.
- Different salt mixtures used in this processes are named according to their carbon potential activity. Besides sodium or potassium cyanide, the bath contains (i) Sodium and potassium chloride (ii) Barium chloride which acts as an activator.



- Some beneficial nitrogen diffusion may also take place through oxidation of CN to CNO . In liquid carburizing, heating time is short and heat transfer is rapid. There is complete uniformity of the carburized layer in the component.
- This process gives a thin and clean hardened layer of $\sim 0.08mm$ thick.



Gas Carburizing

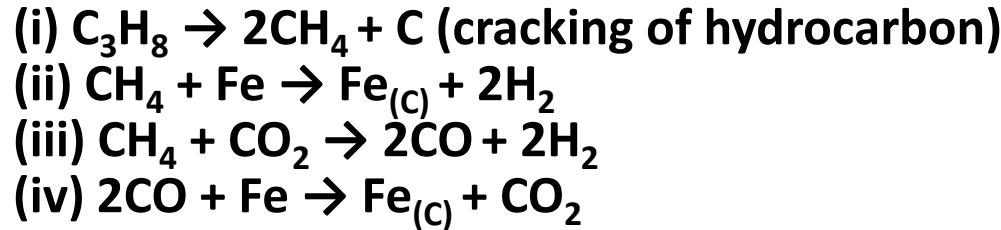
- This is the most widely used method of carburizing. It is carried out in **retort type**, **sealed quench type**, or **continuous pusher type furnaces**. These **furnaces** are either **gas fired** or are heated **electrically**. Gas carburizing temperature varies from 870-950 °C.
- Gas atmosphere for carburizing is produced from **liquid (methanol, isopropanol)** or **gaseous hydrocarbons (propane and methane)**. An endothermic gas generator is used to supply endothermic gas.
- A mixture of propane or methane with air is cracked in hot retort of an endo-gas generator to form carrier gas, whose dew point is adjusted at about +4 °C by proper gas/air ratio. The approximate composition of this gas is as follows.
- Such a gas acts as a ‘carrier gas’ for the process. Furnace chamber is purged with this gas to maintain a slightly positive pressure. This in turn prevents infiltration of air from atmosphere.
- This gas also prevents oxidation of the steel during heating. When the material reaches carburizing temperatures, propane or methane is introduced to maintain a specific carbon potential.

Nitrogen	40%
Hydrogen	40%
Carbon monoxide	20%
Carbon dioxide	0.3%
Methane	0.5%
Water vapour	0.8%
Oxygen	In traces



Contd...

- During gas carburizing, the following reactions take place:



- Carburizing occurs mainly due to conversion of CO to CO_2 through reaction (iv). Hydrogen reacts with CO_2 and increases CO concentration by the reaction:



- Traces of O₂ are also present due to the following reactions:



- Average concentrations of CO_2 , H_2O , and O_2 are 0.2%, 0.5% and 10^{-14} ppm respectively.
- One of the recent developments in the gas carburizing technique is the use of nitrogen as a carrier gas. Normally, nitrogen gas is used with some minor additives. Carbon potential is controlled by adjusting the level of oxidizing constituents.
- Currently the cost of equipment for this modified process is high. Also, skilled and well trained operators are required for successful operation of this process.



Vacuum Carburizing

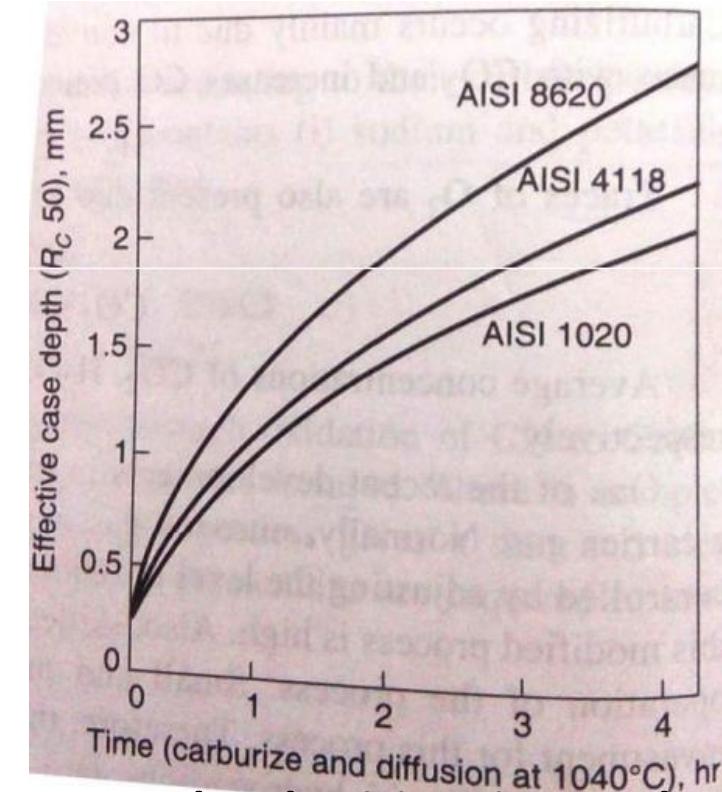
- The first commercial application of vacuum carburizing started in the early 1970s. Vacuum carburizing is a processes of carburizing, carried out either in **vacuum or in reduced pressure**. The main advantage of the process lies in the **tremendous energy saving** associated with it.
- Carburizing in vacuum or reduced pressure is carried out in **two stages**. In the **first stage**, carbon is made available to the steel for absorption.
- In the **second stage**, diffusion of the carbon takes place within the steel piece and results in appropriate concentration of carbon and depth of carburizing.
- In vacuum carburizing, there is accurate control on the amount of carbon absorbed. Also, as the process takes place at a relatively higher temperature, carbon absorption is quite rapid.

- To start the process, the job is introduced into the furnace which is then evacuated. After achieving the required degree of vacuum, the furnace is heated up to a carburizing temperature which lies in the range 925-1050 °C. In this temperature range, austenite which is formed is unsaturated with respect to carbon.
- A gaseous hydrocarbon such as methane or propane is then introduced into the furnace. As soon as the hydrocarbon in gaseous form comes in contact with the surface of the job, it cracks. As a result, a very thin layer of extremely fine carbon is deposited on the surface.
- This carbon is immediately absorbed by the steel till saturation is attained. The process continues till sufficient carbon is absorbed and the required case depth is formed the inflow of gas is then stopped and the excess gas is removed by vacuum pumps.

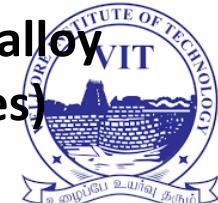


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- At this point, the second stage or controlled diffusion cycle commences. During this stage the required carbon concentration is formed. Vacuum carburizing can be carried out either by continuous flow of gas during the carburizing cycle or by short cycles of carburizing and diffusion.
- **Advantages**
- Since heating is carried out by radiation, there is improved efficiency due to the presence of vacuum.
- Heat zones occupy less volume.
- It is not necessary to keep the furnace on throughout the process. It can be heated and cooled rapidly as and when required.
- Absence of atmosphere, so that free from oxides, micro cracks, and decarburization.
- The quantity of gas required is only about 1% of the requirement in conventional processes.

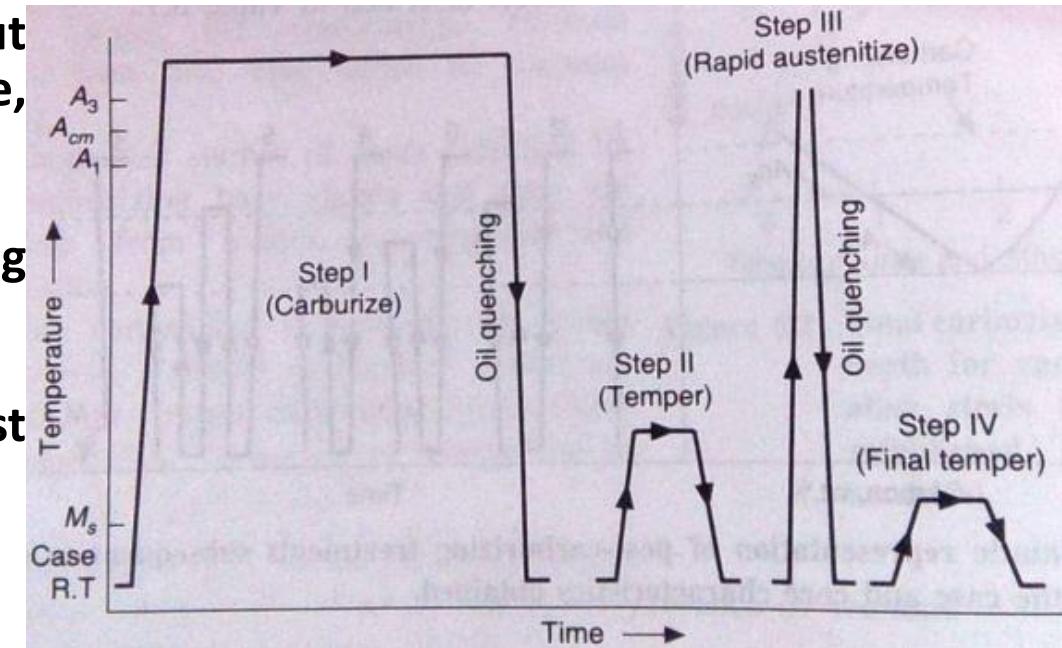


Total carburizing time and case depth for various carbon and alloy steels (as-quenched samples)



Post-Carburizing Heat Treatments

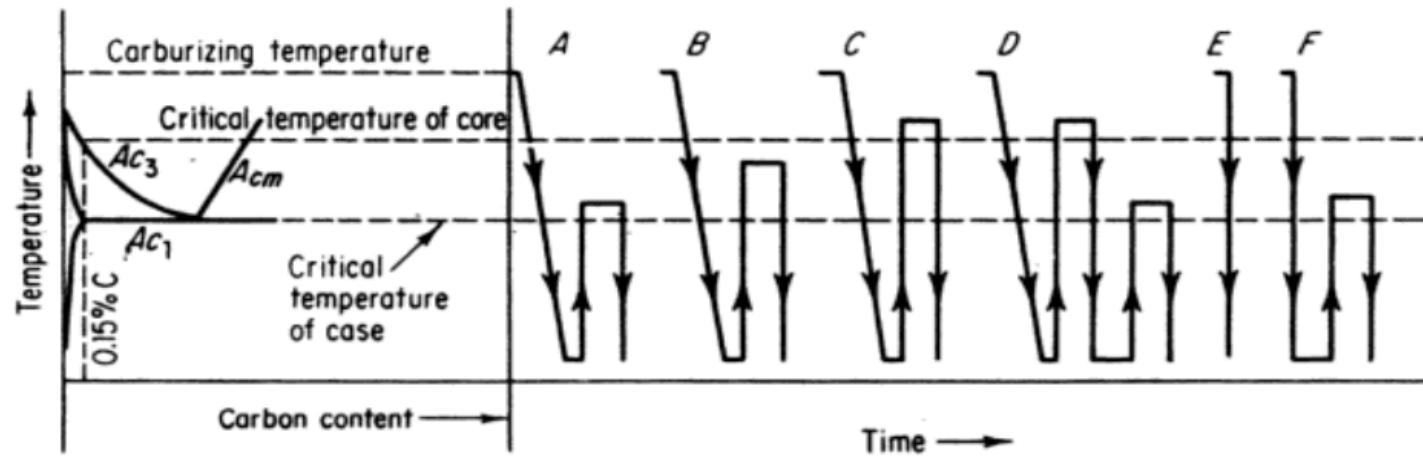
- The objectives of this post-carburizing heat treatment are to (i) improve the microstructure and refine coarser grains of core and case of carburized steel (ii) achieve high hardness at the surface; and (iii) break the carbide network in the carburized case, which may be formed due to higher carbon content (1.0%)
- A procedure has been devised to obtain maximum case hardness and very fine grain size
- Step 1: Work piece is heated to about 1040°C (about 120°C above the normal range) for a short time, followed by quenching in oil bath.
- Step 2: Tempering at about 370°C for converting retained austenite into bainitic microstructure.
- Step 3: Rapid austenising by induction heating just above Ac_3 temperature, followed by oil quenching.
- Final step consists of tempering at about 180°C .
- This four-step heat treatment gives maximum case hardness (around 900 DPH) with very fine grained case and core.



Recommended heat treatment cycle for maximizing case hardness along with grain refinement



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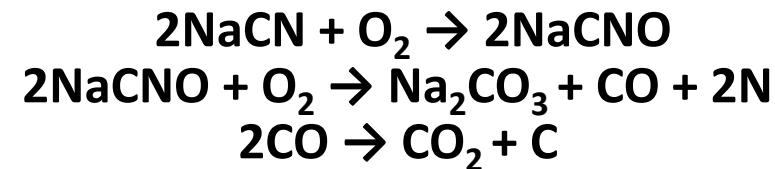


TREATMENT	CASE	CORE
A – best adapted to fine grained steels	Refined; Excess carbide not dissolved	Unrefined; soft and machinable
B-best adapted to fine grained steels	Slightly coarsened; some solution of excess carbide	Partially refined; stronger and tougher than A
C-best adapted to fine grained steels	Somewhat coarsened; solution of excess carbide favored; austenite retention promoted in highly alloyed steels.	Refined: maximum core strength and hardness; better combination of strength and ductility than B
D-best treatment for coarse grained steels	Refined solution of excess carbide favored; austenite retention minimized	Refined; soft and machinable; maximum toughness and resistance to impact
E-adapted to fine grained steels only	Unrefined with excess carbide dissolved; austenite retained; distortion minimized	Unrefined but hardened
F-adapted to fine grained steels only	Refined; solution of excess carbide favored; austenite retention minimized	Unrefined; fair toughness



Cyaniding and Carbo-Nitriding

- In cyaniding and carbo-nitriding processes, the surface layer of steel (with 0.3-0.4% C) is hardened by addition of both carbon and nitrogen.
- In this case that contain both carbon and nitrogen are produced in liquid salt baths (cyaniding) or by use of gas atmospheres (carbo-nitriding). The temperatures used are generally lower than those used in carburizing, being between 750-900 °C.
- Exposure is for a shorter time, and thinner cases are produced, up to 0.010 in. for cyaniding and up to 0.030 in. for carbo-nitriding.
- In cyaniding is done in a liquid bath of NaCN, with the concentration varying between 30 and 97%. Both carbon and nitrogen enter the steel via the following reactions:



- Carbon and nitrogen so formed in atomic form diffuse into the steel and give thin wear resistant layer of the carbo-nitride ϵ -phase.
- The temperature used for cyaniding is lower than that for carburizing and in the range of 800-870 °C. the time of cyaniding is 0.5-3 hour to produce a case depth of 0.25 mm or less.
- Cyaniding process is not suitable for hardening those parts which are subjected to shock, fatigue and impact because nitrogen addition has adverse effects on such properties of steels.



Contd...

- Carbo-nitriding is a case-hardening process in which a steel is heated in a gaseous atmosphere of such composition that carbon and nitrogen are absorbed simultaneously.
- This process is also known as dry cyaniding or gas cyaniding. It is the gas carburizing process modified by the addition of anhydrous ammonia.
- The decomposition of ammonia provides the nitrogen, which enters the steel along with carbon.
- A typical gas mixture consists of 15% NH_3 , CH_4 , and 80% of neutral carrier gas. The temperature used is 750-900 °C. With increasing temperature, a greater proportion of carbon enters the steel.
- The presence of nitrogen in the austenite accounts for the major differences between carbo-nitriding and carburizing.
- Carbon-nitrogen austenite is stable at lower temperatures than plain-carbon austenite and transforms more slowly on cooling. Carbo-nitriding therefore can be carried out at lower temperatures and permits slower cooling rates than carburizing in the hardening operation.
- In this process, surface hardenability, wear resistance and corrosion resistance are better than in the carburizing process. But the time required for heat treatment is longer than that for carburizing.



Nitriding

- In contrast to the processes described before, nitriding is carried out in the ferrite region. Consequently, no phase change occurs after nitriding .
- This part to be nitrided should possess the required core properties prior to nitriding. Pure ammonia decomposes to yield nitrogen which enters the steel:

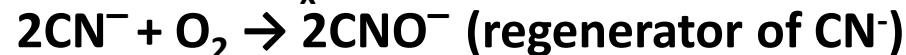


- The solubility of nitrogen in ferrite is small. Most of the nitrogen that enters the steel forms hard nitrides (e.g. Fe_3N). A typical nitriding steel contains alloying elements of 1%Al, 1.5%Cr and 0.2%Mo. Al, Cr, and Mo form very hard and wear resistant nitrides.
- The temperature of nitriding is 500-590 °C. the time for a case depth of 0.02mm is about 2 hour. In addition with wear resistance, it also increases the resistance of a carbon steel to corrosion in moist atmospheres.
- A common problem encountered in nitriding is the formation of γ' nitride (Fe_4N) on the outer layers of the case, known as the “white layer”, as it looks white under the microscope. This layer is very brittle and tends to crack. It must be removed by final grinding operation. Its formation can be minimized by maintaining the correct ratio of NH_3/H_2 in the gas mixture during the heat treatment.
- There are two ways by which white layer can be totally suppressed,
 - Floe process or double stage nitriding, where a white layer is first produced and then decomposed
 - Ion nitriding process or Plasma nitriding



Salt Bath Nitro-Carburizing

- In this process, besides nitrogen, carbon atoms are also diffused into the case of steel component at 570-580 °C in salt baths. The salt baths are of two types, namely, those containing cyanide and others which do not contain any cyanide.
- Cyanide-free salt baths are more popular because these are not hazardous. The base salt contains a mixture of sodium and potassium cyanates and carbonates.
- The time for obtaining a case depth of 10-15 µm is about 1½ hours for low carbon unalloyed steels.
- Reactions that take place in the bath are as follows.

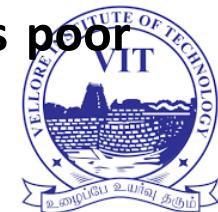


- One of the recent developments is to destroy cyanate and the small percentage of cyanide in the drag-out salt. This is achieved by quenching in oxidizing quenching (cooling) salt. Such a treatment eliminates the need for neutralization plant.
- This process can be used for any ferrous material; the time taken for treatment is short. However, it is not suitable for very large objects and odd shaped components.
- Limitation of the processes is that the typical treated layers are very thin and nitro carburizing atmospheres/salts are difficult to handle safely.



Boronizing

- Boronizing is one of the recent methods of surface hardening, which may be applied to **any ferrous material** but is generally adopted for carbon steels and tool steels.
- In the case of pack process, the components are packed in heat resistant boxes with mixtures of granules or paste of **boron carbide or other boron compounds** with addition of activators and diluents at 900-1000 °C.
- **Boron diffuses inwards and iron borides (FeB and Fe₂B) layers** are formed. On the outer surface, FeB phase forms, While in the interior, Fe₂B phase is formed. FeB phase is more brittle and is not desirable.
- Higher temperatures, longer treatment times and high alloy steels favour the formation of FeB phase. The boride layers are very hard. The hardness of boride layers on steel ranges between 1500 and 2100 VHN.
- Boride layer depths range from 0.012-0.127 mm, depending on material and application. The treatment time required for a case depth of 0.15 mm is 6hours at about 900 °C.
 - Thick layers (up to 0.127 mm) – for abrasive wear
 - Thin layer (up to 0.025 mm) – for adhesive wear and friction reduction
- Boronizing increases tool and mold life by improving resistance to abrasive, sliding and adhesive wear. It reduces the use of lubrication as have low coefficient of friction. But high process temperature may lead to the distortion of the component. Moreover, the component shows poor fatigue and corrosion resistance.



Chromizing

- Like Boronizing process, Chromizing is also used for surface hardening of both carbon and tool steels.
- There are **two basic types of chromizing** : Pack chromizing and gaseous chromizing. The components to be chromized are packed with **fine chromium powder and additives**.
- A typical chromizing mixture consists of 60% Cr or ferro chrome (with carbon content not exceeding 0.1%), 0.2% ammonium iodide, and 39% kaolin powder.
- Diffusion of chromium takes place at 900-1020 °C, and chromium carbide is formed on the surface of steel. The treatment time needed for achieving a case depth of 0.02-0.04 mm is 12 hours at 900-1020 °C. Hardness of chromium carbide layer is about 1500 VHN.
- **HARD CHROMIZING** : If the steel, which to be chromized, **contains enough carbon (minimum 0.35%)**, a corrosion and wear resistant chromium layer will be formed on the surface of the work-piece during the chromizing treatment.
- **SOFT CHROMIZING** : On steel, **with low carbon content (<0.35%)**, a chromium carbide layer cannot be formed. Instead a chromium diffusion layer builds up during the chromizing process which can reach up to 200 μ m in thickness and a chromium content of upto 35%. The high chromium content endows the work piece with an excellent resistance against corrosion and oxidation while maintaining its ductility.
- Chromizing leads to excellent corrosion resistance under a variety of severe conditions. High temperature oxidation resistance is also improved significantly. Components may undergo bending and flanging operations without spalling. Hardness of chromium carbide layer is about 1500VHN.

