LECTURE NOTES ON

MM-15-015: HEAT TREATMENT

6th Semester, MME
HEAT TREATMENT

Avala Lava Kumar
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla-768018
E-mail: lavakumar.vssut@gmail.com Phone: (+91) (7077110110)

D.K.Mishra
Department of MME, VSSUT, Burla – 768018
E-mail: dinesh.igit@gmail.com Phone: (+91) 7377483380

Dr. S.K.Badjena
Department of MME, VSSUT, Burla – 768018
E-mail: skbadjena@gmail.com Phone: (+91) 8455938473
The aim of this course is to gain an understanding of the role of heat treatment on the development of microstructure and properties of metallic materials. The course will highlight a number of commercially-significant applications where heat treatment are important.

This course covers the theory of heat treatment including the kinetic principles of solid state transformations. The influence of time on phase transformation is investigated. The interpretation of IT and CT diagrams to predict transformations and resulting microstructures is covered. Hardenability of steel is studied including factors influencing hardenability and the use of hardenability curves in the selection of steels for given applications. The effect of thermal gradients and phase transformations on distortion and residual stress in heat treated products is studied. With addition of this it covers heat treatment of some selected non-ferrous alloys and ferrous alloys.

The course is to supply the student with a basic understanding of the modern heat treatment processes and reheating principles. Upon completing the required coursework, the student can explain the reasons for the heat treatment and its effects on the final properties of the product. With the help of a short theoretical background.
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Chapter Name</th>
<th>Slide No</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Foundation</td>
<td>6-55</td>
</tr>
<tr>
<td>2</td>
<td>Principles of heat treatment of steels</td>
<td>56-133</td>
</tr>
<tr>
<td>3</td>
<td>Heat treatment processes for steels</td>
<td>134-170</td>
</tr>
<tr>
<td>4</td>
<td>Hardenability</td>
<td>171-196</td>
</tr>
<tr>
<td>5</td>
<td>Quenching technology</td>
<td>197-231</td>
</tr>
<tr>
<td>6</td>
<td>Surface hardening treatment of steels</td>
<td>232-241</td>
</tr>
<tr>
<td>7</td>
<td>Thermo chemical treatments of steels</td>
<td>242-259</td>
</tr>
<tr>
<td>8</td>
<td>Thermo mechanical treatment</td>
<td>260-272</td>
</tr>
<tr>
<td>9</td>
<td>Cast irons</td>
<td>273-308</td>
</tr>
<tr>
<td>10</td>
<td>Heat treatment of selected steels</td>
<td>309-334</td>
</tr>
<tr>
<td>11</td>
<td>Heat treatment of non ferrous alloys</td>
<td>335-395</td>
</tr>
</tbody>
</table>
REFERENCES

- Steel heat treatment: Metallurgy and Technologies
  George E. Totten
  CRC Press, Taylor & Francis Group

- Heat Treatment: Principles and Techniques
  T.V. Rajan, C.P. Sharma, and Ashok Sharma
  PHI Learning Private Limited

- Heat Treatment of Materials
  Vijendra Singh
  Standard Publishers Distributors, Delhi

- Phase Transformations & Heat Treatment
  Prof. M.P. Gururajan
  NPTEL web course

- Practical Heat Treating
  Howard E. Boyer
  American society for metals

- Introduction to Physical Metallurgy
  Sidney H. Avner
  McGraw Hill Education (India) Pvt Ltd
Avala Lava Kumar : D.K. Mishra : Dr. S.K. Badjena
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla -768018
*E-mail: lavakumar.vssut@gmail.com
Heating and cooling a solid metal or alloy in a way so as to obtain specific conditions and/or properties.
To increase strength, hardness and wear resistance (*bulk hardening*, *surface hardening*)

To increase ductility and softness (*Tempering*, *Recrystallization Annealing*)

To increase toughness (*Tempering*, *Recrystallization annealing*)

To obtain fine grain size (*Recrystallization annealing*, *Full annealing*, *Normalizing*)

To remove internal stresses induced by differential deformation by cold working, non-uniform cooling from high temperature during casting and welding (*Stress relief annealing*)

To improve machinability (*Full annealing and Normalizing*)

To improve cutting properties of tool steels (*Hardening and Tempering*)

To improve surface properties (*surface hardening*, *high temperature resistance-precipitation hardening*, *surface treatment*)

To improve electrical properties (*Recrystallization*, *Tempering*, *Age hardening*)

To improve magnetic properties (*Hardening*, *Phase transformation*)

**Heat Treatment Process variables**

- Temperature
- Holding time
- Heating rate
- Cooling rate
- Furnace atmosphere
Classification of steels

- Compositions, such as carbon (or non alloy), low-alloy, and alloy steels
- Manufacturing methods, such as converter, electric furnace, or electroslag remelting methods
- Application or main characteristic, such as structural, tool, stainless steel, or heatresistant steels.
- Finishing methods, such as hot rolling, cold rolling, casting, or controlled rolling and controlled cooling.
- Product shape, such as bar, plate, strip, tubing, or structural shape
- Oxidation practice employed, such as rimmed, killed, semikilled, and capped steels.
- Microstructure, such as ferritic, pearlitic, martensitic, and austenitic
- Required strength level, as specified in the American Society for Testing and Materials (ASTM) standards.
- Heat treatment, such as annealing, quenching and tempering, air cooling (normalization), and thermo-mechanical processing.
- Quality descriptors and classifications, such as forging quality and commercial quality.
### Classification of steels

#### Steels

<table>
<thead>
<tr>
<th>Classification</th>
<th>Low Alloy</th>
<th>High Alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbon</strong></td>
<td>low carbon</td>
<td>high carbon</td>
</tr>
<tr>
<td></td>
<td>&lt;0.25 wt% C</td>
<td>0.6-1.4 wt% C</td>
</tr>
<tr>
<td><strong>Additions</strong></td>
<td>none</td>
<td>Cr, Ni, Mo</td>
</tr>
<tr>
<td><strong>Name</strong></td>
<td>plain HSLA</td>
<td>tool austenitic stainless</td>
</tr>
<tr>
<td><strong>Example</strong></td>
<td>1010</td>
<td>304</td>
</tr>
</tbody>
</table>

#### Example Table

<table>
<thead>
<tr>
<th>Hardenability</th>
<th>TS</th>
<th>EL</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>+</td>
<td>auto struc. sheet</td>
</tr>
<tr>
<td>++</td>
<td>0</td>
<td>+</td>
<td>bridges towers press. vessels</td>
</tr>
<tr>
<td>++</td>
<td>+</td>
<td>0</td>
<td>crank shafts bolts hammers blades</td>
</tr>
<tr>
<td>++</td>
<td>++</td>
<td>-</td>
<td>pistons gears wear applic.</td>
</tr>
<tr>
<td>++</td>
<td>++</td>
<td>--</td>
<td>wear applic.</td>
</tr>
<tr>
<td>++</td>
<td>++</td>
<td>++</td>
<td>drills saws dies</td>
</tr>
</tbody>
</table>

**Increasing strength, cost, decreasing ductility**

**Example Steels**: 1010, 4310, 1040, 4340, 1095, 4190, 304
Iron is an allotropic metal, which means that it can exist in more than one type of lattice structure depending upon temperature. A cooling curve for pure iron is shown below:

- Liquid
- \(\delta\) (delta) Fe - B.C.C
- \(\gamma\) (gamma) Fe - F.C.C
- \(\alpha\) (alpha) Fe - B.C.C

Can be other allotropic structures are possible?....?
Effect of pressure on allotropy of Iron

This line slopes upward as at constant T if we increase the P the gas will liquefy as liquid has lower volume (similarly the reader should draw horizontal lines to understand the effect of pressure on the stability of various phases- and rationalize the same).

Phase fields of non-close packed structures shrink under higher pressure

Phase fields of close packed structures expand under higher pressure

These lines slope downward as: Under higher pressure the phase with higher packing fraction (lower volume) is preferred

The face centered tetragonal (FCT) iron is coherently deposited iron grown as thin film on a \{100\} plane of copper substrate. Growing Trigonal iron on mis-fiting \{111\} surface of a face centered cubic copper substrate.
The Fe-C (or more precisely the Fe-Fe$_3$C) diagram is an important one. Cementite is a metastable phase and ‘strictly speaking’ should not be included in a phase diagram. But the decomposition rate of cementite is small and hence can be thought of as ‘stable enough’ to be included in a phase diagram. Hence, we typically consider the Fe-Fe$_3$C part of the Fe-C phase diagram.

In the phase diagram, temperature is plotted against composition. Any point on the diagram therefore represents a definite composition and temperature. The phase diagram indicates the phases present and the phase changes that occur during heating and cooling. The relative amounts of the phases that exist at any temperature can also be estimated with the help of lever rule.

A portion of the Fe-C diagram – the part from pure Fe to 6.67 wt.% carbon (corresponding to cementite, Fe$_3$C) – is technologically very relevant.

Cementite is not a equilibrium phase and would tend to decompose into Fe and graphite. This reaction is sluggish and for practical purpose (at the microstructural level) cementite can be considered to be part of the phase diagram. Cementite forms as it nucleates readily as compared to graphite.

Compositions upto 2.1%C are called steels and beyond 2.1% are called cast irons. In reality the classification should be based on ‘castability’ and not just on carbon content.

Heat treatments can be done to alter the properties of the steel by modifying the microstructure → we will learn about this in coming chapters.
Fe-Fe$_3$C metastable phase diagram

- **Peritectic**: $L + \delta \rightarrow \gamma$
- **Eutectic**: $L \rightarrow \gamma + Fe_3C$
- **Liquid (L)**: $L \rightarrow \gamma + Fe_3C$
- **L + Fe$_3$C**
- **Hypo Eutectic**: 0.16 %C
- **Hyper Eutectic**: 0.51 %C
- **Eutectoid**: $\gamma \rightarrow \alpha + Fe_3C$
- **Pearlite**: $[\alpha (Ferrite) + Fe_3C (Cementite)] = Pearlite$
- **Ledefurite**: $[\gamma (Austenite) + Fe_3C (Cementite)] = Ledefurite$
- **Pearlite**: $[\alpha (Ferrite) + Fe_3C (Cementite)] = Pearlite$
- **Steels**: 0.025 %C
- **Cast Irons**: 0.008 %C

Temperatures:
- Peritectic: 1493ºC
- Eutectic: 1147ºC
- Hypo Eutectoid: 910ºC
- Hyper Eutectoid: 723ºC

% Carbon:
- Fe: 0.008 - 6.7
- Fe$_3$C: 0.14
Solubility of carbon in Fe = f (structure, temperature)

Where is carbon located in iron lattice?

Octahedral sites

- 6 faces sharing with two sides (6/2)=3
- 12 edges sharing with four sides (12/4)=3
- Total sites is (3+3), 6 per unit cell
- Every one Fe atom we have 3 interstitial sites

One interstitial site in center plus
- 12 edges sharing with four sides (12/4)=3
- Total sites is (1+3), 4 per unit cell
- Every one Fe atom we have 1 interstitial site
Why concentration of carbon in α-Fe with BCC structure is less than γ-Fe with FCC structure?

- **FIRST LET US CONSIDER FCC STRUCTURE (γ-Fe)**
- Packing factor of FCC lattice 0.74
- This indicates the presence of voids. Let us discuss it more elaborately.
- In a FCC crystal there are mainly two types of voids:
  - Tetrahedral: coordination number (CN) is 4. That means the void is surrounded by 4 atoms.
  - Octahedral: CN is 6. That means the void is surrounded by 6 atoms.
- There are 8 tetrahedral voids in a unit cell. That means 2 voids per atom.
- There are 4 octahedral voids in a unit cell. That means 1 void per atom.
- However, impurities prefer to occupy octahedral voids.
- Because the ratio of the radius of the tetrahedral void to atom is 0.225 and the same for the octahedral void is 0.414.
- The ratio of the radius of the carbon atom (size is 77 pm) to Fe (when it has FCC crystal) is 0.596.
- So when a carbon atom occupies any void, lattice will be distorted to increase the enthalpy.
- Distortion will be less if it occupies the octahedral voids.
- Although it increases the enthalpy, carbon atoms will be present up to a certain extent because of the gain in entropy, as explained previously, which decreases the free energy.
Carbon Solubility in Iron

**FCC**

- Size of Fe atom (CCP crystal): $r_{FCC}^{Fe} = 1.292 \, \text{Å}
- Size of the OV: $x_{FCC}^{Fe} (oct) = 0.534 \, \text{Å}$
- Size of Carbon atom: $r^{C} = 0.77 \, \text{Å}$

**BCC**

- Size of Fe atom (BCC crystal): $r_{BCC}^{Fe} = 1.258 \, \text{Å}
- Size of the TV: $x_{BCC}^{Fe} (d.tet) = 0.364 \, \text{Å}$
- Size of the OV: $x_{BCC}^{Fe} (d.oct) = 0.195 \, \text{Å}$

Note the difference in size of the atoms.

**Relative sizes of voids w.r.t atoms**

- Size of the largest atom which can fit into the tetrahedral is 0.225 and octahedral void is 0.414
- Size of the largest atom which can fit into the $d.tetrahedral$ is 0.29 and $d.octahedral$ void is 0.154
Why concentration of carbon in α-Fe with BCC structure is less than γ-Fe with FCC structure?

- NOW LET US CONSIDER THE BCC UNIT CELL (α-Fe)
- Packing factor of BCC lattice 0.68. So total void in a BCC unit cell is higher than FCC cell.
- However, there are 12 (6 per atom) tetrahedral and 6 (3 per atom) octahedral voids present. This number is higher than the number of voids present in a FCC unit cell.
- Unlike voids in FCC lattice, in a BCC lattice the voids are distorted. That means if an atom sits in a void, it will not touch all the host atoms.
- The ratio of the radius of tetrahedral void to atom is 0.29 and the radius of octahedral void to atom is 0.155.
- The ratio of the radius of the C atom (size is 77 pm) to Fe (when it has BCC crystal) is 0.612. So it is expected that in a BCC unit cell, impurities should prefer tetrahedral voids.
- However, although the octahedral void size is small, planar radius which has 4 atoms on the same plane is 79.6 pm, which is larger that the C atom size. That means it needs to distort only other two atoms.
- On the other hand if C sits in the tetrahedral void it has to distort all four atoms. So in α–Fe with BCC unit cell C occupies the octahedral voids.
- Now the octahedral void size in γ-Fe (FCC) is higher than α-Fe (BCC). So naturally the distortion in a BCC cell will be higher and the activation energy for impurities to occupy a void in a BCC cell also will be higher.
- This is the reason that we find much lower solubility limit of C in α-Fe.
Why carbon preferentially sits in the apparently smaller octahedral void in BCC?

Ignoring the atom sitting at B and assuming the interstitial atom touches the atom at A

\[ OA = r + x_A = \frac{\sqrt{2}a}{2} \]
\[ r + x_A = \frac{2\sqrt{6}r}{3} \]
\[ \frac{x_A}{r} = \left( \frac{2\sqrt{6}}{3} - 1 \right) = 0.6329 \]
\[ OX = x_A = 0.796 \text{Å} \quad OY = x_B = 0.195 \text{Å} \quad x_{BCC}^{Fe} (d.tet) = 0.364 \text{Å} \]
Characteristics of phases appeared in Fe-Fe$_3$C phase diagram
Ferrite ($\alpha$)

- It is an interstitial solid solution of a small amount of carbon dissolved in $\alpha$ iron. The maximum solubility is 0.025%C at 723ºC and it dissolves only 0.008%C at room temperature. *It is the softest structure that appears on the diagram.*
- *Ferrite is ferromagnetic at low temperatures but loses its magnetic properties with the rise of temperatures with major loss at curies temperatures, 768ºC and above this temperature, it becomes non magnetic (paramagnetic).*
- The crystal structure of ferrite ($\alpha$) is B.C.C
- Tensile strength – 245 Mpa, Yield strength 118 Mpa
- Elongation – 40-50% in 2 in.
- Hardness - 95 VPN

\[\alpha (\text{Ferrite}) \text{ contains B.C.C structure}\]

\[\alpha (\text{Ferrite}) - 90X\]
Cementite or iron carbide, chemical formula Fe$_3$C, contains 6.67%C by weight and it is a metastable phase.

It is typically hard and brittle interstitial compound of low tensile strength (35 Mpa) but high compressive strength and high hardness ~800VPN.

It is the hardest structure that appears on the diagram.

It has a complex orthorhombic crystal structure with 12 iron atoms and 4 carbon atoms per unitcell.

It is slightly ferromagnetic up to 210ºC and paramagnetic above it. Melting point around 1227ºC.
Pearlite (α+Fe₃C)

- Pearlite is the eutectoid mixture containing 0.80 %C and is formed at 723°C on very slow cooling.
- It is very fine platelike or lamellar mixture of ferrite and cementite. The fine fingerprint mixture called pearlite is shown in below figure.
- The weight % of these two phases are thus in ratio 8:1
- Tensile strength – 120,000 psi or 825 Mpa
- Elongation – 20 percent in 2 in.
- Hardness – HRC 20, HRB 95-100, or BHN 250-300

Remember…!

Pearlite is a not a phase but combination of two phases (ferrite + cementite)
It is an interstitial solid solution of a small amount of carbon dissolved in γ iron and has FCC crystal structure. The maximum solubility is 2.1%C at 1147°C.

Austenite is soft, ductile tough and malleable (FCC structure) and non magnetic (paramagnetic).

Steels are commonly rolled and forged above about 1100°C when they are in austenite state due to its high ductility and malleability, which is also due to its FCC structure.

- Tensile strength – 150,000 psi or 1035 Mpa
- Elongation – 10% in 2 in.
- Hardness - 395 VPN and Toughness is high.
Ledeburite is the eutectic mixture of austenite and cementite. It contains 4.3% C and is formed at 1147ºC.
- Structure of ledeburite contains small islands of austenite are dispersed in the carbide phase.
- Not stable at room temperature

The pearlite is resolved in some regions where the sectioning plane makes a glancing angle to the lamellae. The ledeburite eutectic is highlighted by the arrows. At high temperatures this is a mixture of austenite and cementite formed from liquid. The austenite subsequently decomposes to pearlite.
Interstitial solid solution of carbon in iron of body centered cubic crystal structure. (δ iron) of higher lattice parameter (2.89Å) having solubility limit of 0.09 wt% at 1495°C with respect to austenite. The stability of the phase ranges between 1394-1539°C.

It is a high temperature phase and is a high temperature manifestation of α ferrite.

This is not stable at room temperature in plain carbon steel. However it can be present at room temperature in alloy steel specially duplex stainless steel.

δ-ferrite in dendrite form in as-cast Fe-0.4C-2Mn-0.5Si-2Al0.5Cu
Invariant Reactions in Fe-Fe$_3$C Phase Diagram
The invariant peritectic reaction in Fe-Fe₃C diagram is given by

\[ L + 0.51\%C + \delta\text{-ferrite} + 0.1\%C \xrightarrow{\text{Cool \ 1495\ºC}} \text{Austenite (}\gamma\text{)} + 0.17\%C \]

Thus Liquid, wt% is

\[ L = \frac{0.16 - 0.1}{0.51 - 0.1} \times 100 = 14.63\% \]

Thus \( \delta \text{-ferrite, wt % is} \)

\[ \delta(\text{ferrite}) = \frac{0.51 - 0.16}{0.51 - 0.1} \times 100 = 85.37\% \]

Fe-0.16\%C steel is a peritectic steel because only this steel undergoes above reaction completely.

Peritectic reaction is of some importance during freezing of steels (carbon from 0.1 to 0.51\% particularly under fast cooling conditions, when micro segregation may result, otherwise no commercial heat treatment is done in this region.

Unfortunately these temperatures are attained during heating of steels for forging or rolling etc., then severe overheating and burning results in steels turning them to scrap form.
The invariant Eutectic reaction in Fe-Fe$_3$C diagram is given by

\[
\text{Liquid (L)} \xrightarrow{\text{Cool}}\text{Austenite (γ)} + \text{Cementite} \\
0.17\% \text{C} \quad \text{1147°C} \quad 2.11\% \text{C} + 6.67\% \text{C}
\]

Thus Austenite, wt% is \( \gamma = \frac{6.67 - 4.3}{6.67 - 2.11} \times 100 = 51.97\% \)

Thus cementite, wt % is \( Fe_3C = \frac{4.3 - 2.11}{6.67 - 2.11} \times 100 = 48.03\% \)

Fe-4.3%C alloy is called eutectic cast iron as it is the lowest melting point alloy, which is single phase liquid (100%) of 4.3% carbon at the eutectic temperature, 1147°C just attained and undergoes eutectic reaction completely at this constant eutectic temperature to give a mixture of two different solids, namely austenite and cementite, solidifying simultaneously. The eutectic mixture called Ledeburite.

As Fe-C alloys having more than 2.11% carbon are classed as cast irons, the Fe-C alloys having carbon between 2.11 and 4.3% are called hypo eutectic cast irons, where as those having carbon between 4.3% and 6.67% are called hypereutectic cast irons. Alloys of Fe with 4.3% carbon is called eutectic cast iron.
The invariant Eutectoid reaction in Fe-Fe₃C diagram is given by

\[
\text{Austenite (γ)} \quad \overset{\text{Cool}}{\rightleftharpoons} \quad \text{Ferrite (α)} + \text{Cementite}
\]

\[
0.8\%C \quad 727^\circ C \quad 0.02\%C \quad 6.67\%C
\]

- Thus Ferrite, wt% is \( \alpha = \frac{6.67 - 0.8}{6.67 - 0.02} \times 100 = 88\% \)

- Thus cementite, wt % is \( Fe_3C = \frac{0.8 - 0.02}{6.67 - 0.02} \times 100 = 12\% \)

During cooling austenite of 0.8% at constant eutectoid temperature, 727°C undergoes eutectoid transformation to form a mixture of ferrite (C%=0.02%) and cementite i.e., there are alternate lamellae of ferrite and cementite.

This eutectoid mixture of ferrite and cementite is called PEARLITE, because of its pearly appearance under optical microscope.

The weight % of these phases are thus 8:1. The densities are (α-7.87 gm/cm³) and (Fe₃C- 7.70 gm/cm³) are quite comparable. Thus the Volume % also approx 8:1. Thus ferrite lamilla is 8 times thicker than cementite lamilla. as the two boundaries of cementite plate are close together, they may not resolved separately under the microscope, instead of two lines, it appears a single dark line.
Phase changes that occur upon passing from the $\gamma$ region into the $\alpha + Fe_3C$ phase field.

Consider, for example, an alloy of eutectoid composition (0.8% C) as it is cooled from a temperature within the $\gamma$ phase region, say 800ºC – that is, beginning at point ‘a’ in figure and moving down vertical $xx'$. Initially the alloy is composed entirely of the austenite phase having composition 0.8 wt.% C and then transformed to $\alpha + Fe_3C$ [pearlite]

The microstructure for this eutectoid steel that is slowly cooled through eutectoid temperature consists of alternating layers or lamellae of the two phases $\alpha$ and $Fe_3C$

The pearlite exists as grains, often termed “colonies”; within each colony the layers are oriented in essentially the same direction, which varies from one colony to other.

The thick light layers are the ferrite phase, and the cementite phase appears as thin lamellae most of which appear dark.
Eutectoid Structure

Schematic representation of the formation of pearlite from austenite; direction of carbon diffusion indicated by arrows.

Pearlite in SEM

Pearlite in optical microscope 500X

Pearlite in AFM
Hypo eutectoid region – 0.008 to 0.8 %C

Consider vertical line yy' in figure, at about 875°C, point c, the microstructure will consist entirely of grains of the $\gamma$ phase.

In cooling to point d, about 775°C, which is within the $\alpha+\gamma$ phase region, both these phases will coexist as in the schematic microstructure. Most of the small $\alpha$ particles will form along the original $\gamma$ grain boundaries.

Cooling from point d to e, just above the eutectoid but still in the $\alpha+\gamma$ region, will produce an increased fraction of the $\alpha$ phase and a microstructure similar to that also shown: the $\alpha$ particles will have grown larger.
Just below the eutectoid temperature, at point f, all the γ phase that was present at temperature e will transform pearlite. Virtually there is no change in α phase that existed at point e in crossing the eutectoid temperature – it will normally be present as a continuous matrix phase surrounding the isolated pearlite colonies.

Thus the ferrite phase will be present both in the pearlite and also as the phase that formed while cooling through the α+γ phase region. The ferrite that is present in the pearlite is called eutectoid ferrite, whereas the other, is termed proeutectoid (meaning pre- or before eutectoid) ferrite.
- Hyper eutectoid region – 0.8 to 2.1 %C
- Consider an alloy of composition C₁ in figure that, upon cooling, moves down the line zz’. At point g only the γ phase will be present and the microstructure having only gamma grains.
- Upon cooling into the γ + Fe₃C phase field – say to point h – the cementite phase will began to form along the initial γ grain boundaries, similar to the α phase in point d. This cementite is called proeutectoid cementite that which forms before the eutectoid reaction.
- As the temperature is lowered through the eutectoid to point I, all remaining austenite of eutectoid composition is converted into pearlite; thus the resulting microstructure consists of pearlite and proeutectoid cementite as microconstituents.
Hypo Eutectoid Region

- Pearlite
- Cementite network

Scale:
- 40μm
- 400μm
When the carbon content of steels is much away from the eutectoid carbon, then distinction can easily be made between hypoeutectoid steels and the hypereutectoid steel. Nital is the common etching agent.

**Shape of the phases**

- Proeutectoid ferrite appears as grains which are quite wide, polyhedral and the grain boundaries in between neighboring ferrite grains can be seen.

- The films of proeutectoid cementite generally are much thinner, have irregular outlines and bounded by sharp lines. These are present as network of needles or platelets. Cementite looks much brighter and sharp because of its hardness and etching characteristics.

- Major difference is cementite is present as network at the grain boundaries of pearlite (at RT), whereas ferrite is present as grains (equiaxed polyhedral grains) with grain boundaries in between ferrite grains (if etched properly).
Cementite is very hard (~800 VPN) and ferrite is (~95 VPN). Micro hardness testing can be done to distinguish between ferrite and cementite.

A simple scratch test can be done. Make a scratch on the polished and etched surface of the steel and then, examine the point of the scratch where it enters the white proeutectoid phase from the pearlite.

If the scratch widens on entering, it is the soft phase ferrite, and if it thins in white phase, then the white phase is much harder than pearlite, i.e, it is cementite.

Nital etching causes cementite as well as ferrite to look white under microscope. A sodium picrate solution used either boiling or electrolytically, darkens Fe₃C but not ‘α’.

Another etchant based on sodium thiosulphate and ammonium nitrate gives colors ferrite but not cementite.
Fe-Fe₃C phase diagram (microstructural aspects)

L=liquid, Cm=cementite, LB=ledeburite, δ=delta ferrite, α=alpha ferrite, α'=alpha ferrite (0.00005 wt% C), γ=austenite, P=pearlite, eu=eutectic, ed=eutectoid, I=primary, II=secondary, III=tertiary

Temperature, °C

Weight percent carbon

A₁=727°C
A₂=668/770°C
A₃=1495°C
A₄=1147°C
A₅=1394°C
A₆=1227°C
A₇=910°C
A₈=1539°C

δ+L
L+γ
L+Cm I
L+ γ I
γ I'( γII +Cm II )+LB' ( γ' eu ( γII +Cm II )+Cm eu )
γ
δ
δ+ γ
δ+L
A 4 =1147˚C
A 5 =1495˚C
A 2 =668/770˚C

Evolution of Microstructures on equilibrium cooling

- Sequence of evolution of microstructure can be described by the projected cooling on compositions A, B, C, D, E, F.

  - At composition A
    \[ L \rightarrow \delta + L \rightarrow \delta \rightarrow \delta + \gamma \rightarrow \gamma \rightarrow \gamma + \alpha_i \rightarrow \alpha \rightarrow \alpha' + Cm_{III} \]

  - At composition B
    \[ L \rightarrow \delta + L \rightarrow L + \gamma_i \rightarrow \gamma \rightarrow \alpha_i + \gamma \rightarrow \alpha_i + (P(\alpha_{ed} + Cm_{ed})) \rightarrow \alpha_i(\alpha' + Cm_{III}) + P(\alpha_{ed}(\alpha_{ed}' + Cm_{III}) + Cm_{ed}) \]

  - At composition C
    \[ L \rightarrow L + \gamma_i \rightarrow \gamma \rightarrow \gamma_{II} + Cm_{II} \rightarrow P(\alpha_{ed} + Cm_{ed}) + Cm_{II} \rightarrow P(\alpha_{ed}(\alpha_{ed}' + Cm_{III}) + Cm_{ed}) + Cm_{II} \]

  - At composition D
    \[ L \rightarrow L + \gamma_i \rightarrow \gamma_i + LB \rightarrow \gamma_i(\gamma_{II} + Cm_{II}) + LB'(\gamma_{eu}(\gamma_{II} + Cm_{II}) + Cm_{eu}) \]
    \[ \rightarrow (P(\alpha_{ed} + Cm_{ed}) + Cm_{II}) + LB'(P(\alpha_{ed} + Cm_{ed}) + Cm_{II} + Cm_{eu}) \]
    \[ \rightarrow (P(\alpha_{ed}(\alpha_{ed}' + Cm_{III}) + Cm_{ed}) + Cm_{II}) + LB'(P(\alpha_{ed}(\alpha_{ed}' + Cm_{III}) + Cm_{ed}) + Cm_{II} + Cm_{eu}) \]
Sequence of evolution of microstructure can be described by the projected cooling on compositions A, B, C, D, E, F.

- At composition E

\[
L \rightarrow L + Cm_l \rightarrow LB(\gamma_{eu} + Cm_{eu} + Cm_l) \rightarrow LB'(\gamma_{eu} (\gamma_{II} + Cm_{II}) + Cm_{eu}) + Cm_l
\]

\[
\rightarrow LB'(P(\alpha_{ed} + Cm_{ed}) + Cm_{II}) + Cm_{eu}) + Cm_l
\]

\[
\rightarrow LB'(P(\alpha_{ed} (\alpha'_{ed} + Cm_{III}) + Cm_{ed}) + Cm_{II}) + Cm_{eu}) + Cm_l
\]

- At composition F

\[
L \rightarrow Fe_3C
\]
Application of Lever rule in Fe-Fe$_3$C phase diagram
For a 99.6 wt% Fe-0.40 wt% C at a temperature just below the eutectoid, determine the following:

a) The amount of Fe₃C, ferrite (α) and pearlite

b) The amount of pearlite and proeutectoid ferrite (α)

---

**Solved Example**

For a 99.6 wt% Fe-0.40 wt% C at a temperature just below the eutectoid, determine the following:

a) The amount of Fe₃C and ferrite (α)

Percentage of Fe₃C = \( \frac{0.4 - 0.025}{6.67 - 0.025} \times 100 \)

Percentage of Fe₃C in 0.4 %C steel is 5.64 %

Percentage of Ferrite (α) in 0.4 %C steel = (100 - 5.64)%

Percentage of ferrite in 0.4 %C steel = 94.36%

or

Percentage of ferrite = \( \frac{6.67 - 0.4}{6.67 - 0.025} \times 100 \) = 94.36%
b) Phase fraction of pearlite and proeutectoid ferrite (α)

\[ \text{Percentage of pearlite} = \frac{0.4 - 0.025}{0.8 - 0.025} \times 100 \]

Percentage of pearlite = 48%

Percentage of proeutectoid ferrite (α) in 0.4 % C steel = (100 - 48)%

Percentage of proeutectoid ferrite (α) = 52%

or

\[ \text{Percentage of proeutectoid ferrite} = \frac{0.8 - 0.4}{0.8 - 0.025} \times 100 = 52\% \]
In general, $A_0$ – Subcritical temperature, $A_1$ - lower critical temperature, $A_3$ - upper critical temperature, $A_4$ – Eutectic temperature, $A_5$ – Peritectic temperature and $A_{cm}$ - γ/γ+cementite phase field boundary.

While heating we denoted as $Ac_1$, $Ac_2$, $Ac_3$ etc., ‘c’ stands for chauffage (French word), which means heating and while cooling we denoted as $Ar_1$, $Ar_2$, $Ar_3$ etc., ‘r’ stands for refroidissement, (French word) which means cooling.
The upper – and lower critical temperature lines are shown as single lines under equilibrium conditions and are sometimes indicated as $A_{e3}, A_{e1}$ etc. When the critical lines are actually determined, it is found that they do not occur at the same temperature.

The critical line on heating is always higher than the critical line on cooling. Therefore, the upper critical line of a hypo eutectoid steel on heating would be labeled $A_{C3}$ and the same line on cooling $A_{r3}$. The rate of heating and cooling has a definite effect on the temperature gap between these lines.

The results of thermal analysis of a series of carbon steels with an average heating and cooling rate of 11ºF/min are shown in the figure.

Final word...! with infinitely slow heating and cooling they would probably occur at exactly the same temperature.
Mn, Ni, Co, Cu, Zn increase the range in which γ-phase, or austenite is stable [by raising $A_4$ and lowering $A_3$ temperature and also tend to retard the separation of carbides.

These elements have γ-phase FCC crystal structure (or similar structure) in which these elements are more soluble than ferrite, and that is why, in the $(\alpha+\gamma)$ two phase equilibrium, these segregate in austenite in preference to ferrite.

Elements like carbon and nitrogen (interstitial solid solution forming elements) are also austenite stabilizers.

Cr, W, Mo, V, Si, Al, Be, Nb, P, Sn, Ti, Zr increase the range of α-phase (by lowering $A_4$ and raising $A_3$ temperatures).

These elements have α phase BCC crystal structure (or similar structure) and thus in $(\alpha+\gamma)$ two phase equilibrium, these elements segregate in ferrite in preference to austenite. These elements decrease the amount of carbon soluble in austenite, and thus tend to increase the volume of the free carbide in the steel for a given carbide content.

Chromium is a special case of these elements as at low concentrations, chromium lowers $A_3$ temperature and raises $A_4$, but at high concentrations raises $A_3$ temperature. Overall, the stability of austenite is continuously decreased.
Effect of alloying elements on Austenite phase region Mn, Cr

- Mn is Austenite stabilizer
- Expansion of γ phase field with ↑ Mn

Outline of the γ phase field

- Cr is Ferrite stabilizer
- Shrinking γ phase field with ↑ Cr

Temperature

<table>
<thead>
<tr>
<th>C (%)</th>
<th>0</th>
<th>0.4</th>
<th>0.8</th>
<th>1.2</th>
<th>1.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Cr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% Cr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12% Cr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15% Cr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

0.35% Mn

6.5% Mn
Important elements, in this class, are arranged in order of increasing affinity for carbon, and thus the carbide forming potential of the element:

\[
\text{Fe} \rightarrow \text{Mn} \rightarrow \text{Cr} \rightarrow \text{W} \rightarrow \text{Mo} \rightarrow \text{V} \rightarrow \text{Ti} \rightarrow \text{Nb} \rightarrow \text{Ta} \rightarrow \text{Zr}
\]

For example, vanadium is added in steel having chromium and molybdenum with insufficient carbon, then vanadium first removes carbon from chromium carbide, the remaining vanadium then removes carbon from molybdenum carbide and forms its own carbide. The released Cr and Mo dissolve to form solid solution in austenite.

**Carbide forming elements**

- Si, Ni, Cu, Al are common graphitizers. Small amount of these elements in steel can graphitize it and thus, impair the properties of steel unless elements of austenite stabilizers are present to counteract the effect.

**Graphitising elements**

- Co is the only element which neither forms carbide, nor causes graphitisation.
All the elements lower the eutectoid carbon content. Titanium and molybdenum are the most effective in lowering it.

For example, a steel with 5% Cr has its eutectoid point at 0.5%C as compared to 0.8% in carbon steels. High speed steel has eutectoid point at 0.25% carbon.

Elements like Ni, Mn i.e., the austenite stabilizers lower the eutectoid temperature (727°C). Ferrite stabilizers like Cr, V, W etc. raise the eutectoid temperature.
Limitations on Fe-Fe$_3$C phase diagram

- Fe-Fe$_3$C diagram represents behavior of steels under equilibrium conditions, whereas the actual heat treatments of steels are normally under non-equilibrium conditions.
- The diagram does not indicate the character of transformation of austenite such as to bainite, or martensite.
- The diagram does not indicate the presence of metastable phases like martensite, or bainite.
- It does not indicate the temperature of start of martensite $M_s$ or bainite $B_s$.
- It does not indicate the kinetics of the transformation of austenite to martensite, bainite or even pearlite.
- It does not indicate the possibilities of suppressing the pearlitic or bainitic transformations.
Solid Solution Strengthening

- Solid solution strengthening is a phenomenon that occurs when the number of impurity atoms in the lattice of the basic element is so small that they are incapable of forming both stable and metastable precipitation phases under any thermal treatment conditions.

- Consider the influence of carbon, which is statistically uniformly distributed in the lattice of the $\alpha$-iron, on the structure and properties of $\alpha$-iron. Solubility of carbon in $\alpha$-iron is much lower than in the $\gamma$-iron. It forms interstitial solid solutions with both irons.

- However, whereas the $\gamma$-iron lattice has sufficiently large pores for implantation of carbon atoms, the cubic lattice of the $\alpha$-iron suffers, upon introduction of carbon atoms, a tetragonal distortion similar to the one of the martensite lattice, except that in the former case the distortion is much smaller.

- In addition, implantation of carbon atoms causes the entire lattice of the $\alpha$-iron to expand somewhat. For example, at a carbon content of 0.015% the lattice constant increases at room temperature by 0.025c.

- The yield stress rises most dramatically with an increase in the carbon concentration from $10^{-7}$ to $10^{-4}$ - $10^{-3}$ %. The influence that carbon exerts on plastic deformation resistance of the $\alpha$-phase is due to both its strong interaction with dislocations and pinning of the dislocations and elastic deformations arising as a result of the tetragonal distortion of the $\alpha$-phase lattice after implantation of carbon atoms.

- Dissolution of part of the carbon in the $\alpha$-phase and suggests that the solid solution strengthening of the phase is one of the factors providing the high strength properties of intermediate transformation products.
Strengthening mechanisms in steels

Grain Size Refinement

- Austenite passes to other phases during cooling, its grain size represents an important characteristic of steel. This is due to the fact that all structural components are formed within each separate crystal.

- The smaller the austenite grains, the finer the network of excess ferrite at their boundaries and the smaller the pearlite colonies and martensite crystals. Therefore, a fine grain corresponds to a fine crystal fracture of steel and vice versa at the temperatures where austenite has already precipitated.

- Impact strength is especially sensitive to the austenite grain size, and it decreases with grain enlargement. A decrease in the dimensions of pearlite colonies inside the initial austenite grain favors a rise in impact strength also.

- Although the grain size has a considerable effect on impact strength, its influence is small if any on the statistical characteristics of mechanical properties such as hardness, fracture stress, yield stress, and specific elongation. Only the actual grain size affects steel properties, the inherited size has no effect.

- However, the technological process of heat treatment is determined by the inherited grain. For example, a hereditarily fine-grained steel may be deformed at a higher temperature with the assurance that the coarse-grained structure will not occur.
In the majority of metal alloys, precipitation of supersaturated solid solutions formed during quenching is followed by precipitation of disperse particles enriched in atoms of the alloying components. It was found that the strength (hardness) of the alloys increases with the precipitation of these particles. The increment in the value of these characteristics increases as the dispersion and volume fraction of the particles increase. This phenomenon has been referred to as dispersion strengthening.

When a solid solution of carbon in $\alpha$-iron is cooled below point $A_1$, carbon should precipitate as cementite with lowering of the carbon solubility and a decrease in temperature. This process is realized under sufficiently slow cooling, which is accompanied by diffusion processes, leading to the formation of cementite.

In the case of abrupt cooling, e.g., water quenching, carbon has no time to precipitate. A supersaturated a solid solution appears. At room temperature the retained amount of carbon can correspond to its maximum solubility of 0.018%. During subsequent storage at room temperature (natural aging) carbon tends to precipitate from the solid solution. Carbon enriched regions appear predominantly in defective sections of the matrix. Precipitation of carbon from a supersaturated solid solution during natural aging results in improvement of its strength characteristics and hardness. However, plastic characteristics—reduction of area, specific elongation, and impact strength are impaired. A clearly pronounced yield stress appears after a long natural aging. Hardness may increase by 50% over that of the as quenched state. The phenomenon of dispersion strengthening is observed.
An important method used to strengthen steels is deformation strengthening. Strengthening achieved with crystal deformation can be judged from the shape of stress–strain curves.

The actual shape of these curves largely depends on the crystal lattice type of the metal, its purity, and thermal treatment.

In the case of cubic lattice metals, strengthening curves are parabolic, whereas for hexagonal lattice metals a nearly linear dependence is observed between the stress and the strain.

This fact suggests that plastic deformation strengthening is determined mainly by the interaction of dislocations and is associated with the structural changes that impede the movement of dislocations.

Metals with a hexagonal lattice are less prone to deformation strengthening than cubic lattice metals because the hexagonal lattice has fewer easy slip systems.

In cubic lattice metals, the slip proceeds in several intersecting planes and directions.
Principles of heat treatment

Avala Lava Kumar : D.K.Mishra : Dr.S.K.Badjena
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla -768018

*E-mail : lavakumar.vssut@gmail.com
Formation of austenite is a preliminary step for any heat treatment process.

Formation of austenite in eutectoid steel differs from that of hypoeutectoid and hypereutectoid steels in the sense that in the former case it occurs at a particular temperature ($A_{C1}$) whereas for the latter it takes place over a range of temperature.

At 1147°C, the maximum solubility of carbon in FCC iron is about 2 percent. Therefore, at this temperature, regions around the cementite layer will be enriched with carbon because of diffusion.
The maximum diffusion of carbon atoms will take place from the cementite at the ferrite-cementite interface. As sufficient number of interfaces are available, austenite nuclei will be formed at the interface.

By gradual dissolution of carbon of cementite into gamma iron, primary austenite/grains are formed. These primary austenitic grains dissolve the surrounding ferrite and austenitic grains grow at the expense of ferrite.

The growth rate of austenite is higher than the rate of dissolution of the cementite into austenite because austenitic grain growth takes place because of the transformation of alpha iron to gamma iron and diffusion of carbon atoms from austenite to ferrite. This explains the experimentally observed fact that dissolving of ferrite is completed before that of cementite.

The austenite thus formed at eutectoid temperature is not homogeneous. The carbon concentration is higher in these regions which are adjacent to the original cementite lamellae than those which are adjacent to the ferrite mass.

Chemically homogeneous austenitic grains are obtained by holding (holding time should be sufficient to diffuse properly) steel above the eutectoid temperature.
The formation of austenite on heating always occurs at a temperature higher than that predicted by the Fe-Cementite phase diagram.

To study the kinetics of austenite formation is to heat a number of steel samples to different temperatures above the eutectoid temperature.

Heating is done by immersing samples in constant temperature baths. A number of samples are immersed in a constant temperature bath and are taken out one by one after a definite interval of time followed by immediate quenching which will result in the formation of austenite from transformed austenite.

The amount of martensite formed will depend on the amount of transformed austenite which in turn will depend on the temperature at which the steel sample has been heated and the holding time at that temperature.

From the figure, we can concluded that the lower transformation temperature, the more is the time required to complete the transformation.

Any property which changes with the formation of austenite, and/or with martensite formed by quenching of transformed austenite, can be utilized this purpose.
The relationship between transformation temperature and transformation time has been derived by taking into consideration the effect of superheating. An analysis of figure leads to the following conclusions:

- Transformation is completed in a short period at high transformation temperature.
- For higher heating rates, transformation will start at higher temperature, whereas for slower heating rate, transformation will start at lower temperature.
- For any given practical rate of heating, the formation of austenite will occur over a range of temperature, and not at constant temperature.

For the formation of austenite at a constant temperature, the heating rate should be extremely slow, and the two curved lines will converge to a single point located at eutectoid temperature line.

The end of transformation curve does not reveal any information about the nature (homogeneity) of austenite. The curved line ensures that all the pearlite has been transformed into austenite. In order to attain homogeneous austenite, the steel has to be heated to still higher temperatures.
The processes of austenite formation on heating proceeds by nucleation and growth reaction. Therefore, the factors which can vary either the rate of nucleation or the rate of growth or both will change the kinetics of austenite formation. Two such parameters are transformation temperature and holding time at transformation temperature.

The kinetics of austenite transformation is governed to great extent, by the nature of pearlite. The number of possible austenite nuclei will increase with the increase in interfacial area. The interfacial area can be increased in two ways: by increasing the cementite contents, and by decreasing the interlamellar spacing. This is the reason why high carbon steels austenitize more rapidly than low carbon steels.

The closer the ferrite-cementite lamellae, the higher will be the rate of nucleation. Also, the carbon atoms have to diffuse for smaller distances in order to enrich low carbon regions.

Therefore, the rate of growth of primary austenitic grains will also be higher in this case. This explains why pearlitic structure with less interlamellar spacing is transformed faster to austenite.

The kinetics of austenite transformation for coarse pearlitic structure is slow for the reason given above. The kinetics of austenitic transformation from granular pearlite is slower than that of lamellar pearlite for same reasons.

The kinetics of transformation will further decrease with increase in the size of globular cementite particles. Quenched structure will also transform to austenite more rapidly than the granular pearlitic structure.
Austenitic Grain Size

- The size of austenitic grains is the most important structural characteristic of heated steel. The austenitic grain size strongly effects its own transformation behavior and the mechanical properties of the microstructures formed from austenite.

- Austenitic grain boundaries are preferred sites for the nucleation of pro-eutectoid phases and pearlite, which are diffusion controlled transformation products.

- Coarse austenitic grains having less grain boundary area, have fewer nucleating sites, thus diffusion-controlled transformation of austenite is retarded paving way for easy transformation to martensite (Diffusionless transformation product).

- The impact toughness of steel is most sensitive to the size of the austenite grains in the hardened and tempered state. The charpy impact value improves with decreasing austenitic grain size to the extent that its value for a fine-grained steel can exceed several times that of a coarse grained steel of the same grade.

- The reason, partly is due to segregation of impurity atoms to the austenitic grain boundaries during Austenitisation (more segregation takes place if grain boundary area is less as is the case in coarse grained steels), and thus the fracture frequently takes place along prior austenitic grain boundaries.

- The co-segregation of impurities like Sb, P, Sn, As along the large angle grain boundaries of austenitic grains weakens the adhesion at these boundaries to cause fracture along them. Such intergranular fracture is quite brittle.

- In alloys of Fe-Ni, and Fe-Ni-C, the $M_s$ temperature is lowered significantly by decreasing the austenitic grain size, probably due to higher strength of fine grained austenite, which in turn increases the shear resistance of austenite to transform martensite.
At temperatures just above the upper critical temperature, when the structure is fully austenitic, that is just after the transformation is complete, the initial grain size of austenite is fine (though more disperse is the initial structure, the finer is the austenite grain formed).

As the temperature is raised further, or holding time at a given temperature is increased, then grain coarsening occurs. This behavior is schematically illustrated.

Austenitic grain growth is a natural spontaneous process and is caused by the tendency to reduce the surface energy by reducing the total surface area of the grain boundaries. A high temperature accelerates the rate of this processes.

Driving force is the surface energy stored as grain boundary energy. Certain grains grow at the expense of smaller grains, which due to their less stable.
Depending on the tendency of steel to grain growth, steels can be classified into two broad groups:

- Inherently fine grained steels
- Inherently coarse grained steels

Inherently fine grained steel resists the growth of austenitic grains with increasing temperature. The kinetics of austenite grain growth is very slow and the steel remains fine grained even at temperatures as high as 1000°C or 1050°C.

On the other hand, grains of inherently coarse grained steel grow abruptly with increasing temperature, and so a steel with coarse grains is obtained.

In the presence of ultramicroscopic particles of oxides, carbides and nitrides which prevent grain growth. These particles are refractory in nature, i.e., they can withstand high temperatures and are generally present at grain boundaries of austenite. Therefore, they act as barriers to the growth of austenitic grains.

Intensive grain coarsening of inherently fine grained steels above a particular temperature is due to the dissolution of ultrafine particles of carbides, oxides and nitrides in the matrix (austenite). After dissolution, no particles are left to offer resistance to grain growth.
Measurement of austenitic Grain Size

ASTM standard grain size number

- This is the most common method of measuring grain size, where the grain size is reported as ASTM (American Society of Testing Materials) grain size number. The method is used for equiaxed grains.

- The grain size is determined in a microscope at a magnification of 100X by comparing with ASTM standard grain size charts and the matching number of the grain size is reported. So, that it is also called grain comparison method.

- This is the simplest and, yet least quantitative, method. Because the comparison of grain structures may be influenced by the overall type of microstructure, four standard categories of grain size plates are used for comparison.

  - PLATE 1: Untwinned grains, flat-etch at 100X
    Includes grain size numbers 00, 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, and 10.

  - PLATE 2: Twinned grains, flat-etch at 100X
    Includes grain size numbers 1, 2, 3, 4, 5, 6, 7, and 8.

  - PLATE 3: Twinned grains, contrast-etch at 75X
    Includes nominal grain diameters of 0.2, 0.15, 0.12, 0.09, 0.07, 0.06, 0.05, 0.045, 0.035, 0.025, 0.020, 0.015, 0.010, and 0.005mm.

  - PLATE 4: Austenite grains in steel at 100 X
    Includes grain size numbers 1, 2, 3, 4, 5, 6, 7, and 8.
The ASTM grain size number, $N$, is related to the number of grains per square inch at 100 X magnification, $n$, by the relationship,

$$n = 2^{N-1}$$

Where, $N$ is the ASTM grain size number, and $n$ is the number of grains per square inch at 100X.

ASTM has modified the equation to:

$$G = -2.9542 + 1.4427 \ln n_a$$

Where, $G$ is the ASTM grain size number, and $n_a$ is the number of grains per mm$^2$ at 1X.

Table (next page) gives ASTM grain size number with corresponding average number of grains at 100X per square inch, average grain diameter in mm and average number of grains per square millimeter at 1X. Figure illustrates the same.
### ASTM Grain Size Numbers

<table>
<thead>
<tr>
<th>ASTM Grain size number N</th>
<th>Ave. No. of grains per square inch. At 100X</th>
<th>Ave. Diameter of grain as sphere at 1 X mm</th>
<th>Grains per millimeter square at 1X</th>
</tr>
</thead>
<tbody>
<tr>
<td>00</td>
<td>¼</td>
<td>0.51</td>
<td>3.9</td>
</tr>
<tr>
<td>0</td>
<td>½</td>
<td>0.36</td>
<td>7.8</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.25</td>
<td>15.5</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0.18</td>
<td>31.0</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>0.125</td>
<td>62.0</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.090</td>
<td>124.0</td>
</tr>
<tr>
<td>5</td>
<td>16</td>
<td>0.065</td>
<td>248.0</td>
</tr>
<tr>
<td>6</td>
<td>32</td>
<td>0.045</td>
<td>496.0</td>
</tr>
<tr>
<td>7</td>
<td>64</td>
<td>0.032</td>
<td>992.0</td>
</tr>
<tr>
<td>8</td>
<td>128</td>
<td>0.022</td>
<td>1980.0</td>
</tr>
<tr>
<td>9</td>
<td>256</td>
<td>0.016</td>
<td>3970.0</td>
</tr>
<tr>
<td>10</td>
<td>512</td>
<td>0.011</td>
<td>7940.0</td>
</tr>
<tr>
<td>11</td>
<td>1024</td>
<td>0.008</td>
<td>15870.0</td>
</tr>
<tr>
<td>12</td>
<td>2048</td>
<td>0.006</td>
<td>31,700.0</td>
</tr>
</tbody>
</table>
A steel has ASTM grain size number 6. What is the average number of grains per mm$^2$ in this steel at $1X$?

**Solution**

\[
G = -2.9542 + 1.4427 \ln n_a
\]

\[
n_a = \exp \left( \frac{6 + 2.9542}{1.4427} \right)
\]

\[
= 496 \text{mm}^{-2} = 496 \times 10^6 \text{m}^{-2}
\]

Calculate the average area of a grain if the steel has ASTM grain size number 7? Calculate in inch$^2$ as well as in mm$^2$.

**Solution**

\[
n = 2^{N-1} = 2^{7-1} = 64 \text{ grains/in}^2 \text{ at 100X}
\]

\[
= \frac{64}{(0.01)(0.01)} = 640,000 \text{ grains/in}^2 \text{ at 1X}
\]

Thus area of one grain \[
= \frac{1}{640000} \text{ in}^2 = 0.0010078 \text{mm}^2
\]

Or

\[
n = \frac{64}{(0.01)(0.01)} \times \frac{1}{645} = \frac{645}{640000} = 0.0010078 \text{mm}^2
\]
This is also known Grain counting method. The basic steps of procedure are as follows:

a) Inscribe a circle (or other shape) of known area, A, on an image of magnification, M.
b) Count the number of grains that are completely within the area.
c) Count the number of grains that are partially within the area.
d) Divide the result from (c) by 2.
e) Add the result from (d) to the result from (b).
f) Divide the result from (e) by A.
g) Convert the result from (f) to grains/in\(^2\) @ 100X
h) Use the definition of ASTM grain size number to determine n.

This method above can be used in every case. The only step that may be confusing is (g), where the magnification must be accounted for. The result from (f) will be given in grains per unit area, measured on the image of magnification, M. To convert this to the 100X equivalent, multiply the result by \((M/100)^2\).

For this method, the standard suggests that an area of 5000mm\(^2\) be used for the grain count, so long as this area encompasses at least 50 grains.

The standard also includes a table that provides a “Jeffries Multiplier” corresponding to several magnifications (next page).
### Relationship between magnification used and Jeffries Multiplier, f, for an area of 5000mm² (a circle of 79.8 mm diameter) (f=0.0002M²)

<table>
<thead>
<tr>
<th>Magnification Used, M</th>
<th>Jeffries Multiplier, f, to obtain Grains/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0002</td>
</tr>
<tr>
<td>10</td>
<td>0.02</td>
</tr>
<tr>
<td>25</td>
<td>0.125</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
</tr>
<tr>
<td>75</td>
<td>1.125</td>
</tr>
<tr>
<td>100</td>
<td>2.0</td>
</tr>
<tr>
<td>150</td>
<td>4.5</td>
</tr>
<tr>
<td>200</td>
<td>8.0</td>
</tr>
<tr>
<td>250</td>
<td>12.5</td>
</tr>
<tr>
<td>300</td>
<td>18.0</td>
</tr>
<tr>
<td>500</td>
<td>50.0</td>
</tr>
<tr>
<td>750</td>
<td>112.5</td>
</tr>
<tr>
<td>1000</td>
<td>200.0</td>
</tr>
</tbody>
</table>

If A = 5000mm², the multiplier indicated by this table can be multiplied by the result from step (f) to yield the grain count in terms of grains/mm² @ 1X.
A photomicrograph taken at 250X shows 3.4 grains per cm². What is the ASTM grain size number?

**Solution**

Number of grains per mm² at 1X

\[
\text{Number of grains per mm}^2 \text{ at 1X} = \frac{3.4 \times 250 \times 250}{10 \times 10} = 2125
\]

\[
G = -2.9542 + 1.4427 \ln 2125
\]

ASTM No. = 8.1
Heyn’s Intercept Method

This is also known linear intercept method. The basic steps of procedure are as follows:

a) On a single field of view, randomly place one or more straight test lines of known combined total length, L

b) Count the total number of intercepts, P, between the test lines and the grain boundaries. Triple junctions count as 1.5. If P<50, use additional lines

c) Divide the number of intercepts, P, obtained from (b) by the total length, L.

d) Repeat (a-c) for 2-4 additional fields of view.

e) Obtain PL as the average of the result from (c) for all fields of view

f) The ASTM grain size number is given as

\[ n = -3.3 + 6.65 \log_{10}(P_L) \]

Where PL is given in mm⁻¹
Suppose that 5 field of view, at 200X, were used for the measurements resulting in the following data.

<table>
<thead>
<tr>
<th>Field of view</th>
<th>Test line length (mm)</th>
<th>Number of intercepts</th>
<th>$P_L$ (mm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>337</td>
<td>71</td>
<td>42.2</td>
</tr>
<tr>
<td>2</td>
<td>216</td>
<td>45</td>
<td>41.6</td>
</tr>
<tr>
<td>3</td>
<td>402</td>
<td>89</td>
<td>44.2</td>
</tr>
<tr>
<td>4</td>
<td>529</td>
<td>113</td>
<td>42.8</td>
</tr>
<tr>
<td>5</td>
<td>395</td>
<td>81</td>
<td>41.0</td>
</tr>
</tbody>
</table>

From the table, the average value of $P_L$ is found to be 42.36 mm$^{-1}$. Using the below equation

$$n = -3.3 + 6.65 \log_{10}(P_L) \Rightarrow n = 7.5$$
The dependence of yield stress on grain size is expressed by the well known Hall-Petch equation

\[ \sigma_0 = \sigma_i + K_y D^{-1/2} \]

where \( \sigma_0 \) is the yield stress, \( \sigma_i \) the frictional stress opposing motion of dislocation, \( K_y \) the extent to which dislocations are pillared up at barriers, and \( D \) is the average grain diameter.

An increase in grain size raises the impact transition temperature, and thus makes the steel more prone to failure by brittle fracture.

In general, a coarse grained steel has better creep strength above the equicohesive temperature. Below this temperature, fine grained steels exhibit superior creep strength. It has been observed that cast steels have improved creep strength over forged steels. The basic coarse grain size of cast steel is believed to be responsible for this.

Fatigue strength, similar to creep strength, does not exhibit any basic relationship with grain size. However, fine grained steels have higher fatigue strength as compared to coarse grained steels.

Coarse grained steels has better hardenability than fine grained steel. The reason for this is that coarse grained steel has fewer grain boundaries. Grain boundaries are the region where the rate of diffusion is high. Consequently, formation of pearlite, which is a diffusion controlled processes, starts at grain boundaries. With smaller grain boundary area in coarse grained steels, preferential formation of martensite from austenite takes place on cooling.
The transformation of austenite on cooling is a complex process in the sense that compositional as well as configurational changes are involved. Carbon present in the austenite adjusts itself in such a way that at one end it leaves behind an almost carbon-free phase (ferrite) and on the other it combines with iron to form cementite.

Similarly large scale redistribution of alloying elements takes place when the solubility of the element is restricted in alpha iron, and/or there is a strong tendency for the element to form carbides. Also, the crystal structure changes from $\gamma$-iron to $\alpha$-iron.

The process of decomposition of austenite to ferrite-cementite aggregate is essentially a diffusion controlled process and proceeds by nucleation and growth mechanism. Therefore, any factor, which is able to vary either the rate of nucleation/the rate of growth or both is also able to change the nature of ferrite cementite mixture.

Some of these factors are: nature of austenite under consideration, the temperature of transformation and the presence of alloying elements.

The more the homogeneity of austenite, the better is the probability of getting a lamellar structure. A heterogeneous austenite may result in the transformation of austenite to spheroidized structure. With lowering of the transformation temperature, a harder and finer aggregate of ferrite and cementite results.

The microstructures evolving during austenite decomposition are Ferrite with different morphologies (grain boundary allotriomorphic ferrite, idiomorphic ferrite, Widmanstatten ferrite, and intragranular ferrite), cementite, Pearlite, Bainite and Martensite.
The temperature of transformation controls the nature of decomposed product (of austenite) which in turn decides the resultant properties of steel.

The kinetics of austenitic transformation can be studied best at a constant temperature rather than by continuous cooling.

The constant temperature transformation is also referred to as isothermal transformation which is studied by the following experiment.

Davenport and Bain were the first to develop the TTT diagram of eutectoid steel. They determined pearlite and bainite portions whereas Cohen later modified and included $M_S$ and $M_F$ temperatures for martensite.

There are number of methods used to determine TTT diagrams. The most popular method is salt bath techniques combined with metallography and hardness measurement with addition of this we have other techniques like dilatometry, electrical resistivity method, magnetic permeability, in situ diffraction techniques (X-ray, neutron), acoustic emission, thermal measurement techniques, density measurement techniques and thermodynamic predictions.

TTT diagrams, also called as Isothermal (temperature constant) Transformation diagrams.

For every composition of steel we should draw a different TTT diagram.
Equipments for determination of TTT Diagrams

Salt bath I
Austenitisation heat treatment

Salt bath II
Low-temperature for isothermal treatment

Sample and fixtures
for dilatometric measurements

Dilatometer equipment
For the determination of isothermal transformation (or) TTT diagrams, we consider molten salt bath technique combined with metallography and hardness measurements.

In molten salt bath technique two salt baths and one water bath are used.

Salt bath I is maintained at austenising temperature (780°C for eutectoid steel).

Salt bath II is maintained at specified temperature at which transformation is to be determined (below $A_{c1}$), typically 700-250°C for eutectoid steel.

Bath III which is a cold water bath is maintained at room temperature.

In bath I number of samples are austenite at $A_{1} + 20-40°C$ for eutectoid, $A_{3} + 20-40°C$ for hypo-eutectoid steel and $A_{Cm} + 20-40°C$ for hyper-eutectoid steels for about an hour.

Then samples are removed from bath I and put in bath II and each one is kept for different specified period of time say $t_1$, $t_2$, $t_3$, $t_4$, ............., $t_n$ etc.

After specified times, the samples are removed and quenched in cold water.

The microstructure of each sample is studied using metallographic techniques. The type, as well as quantity of phases, is determined on each sample.

Transformation of austenite to ferrite-cementite mixtures occurs after a definite time (say $t_1$). This time during which transformation does not proceed is known as incubation period.

The magnitude of incubation period provides a qualitative idea about the relative stability of supercooled austenite. Smaller incubation period corresponds to lesser stability of austenite.
Determination of TTT diagram for eutectoid steel

Simple experimental arrangement for determining the kinetics of isothermal austenitic transformation.

Eutectoid section of the iron-carbon diagram.

The progress of austenite transformation:
A-austenite, P-pearlite, M-martensite.

TTT curve of austenite to pearlite for 1080 steel.
Determination of TTT diagram for eutectoid steel

Important points to be noted:

✓ At $T_1$, incubation period for pearlite = $t_2$, Pearlite finish time = $t_4$

✓ Minimum incubation period $t_0$ at the nose of the TTT diagram.

✓ The x-axis is log scale. ‘Nose’ of the ‘C’ curve is in ~sec and just below $T_E$ transformation times may be ~day.

✓ The starting phase (left of the C curve) has to $\gamma$.

✓ To the right of finish C curve is ($\gamma + \text{Fe}_3\text{C}$) phase field. This phase field has more labels included.
Important points to be noted:

- The x-axis is log scale. ‘Nose’ of the ‘C’ curve is in ~sec and just below $T_E$ transformation times may be ~day.

- The starting phase (left of the C curve) has to $\gamma$.

- To the right of finish C curve is ($\gamma$+$Fe_3C$) phase field. This phase field has more labels included.
Possible phases in TTT diagram for eutectoid steel

- Coarse Pearlite R/C 15
- Temperature
- A_e1
- Nose
- 50% F.P + 50% U.B
- Medium Pearlite R/C 30
- Fine Pearlite (F.P) R/C 40
- Upper bainite (U.B) R/C 40
- Coarse Pearlite R/C 15
- Medium Pearlite R/C 30
- Fine Pearlite (F.P) R/C 40
- Temperatures
- Martensite R/C 64
- Metastable austenite + martensite
- M_s, Martensite start temperature
- M_s,50% Martensite
- M_f, Martensite finish temperature
- Log time
- Hardness
- 50% Transformation
- 50% Martensite
- 50% Transformation
As pointed out before one of the important utilities of the TTT diagrams comes from the overlay of micro-constituents (microstructures) on the diagram.

Depending on the T, the (γ+ Fe₃C) phase field is labeled with micro-constituents like Pearlite, Bainite.

The time taken to 1% transformation to, say pearlite or bainite is considered as transformation start time and for 99% transformation represents transformation finish.

We had seen that TTT diagrams are drawn by instantaneous quench to a temperature followed by isothermal hold.

Suppose we quench below (~225°C, below the temperature marked Mₛ), then Austenite transforms via a diffusionless transformation (involving shear) to a (hard) phase known as Martensite. Below a temperature marked Mₐ this transformation to Martensite is complete. Once γ is exhausted it cannot transform to (γ + Fe₃C).

Hence, we have a new phase field for Martensite. The fraction of Martensite formed is not a function of the time of hold, but the temperature to which we quench (between Mₛ and Mₐ).

Strictly speaking cooling curves (including finite quenching rates) should not be overlaid on TTT diagrams (remember that TTT diagrams are drawn for isothermal holds!).
Austenite
Pearlite
Pearlite + Bainite
Bainite

400
600
500
800
723 Eutectoid temperature

Coarse
Fine

Isothermal hold at: (i) T1 gives us Pearlite, (ii) T2 gives Pearlite+Bainite, (iii) T3 gives Bainite. Note that Pearlite and Bainite are both $\alpha + \text{Fe}_3\text{C}$ (but their morphologies are different).

To produce Martensite we should quench at a rate such as to avoid the nose of the start ‘C’ curve. Called the critical cooling rate.

If we quench between $M_s$ and $M_f$ we will get a mixture of Martensite and $\gamma$ (called retained Austenite).

Not an isothermal transformation
In principle two curves exist for Pearlitic and Bainitic transformations → they are usually not resolved in plain C steel (In alloy steels they can be distinct)
In hypo- (and hyper-) eutectoid steels (say composition C₁) there is one more branch to the ‘C’ curve-NP (next slide: marked in red).

The part of the curve lying between \( T_1 \) and \( T_E \) (marked in fig: next slide) is clear, because in this range of temperatures we expect only pro-eutectoid \( \alpha \) to form and the final microstructure will consist of \( \alpha \) and \( \gamma \). (E.g. if we cool to \( T_x \) and hold).

The part of the curve below \( T_E \) is a bit of a ‘mystery’ (since we are instantaneously cooling to below \( T_E \), we should get a mix of \( \alpha + Fe_3C \Rightarrow \) what is the meaning of a ‘pro’-eutectoid phase in a TTT diagram? (remember ‘pro’- implies ‘pre’-)

Suppose we quench instantaneously an hypo-eutectoid composition C₁ to \( T_x \) we should expect the formation of \( \alpha + Fe_3C \) (and not pro-eutectoid \( \alpha \) first).

The reason we see the formation of pro-eutectoid \( \alpha \) first is that the undercooling w.r.t to \( A_{cm} \) is more than the undercooling w.r.t to \( A_1 \). Hence, there is a higher propensity for the formation of pro-eutectoid \( \alpha \).
TTT diagram for Hypo-eutectoid steel

\[ \alpha + Fe_3C \]
Similar to the hypo-eutectoid case, hyper-eutectoid compositions C₂ have a γ+Fe₃C branch.

For a temperature between T₂ and T_E (say T_m (not melting point- just a label)) we land up with γ+Fe₃C.

For a temperature below T_E (but above the nose of the ‘C’ curve) (say T_n), first we have the formation of pro-eutectoid Fe₃C followed by the formation of eutectoid γ+Fe₃C.
Almost all alloying elements (except Al, Co, Si) increase the stability of supercooled austenite and retard both proeutectoid and the pearlitic reaction and then shift TTT curves of start to finish to right or higher timing. This is due to:

- low rate of diffusion of alloying elements in austenite as they are substitutional elements,
- reduced rate of diffusion of carbon as carbide forming elements strongly hold them.
- Alloyed solute reduce the rate of allotropic change, i.e. \( \gamma \rightarrow \alpha \), by solute drag effect on \( \gamma \rightarrow \alpha \) interface boundary.

Additionally those elements (Ni, Mn, Ru, Rh, Pd, Os, Ir, Pt, Cu, Zn, Au) that expand or stabilise austenite, depress the position of TTT curves to lower temperature. In contrast elements (Be, P, Ti, V, Mo, Cr, B, Ta, Nb, Zr) that favour the ferrite phase can raise the eutectoid temperature and TTT curves move upward to higher temperature.

However Al, Co, and Si increase rate of nucleation and growth of both ferrite or pearlite and therefore shift TTT diagram to left. In addition under the complex diffusional effect of various alloying element the simple C shape behaviour of TTT diagram get modified and various regions of transformation get clearly separated. There are separate pearlitic C curves, ferritic and bainitic C curves and shape of each of them are distinct and different.
The effect of alloying elements is less pronounced in bainitic region as the diffusion of only carbon takes place (either to neighboring austenite or within ferrite) in a very short time (within a few second) after supersaturated ferrite formation by shear during bainitic transformation and there is no need for redistribution of mostly substitutional alloying elements.

Therefore bainitic region moves less to higher timing in comparison to proeutectoid/pearlitic region. Addition of alloying elements lead to a greater separation of the reactions and result separate C-curves for pearlitic and bainitic region. Mo encourage bainitic reaction but addition of boron retard the ferrite reaction. By addition of B in low carbon Mo steel the bainitic region (almost unaffected by addition of B) can be separated from the ferritic region.

However bainitic reaction is suppressed by the addition of some alloying elements. $B_s$ temperature (empirical) has been given by Steven & Haynes

$$B_s^{(0C)} = 830 - 270(\%C) - 90(\%Mn) - 37(\%Ni) - 70(\%Cr) - 83(\%Mo)$$

Most alloying elements which are soluble in austenite lower $M_s$, $M_F$ temperature except Al, Co. Andrews gave best fit equation for $M_s$:

$$M_s^{(0C)} = 539 - 423(\%C) - 30.4Mn - 17.7Ni - 12.1Cr - 7.5Mo + 10Co - 7.5Si$$

Effect of alloying elements on $M_F$ is similar to that of $M_s$. Therefore, subzero treatment is must for highly alloyed steels to transform retained austenite to martensite.
The (a) type of TTT diagram is similar to that of carbon steel. In the presence of carbide forming elements super cooled austenite decomposes to a mixture of ferrite and carbides rather than to aggregate of ferrite and cementite.

The (b) type of TTT diagram consists of two minima with respect to the stability of austenite. The upper bay ($\gamma \rightarrow$ pearlite), lower bay ($\gamma \rightarrow$ bainite). Very few steels exhibit such a TTT diagram.

The (c) type of TTT diagram is peculiar in the sense that bainitic region is not present. Such a TTT diagram is obtained, in general, for high alloy steels and Ms region shifted to sub zero region.

The (d) type of TTT diagram does not exhibit pearlitic bay. Under normal conditions either bainite or martensite can be formed.
Carbon and alloying elements affect the transformation of austenite in many ways. As the amount of carbon and most alloying elements increase in steel, the lower part of the curves is progressively lowered because except for aluminium, all the elements lower the $M_s$ temperature.

The austenite stabilizers lower the $Ac_3$ as well as $Ac_1$ temperatures, i.e., these elements (Ni, Mn, C etc) lower the upper part of the TTT curve. This probably is the reason of having overlapping ‘C’ curves for pearlitic and bainitic transformations in plain carbon steel as well as in steels having Ni, etc.

Ferrite stabilizers raise $Ac_3$ as well as $Ac_1$ temperatures. As the TTT curve for such steels get raised upward as well as gets lowered downward, there are invariably two ‘C’ curves—one for pearlitic and the other for bainitic transformations. For example, presence of 0.8% Cr and 0.33% Mo in steel yield two ‘C’ curves.

Andrew suggests the effect of the elements on $Ac_3$ and $Ac_1$ by equations:

\[
Ac_3 = 910 - 203\sqrt{\%C} - 15.2(\%Ni) + 44.7(\%Si) + 104(\%V) + 31.5(\%Mo) + 13.1(\%W)
\]

\[
Ac_1 = 727 - 10.7(\%Mn) - 16.9(\%Ni) + 29.1(\%Si) + 290(\%As) + 16.9(\%Cr) + 6.38(\%W)
\]
Factors affecting on TTT diagram

Effect of grain size

γ=austenite
α=ferrite
CP=coarse pearlite
P=pearlite
FP=fine pearlite
UB=upper Bainite
LB=lower Bainite
M=martensite
Ms=Martensite start temperature
M50=temperature at which 50% martensite is obtained
Mf= martensite finish temperature

Temperature, T vs Log(time, t)

Metastable γ

For finer austenite

50% FP + 50% UB

UB

Metastable γ + M

M
Factors affecting on TTT diagram

Effect of grain size

- All the composition products of austenite nucleate heterogeneously preferentially at the grain boundaries.
- A fine grained steel has larger grain boundary area than a coarse grained steel, and consequently favors nucleation of pearlite, bainite, ferrite, cementite and thus, reduces the incubation period, that means the TTT curve of the fine grained steel is more towards left, significantly in the pearlitic range, than a coarse grained steel of same composition.

Effect of Heterogeneity of Austenite

- Heterogeneous austenite increases transformation time range, start to finish of ferritic, pearlitic and bainitic range as well as increases the transformation temperature range in case of Martensitic transformation and bainitic transformation. Undissolved cementite, carbides act as powerful inoculants for pearlite transformation. Therefore heterogeneity in austenite increases the transformation time range in Diffusional transformation and temperature range of shear transformation products in TTT diagram.
- This heterogeneity of austenite, when the steel is heated to temperatures not higher than 50°C above A₁ is put to advantage to obtain spheroidized pearlite by letting it decompose within 50°C below A₁ to improve the ductility and the machinability (high carbon steels).
Applications of TTT diagrams

**MARTEMPERING**

- This heat treatment is given to oil hardenable and air hardenable steels and thin section of water hardenable steel sample to produce martensite with minimal differential thermal and transformation stress to avoid distortion and cracking.
- The steel should have reasonable incubation period at the nose of its TTT diagram and long bainitic bay.
- The sample is quenched above $M_S$ temperature in a salt bath to reduce thermal stress (instead of cooling below $M_F$ directly) Surface cooling rate is greater than at the centre.
- The cooling schedule is such that the cooling curves pass behind without touching the nose of the TTT diagram. The sample is isothermally hold at bainitic bay such that differential cooling rate at centre and surface become equalize after some time.
- The sample is allowed to cool by air through $M_S-M_F$ such that martensite forms both at the surface and centre at the same time due to not much temperature difference and thereby avoid transformation stress because of volume expansion. The sample is given tempering treatment at suitable temperature.
- The rate of cooling from austenising temperature should avoid formation of pearlitic and bainite. Thus the success of Martempering depends on the incubation period at the pearlitic nose, and also at the bainitic bay, and thus the steel suitable for Martempering should have sufficient hardenability. *Plain carbon steels with dia. > 10mm are difficult to mar-temper and thus, this process is restricted to alloy steels.*
Martempering

\[ \gamma = \text{austenite} \]
\[ \alpha = \text{ferrite} \]
\[ \text{CP} = \text{coarse pearlite} \]
\[ P = \text{pearlite} \]
\[ \text{FP} = \text{fine pearlite} \]
\[ t_0 = \text{minimum incubation period} \]
\[ \text{UB} = \text{upper bainite} \]
\[ \text{LB} = \text{lower bainite} \]
\[ M = \text{martensite} \]
\[ M_S = \text{Martensite start temperature} \]
\[ M_{50} = \text{temperature at which 50% martensite is obtained} \]
\[ M_F = \text{martensite finish temperature} \]
Austempering heat treatment is given to steel to produce lower bainite in high carbon steel without any distortion or cracking to the sample.

The heat treatment is cooling of austenite rapidly in a bath maintained at lower bainitic temperature (above $M_s$) temperature (avoiding the nose of the TTT diagram) and holding it here to equalize surface and centre temperature and till bainitic finish time.

At the end of bainitic reaction sample is air cooled. The microstructure contains fully lower bainite. This heat treatment is given to 0.5-1.2 wt% C steel and low alloy steel.

The product hardness and strength are comparable to hardened and tempered martensite with improved ductility and toughness and uniform mechanical properties. Products do not required to be tempered.

TTT diagram is great help in scheduling Austempering as it fixes
- Temperature of holding of the bath
- Duration of holding time
- Section which can be quenched to avoid pearlite formation
- Whether Austempering is worth while, or not, as the time at the bay may be too long.
Austempering

\[ A_{e1} \]

\[ A_{e3} \]

\[ \alpha + CP \]

\[ \alpha + P \]

FB

FP

UB

50% FP + 50% UB

\[ \gamma = \text{austenite} \]

\[ \alpha = \text{ferrite} \]

CP = coarse pearlite

P = pearlite

FP = fine pearlite

t\[ t_0 \] = minimum incubation period

UB = upper bainite

LB = lower bainite

M = martensite

\[ M_s = \text{Martensite start temperature} \]

\[ M_{50} = \text{temperature at which 50\% martensite is obtained} \]

\[ M_F = \text{martensite finish temperature} \]
Applications of TTT diagrams

ISOTHERMAL ANNEALING

- Isothermal annealing consists of four steps.
  - The first step is heating the steel components similar as in the case of full annealing.
  - The second step is slightly fast cooling from the usual austenitizing temperature to a constant temperature just below $A_1$.
  - The third step is to hold at this reduced temperature for sufficient soaking period for the completion of transformation and the final step involves cooling the steel component to room temperature in air.

- Figure (nextslide) depicts the heat treatment cycles of full annealing and isothermal annealing. The terms $\alpha$, $\gamma$, $P$, $P_s$ and $P_F$ refer to ferrite, austenite, pearlite, pearlite starting and pearlite finish, respectively.

- Isothermal annealing has distinct advantages over full annealing which are given below.
  - Reduced annealing time, especially for alloy steels which need very slow cooling to obtain the required reduction in hardness by the full annealing.
  - More homogeneity in structure is obtained as the transformation occurs at the same time throughout the cross section.
  - Improved machinability and surface finish is obtained after machining as compared to that of the full annealed components.
Isothermal annealing is primarily used for medium carbon, high carbon and some of the alloy steels to improve their machinability.
Patenting is an isothermal heat treatment processes used for producing high strength ropes, springs, and piano wires of normally 0.45% to 1.0% carbon steel. In fact, the strongest material in commercial quantities is the patented and cold drawn wire made from 0.80% to 1.0% carbon steel, containing no martensite. Wires having high ultimate tensile strength of 4830MN/m² with 20% elongation have been reported.

Patenting consists of austenitising steel in continuous furnace to temperature 150-200°C above Ac₃, then cooling rapidly in and holding in a lead, or salt bath maintained at a temperature of 450-550°C (near the pearlitic nose of its TTT curve, i.e., in the lower temperature limit of pearlitic transformation) for sufficient time for austenite to completely transform to finest pearlite (some upper bainite may also form), and then wound on to driven drum.

The eutectoid steel after patenting may have interlamellar spacing as small as 40nm with strength as 1240-1450 Mpa. The process of patenting helps in two ways to obtain high strengths. Patented wires can be cold drawn by large extent (80-90%) without fracture as the soft, weak primary ferrite or brittle cementite is absent and the interlamellar spacing is same every where.

TTT diagram help to fix the time and temperature of holding. The speed of motion of the wire through the bath should be such that it remains in bath for a time slightly greater than the time of completion of pearlitic transformation to avoid any chance of untransformed austenite to bainite or martensite later.
Figure: Patenting (a) Schematic process of patenting, (b) TTT diagram of 0.6% carbon steel
The TTT diagrams are also called Isothermal Transformation Diagrams, because the transformation times are representative of isothermal hold treatment (following a instantaneous quench).

In practical situations we follow heat treatments (T-t procedures/cycles) in which (typically) there are steps involving cooling of the sample. The cooling rate may or may not be constant. The rate of cooling may be slow (as in a furnace which has been switch off) or rapid (like quenching in water).

Hence, in terms of practical utility TTT curves have a limitation and we need to draw separate diagrams called Continuous Cooling Transformation diagrams (CCT), wherein transformation times (also: products & microstructure) are noted using constant rate cooling treatments.

A diagram drawn for a given cooling rate (dT/dt) is typically used for a range of cooling rates (thus avoiding the need for a separate diagram for every cooling rate).

However, often TTT diagrams are also used for constant cooling rate experiments- keeping in view the assumptions & approximations involved.

**Important difference between the CCT & TTT transformations is that in the CCT case Bainite cannot form.**

The CCT diagram for eutectoid steel is considered next.
CCT diagrams are determined by measuring some physical properties during continuous cooling. Normally these are specific volume and magnetic permeability. However, the majority of the work has been done through specific volume change by dilatometric method. This method is supplemented by metallography and hardness measurement.

In dilatometry the test sample is austenitised in a specially designed furnace and then controlled cooled. Sample dilation is measured by dial gauge/sensor. Slowest cooling is controlled by furnace cooling but higher cooling rate can be controlled by gas quenching.
Cooling data are plotted as temperature versus time (Fig. a). Dilation is recorded against temperature (Fig. b). Any slope change indicates phase transformation. Fraction of transformation roughly can be calculated based on the dilation data as explained below.

Fig. a : Schematic cooling curves

Fig. b : Dilation-temperature plot for a cooling curve

Determination of CCT diagram for eutectoid steel
In **Fig. a** curves I to V indicate cooling curves at higher cooling rate to lower cooling rate respectively.

**Fig. b** gives the dilation at different temperatures for a given cooling rate/schedule.

In general slope of dilation curve remains unchanged while amount of phase or the relative amount of phases in a phase mixture does not change during cooling (or heating) however sample shrink or expand i.e. dilation takes place purely due to thermal specific volume change because of change in temperature.

Therefore in **Fig. b** dilation from a to b is due to specific volume change of high temperature phase austenite. But at $T_S$ slope of the curve changes.

Therefore transformation starts at $T_S$. Again slope of the curve from c to d is constant but is different from the slope of the curve from a to b.

This indicates there is no phase transformation between the temperature from c to d but the phase/phase mixture is different from the phase at a to b.

Slope of the dilation curve from b to c is variable with temperature. This indicates the change in relative amount of phase due to cooling.

The expansion is due to the formation of low density phase(s). Some part of dilation is compensated by purely thermal change due to cooling.

Therefore dilation curve takes complex shape. i.e first slope reduces and reaches to a minimum value and then increases to the characteristic value of the phase mixture at c.
Determination of CCT diagram for eutectoid steel

- Therefore phase transformation start at b i.e. at temperature $T_S$ and transformation ends or finishes at c or temperature $T_F$. The nature of transformation has to be determined by metallography.

- When austenite fully transforms to a single product then amount of transformation is directly proportional to the relative change in length. For a mixture of products the percentage of austenite transformed may not be strictly proportional to change in length, however, it is reasonable and generally is being used.

- Cumulative percentage of transformation at in between temperature T is equal to $\frac{YZ}{XZ} \times 100$ where X, Y and Z are intersection point of temperature T line to extended constant slope curve of austenite (ba), transformation curve (bc) and extended constant slope curve of low temperature phase (cd) respectively.

- So at each cooling rate transformation start and finish temperature and transformation temperature for specific amount (10%, 20%, 30% etc.) can also be determined.

- For every type of transformation, locus of start points, isopercentage points and finish points give the transformation start line, isopercentage lines and finish line respectively and that result CCT diagram.

- Normally at the end of each cooling curve hardness value of resultant product at room temperature and type of phases obtained are shown.
CCT diagram for eutectoid steel

- Eutectoid temperature
- Original TTT lines
- Pearlite
- Austenite
- Martensite
- Ms
- Mf
Different cooling rates for eutectoid steel

<table>
<thead>
<tr>
<th>Process</th>
<th>Cooling rate (K/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealing</td>
<td>$10^{-5} - 10^{-3}$</td>
</tr>
<tr>
<td>Air Cooling</td>
<td>1 – 10</td>
</tr>
<tr>
<td>Oil Quenching</td>
<td>~100</td>
</tr>
<tr>
<td>Water Quenching</td>
<td>~500</td>
</tr>
<tr>
<td>Splat Quenching</td>
<td>$10^5$</td>
</tr>
<tr>
<td>Melt-Spinning</td>
<td>$10^6 - 10^8$</td>
</tr>
<tr>
<td>Evaporation, sputtering</td>
<td>$10^9$ (expected)</td>
</tr>
</tbody>
</table>

M = Martensite  P = Pearlite

Water quench

Oil quench

Normalizing

Full anneal

Coarse P

Fine P

M + P

$t$ (s) →
Pearlite typically forms on the grain boundaries of the austenite phase by the nucleation of either the ferrite or cementite; the exact phase that nucleates is decided both by the composition and the structure of the grain boundary.

The nucleation is such that the barrier for nucleation is the lowest; in other words, the nuclei has an orientation relationship with one of the grains such that the interfacial free energy is minimized.

Suppose the first phase to nucleate is cementite; this leads to a depletion of the carbon surrounding this region leading to ferrite nucleation. Ferrite nucleation is also such that the interfacial free energy is minimized; thus, it also has an orientation relationship with the cementite. This process is repeated with the entire grain boundary coated with alternating cementite and ferrite nuclei.
If the composition of the steel is not the eutectoid composition, then, it is possible that proeutectoid ferrite or cementite is nucleated at the grain boundary. The other phase, be it cementite or ferrite, then forms on the incoherent boundary of this proeutectoid phase. This process is shown schematically in Fig.

**Orientation Relation:** Kurdyumov-Sachs

- \((100)_c \parallel (111)_\gamma\)
- \((010)_c \parallel (110)_\gamma\)
- \((001)_c \parallel (112)_\gamma\)

**Nucleation of the eutectoid phases in a system with pro-eutectoid composition**

- The development of Pearlitic microstructure requires cooperative growth of Ferrite and Cementite
- If this cooperation is not established then the resulting microstructure is non-lamellar → *Degenerate Pearlite*
**Eutectoid Transformations**

**Nucleation at GB**

Pearlite in Fe-C alloys

\[ \gamma \rightarrow \alpha + Fe_3C \]

- Low undercooling (below \( A_1 \))
  - Small number of nuclei form which grow without interference
- Large undercooling (below \( A_1 \))
  - High nucleation rate → Site saturation along GB

---

A pearlite colony advancing into an austenite grain. (After L.S. Darken and R.M. Fisher in *Decomposition of Austenite by Diffusional Processes*, V.F. Zackay and H.I. Aaronson (Eds.), by permission of The Metallurgical Society of AIME.)

At relatively larger supersaturations (austenite cooled below the nose of the pearlite transformation), there is another eutectoid product that develops known as bainite; bainite is also a mixture of ferrite and cementite; however, it is microstructurally quite distinct. In the next two subsections, we discuss these microstructural features.

**Upper bainite**

- At the higher end of the temperatures (350-550°C), the microstructure consists of needles of laths of ferrite nucleated at the grain boundary and grown into one of the grains with cementite precipitates between the ferrites; see in Fig.
- The ferrite formed is Widmanstatten; it has a Kurdjumov-Sachs orientation relationship with the austenite grain into which it is growing; it is in this respect, namely the orientation relationship between the ferrite/cementite and the austenite grain in which they grow, that the bainite differs from pearlite.
At low enough temperatures, the bainitic microstructure changes to that of plates of ferrite and very finely dispersed carbides; since the diffusion of carbon is very low at these temperatures (especially in the austenite phase as compared to ferrite), the carbides precipitate in ferrite (and, with an orientation relationship). These carbides that precipitate could be the equilibrium cementite or metastable carbides (such as ε carbide for example). A schematic of lower bainite plate that is formed is shown in Fig.

Pearlite is nucleated by a carbide crystal, bainite is nucleated by a ferrite crystal, and this results in a different growth pattern.

- Acicular, accompanied by surface distortions
- ** Lower temperature → carbide could be ε carbide (hexagonal structure, 8.4% C)
- Bainite plates have irrational habit planes
- Ferrite in Bainite plates possess different orientation relationship relative to the parent Austenite than does the Ferrite in Pearlite
AtIn this topic we will be concerned with phase transformations in which the first phase to appear is that given by the equilibrium phase diagram.

Here we will consider to the diffusional transformation of Fe-C austenite into ferrite.

However, many of the principles are quite general and have analogues in other systems where the equilibrium phases are not preceded by the precipitation of transition phases.

Under these conditions the most important nucleation sites are grain boundaries and the surface of inclusions.

It can be seen in figure (next slide) that ferrite can also precipitate within the austenite grains (intragranular ferrite). Suitable heterogeneous nucleation sites are thought to be inclusions and dislocations. These precipitates are generally equiaxed at low undercoolings and more platelike at higher undercoolings.

In general the nucleation rate within grains will be less than on grain boundaries. Therefore, whether or not intergranular precipitates are observed depends on the grain size of the specimen.

In fine grained austenite for example, the ferrite that forms on grain boundaries will rapidly raise the carbon concentration within the middle of the grains, thereby reducing the undercooling and making nucleation even more difficult.

In a large grained specimen, however, it takes a longer time for the carbon rejected from the ferrite to reach the centers of the grains and meanwhile there will be time for nucleation to occur on the less favorable intragranular sites.
Ferrite nucleates on Austenite grain boundaries and grows with a blocky appearance → **Grain Boundary Allotriomorphs**

Curved interfaces → incoherent
Faceted interfaces → semicoherent

**800°C**

Larger undercooling – Ferrite grows as plates from GB → **Widmannstätten side-plates**

Irrational habit planes

Ferrite can also nucleate within the γ grains heterogeneously at inclusions and dislocations → equiaxed at low undercoolings and plate-like at higher undercoolings.

**750°C**
**Widmannstätten side-plates → become finer with larger undercooling**

**Very Large undercooling – Ferrite grows as needles GB → Widmannstätten needles**
Martensitic transformations

- The name martensite is after the German scientist Martens. It was used originally to describe the hard microconstituent found in quenched steels. Martensite remains of the greatest technological importance in steels where it can confer an outstanding combination of strength (> 3500 MPa) and toughness (> 200 MPa m$^{1/2}$).

- Martensitic transformation is the name for any transformation that takes place in a diffusionless and military manner - that is, these transformations take place through atomic movements which are less than one atomic spacing; and in these transformations atoms change their positions in a coordinated manner (unlike thermally activated diffusional, or, so-called, civilian processes).

- In shape memory alloys such as Ni-Ti (nitinol), it is the martensitic transformation that is responsible for the shape memory effect.

- In this topic, we describe some characteristic features of the martensitic transformations (with specific reference to steels in which, this transformation is responsible for hardening by quenching).

- Since martensitic transformations are diffusionless, necessarily, the composition does not change during the transformation. It is only the crystal structure that changes. For example, in Fe-C alloys, the austenite (fcc) transforms into martensite (bct);

- in Ni-Ti, an ordered bcc (called austenite) transforms to another ordered CsCl type structure (called martensite). Note that since martensitic transformation is diffusionless, if the austenitic phase is ordered, the martensitic phase is also ordered.
Martensitic transformations

- Occur at high supersaturations, without change in composition
- No long range diffusion → Movement of atoms a fraction of the inter-atomic distance
- Nearest neighbour configuration remains unchanged
- Cooperative movement of a large group of atoms → transformation proceeds at the speed of sound in the material
- Thermal activation does not play a role in the growth of the martensitic phase
  Thermal activation may play a role in the nucleation of martensite
- Usually martensite crystals nucleate and grow across the whole grain (in some cases this growth is a function of temperature)
- In some cases the transformation occurs over a period of some time (due to thermally assisted nucleation)
- Martensitic crystals have a specific orientation relationship (OR) with the parent phase
- Planes of the parent lattice on which Martensitic crystals from → Habit planes (*irrational Indices*)
- Interface between Martensite and parent phase → Coherent or Semi-coherent
- At a given temperature (between $M_s$ and $M_f$) the fraction transformed ↑ with plastic deformation (in some cases elastic stress also has a similar effect)
- With prior plastic deformation the transformation temperature can be increased to $M_d$
Characteristics of Martensitic transformations

(a, b) Growth of martensite with increasing cooling below $M_s$
(c-e) Different martensite morphologies in iron alloys

Low C (lathe)

Medium C (plate)
Fe-Ni: Plate

(a, b) Growth of martensite with increasing cooling below $M_s$
(c-e) Different martensite morphologies in iron alloys
Characteristics of Martensitic transformations

- Shape of the Martensite formed → Lathe and Plate morphologies
- Associated with shape change (shear)
- But: Invariant plane strain (*observed experimentally*) → Interface plane between Martensite and Parent remains undistorted and unrotated
- This condition requires
  1) Bain distortion → Expansion or contraction of the lattice along certain crystallographic directions leading to homogenous pure dilation
  2) Secondary Shear Distortion → Slip or twinning
  3) Rigid Body rotation
Martensitic transformation can be understood by first considering an alternate unit cell for the Austenite phase as shown in the figure below.

If there is no carbon in the Austenite (as in the schematic below), then the Martensitic transformation can be understood as a ~20% contraction along the c-axis and a ~12% expansion of the a-axis → accompanied by no volume change and the resultant structure has a BCC lattice (the usual BCC-Fe) → c/a ratio of 1.0.

FCC → BCC

~20% contraction of c-axis
~12% expansion of a-axis
Characteristics of Martensitic transformations

But shear will distort the lattice!

Irrational Habit Plane
(Should remain undistorted and unrotated)

Dilation due to phase transformation
(Rotated due to the transformation)

Shear
(Combine Dilation and Shear leaves Habit Plane Invariant)

But shear will distort the lattice!

Slip

Twinning

Average shape remains undistorted
How does the motion of dislocations lead to a macroscopic shape change?

(From microscopic slip to macroscopic deformation ⇒ a first feel!)

Dislocation formed by pushing in a plane

Step formed when dislocation leaves the crystal

Characteristics of Martensitic transformations
Characteristics of Martensitic transformations
Characteristics of Martensitic transformations

Net shape change
Characteristics of Martensitic transformations

Properties of 0.8% C steel

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Hardness ($R_c$)</th>
<th>Tensile strength (MN / m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse pearlite</td>
<td>16</td>
<td>710</td>
</tr>
<tr>
<td>Fine pearlite</td>
<td>30</td>
<td>990</td>
</tr>
<tr>
<td>Bainite</td>
<td>45</td>
<td>1470</td>
</tr>
<tr>
<td>Martensite</td>
<td>65</td>
<td>-</td>
</tr>
<tr>
<td>Martensite tempered at 250 °C</td>
<td>55</td>
<td>1990</td>
</tr>
</tbody>
</table>
Characteristics of Martensitic transformations

Influence of carbon on the martensite range

Effect carbon on lattice parameters of austenite and martensite

Influence of carbon on the martensite range

Effect carbon on lattice parameters of austenite and martensite
Various ways of showing Martensitic Transformations

(a) Free energy – temperature diagram for Austenite and martensite of fixed carbon concentration
(b) Free energy – composition diagram for the austenite and martensite phases at the $M_s$ temperature.
(c) Iron-carbon phase diagram with $T_0$ as defined in (a), $M_s$ and $M_f$ superimposed.
(d) $M_s$ and $M_f$ in relation to the TTT diagram for alloy $C_0$ in C
At this point, it is worth stopping to ask why a tetragonal martensite forms in iron. The answer has to do with the preferred site for carbon as an interstitial impurity in bcc Fe. Remember: Fe-C martensites are unusual for being so strong (& brittle). Most martensites are not significantly stronger than their parent phases.

Interstitial sites:
- FCC: octahedral sites radius = 0.052 nm
tetrahedral sites radius = 0.028 nm
- BCC: octahedral sites radius = 0.019 nm
tetrahedral sites radius = 0.036 nm

Surprisingly, it occupies the octahedral site in the bcc Fe structure, despite the smaller size of this site (compared to the tetrahedral sites) presumably because of the low modulus in the <100> directions.

One consequence of the occupation of the octahedral site in ferrite is that the carbon atom has only two nearest neighbors. Each carbon atom therefore distorts the iron lattice in its vicinity. The distortion is a tetragonal distortion.

If all the carbon atoms occupy the same type of site then the entire lattice becomes tetragonal, as in the martensitic structure.

Switching of the carbon atom between adjacent sites leads to strong internal friction peaks at characteristic temperatures and frequencies.
Kinetics of Martensitic transformations

Athermal

- Fraction transformed = \( f(T) \) only (between \( M_s \) and \( M_f \))
- At a given \( T \) a certain number of nuclei form which grow at the speed of sound in the material across the whole grain
- The number of nuclei forming increases with decreasing \( T \) ⇒ more transformation
- \( M_s \) and \( M_f \) temperatures increase with increasing grain size

Burst

- At some \( T \) (\( M_b \)) → sudden transformation of a large fraction of parent to Martensite (often with an acoustic effect – click)
- \% transformed during the “burst” → few-over 50%
- The ‘burst’ can be thought of as an extreme form of autocatalytic effect
- Remaining transformation is completed at → • lower \( T \) • longer \( t \)
Kinetics of Martensitic transformations

- Fraction transformed at a given T (between $M_s$ and $M_f$) = $f(t)$ → observed in some alloys at subzero $T$
- At the low T thermal activation of growth does not occur (as usual fast)
- “t effect” is due to small thermal activation required for nucleation of Martensitic plates and autocatalytic effect
- Rate of transformation at a given T ↑ with ↑ grain size (fewer nucleation events give more transformed fraction)

 Isothermal Transformation diagram for Martensitic Transformation in Fe-Ni-Mn alloy
Heat Treatment Processes for Steels

Avala Lava Kumar : D.K.Mishra : Dr.S.K.Badjena
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla -768018
*E-mail : lavakumar.vssut@gmail.com
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
- Not above $A_{cm}$ →to avoid a continuous network of proeutectoid cementite along grain boundaries (→path for crack propagation)
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)
Stress Relief Annealing

Residual stresses → Heat below $A_1$ → Recovery

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

Annihilation of dislocations, polygonization
Annealing

Spheroidization Annealing

Heat below/above $A_1$ (Prolonged holding*)
Cementite plates $\rightarrow$ Cementite spheroids $\rightarrow$ ↑ 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*
**Diffusion Annealing**

- This process also known as homogenizing annealing, is employed to remove any structural non-uniformity.

- Dendrites, columnar grains and chemical inhomogeneities 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.

- Hypoeutectoid 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
Partial Annealing

- Partial annealing is also referred to as intercritical annealing or incomplete annealing. In this process, steel is heated between the A₁ and the A₃ 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 Ac₁ for hypereutectoid 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.
Heat above \( A_3 \) \( \rightarrow \) \( A_{cm} \) \( \rightarrow \) Austenization \( \rightarrow \) Air cooling \( \rightarrow \) Fine Pearlite (Higher hardness)

**Purposes**
- Refine grain structure prior to hardening
- To harden the steel slightly
- To reduce segregation in casting or forgings

- 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

<table>
<thead>
<tr>
<th>Annealed</th>
<th>Normalized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less hardness, tensile strength and toughness</td>
<td>Slightly more hardness, tensile strength and toughness</td>
</tr>
<tr>
<td>Pearlite is coarse and usually gets resolved by the optical microscope</td>
<td>Pearlite is fine and usually appears unresolved with optical microscope</td>
</tr>
<tr>
<td>Grain size distribution is more uniform</td>
<td>Grain size distribution is slightly less uniform</td>
</tr>
<tr>
<td>Internal stresses are least</td>
<td>Internal stresses are slightly more</td>
</tr>
</tbody>
</table>
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 process known as **Hardening**.

The hardening process consists of four steps. The first step involves heating the steel to above $A_3$ temperature for hypoeutectoid steels and above $A_1$ temperature for hypereutectoid steels by 50°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.
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 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 restrains are minimum. R.A is less at surface than center of the part.
Retained Austenite

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.
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.

Subzero 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 subzero 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.
Sub-Zero treatment

Table: Subzero Coolants with Temperature of Application

<table>
<thead>
<tr>
<th>Coolant</th>
<th>Minimum temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry ice (solid Co₂) + Acetone</td>
<td>-78</td>
</tr>
<tr>
<td>Ice + Salt (NaCl)</td>
<td>-23</td>
</tr>
<tr>
<td>Ice + Salt (CaCl₂)</td>
<td>-55</td>
</tr>
<tr>
<td>Liquid air</td>
<td>-183</td>
</tr>
<tr>
<td>Liquid Nitrogen</td>
<td>-196</td>
</tr>
<tr>
<td>Liquid Pentane</td>
<td>-129</td>
</tr>
<tr>
<td>Freon</td>
<td>-111</td>
</tr>
</tbody>
</table>

Figure: Liquid cooled (liquid N₂) 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.
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°C immediately after first quenching and then given the sub-zero treatment.

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 to 1.1%C as hardness increases by 1-3 HRc

Sub-zero treatment has been most extensively used for…!
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.
Tempering

**Objective**
- Relieve Internal stresses
- Restore ductility and toughness
- To improve dimensional stability
- To improve magnetic properties

**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 $\varepsilon$-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 $\varepsilon$-carbide, Fe$_{2.4}$C occurs. *(There are reports of precipitation of eta-carbide, Fe$_2$C and Haggs carbide, Fe$_{2.2}$C.)*

- $\varepsilon$-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 $c = 4.33\AA$, $a = 2.73\AA$, $c/a = 1.58\AA$ and forms as small (0.015-0.02 $\mu$m) 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 $\varepsilon$-carbide.

- In this stage volume ↓ because specific volume of martensite ↓ due to rejecting of C atoms.
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 $\varepsilon$-carbide). The matrix in lower bainite is cubic ferrite ($c/a = 1$), where as in tempered martensite, the low tetragonal martensite has $c/a \approx 1.014$

- When retained austenite changes to lower bainite, their takes place increase in volume.

Third stage of Tempering

- Third Stage of tempering temperature lies between 200-350°C. In this stage of tempering, $\varepsilon$-carbide dissolves in matrix, and low tetragonal martensite losses its completely its carbon and thus, the tetragonality to become ferrite.

- Cementite forms as rods at interfaces of $\varepsilon$-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 in around 0.25%
Tempering of plain carbon steels

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°C to 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 tempering temperature (1 hour at each temperature) on hardness and reactions.
The presence of alloying elements, steels can change their nature and properties effectively.

Most common elements (except cobalt) 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°C), where these elements have good diffusivity to take part in tempering reactions.
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 chromium in 0.35%C steel on tempering

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

Effect of increasing chromium in 0.35%C steel on tempering
Tempering of alloy steels

- Element, such as, silicon dissolves in $\varepsilon$-carbide to stabilize it. Steels with 1-2% silicon have $\varepsilon$-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 $(\text{Fe, Mn})_3\text{C}$.

- Martensite in plain carbon steels loss 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.
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
In alloy steels, having larger amounts of strong carbide forming elements like Mo, Ti, V, Nb, W, Cr etc., and carbon, 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 to 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 replace 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.
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:

\[ \text{Rate} = \frac{1}{t} = Ae^{-Q/RT} \]

Where, \( t \) is the time of tempering to develop a given hardness, 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:

\[ H = f[te^{-Q/RT}] \]

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

\[ Q = T[\ln t - \ln t_0] = f(H) \]

As \( t_0 \) constant then

\[ H = f[T(C + \ln t)] \]

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., \( T(C + \ln t) \) is called the Hollomon and Jaffe tempering parameter. (hardness in vickers is preferable)
## Temperature and colours for Heating and Tempering of Steel

<table>
<thead>
<tr>
<th>Colours of Hot Solid metal</th>
<th>°C</th>
<th>Process of Heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>White</td>
<td>1500</td>
<td>High speed steel hardening (1230-1300°C)</td>
</tr>
<tr>
<td>Yellow white</td>
<td>1300</td>
<td>High speed steel hardening (1230-1300°C)</td>
</tr>
<tr>
<td>Yellow</td>
<td>1100</td>
<td>High speed steel hardening (1230-1300°C)</td>
</tr>
<tr>
<td>Orange Red</td>
<td>1000</td>
<td>Alloy steel hardening (800-1100°C)</td>
</tr>
<tr>
<td>Light-Cherry-Red</td>
<td>900</td>
<td>Carbon steel hardening</td>
</tr>
<tr>
<td>Cherry-red</td>
<td>800</td>
<td>Carbon steel hardening</td>
</tr>
<tr>
<td>Dark-red</td>
<td>700</td>
<td>High speed steel tempering (500-600°C)</td>
</tr>
<tr>
<td>Vary dark-red</td>
<td>500</td>
<td>Carbon steel tempering (150-575°C)</td>
</tr>
<tr>
<td>Black red in dull light, or darkness</td>
<td>400</td>
<td>Carbon steel tempering (150-575°C)</td>
</tr>
<tr>
<td>Steel gray</td>
<td>300</td>
<td>Carbon steel tempering (150-575°C)</td>
</tr>
</tbody>
</table>

### Colour of Oxide film

<table>
<thead>
<tr>
<th>Colour of Oxide film</th>
<th>°C</th>
<th>Parts Heat treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel Gray</td>
<td>327</td>
<td>Cannot be used for cutting tools</td>
</tr>
<tr>
<td>Pale-light blue</td>
<td>310</td>
<td>For springs</td>
</tr>
<tr>
<td>Purple</td>
<td>282</td>
<td>Spring and screw drivers</td>
</tr>
<tr>
<td>Brown</td>
<td>270</td>
<td>Axes, wood cutting tools</td>
</tr>
<tr>
<td>Gold</td>
<td>258</td>
<td>Shear blades, hammer faces, cold chisels</td>
</tr>
<tr>
<td>Dark-straw-light-brown</td>
<td>240</td>
<td>Punches and Dies</td>
</tr>
<tr>
<td>Light-Straw-Yellow</td>
<td>220</td>
<td>Steel cutting tools, files, paper cutters</td>
</tr>
</tbody>
</table>
Embrittlement during Tempering

- Normally, as the tempering progresses, the hardness and the strength decreases, but the ductility and impact strength increase. But in certain steels, there is an unexpected decrease of the impact strength in certain ranges of temperatures. This indicates that there are two main types of embrittlement during tempering.
  - Tempered Martensite Embrittlement (TME)
  - Temper Embrittlement

- Both these embrittlement raise the impact transition temperature (ITT) to higher temperature. Figure (below) indicates the increase in impact transition temperature, $\Delta$(ITT) due to TE in SAE 3140 steel.

Temper-embrittlement in SAE 3140 steel shifts the impact transition temperature to higher temperature. $\Delta$(TTT) indicates the amount of increase.
Embrittlement during Tempering

- Normally, the degree of both type of embrittlement is expressed in terms of relative displacements of ITT i.e., by Δ (ITT) illustrated in figure (in previous slide).
- In both the transgranular fracture mode is replaced by an intergranular (IG) mode below the transition temperature, i.e., these show bright inter crystalline fracture along original austenite grain boundaries.
- Inspite of these similar effects, the two types of embrittlement are two separate phenomena, which occur in two different temperature ranges. Moreover, TME is a much faster process usually occurring in one hour, where as TE takes many hours.
- Temper embrittlement is of mush greater concern from practical point of view, as the rotors and shafts of power generating equipment even after tempering above 600°C, develop it when thick section cool very slowly through the range (450-600°C)

Schematic illustration of effect of tempering temperature on impact strength in steels prone to embrittlement during tempering.
As TME develops after tempering in range 260°C to 370°C, it is called as “350°C” embrittlement, or 500°F embrittlement. It is called ‘one-step embrittlement’ as during heating only in this range, TME develops. It is also called ‘irreversible embrittlement because a steel embrittled by tempering in this range, if heated further to above 400°C (above the critical range), becomes tougher, and the tempered martensite embrittlement does not occur again if cooled down to or tempered in the range of 260°C to 370°C again.

All steels, including the plain carbon steels are prone to irreversible embrittlement to some extent, and that is why tempering range of 260°C- 370°C is avoided in all steels, though it is a malady of low alloy steels.

The embrittlement is associated with the change in the structure of carbide from epsilon (ε) to cementite in the form of a film at the grain boundaries.

On tempering at higher temperatures, this film disappears and can not be restored, on repeated heating in 260°C-370°C temperature range.

Although, tempered martensite embrittlement is concurrent with the precipitation of cementite, but such precipitation is not in itself the cause of loss of impact toughness, as the embrittlement is does not occur if P, Sb, Sn, As, or N are not present in steel.

Addition of sufficient silicon to the steel inhibits the formation of cementite in the critical range, as silicon dissolved in epsilon carbide, increases its stability, and thus embrittlement does not occur.
Temper embrittlement

- The sickness of alloy steels occurs when they are tempered in the range 450°C to 600°C. It is also called reversible embrittlement (as well as two step embrittlement), because it occurs, when steels are tempered in this range, but gets removed, when heated to high temperatures, but occurs again on slow continuous cooling through this range from that high temperature (>600°C). The degree of embrittlement depends on the rate of cooling in the range 600-450°C.

- The phenomena of temper embrittlement results in loss of toughness as measured by notched impact test (without affecting very much the hardness, Y.S, UTS, elongation and fatigue properties), and a rise in ductile to brittle transition temperature occurs, with an intergranular (IG) fracture, below the transition temperature along the original austenitic grain boundaries.

- Carbon steels in general, but with less than 0.5% Mn, do not show temper embrittlement. Alloy steels of high purity do not show it. It is caused primarily by Sb and P and secondarily by Sn or As (even in amounts as low as 0.01%) in presence of elements like Ni, Mn, Cr, Si in steels. The highest effect is in Ni-Cr and Mn-Cr steels. Presence of elements like Mo, Ti, Zr delay, or remove embrittlement.

- The characteristic features of temper embrittlement are best explained by the concept of co-segregation. The impurity solutes are the surface active elements in iron, i.e., these reduce the grain boundary energy, and thus reduce the cohesion. Elements like Sb, P, As, Sn, interact with certain elements like Ni and Mn in steels.
Temper embrittlement

- These interactions lead to co-segregation of alloying elements and the impurity elements such as between Ni-Sb, Ni-P-Ni-Sn and Mn-Sb. The reason of co-segregation is the stronger interaction between them than, between either of these and iron.

- If the interaction is very strong then, co-segregation does not occur, but a scavenging effect is got, as happens between Mo-P, Ti-P, which is the cause of elimination of embrittlement by 0.5% Mo in such steels. If larger amount of Mo, Ti, Zr are present, then these elements slowly react with carbon to form stable carbides releasing the impurity atoms to segregate to the boundaries.

- Additional segregation may take place, when two alloying elements are present simultaneously, such as Ni and Cr. At high temperatures (>600°C), thermal vibrations make the equilibrium segregation low enough not to cause embrittlement, and at lower temperature (<450°C), the diffusion of the elements is too low to cause enough co-segregation within the normal tempering time.

- The following methods are normally recommended to minimize the effect of Temper embrittlement
  - Keep the impurities such as Sb, P, Sn, As as low as possible
  - Alloy the steel with Mo (0.5-0.75%)
  - Quench from tempering at higher temperatures
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

Avala Lava Kumar : D.K. Mishra : Dr. S.K. Badjena
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla - 768018

*E-mail: lavakumar.vssut@gmail.com
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

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

Typical hardness test survey made along a diameter of a quenched cylinder.
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.
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
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
Severity of Quenching media

<table>
<thead>
<tr>
<th>Process</th>
<th>Variable</th>
<th>H Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>No agitation</td>
<td>0.02</td>
</tr>
<tr>
<td>Oil quench</td>
<td>No agitation</td>
<td>0.2</td>
</tr>
<tr>
<td>&quot;</td>
<td>Slight agitation</td>
<td>0.35</td>
</tr>
<tr>
<td>&quot;</td>
<td>Good agitation</td>
<td>0.5</td>
</tr>
<tr>
<td>&quot;</td>
<td>Vigorous agitation</td>
<td>0.7</td>
</tr>
<tr>
<td>Water quench</td>
<td>No agitation</td>
<td>1.0</td>
</tr>
<tr>
<td>&quot;</td>
<td>Vigorous agitation</td>
<td>1.5</td>
</tr>
<tr>
<td>Brine quench (saturated Salt water)</td>
<td>No agitation</td>
<td>2.0</td>
</tr>
<tr>
<td>&quot;</td>
<td>Vigorous agitation</td>
<td>5.0</td>
</tr>
<tr>
<td>Ideal quench</td>
<td></td>
<td>∞</td>
</tr>
</tbody>
</table>

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 $H$

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

$f \rightarrow$ heat transfer factor  
$K \rightarrow$ 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 $\infty$ ($\Rightarrow H = \infty$)
Grossman’s critical diameter method

- 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

- $D_I = D_C$ for $H = \infty$
- $D_I > D_C$ 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 $H$. 
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.
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.
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 (see 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.
**Jominy sample**

- $t_0$ = Minimum incubation period at the nose of the TTT diagram,
- $t'_0$ = Minimum incubation period at the nose of the CCT diagram

- **M** – Martensite
- **P** – Pearlite
- **F.P** – Fine pearlite
- **C.P** – Coarse pearlite
- **M$_S$** – Martensite start
- **M$_F$** – Martensite finish
- **T$_E$** – Eutectoid temp.
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.

$D_1$ (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.

**Variation of hardness along a Jominy bar**

**Grossman chart used to determine the hardenability of a steel bar**
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 also declines.

The effect of alloying elements in the hardenability is shown in Figure (b) (next page). 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).
Estimation of Hardenability from chemical composition

For example, for a steel of grain size ASTM 8, with 0.5% carbon, 0.6% Mn, 1% Cr and 2% Ni, $D_1 = 0.22 \times 3.00 \times 3.17 \times 1.77 = 3.70$ 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
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:

$$D_I = D_{Critical} \times F_{Mn} \times F_{Cr} \times F_{Ni} \times F_{Si} \times F_{Mo}$$

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

<table>
<thead>
<tr>
<th>Carbon</th>
<th>No. 6</th>
<th>No. 7</th>
<th>No. 8</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.0814</td>
<td>0.0750</td>
<td>0.0697</td>
<td>1.167</td>
<td>1.035</td>
<td>1.018</td>
<td>1.080</td>
<td>1.15</td>
</tr>
<tr>
<td>0.10</td>
<td>0.1153</td>
<td>0.1065</td>
<td>0.0995</td>
<td>1.333</td>
<td>1.070</td>
<td>1.036</td>
<td>1.216</td>
<td>1.30</td>
</tr>
<tr>
<td>0.15</td>
<td>0.1413</td>
<td>0.1315</td>
<td>0.1212</td>
<td>1.500</td>
<td>1.105</td>
<td>1.055</td>
<td>1.324</td>
<td>1.45</td>
</tr>
<tr>
<td>0.20</td>
<td>0.1623</td>
<td>0.1509</td>
<td>0.1400</td>
<td>1.667</td>
<td>1.140</td>
<td>1.073</td>
<td>1.432</td>
<td>1.60</td>
</tr>
<tr>
<td>0.25</td>
<td>0.1820</td>
<td>0.1678</td>
<td>0.1560</td>
<td>1.833</td>
<td>1.175</td>
<td>1.091</td>
<td>1.540</td>
<td>1.75</td>
</tr>
<tr>
<td>0.30</td>
<td>0.1991</td>
<td>0.1849</td>
<td>0.1700</td>
<td>2.000</td>
<td>1.210</td>
<td>1.109</td>
<td>1.648</td>
<td>1.90</td>
</tr>
<tr>
<td>0.35</td>
<td>0.2154</td>
<td>0.2000</td>
<td>0.1842</td>
<td>2.167</td>
<td>1.245</td>
<td>1.128</td>
<td>1.756</td>
<td>2.05</td>
</tr>
<tr>
<td>0.40</td>
<td>0.2300</td>
<td>0.2130</td>
<td>0.1976</td>
<td>2.333</td>
<td>1.280</td>
<td>1.246</td>
<td>1.864</td>
<td>2.20</td>
</tr>
<tr>
<td>0.45</td>
<td>0.2440</td>
<td>0.2259</td>
<td>0.2090</td>
<td>2.500</td>
<td>1.315</td>
<td>1.164</td>
<td>1.972</td>
<td>2.35</td>
</tr>
<tr>
<td>0.50</td>
<td>0.2580</td>
<td>0.2380</td>
<td>0.2200</td>
<td>2.667</td>
<td>1.350</td>
<td>1.182</td>
<td>2.080</td>
<td>2.50</td>
</tr>
<tr>
<td>0.55</td>
<td>0.2730</td>
<td>0.2510</td>
<td>0.2310</td>
<td>2.833</td>
<td>1.385</td>
<td>1.201</td>
<td>2.188</td>
<td>2.65</td>
</tr>
<tr>
<td>0.60</td>
<td>0.284</td>
<td>0.262</td>
<td>0.2410</td>
<td>3.000</td>
<td>1.420</td>
<td>1.219</td>
<td>2.296</td>
<td>2.80</td>
</tr>
<tr>
<td>0.65</td>
<td>0.295</td>
<td>0.273</td>
<td>0.2551</td>
<td>3.167</td>
<td>1.455</td>
<td>1.237</td>
<td>2.404</td>
<td>2.95</td>
</tr>
<tr>
<td>0.70</td>
<td>0.306</td>
<td>0.283</td>
<td>0.260</td>
<td>3.333</td>
<td>1.490</td>
<td>1.255</td>
<td>2.512</td>
<td>3.10</td>
</tr>
<tr>
<td>0.75</td>
<td>0.316</td>
<td>0.293</td>
<td>0.270</td>
<td>3.500</td>
<td>1.525</td>
<td>1.273</td>
<td>2.620</td>
<td>3.25</td>
</tr>
<tr>
<td>0.80</td>
<td>0.326</td>
<td>0.303</td>
<td>0.278</td>
<td>3.667</td>
<td>1.560</td>
<td>1.291</td>
<td>2.728</td>
<td>3.40</td>
</tr>
<tr>
<td>0.85</td>
<td>0.336</td>
<td>0.312</td>
<td>0.287</td>
<td>3.833</td>
<td>1.595</td>
<td>1.309</td>
<td>2.836</td>
<td>3.55</td>
</tr>
<tr>
<td>0.90</td>
<td>0.346</td>
<td>0.321</td>
<td>0.296</td>
<td>4.000</td>
<td>1.630</td>
<td>1.321</td>
<td>2.944</td>
<td>3.70</td>
</tr>
<tr>
<td>0.95</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.167</td>
<td>1.665</td>
<td>1.345</td>
<td>3.052</td>
<td>-</td>
</tr>
<tr>
<td>1.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.333</td>
<td>1.700</td>
<td>1.364</td>
<td>3.160</td>
<td>-</td>
</tr>
</tbody>
</table>
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.
The industrial products of steels may change composition and average grain size from batch to batch, therefore, the measured hardenability of a given type of steel should be presented as a band rather than a single line, as demonstrated by the Figure at right.

Hardenability data now exists for a wide range of steels in the form of maximum and minimum end-quench hardenability curves, usually referred to as hardenability bands.

This data is available for very many of the steels listed in specifications such as those of the American Society of Automotive Engineers (SAE), the American Iron and Steel Institute (AISI) and the British Standards.
Factors effecting 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 effects 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.
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 $\gamma$-grain boundary surface the easier it is for pearlite to form rather than martensite
- Smaller $\gamma$-grain size $\rightarrow$ lower hardenability
- Larger $\gamma$-grain size $\rightarrow$ higher hardenability
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.
Factors effecting Hardenability

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.
Factors effecting Hardenability

- Cr, Mo, W, Ni
- Temperature
- Time

- **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

Exceptions
Factors effecting Hardenability

- All steels have 0.4wt% 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.
Boron is added to steel for only one reason-to increase hardenability. Boron-treated steels have certain peculiar characteristics.

Boron increases hardenability in hypoeutectoid 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 to 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 $\alpha$-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 $\text{Fe}_{23}(\text{BC})_6$ are formed there and to some extent they assume an orientation coherent with one of the two austenite grains between them which separate out.
Atomic contact is thereby established between Fe\textsubscript{23}(BC)\textsubscript{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

$$B_F = \frac{D_i \text{with} 'B'}{D_i \text{without} 'B'}$$

$D_i$ (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. 15. 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\textsubscript{2}B in austenite grain boundaries.
Quenching Technology

Avala Lava Kumar : D.K.Mishra : Dr.S.K.Badjena
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla -768018

*E-mail : lavakumar.vssut@gmail.com
Schematic principles of heating methods. (a) Heating in furnace kept at required temperature, more difference of temperature between surface and center than (c) though heating rate is faster here; (b) Heating in a furnace originally at a high temperature than required. Faster heating than (a) but difference of temperature between surface and center is largest; (c) Heating with furnace, difference of temperature between surface and center at any instant is small. Takes more time than (a) & (b); (d) Method tending to decrease distortion during heating; (e) Heating method of high speed steel (Large tool of intricate shapes)
The outstanding importance of steels in engineering is based on their ability to change mechanical properties over a wide range when subjected to controlled heat treatment.

For unalloyed carbon steels, for example, the hardness can be increased by up to 500% just by changing the cooling rate from the austenitizing temperature from extremely slow to extremely fast.

However quenching at a rate faster than in still air does not only determine the desired mechanical properties but is an important side effect of quenching is the formation of thermal and transformational stresses that lead to changes in size and shape and thus may result in quenching cracks that damage the work piece.

schematically represents the coupling effects among the three different characteristics of quenching—cooling rate, metallic structure, and internal stresses.
The coupling effects between temperature distribution during quenching, metallic structure, and stresses require correct cooling rate during heat treatment.

This includes sufficient reproducibility and predictability of quenching performance as well as the ability to exactly control quenching intensity by varying the type of quenchant and its physical state.

The main objective of the quenching process is to achieve the desired microstructure, hardness, and strength while minimizing residual stresses and distortion.

The most common quenchants in hardening practice are liquids including water, water that contains salt, aqueous polymer solutions, and hardening oils. Inert gases, molten salt, molten metal, and fluidized beds are also used.

Quenching techniques used for liquid media are immersion quenching and spray quenching. Immersion quenching, where the part is submerged into an un-agitated or agitated quenchant, is the most widely used.

The quenching intensity can be changed by varying the type of quenchant, its concentration and temperature, and the rate of agitation.

Spray quenching refers to spraying the liquid through nozzles onto those areas of the hot work piece where higher cooling rates are desired.

The heat transfer is mainly determined by the impingement density and its local distribution.
We can explain cooling rate effect by considering the transformation behavior during very slow cooling of an unalloyed steel with 0.45 wt% carbon (1040 steel) from austenitizing temperature (about 850°C) is described by the metastable iron–cementite equilibrium diagram.

Influence of cooling rate on the transformation temperatures of austenite. (a) Metastable iron–cementite equilibrium diagram; (b) change of transformation temperatures of a 1040 steel with increasing cooling rate; (c) CCT diagram of a 1040 steel.
Microstructures of a 1040 steel obtained with increasing cooling rate from austenitizing temperature (850°C). Magnification 1000.

(a) Globular cementite (gray) in a ferritic matrix (white), after tempering at 680°C over 60 h starting from a ferrite–pearlite microstructure;

(b) proeutectoid ferrite (white) and pearlite (dark) in a normalized structure. Heat treatment: 850°C/still air;

(c) pearlite–ferrite (white) and carbide (dark) in an arrangement of parallel plates, and small amounts of proeutectoid ferrite (white);

(d) bainite. Heat treatment: 850°C/oil;

(e) martensite. Heat treatment: 850°C/water;

(f) widmannstatten structure. Heat treatment: 1100°C/still air.
The hardness of steels increases with the concentration of carbon dissolved in austenite before quenching.

Effect of carbon concentration on (a) hardness for structures with different martensite content; (b) temperature for starting and completing the martensite formation $M_s$ and $M_f$; (c) retained austenite.
As described in the previous section, the concentration of carbon dissolved in austenite before quenching has a great effect on hardness and strength. While carbon is placed at interstitial locations in the iron lattice, alloying elements are dissolved at the original lattice sites.

The additional warping of the iron lattice due to the alloying elements causes only a slight increase in hardness but strongly affects the mobility of carbon, which results in a drastically reduced transformation rate.

This influence can be used to produce steels whose transformation characteristics are adapted to the desired microstructure and to the geometry of the parts to be quenched.

The internal stresses formed during quenching have a decisive influence on the transformation behavior of austenite as already described in introductory part of this chapter.

Depending on the chemical composition and the cooling rate, austenite can transform in the pearlite, bainite, or martensite range.

All these phase transformations are accompanied by volume expansion. The change of length during slow and rapid cooling of unstressed and tensile stressed austenite is shown in Figure (next page).
After cooling austenite at a very slow cooling rate, close to the equilibrium, ferrite and pearlite are formed in the temperature range between $\text{Ar}_3$ and $\text{Ar}_1$ temperatures (continuous line).

With fast cooling rates (dashed lines), the diffusion controlled transformations are suppressed, and below the martensite start temperature, $M_S$, the unstressed austenite transforms into martensite with an increase in specific volume.

If tensile stresses occur within the sample, the martensite start temperature increases from $M_S$ to $M_S'$ and larger changes of length occur. The opposite is true for compressive stresses. This phenomenon is called transformation plasticity.

The volume changes of the ferritic–pearlitic transformation as well as those of the martensitic transformation are due to the transformation of the face-centered cubic austenite crystal lattice into the body-centered cubic ferrite lattice or the tetragonal deformed martensite lattice. The ferritic and martensitic crystal lattices have a higher specific volume.
Previously it was shown that the cooling rate and the shape of the cooling curve influence the course of phase transformations, residual stresses and distortion.

In quench hardening, fast cooling rates, depending on the chemical composition of the steel and its section size, are frequently applied to prevent diffusion controlled transformations in the pearlite range and to obtain a structure consisting mainly of martensite and bainite.

However, the reduction of undesirable thermal and transformational stresses due to volume changes usually requires slower cooling rates.

Quenching processes therefore require the selection of cooling rates that are fast enough to permit the desired micro structure to form but slow enough to minimize residual stresses and distortion.

These considerations have resulted in different quenching methods such as

- Direct quenching,
- Interrupted quenching (Mar-quenching, Austempering, Isothermal Annealing)
- Spray quenching,
- Gas quenching
- Fog quenching.

The time temperature cycles that can be obtained with different quenching methods are shown in Figure (next page) for the center and surface of the quenched part together with the time temperature transformation diagram.
Quenching Processes

Direct Quenching

- Direct quenching, the most common quenching technique, refers to the quenching of the part from the austenitizing temperature directly to room temperature by immersion into a vaporizable liquid quenchant. Petroleum solutions or aqueous polymer solutions are often used for this process.

Interrupted Quenching

- Interrupted quenching consists of rapidly quenching steel from the austenitizing temperature to a temperature above the $M_S$ temperature, where it is held for a time sufficient to affect the desired transformation and then cooled in air.

- Interrupted quenching comprises three different quenching techniques: mar-quenching, Austempering, and isothermal annealing—which differ in the temperature at which quenching is interrupted and the time for which the steel is held at this temperature. The quenchants usually used for interrupted quenching are molten salt baths and specialty oils such as mar-tempering oils.

- Mar-quenching consists in rapidly quenching the steel to a temperature just above the $M_S$ temperature, holding it at this temperature to equalize the temperature throughout the work piece, and then removing it from the bath before transformation into bainite begins.

- Austempering is similar to mar-quenching in that the steel is rapidly quenched from the austenitizing temperature to a temperature above $M_S$ but differs in that the work piece is held at temperature for sufficient time to allow an isothermal transformation into bainite.
Isothermal annealing, differs from mar-quenching and austempering in that the bath temperature is sufficiently high that isothermal transformation into pearlite occurs. Pearlite exhibits high toughness and sufficient strength to be the optimal structure for parts such as wires or cables and railroad rails.

Cooling curves for the center and the surface of quenched parts for different quenching methods correlated to a time–temperature transformation schematic diagram. (a) Direct quenching; (b) mar-quenching; (c) austempering; (d) isothermal annealing or pearlitizing.
Spray Quenching

- Spray quenching with a liquid quenchant, generally water or an aqueous polymer solution, at sufficiently high pressures on the surface of the workpiece produces fast cooling rates because the liquid droplets impact the surface and cause a high rate of heat transfer.
- The rate of heat extraction can be varied over a wide range by varying the quantity of the sprayed liquid or by spraying a mixture of water and air (fog quenching). Compared to immersion quenching, spray quenching allows better control in cooling the workpiece.

Gas Quenching

- In gas quenching, heat removal is achieved by blowing a stream of gas over the workpiece, sometimes after austenitizing it in a vacuum furnace. Usually, the cooling rate is faster than that obtained in still air but slower than that achieved in oil and is controlled by the type, pressure, and velocity of the cooling gas. Inert gases including helium, argon, and nitrogen are most commonly used.

Fog Quenching

- The fog-quenching is very profitable for quenching of cast or forged steel pieces, because it can control the cooling rate in a wide range, and make uniform cooling at various sections of a material with complicated shape by controlling the flow rates of water and compressed air.
During quenching in liquid media with boiling temperatures far below the initial temperature of the body, three stages of heat removal occur. These are referred to as:

1. The film boiling or vapour blanket stage,
2. The nucleate boiling stage, or Vapour-transport cooling stage
3. The convection stage.

**Vapour-blanket cooling stage**

- In this stage, quenching medium is vaporized at the surface of the metal and forms a thin stable layer.
- Cooling is by conduction and radiation.
- Cooling rate is relatively slow

**Vapour-transport cooling stage**

- This stage starts when the metal has cooled to a temperature at which the vapor film is no longer stable.
- Wetting of the metal surface by the quenching medium and violent boiling occur. Heat is removed from the metal very rapidly as the latent heat of vaporization. This is the fastest stage of cooling.
Liquid cooling stage

- This stage starts when the surface temperature of the metal reaches the boiling point of the quenching liquid.
- Vapor no longer forms, so cooling is by conduction and convection through the liquid. The rate of cooling is slowest in this stage.

- Some typical examples of the wetting sequences on steel and silver samples quenched in water, oil, and aqueous polymer solutions are depicted in following figures.
Wetting process on the surface of CrNi steel specimens quenched from 850°C into water and oil. (a) Cylinder (25-mm diameter × 100mm) in water at 30°C flowing at 0.3 m/s; (b) cylinder (25-mm diameter × 100 mm) in oil at 60°C flowing at 0.3 m/s; (c) prismatic cylinder (15 × 15 × 45mm) in water at 60°C without forced convection.
The wetting process can be strongly influenced by the addition of additives. Figure a and b (next page) show two wetting sequences that were obtained in water with different chemical admixtures.

On the surface of the sample, a polymer film forms that provides a uniform breakdown of the vapor blanket and reduces heat transfer in the lower temperature range. When the polymer film has completely redissolved, heat transfer is achieved entirely by convection.

The velocity of the spreading wetting front and the time interval of the simultaneous presence of film boiling and nucleate boiling can be strongly influenced by changing the physical properties of the quenchant and the sample. The items varied are:

- Type of quenchant as described by its boiling temperature, viscosity, thermal capacity, and surface tension
  - Additives to the quenchant, and their concentration
  - Temperature and agitation rate of the quenchant
  - Thermal characteristics of the body and its transformation behavior
  - Surface roughness of the body and surface layers
  - Geometry and initial temperature distribution of the sample

The influence of some selected properties on the time when wetting starts $t_s$, the time when wetting is finished $t_f$, the time interval of wetting is given by $\Delta t_w = t_f - t_s$
Wetting process on the surface of cylindrical samples which is quenched in water with different admixtures. (a) CrNi steel cylinder (25-mm diameter × 100 mm) quenched in 5% aqueous polymer solution at 30°C without forced convection and (b) silver cylinder (15-mm diameter × 45 mm) quenched in a 10% aqueous polymer solution with a chemical additive at 25°C without forced convection.
Quenching as a Heat Transfer problem

- When a part is heated to a specified temperature, heat is transferred to it by the furnace. Conversely, when the part is quenched, heat is transferred to the surrounding medium. This produces localized temperature gradients where there is conductive heat transfer from the higher temperature region to the lower temperature region. The heat transfer rate per unit area is proportional to the local temperature gradient and can be expressed by Fourier’s law of heat transfer,

\[ Q = -\lambda A \frac{dT}{dx} \]

- where \( Q \) is the heat transfer rate in J/s, \( \lambda \) is the thermal conductivity in J/(s m K), \( A \) is the unit area in m\(^2\), \( T \) is the temperature in K, and \( x \) is a local coordinate. The minus sign is inserted because the heat flows from higher to lower temperature areas according to the second law of thermodynamics.

- Heat transfer in a solid where temperature changes with time and no heat sources are present within the body is

\[ \frac{\partial T}{\partial t} = a \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \]

- where \( t \) is the time in s, \( a \) is the thermal diffusivity in m\(^2\)/s, and \( x, y, \) and \( z \) are local coordinates. According to above Equation the temperature distribution within a body depends not only on the local temperature gradients but also on the thermal diffusivity, which includes all thermodynamic parameters of the material.
The thermal diffusivity \( a \) is defined as

\[
a = \frac{\lambda}{\rho C_p}
\]

where \( \rho \) is the density in kg/m\(^3\) and \( C_p \) is the specific heat capacity under constant pressure in J/(kg K). The larger the value of \( a \), the more quickly heat will diffuse through the material.

A high value of ‘\( a \)’ can be achieved by either high thermal conductivity \( \lambda \) or low heat capacity \( \rho C_p \), which means that less of the heat moving through the material is absorbed which will increases the temperature of the material.

This fact is illustrated by faster cooling of silver relative to austenitic steels.

Another important problem for the determination of the cooling behavior of steels concerns heat transfer across the surface of the body to the surrounding medium. This is mathematically described in terms of the (interfacial) heat transfer coefficient ‘\( a \)’:

\[
\alpha = \frac{Q}{A(T_1 - T_2)}
\]

where the units of ‘\( a \)’ are J/(s m\(^2\)K), \( T_1 \) is the surface temperature of the body, and \( T_2 \) is the temperature of the medium. Determination of the heat transfer coefficient is based on Fourier’s law of heat transfer, which states that heat flow across the surface of a body is proportional to the temperature gradient at the surface.
## Process Variables Affecting Cooling Behavior and Heat Transfer

- Immersion Quenching
- Bath Temperature
- Effect of Agitation
- Effect of Quenchant Selection
- Surface Oxidation and Roughness Effects
- Effect of Cross-Section Size on Cooling
- Effects of Cooling Edge Geometry
- Effects of Steel Composition
Heat transfer during immersion quenching is influenced by many factors such as the dimensions and shape of the part that is quenched, the quenchant, and the quenching facility.

In the heat treatment shop only a few of these parameters can be realistically varied, including bath temperature, agitation rate, and the quantity and racking arrangement of the parts during the quenching process.

Of these, only agitation is readily varied during the quench, because rapid bath temperature changes and variation of the quenchant (and concentration, if an aqueous polymer solution is used) can not realistically be accomplished during the quenching process itself.
The principal mechanism of heat transfer for vapor blanket cooling during immersion quenching is illustrated in Figure. Heat is transported across the surface through the vapor blanket by conduction \( q_h \) and radiation \( q_g \).

Only a fraction of the heat is released to the liquid by convection \( q_{\alpha} \). The remainder \( q_v \) vaporizes and stabilizes the fluid into the vapor blanket. The hot vapor flows upward, and at the vapor–liquid interface bubbles pass from the vapor film into the fluid, especially at the top of the cooling workpiece.

A local decrease of the thickness \( \delta \) of the vapor film immediately increases the heat flow by conduction \( q_h \), resulting in additional vaporization of the fluid, thus sustaining the vapor film.

When the surface temperature decreases, the thickness \( \delta \) of the vapor film is reduced until the fluid contacts the hot metal, which is the start of wetting.

With increasing water temperature the duration of film boiling increases, which is indicated by the delayed transition from low cooling to fast cooling. In addition, the cooling rates of the three different stages of heat transfer are reduced.
Effect of Agitation

- In addition to bath temperature, the stability of the vapor film is greatly influenced by the velocity profile in the liquid. As illustrated in the lower part of Figure, the velocity profile is caused by the buoyancy-driven vapor flow and possibly by agitation (forced convection).
- A high flow velocity increases the heat transfer by convection \( q_{\alpha} \) and reduces, therefore reducing the duration of film boiling. With agitation, heat transfer during the three stages of cooling is increased.

![Cooling curves](image)

Effect of quenchant velocity on cooling curves in the center of an austenitic stainless steel specimen (25-mm diameter × 100mm) quenched (a) into water at 60°C and (b) into a 10% aqueous polymer solution at 30°C.
The quenchant also exhibits dramatic effects on cooling behavior. The cooling curves in the below figure were obtained with a 25-mm diameter probe quenched in water at two temperatures, a 10% aqueous polymer solution, and a fast quenching oil. All quenchants were evaluated at 0.6 m/s. Using the same probe size (cross-section) and flow velocity, different cooling curves were obtained for each quenchant.

Influence of different quenchants, some with different bath temperature, on cooling curve behavior (agitation velocity of 0.6 m/s)
The surface roughness of the body and surface layers, such as oxides or organic substances, also strongly influences the cooling process. Chromium-alloy steels are oxidation-resistant due to concentration of chromium oxide at the surface. Oxide layers have greater surface roughness and a lower thermal conductivity.

In Figure, the time interval of wetting \((t_f - t_s)\) of austenitic stainless steel cylinders heated to 850°C in an oxidizing atmosphere after annealing at 820°C for 20 h in air is compared to that of similar cylinders heated to the same temperature in a protective, reducing atmosphere. Water at 20 and 50°C flowing at various flow velocities was used as the quenchant. The wetting time is shorter for the oxidized surface and is further reduced with increasing liquid flow velocity sustained by a decreasing bath temperature as shown in Figure.

Influence of surface oxidation on the time interval of wetting \((t_f - t_s)\) of an austenitic stainless steel specimen (15-mm diameter × 45mm) quenched into water at two bath temperatures, 20 and 50°C. Oxidized surface: after annealing 20 h at 820°C in oxidizing atmosphere. Bright surface: after heating in protective atmosphere.
Effect of cross-section size on cooling

- The ratio of surface area to mass is an important factor in determining the actual cooling rate, because only the surface of a part which is in contact with the quenching medium.
- Thin plates and small diameter wires have a large ratio of surface area to mass and therefore rapid cooling rates.

\[
\text{For Cylinder } \quad \frac{\text{Surface area}}{\text{Mass}} = \left( \frac{\pi DL}{(\pi/4)D^2Lp} \right)
\]

- The calculation shows that the ratio is inversely proportional to diameter if the diameter is increased, the ratio of surface area to mass decreases, and the cooling rate decreases.
- The heat in the interior of the piece must be removed by conduction, through the body of the piece, eventually reaching the surface and the quenching medium. Therefore the cooling rate in the interior is less than that at the surface.
- If such variation in cooling rates exists across the radius of a bar during cooling, it is to be anticipated that variations in hardness would be evident when the bars are cut and hardness surveys made on the cross section. A considerable temperature difference between the surface and the center during quenching (see in next slide).
- This temperature difference will give rise to stresses during heat treatment called residual stresses, which may result in distortion and cracking of the piece.
Effect of cross-section size on cooling

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

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
Effect of cooling edge geometry

- As the initial rupture of the vapor blanket is always related to the decrease of surface temperatures below the wetting temperature, wetting behavior is strongly influenced by the radius of the lower edge of a cylindrical steel sample.

- A sharp edge will cause high heat removal rates across the surface and a premature breakdown of the vapor blanket. Increasingly, the lower surface radius from a rounded edge to a radius of 2.5 mm reduces the initial wetting temperature and the influence of bath temperature is diminished due to the greater thickness of the vapor blanket.

- The heating time $t_h$ is more for thicker parts. Comparing the simple shapes (figure below) of the same steel under similar conditions, the relative heating time ($t_h$) is 1 for the sphere, 2.5 for the parallelepiped, 2 for the cylinder, and 4 for the plate.
The chemical composition of steel determines the thermodynamic parameters of the material, the transformation behavior of austenite, and oxidation of the surface and therefore influences the wetting and cooling behavior during quenching.

The effect of chemical composition on cooling curves and cooling rate curves produced in the center of steel cylinders with 25-mm diameter quenched in water at 60°C and 0.3 m/s agitation is illustrated in Figure. All samples were austenitized at 850°C, except the 20MnCr5 steel, which was austenitized at 870°C.

Cooling curves for different alloys were obtained with the same diameter and cooling conditions. High cooling rates for 1045 carbon steel are related directly to its high thermal conductivity.

The minima in the cooling rate curves are caused by the latent heat of transformation of austenite into ferrite–pearlite, bainite, or martensite. The transformation temperature and the amount of latent heat depend on the hardenability of the steel grade and the cooling rate.

Influence of the chemical composition of steels on the cooling behavior of 25 × 100mm steel bars quenched into different fluids flowing at 0.3 m/s. Center cooling curves and cooling rate curves for 30°C water.
Distortion mechanisms

The shape and size changes of a part during heat treating can be attributed to three fundamental causes:

- **Residual stresses that cause shape change when they exceed the material yield strength.** This will occur on heating when the strength properties decline.
- **Stresses caused by differential expansion due to thermal gradients.** These stresses will increase with the thermal gradient and will cause plastic deformation as the yield strength is exceeded.
- **Volume changes due to transformational phase change.** These volume changes will be contained as residual stress systems until the yield strength is exceeded.
- **Residual stresses that remain in the part after the force has disappeared.** Residual stresses always arise from a nonuniform plastic deformation.
- **In the case of heat treatment, this nonuniform plastic deformation may be caused by the temperature gradient or the phase change or usually a combination of both factors during cooling.**
- **Residual stresses are a very serious problem in heat treatment, since they often result in distortion or cracking and in some cases in premature failure of the part in service.**
- **Consider the effect of temperature gradient alone.** It was shown earlier, under the effect of size and mass, that during quenching the surface is cooled more rapidly than the inside.
- **Almost all solids expand as they are heated and contract as they are cooled.** This means that at the end of 10 s (for example) the surface, since it is at a much lower temperature, should have contracted much more than inside.
Thermal stresses may be calculated from the following formula:

\[ S = \alpha \cdot E \cdot \Delta T \]

Where

- \( S \) = Thermal stress, psi
- \( \alpha \) = Coefficient of linear expansion in./in.\(^\circ\)F
- \( E \) = Modulus of elasticity, psi
- \( \Delta T \) = Difference in temperature, \(^\circ\)F

The stress distribution is plotted schematically in below figure.

The stress distribution across the dia. Due to temperature gradient. Dotted curve indicates a truer representation of the stress distribution.

The area in tension must balance the area in compression in order for the stresses to be in equilibrium across the cross section.
Residual stresses

- However since the outside and inside are attached to each other, the inside, being longer, will prevent the outside from contracting as much as it should.
- It will therefore elongates the outside layer, putting them in tension while the inside in turn will be in compression.
- In general, the tensile stress on the surface may reach a very high value. If this stress exceeds the ultimate strength of the material, cracking will occur.
- In the case of steel, however, thermal stresses alone very rarely lead to cracking. If the stress is below the yield strength of the steel, the stress will be borne elastically.
- When the entire piece has reached room temperature, $\Delta T = 0$, and therefore, since the thermal stress will be zero, there will be no distortion.
- If the stress exceeds the yield strength, the surface layer will be plastically deformed or permanently elongated. At room temperature the surface will have residual compressive stress and the inside, residual tensile stress.
- Let us consider the combined effect of temperature gradient and phase change for two possibilities: *Through-Hardened steel and Shallow-Hardened steel*
- The next two slides shows the surface- and center- cooling curves superimposed on the I-T diagram for the *through hardened steel* and *shallow hardened steel*.
- In many applications, the tensile stress developed by the external force is maximum at or near the surface. For these applications, shallow hardened or case-hardened parts are preferred.
Residual stresses

Through-Hardened Condition

Center cooling curve

A+F+C F+C

STRESS CONDITION

SURFACE CENTER

First Temperature gradient

Tension Compression

Second
A \rightarrow M of surface

Compression Tension

Third
A \rightarrow M of center

Tension Compression

Possible fracture in Through-Hardened steel
Residual stresses

Shallow-Hardened Condition

Center cooling curve

STAGE

First
Temperature gradient

Second
A → M of surface
A → P of center

Third
Cooling of center to room temperature

STRESS CONDITION

<table>
<thead>
<tr>
<th>STAGE</th>
<th>STRESS CONDITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>SURFACE</td>
<td>CENTER</td>
</tr>
<tr>
<td>First</td>
<td>Tension</td>
</tr>
<tr>
<td>Second</td>
<td>Compression</td>
</tr>
<tr>
<td>Third</td>
<td>Greater Compression</td>
</tr>
</tbody>
</table>

Possible fracture in Shallow-Hardened steel

Temperature

Surface cooling curve

1st stage
2nd stage
3rd stage

Time, log scale

Crack

Tension layers

Compression layers

Possible fracture in Shallow-Hardened steel
Surface Hardening treatment of steels

Avala Lava Kumar: D.K. Mishra: Dr. S.K. Badjena
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla - 768018

*E-mail: lavakumar.vssut@gmail.com
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
  - Spinning: Torch is stationary while work piece rotates
  - Progressive-spinning: Torch moves over a rotating work piece.
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 $A_c_3$ 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.
Induction Hardening

A coil to be used internally for heating bores applications.

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

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.
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 to 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 reentrant 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

  \[
  \text{casedepth}(\text{mm}) = -0.11 + \frac{3.02P}{(D_bV)^{1/2}} \quad P = \text{laser power, } D_b = \text{Incident beam diameter} \\
  V = \text{traverse speed (mm/s)}
  \]
- 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 upto 0.75 mm can be achieved by this method. A minicomputer is used to control voltage, current, beam time and focus.
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
- Macrostructure 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.
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

The specimen is cut perpendicular to the hardened surface at a predecided 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.
Taper-grind procedure

- This method is suitable for light and medium cases, and is illustrated in the 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.

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.
Case Depth Measurements in Steels

**Macrostructure 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 X20.

**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 treatment of steels

Avala Lava Kumar : D.K.Mishra : Dr.S.K.Badjena
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla -768018
*E-mail : lavakumar.vssut@gmail.com
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 thermochemical 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%. 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

$$Fe + 2CO \rightarrow Fe_{(c)} + CO_2$$

Where $Fe_{(c)}$ 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, $Fe + 2CO \rightarrow Fe_{(c)} + CO_2$ 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.
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% \( \text{BaCO}_3 \) 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
   \[
   \text{BaCO}_3 \rightarrow \text{BaO} + \text{CO}_2
   \]
   \[
   \text{CO}_2 + C \rightarrow 2\text{CO}
   \]

ii. Carbon monoxide reacts with the surface of steel:
   \[
   2\text{CO} + \text{Fe} \rightarrow \text{Fe(c)} + \text{CO}_2
   \]

iii. Diffusion of carbon into steel

iv. \( \text{CO}_2 \) formed in step (ii) reacts with “C” in the coal
   \[
   \text{CO}_2 + C \leftrightarrow 2\text{CO}
   \]

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

\[
\text{casedepth} = k\sqrt{t} \quad \text{Where } k \text{ is constant}
\]

Generally, carburizing time varies from 6 hours to 8 hours, and case depth obtained varies from 1 mm to 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°C and 900°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

\[
BaCl_2 + 2NaCN \rightarrow Ba(CN)_2 + 2NaCl
\]

\[
Ba(CN)_2 + Fe \rightarrow Fe(c) + BaCN_2
\]

- 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 ~0.08mm thick.
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°C to 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 endogas 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.

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

Such a gas acts as a ‘carrier gas’ for the process. Furnace chamber is purged with this gas to gas 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.
Gas Carburizing

During gas carburizing, the following reactions take place:

i. \( C_3H_8 \rightarrow 2CH_4 + C \) (cracking of hydrocarbon)

ii. \( CH_4 + Fe \rightarrow Fe(C) + 2H_2 \)

iii. \( CH_4 + CO_2 \rightarrow 2CO + 2H_2 \)

iv. \( 2CO + Fe \rightarrow Fe(C) + CO_2 \)

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

\[ H_2 + CO_2 \rightarrow CO + H_2O \]

Traces of O\(_2\) are also present due to the following reactions:

\[ 2CO_2 \rightarrow 2CO + O_2 \]

\[ CO_2 + Fe \rightarrow Fe(C) + O_2 \]

Average concentrations of CO\(_2\), H\(_2\)O, 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.
The first commercial application of vacuum carburizing started in the early 1970s. Vacuum carburizing is a process 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 continuous 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.
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)
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 $A_c_3$ 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.
## Post-Carburizing Heat treatments

<table>
<thead>
<tr>
<th>TREATMENT</th>
<th>CASE</th>
<th>CORE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A – best adapted to fine grained steels</td>
<td>Refined; Excess carbide not dissolved</td>
<td>Unrefined; soft and machinable</td>
</tr>
<tr>
<td>B - best adapted to fine grained steels</td>
<td>Slightly coarsened; some solution of excess carbide</td>
<td>Partially refined; stronger and tougher than A</td>
</tr>
<tr>
<td>C - best adapted to fine grained steels</td>
<td>Somewhat coarsened; solution of excess carbide favored; austenite retention promoted in highly alloyed steels.</td>
<td>Refined: maximum core strength and hardness; better combination of strength and ductility than B</td>
</tr>
<tr>
<td>D - best treatment for coarse grained steels</td>
<td>Refined solution of excess carbide favored; austenite retention minimized</td>
<td>Refined; soft and machinable; maximum toughness and resistance to impact</td>
</tr>
<tr>
<td>E - adapted to fine grained steels only</td>
<td>Unrefined with excess carbide dissolved; austenite retained; distortion minimized</td>
<td>Unrefined but hardened</td>
</tr>
<tr>
<td>F - adapted to fine grained steels only</td>
<td>Refined; solution of excess carbide favored; austenite retention minimized</td>
<td>Unrefined; fair toughness</td>
</tr>
</tbody>
</table>
In cyaniding and carbonitriding 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 (carbonitriding). 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 0.010in. For cyaniding and up to 0.030in. For carbonitriding.

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:

\[
2NaCN + O_2 \rightarrow 2NaCNO
\]

\[
2NaCNO + O_2 \rightarrow Na_2CO_3 + CO + 2N
\]

\[
2CO \rightarrow CO_2 + C
\]

Carbon and nitrogen so formed in atomic form diffuse into the steel and give thin wear resistant layer of the carbonitride 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.
Cyaniding and Carbonitriding

- **Carbonitriding** 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% NH₃, CH₄, 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 carbonitriding and carburizing.
- Carbon-nitrogen austenite is stable at lower temperatures than plain-carbon austenite and transforms more slowly on cooling. Carbonitriding 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.
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:

\[
2NH_3 \rightarrow 2[N]_Fe + 3H_2
\]

The solubility of nitrogen in ferrite is small. Most of the nitrogen that enters the steel forms hard nitrides (e.g. Fe₃N). 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 (Fe₄N) 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 NH₃/H₂ 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
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.

\[ 4NCO^- \rightarrow CO_3 + CO + 2N + 2CN \]
\[ XFe + N \rightarrow FexN \]
\[ 2CN^- + O_2 \rightarrow 2NCO^- (\text{regeneration of } CN^-) \]
\[ 3CO_3 + \text{regenerator} \rightarrow 6NCO^- + XH_2O (\text{regenerator of } CO_3^-) \]

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 nitrocarburizing atmospheres/salts are difficult to handle safety.
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 Fe$_2$B) layers are formed. On the outer surface, FeB phase forms, While in the interior, Fe$_2$B 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 to 0.127 mm, depending on material and application. The treatment time required for a case depth of 0.15 mm is 6 hours 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 200μm in thickness and a chromium content of up to 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 1500 VHN.
Thermomechanical Treatment

Avala Lava Kumar : D.K.Mishra : Dr.S.K.Badjena
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla -768018

*E-mail : lavakumar.vssut@gmail.com
Introduction

- As the name suggests- ‘Thermo’ means heat and ‘mechanical’ means deformation process: thermo-mechanical treatment, thus involves simultaneous application of various combinations of heat treatments and deformation processes in order to change its shape, refine the microstructure to improve properties of the alloys.

- Generally, increased strength with improvement in ductility and/or toughness are the chief objectives of thermo-mechanical treatments. Thermomechanical treatments can be classified based on the timing of deformation of austenite during the heat treatment as illustrated in below.

Classification of Thermomechanical Treatments (TMT)

I. Above critical TMT (above \( \text{Ae}_3 \)) → Controlled hot rolling, High temperature thermo-mechanical treatment (HTMT)

II. Inter-critical TMT (between \( \text{Ae}_3 \) and \( \text{Ae}_1 \))

III. Sub-critical TMT (below \( \text{Ae}_1 \))
   - Deformation prior to austenite transformation → Ausforming-ausworking, ausrolling; Low temperature thermo-mechanical treatments (LTMT)
   - Deformation during transformation (Isoforming)
   - Deformation after transformation
Very high strength levels are obtained by controlled rolling. This process consists of heating steel above the upper critical temperature, i.e., stable austenitic temperature range. Austenite thus obtained is deformed, and conditions are so maintained that fine grains of recrystallized austenite are obtained. The grain growth tendency is checked by the hot working process variables and by the presence of second phase particles.

Second phase particles are generally carbides of microalloying elements such as niobium, vanadium and titanium. Fine austenitic grains will result in fine ferritic grains in the final structure. Ferritic grains nucleate at austenitic grain boundaries.

Thus, the finer the austenitic grains, the better will be the ferritic grains. Therefore, it is very essential to check grain growth during Recrystallization.

Carbides of microalloying elements not only control the growth of austenitic grains but also retard the rate of recrystallization. However, the carbide of microalloying elements are effective only up to about 1050°C, and so rolling should be performed below this temperature.

Heavy deformation during rolling elongates the austenitic grains, thereby increasing the grain boundary area. This results in the availability of larger number of nucleation sites for ferrite.

In order to have maximum strengthening, heavy deformation and low finishing temperature should be chosen. The process is widely employed for high strength low alloy steels.
Hot-Cold Working : HTMT

- Hot-Cold working process consists of heating steel above the upper critical temperature. Stable austenite present at this temperature is deformed heavily in such a way that no recrystallization takes place.
- This non-recrystallized austenite is transformed into martensite by rapid quenching. In this process, work is carried out at minimum possible temperature above the austenitizing temperature. In order to control recrystallization, alloying elements such as vanadium, titanium or niobium are added to steel. The steel so obtained strong directional properties.
- Mechanical properties, such as strength, ductility, impact and fatigue strength are considerably improved by this process.

Schematic representation of HTMT and LTMT processes

Hot –Cold working TMT cycle
Ausforming is consists of heating steel above the upper critical temperature so as to get austenite. This austenite is supercooled to a temperature below the recrystallization temperature of the steel. The austenite so supercooled is deformed heavily. It is then quenched to obtain completely martensitic structure and then tempered.

Not all steels can be given this treatment. Only steels which possess sufficient gap between pearlitic and bainitic C-curves are suitable for this purpose. In addition the pearlitic and bainitic C-curves should have sufficiently long incubation period. This ensures availability of sufficient time for deformation.

Carbon is essential for Ausforming, at least a minimum of about 0.05 to 0.10%, but larger additions produce little effect, although steels normally have 0.3 to 0.4% carbon.

Strong carbide forming elements such as molybdenum, niobium, vanadium, titanium not only display the TTT curves towards right, but form a fine dispersion of their carbides which resists softening (coarsening) during tempering and increase the strength of the steels.
Ausforming process variables

- Austenitizing temperature
- Rate of cooling from austenitizing temperature to deformation temperature
- Temperature of deformation
- Amount of deformation

Structural changes

- Refinement of the martensite plates, or packets
- Increase in dislocation density (~10^{13} \text{ cm}^{-2}) in martensite. Martensite plates may have inherited fine dislocation substructures from austenite.
- Change in the size, amount and distribution of carbides.
- Development of texture in the martensite

Strengthening factors

- Major contribution is due to fine dispersion of alloy carbides associated with dislocations.
- The presence of alloying elements which raise the stacking fault energy (SFE) of austenite, for example Ni, raises SFE, reduces the strengthening effect. In contrast, the strengthening effect associated with ausforming is increased considerably in the presence of elements which reduces the SFE of the austenite. (\textit{Mn lower SFE, raises rate of work hardening})
The isoforming process consists of deforming steel below the lower critical temperature during transformation. The resultant product of transformation may be either fine pearlite or bainite, depending on the prevailing conditions. The process is called isoforming because transformation proceeds isothermally.

The steel is first heated above upper critical temperature and then quenched immediately to a temperature of about 650°C, i.e., in the vicinity of nose of the TTT curve. Mechanical working is carried out at this temperature.

Sufficient time should be available at this temperature for carrying out the deformation process and for the metastable austenite to transform isothermally to pearlite. Just after the completion of the transformation, steel is quenched. The larger the deformation or lower the deformation temperature, the greater is the level of strength developed in the steel.

Bainitic structure can be achieved in the final product in the same way as discussed above with minor modifications. In this case stable austenite is supercooled to a temperature range where it transforms to bainite, steel is deformed during the transformation of metastable γ to bainite.
Marstraining

- In the marstraining process, steel is heated above austenitizing temperature, followed by rapid quenching so as to get a martensitic structure. Since as-as-quenched is very hard and brittle, it is partially tempered to restore ductility.
- The ductility martensite thus obtained is cold worked. Only small deformations can be employed in this case because of the rapid rate of work hardening of martensite. This cold worked structure is re-tempered.
- The second tempering temperature should be lower than the first one. The process produces strain ageing and results in significant improvement in yield strength and tensile strength levels. It is believed that epsilon carbide formed at low tempering temperature dissolves during deformation.
- The dislocation-carbon interaction thus obtained hinders the movement of dislocations on re-tempering, and mechanical strength of the steel is improved. Since bainite is relatively soft as compared to martensite, it can be cold worked easily.
- The strain tempering response of bainite is found to be better than that of martensite in the sense that, for a given strength value, better ductility can be obtained.
- The first stage of the process, i.e., pre-tempering, which is carried out to impart some ductility to the steel for cold working, can be dispensed with in the case of strain tempering of bainite.
Cryoforming or Zerolling

- It consists of heating steel above the upper critical temperature. From this temperature, steel is rapidly quenched to sub-zero temperature. Then it is plastically deformed at sub-zero temperature, which is accompanied by high rate of work hardening.
- The transformation of a part of austenite to martensite takes place during deformation, and martensite thus produced has better yield strength, tensile strength and hardness.
- When austenite gets transformed into martensite at sub-zero temperature, a noise similar to crying is produced. This crying like sound is produced because both deformation and transformation proceed simultaneously.
- The process is well suited to steels which cannot be strengthened by cold working because of the high rate of work hardening, resulting in loss of ductility in rapid rate.
- The only drawback associated with the process is that a part of austenite is stabilized. This in turn transforms to hard and brittle martensite during service at room temperature.
- Martensite so formed may cause brittleness.
In this process, steel is plastically deformed. Such steel is rapidly heated to austenitizing temperature, followed by rapid cooling. The treatment does not result in complete elimination of strain-hardening effect developed by deformation given prior to austenitizing. Therefore, the steels thus treated are associated with some strain-hardening effect developed by deformation given prior to austenitizing. Therefore, the steels thus treated are associated with some strain-hardening effect.

The magnitude of residual strain hardening effect depends on the chemical composition of steel, amount of deformation, rate of deformation, rate of heating to austenitizing temperature, and the austenitizing temperature.
Thermomechanical treatment of non-ferrous alloys is commonly applied to the age-hardenable alloys. The process consists of plastic deformation of alloys followed by aging treatment. This is in contrast to thermo mechanical treatment applicable to steel, which consists of plastic deformation and simultaneous phase transformation.

Al, Cu, and Ni base precipitation hardenable alloys have been successfully subjected to thermomechanical treatment. Depending on the temperature of deformation, the process can be divided into two classes, namely:

- Low temperature thermomechanical treatment (LTMT)
- High temperature thermo mechanical treatment (HTMT)

![LTMT and HTMT cycle for an age hardening alloy](image-url)
**Thermomechanical Treatment of Non-Ferrous Alloys**

---

### Low temperature thermomechanical treatment (LTMT)

- Low temperature thermomechanical treatment of non-ferrous alloys consists of heating alloy to a single phase structure (solutioning).
- From this temperature, alloy is rapidly cooled so that it retains the high temperature phase which is generally a supersaturated solid solution of alloying elements in base metal.
- This supersaturated solid solution is subjected to cold deformation. The cold-worked alloy is then aged at room temperature or at slightly higher temperatures.
- For a given alloy, such a treatment results in better yield strength and tensile strength than simple age hardening treatment. However, ductility will be comparatively poor.
- The strengthening mechanism during low temperature thermomechanical treatment of non-ferrous alloys can be explained on the basis of strain hardening and interaction between crystal defects and precipitated particles.

---

### High temperature thermomechanical treatment (HTMT)

- High temperature thermomechanical treatment includes heating of the alloy to get a single phase structure. It is followed by deformation of the alloy.
- The hot deformed solid solution is quenched rapidly and then aged. Hot deformation results in increased dislocation density and strain hardening. Here the extent of strain hardening will be less than in LTMT because of dynamic recrystallization and dynamic polygonization.
The desired structure can be developed in hot deformed alloy by controlling the temperature, rate and degree of deformation. The structure may be either strain hardened, recrystallized and polygonized, or mixed.

The HTMT consists of hot deforming solid solution (single phase) in such a way that either non-recrystallized or very feebly recrystallized structure is attained in the hot deformed alloy. Once this non-recrystallized structure is quenched, it will produce a structure with high dislocation density and crystal defects.

On aging such a structure will develop better mechanical properties, specially tensile and yield strength improved properties are obtained by HTMT under a set of optimum conditions. These conditions are as follows.

- The structure of hot deformed supersaturated solid solution should be non-recrystallized
- Dynamic recrystallization during hot deformation should be prevented effectively.
- The degree of supersaturation should be sufficient so that considerable amount of precipitation should take place to induce significant hardening effect.

Optimum combination of strength and ductility is obtained by this treatment. Improved ductility is essentially due to more uniform precipitation from the supersaturated solid solution and very fine grain size.
Iron - Graphite Phase diagram

CAST IRONS

Avala Lava Kumar
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla -768018
E-mail: lavakumar.vssut@gmail.com
The true equilibrium diagram for iron and carbon is generally considered as iron-graphite phase diagram (next slide).

Earlier we learn about iron-iron carbide phase diagram and it is not a true equilibrium diagram, generally it is called metastable iron - iron carbide phase diagram.

Cementite (Fe₃C) is a metastable compound, and under some circumstances it can be made to dissociate or decompose to form ferrite and graphite, according to the reaction

\[ Fe₃C \rightarrow 3Fe + C \]

For explain of cast irons we will refers to both Iron-Iron carbide phase diagram and Iron-Graphite phase diagram.

Earlier we are studied steel microstructures from Iron-Cementite phase diagram. Same as earlier now we will learn the characteristic features of CAST IRONS with the help of Iron-Graphite phase diagram.

Cast irons are a class of ferrous alloys with carbon contents above 2.14 wt%; in practice, however, most cast irons contain between 3.0 and 4.5 wt% C and, in addition, other alloying elements.

The ductility of cast iron is very low and brittle, it cannot be rolled, drawn, or worked at room temperature. However they melt readily and can be cast into complicated shapes which are usually machined to final dimensions. Since casting is the only suitable process applied to these alloys, they are known as cast irons.
Iron – Graphite Phase Diagram

Temperature °C → 0.09% C

0.09% C
0.021
0.021

0.09% C
0.021
0.021

Fe
1539
1395
1493

0.09% C
0.021
0.021
Classification of cast irons

CAST IRONS

- Grey CI
- Ductile/Nodular CI
- White CI
- Malleable CI
- Compacted Graphite CI
- Alloy CI

Good castability $\Rightarrow C > 2.4\%$

Malleabilize

Stress concentration at flake tips avoided
Most common alloying element of Cast Irons is Silicon for various reasons, which include the manipulation of temperatures required to achieve desired microstructures.

For example, increases the stability of solidification of Graphite phases. Decreases the stability of the solidification of $\text{Fe}_3\text{C}$. Eutectic and eutectoid temperatures change from single values to temperature ranges. Eutectic and eutectoid compositions are affected.

Carbon Equivalent (CE): a measure of the equivalency of Carbon coupled with other alloying elements to that of just Carbon. An easier basis for classifying the properties of a multi-alloy material.

$$\text{CE} = \%\text{C} + \frac{1}{3}\%\text{Si} = 4.3$$

(hypoeutectic) $< \text{CE} = 4.3 <$ (hypereutectic), with the addition of phosphorus

$$\text{CE} = \%\text{C} + \frac{1}{3}(\%\text{P} + \%\text{Si})$$
Graphite structure is a factored crystal bounded by low index planes.

Growth occurs along \((10\overline{1}0)\) & \((0001)\) planes (direction A & C). Unstable growth occurs along direction A, giving the Graphite microstructure rough, poorly defined, edges in certain areas.

When grown from the solidification of liquid Iron Carbon alloys, Graphite takes on a layer structure. Among each layer covalent chemical bonds with strengths between \((4.19 \times 10^5\) to \(5 \times 10^5\) J/mol.) exist. Between layers weaker bonds exist on the order of \((4.19 \times 10^3 – 8.37 \times 10^3\) J/mol.

The structure of the Graphite depends on the chemical composition, the ratio of temperature gradient to growth rate, and the cooling rate. Such structures are:

![Crystalline structure of graphite, A and C possible growth directions](image)
Such structures are (a) Flake or Plate Graphite, (b) Compacted vermicular graphite, (c) Coral Graphite, (d) Spheroidal Graphite.

A wide variety of compounds and certain metals have been claimed to serve as either inoculants or nuclei for Flake Graphite growth. (Silicon dioxide, silicates, sulfides, boron nitride, carbides, sodium, potassium, calcium, etc..!)

Two methods of growth is possible. The nucleation of Flake Graphite Iron occurs mainly on silicon dioxide particles. Another one, Salt like carbides containing the ion Carbon are used as inoculants. Such carbides include NaHC\textsubscript{2} & KHC\textsubscript{2} from Group I, CaC\textsubscript{2}, SrC\textsubscript{2}, BaC\textsubscript{2} from group II, and YC\textsubscript{2} & LaC\textsubscript{2} from group III.
The solidification of a sample is represented mathematically by the relationship

\[
\frac{dQ}{dT} = V \rho \frac{dT}{dt}
\]

Where \( V \) is the volume of the sample, \( \rho \) is the density, \( C_P \) is the heat capacity, and \( \frac{dT}{dt} \) is the cooling rate of the liquid. \( \frac{dT}{dt} \) is the slope of the cooling curve before solidification begins.

When the liquid cools below the liquidus temperature, crystals nucleate and begin to grow. The rate is thus re-expressed as

\[
\frac{dQ}{dT} = (V \rho C_P + \rho \Delta H \frac{df}{dt}) \frac{dT}{dt}
\]

Where \( \Delta H \) is the heat of solidification and \( \frac{df}{dt} \) is the volume fraction of solid formed at a changing temperature.

Cooling curve for an Iron-carbon alloy with 3.2%C. The solidification starts with a primary precipitation of austenite, followed by a eutectic temperature.
In which all the C is in the combined form as Fe$_3$C (Cementite)

The typical microstructure of white cast iron (see next slide), consisting of dendrites of transformed austenite (pearlite) in a white interdendritic network of cementite.

Microstructure → Pearlite + Lедебурит + Cementite

White cast iron contains a relatively large amount of cementite as a continuous interdendritic network, it makes the cast iron hard and wear-resistant but extremely brittle and difficult to machine.

‘completely white’ cast irons are limited in engineering applications because of this brittleness and lack of machinability. mainly used in liners for cement mixers, ball mills and extrusion nozzles.

A large tonnage of white cast iron is used as a starting material for the manufacturer of malleable cast iron.

Hardness: 375 to 600 BHN, Tensile strength: 135-480 Mpa, Compressive strength: 1380 - 1725 Mpa

White cast irons fall into three major groups: Nickel Chromium White Irons: containing 3-5%Ni, 1-4%Cr. Identified by the name Ni-Hard iron. The chromium-molybdenum irons (high chromium irons): 11-23%Cr, 3%Mo, and sometimes additionally alloyed with Ni or Cu. 25-28%Cr White Irons: contain other alloying additions of Molybdenum and/or Nickel up to 1.5%
Typical white cast iron contains 2.5-3.5% C, 0.4-1.5% Si, 0.4-0.6% Mn, 0.1-0.4% P, 0.15% S, and balance Fe.

During solidification, high internal stresses may be developed due to varying cooling rates across the cross section. These stresses can be relieved by heating white cast iron to about 500-550°C.
Gray cast iron is obtained by cooling the molten metal slowly during solidification. A typical gray cast iron contains 2.5-3.5% C, 1.4-2.8% Si, 0.5-0.8% Mn, 0.1-0.9% P, and 0.06-0.12% S.

Fractured surface of gray cast iron appears grey because of the presence of graphite. Hence the alloy is termed gray cast iron.

In the manufacture of gray cast iron the tendency of cementite to separate into graphite and austenite or ferrite is favored by controlling alloy additions and cooling rates.

These alloys solidify by first forming primary austenite. The initial appearance of combined carbon is in the cementite resulting from the eutectic reaction. With proper control of carbon content, temperature and the proper amount of graphitizing elements notably silicon, magnesium cerium and, alloy will follow the stable iron – graphite equilibrium diagram.

For most of these cast irons, the graphite exists in the form of flakes (similar to corn flakes), which are normally surrounded by an α-ferrite or pearlite matrix.

Mechanically, gray iron is comparatively weak and brittle in tension as a consequence of its microstructure; the tips of graphite flakes are sharp and pointed, and may serve as points of stress concentration when an external tensile stress is applied. Strength and ductility are much higher under compressive loads.

Gray irons are very effective in damping vibrational energy. Base structures for machines and heavy equipment that are exposed to vibrations are frequently constructed of this material. In addition, gray irons exhibit a high resistance to wear.
Furthermore, in the molten state they have a high fluidity at casting temperature, which permits casting pieces having intricate shapes; also, casting shrinkage is low.

Finally, and perhaps most important, gray cast irons are among the least expensive of all metallic materials.

Gray irons having different type of microstructures, it may be generated by adjustment of composition and/or by using an appropriate heat treatment.

For example, lowering the silicon content or increasing the cooling rate may prevent the complete dissociation of cementite to form graphite. Under these circumstances the microstructure consists of graphite flakes embedded in a pearlite matrix.

Tensile strength of gray cast iron varies from 100 Mpa to 340 Mpa

Comparison of the relative vibrational damping capacities of (a) steel and (b) gray cast iron
Grey Cast Iron

\[ \text{Fe-C-Si + (Mn, P, S)} \rightarrow \text{Invariant lines become invariant regions in phase diagram} \]

- \( < 0.1\% \rightarrow \text{retards graphitization; } \uparrow \text{size of Graphite flakes} \)
- \( < 1.25\% \rightarrow \text{Inhibits graphitization} \)
- \( \epsilon \in [2.4\% \text{ (for good castability)}, 3.8 \text{ (for OK mechanical properties)}] \)

- \( \text{Fe-C-Si} + (\text{Mn, P, S}) \rightarrow \text{Invariant lines become invariant regions in phase diagram} \)

- \( \text{Si} \in (1.2, 3.5) \rightarrow \text{C as Graphite flakes in microstructure (Ferrite matrix)} \)

- \( \uparrow \text{volume during solidification } \Rightarrow \text{better castability} \)

Most of the ‘P’ combines with the iron to form iron phosphide (Fe\(_3\)P). This iron phosphide forms a ternary eutectic known as steadite, contains cementite and austenite (at room temperature pearlite).

\[ L \rightarrow \gamma + (Fe_3C) \rightarrow \alpha + Fe_3C + (Fe_3C) \]

- L (Lededurite) \rightarrow \gamma + Fe_3C \rightarrow \alpha + Fe_3C + (Fe_3C) \]

- Si \( \uparrow \Rightarrow C_{\text{eutectoid}} \)
Grey Cast Iron

Graphite flakes

Ferrite matrix

Pearlite matrix

500 X

286
The heat treatment given to grey cast iron may be classified as:

- Stress relieving
- Annealing
  - Ferritizing annealing
  - Full annealing
  - Graphitizing annealing
- Normalizing
- Hardening and Tempering

**Stress Relieving**

- The purpose of stress relieving in grey cast iron is to relieve residual stresses introduced during solidification, due to different cooling rates prevalent at various section of castings.
- Residual stresses adversely affect strength and cause distortion and may even result in cracking in some cases.
- The temperature of stress relieving is kept much below $Ac_1$ temperature. For maximum stress relief without changing the microstructure, a temperature range 538-565°C is recommended.
- In this temperature range, about 80% of the residual stresses are removed with holding time of about one hour. When held at 590°C, more than 85% of the stresses can be removed.
The purpose of annealing is to soften the grey cast iron and to improve its machinability by minimizing or eliminating massive eutectic carbides.

Three types of annealing treatment are given to grey cast iron: ferritizing annealing, full annealing, and graphitizing annealing.

**FERRITIZING ANNEALING**: To improve machinability in unalloyed or low alloy grey cast iron of normal composition, ferritizing annealing treatment is carried out.

In this treatment, pearlitic carbide transforms to ferritic matrix and graphite. Ferritic matrix is soft. Above 590°C, the rate of decomposition of iron carbide to ferrite and graphite increases significantly, and at 760°C the rate of decomposition is maximum.

Therefore for most gray cast irons, the ferritizing annealing temperature is kept between 700°C and 760°C, and the recommended holding time is 1 hour per 25 mm of section.

Normally, after ferritizing annealing, the annealed specimens are cooled at a rate varying from 100°C/hour to 300°C/hour.

**FULL ANNEALING**: If alloy content is high in grey cast iron, then it is difficult to decompose iron carbide into ferrite and graphite at 760°C.

Therefore, under such conditions, full annealing treatment is adopted. For this treatment, casting is heated to a suitable temperature between 790°C and 900°C and held about 1 hour. Then it is cooled slowly between 790°C and 680°C.
Annealing

- **GRAPHITIZING ANNEALING**: The purpose of graphitizing annealing is to convert massive iron carbide into pearlite and graphite. The treatment is carried out at 900-955°C.

- At this temperature, massive carbide dissolves in austenite which later decomposes to pearlite and graphite on cooling.

- Above 925°C, Fe$_3$P may also melt. Holding time varies from 15 minutes to several hours.

Normalizing

- The purpose of normalizing treatment for grey cast is to improve mechanical properties such as hardness and tensile strength.

- This treatment also helps restore as cast properties which have been modified by other heating processes such as graphitizing or pre-heat and post-heat treatment of welded joints.

- Normalizing temperature is kept above transformation range, i.e., 885-925°C. Holding time recommended for gray cast iron at normalizing temperature is about 1 hour per 25 mm of maximum thickness.

- Heating temperature significantly affects the mechanical properties, e.g., hardness and tensile strength as also the microstructure.

- Alloying elements such as Cr, Mo, and Ni enhance the strengthening due to normalizing.
The purpose of hardening and tempering in grey iron is to improve its strength and wear resistance. After this treatment, the wear resistance of pearlitic grey cast iron increases four to five times.

Ordinarily, grey iron is furnace or salt bath hardened from a temperature of about 860-870°C. The transformation range can extend by more than 55°C above the Ac1 temperature. Approximately Ac1 temperature of unalloyed grey iron is related to silicon and Manganese content by the relation

\[
\text{Ac}_1 (°C) = 730 + 28.0 (%\text{Si}) - 25.0 (%\text{Mn})
\]

Tempering treatment increases the toughness and relieves internal stresses which may be developed during quenching. Due to tempering hardness decreases.

To achieve maximum toughness in grey iron, tempering temperature of about 370°C is recommended. After tempering at this temperature, the matrix retains a hardness level of 472 BHN.

Increase in wear resistance in grey cast iron is achieved by producing a structure consisting of graphite embedded in a martensitic matrix through heat treatment.

Flame or induction hardening of grey iron is not so common as furnace hardening because, for adopting the first two methods, a relatively large content of combined carbon is required since very little time is available for carbon to dissolve in austenite. Water is often used as a quenchant with flame or induction hardening where only the outer case is hardened.
Ductile Cast Iron: Spheroidal Graphite (SG) iron

- Ductile cast iron also called as Nodular cast iron, and Spherulitic cast iron.
- Graphite nodules instead of flakes (*in 2D section*)
- Mg (0.03-0.06)%, Ce, Ca (or other spheroidizing) elements are added
- The elements added to promote spheroidization react with the solute in the liquid to form heterogeneous nucleation sites
- The alloying elements are injected into mould before pouring
- It is thought that by the modification of the interfacial energy the ‘c’ and ‘a’ growth direction are made comparable leading to spheroidal graphite morphology
- The graphite phase usually nucleates in the liquid pocket created by the pro-eutectic $\gamma$
- As compared to flaky graphite in grey cast iron, spheroidal graphite does not weaken the matrix considerably. For this reason the mechanical properties of SG iron are superior to gray iron.
- SG iron has tensile strength of 400-700 Mpa, Yield strength 270-390 Mpa, and percentage of elongation 10-20.
- Approx. chemical composition of SG iron is 3.0-3.6%C, 2.0-2.5%Si, 0.6%Mn, 0.04 max P, 0.04 max S, and balance Fe.
Ductile Cast Iron: Spheroidal Graphite (SG) iron

- Ferrite
- Graphite nodules

With Ferritic Matrix
With (Ferrite + Pearlite) Matrix
With Pearlitic matrix
The normalizing, hardening, and austempering heat treatment, which involve Austenitisation, followed by controlled cooling or isothermal reaction, or a combination of the two, can produce a variety of microstructures and greatly extend the limits on the mechanical properties of ductile cast iron.

These microstructures can be separated into two broad classes

- Those in which the major iron-bearing matrix phase is the thermodynamically stable body-centered cubic (ferrite) structure.
- Those with a matrix phase that is a meta-stable face-centered cubic (austenite) structure. The former are usually generated by the annealing, normalizing, normalizing and tempering, or quenching and tempering processes.

The latter are generated by austempering, an isothermal reaction process resulting in a product called austempered ductile iron (ADI).

Other heat treatments in common industrial use include stress-relief annealing and selective surface heat treatment. Stress-relief annealing does not involve major microstructural transformations, whereas selective surface treatment (such as flame and induction surface hardening) does involve microstructural transformations, but only in selectively controlled parts of the casting.
Stress Relieving: 540 - 595°C reduces warping and distortion during subsequent machining.

Annealing: Full feritizing Annealing used to remove carbides and stabilized Pearlite, heat to 900°C, holding long enough to dissolve carbides, then cooling at a rate of 85°C/h to 705°C, and still air cooling to room temperature. Also improves low temperature fracture resistance but reduces fatigue strength.

Normalizing, Quenching, And Tempering: heated to 900°C, held for 3 hours (allowing 1h/25mm or 1h/in of cross section to reach that temperature). The air blasted or oil quenched. Followed by tempering between 540 - 675°C. Used to achieve grade 100-70-03. Hardness’s as high as 255HB, increase short time fatigue strength, decreases fatigue life. Increases tensile and yield strengths at the expense of ductility.

Relationship between austempering temperature and the strength and ductility of a 1.5Ni-03.Mo alloyed ductile iron. Austenitizing temperature was 900°C.
Spheroidal Graphite (SG) iron : Heat treatment

- **AUSTEMPERING**: Used to achieve Austempered Ductile Iron, requires two stages. Stage 1: heating to and holding at 900°C. Stage 2: quenching and isothermally holding at the required austempering temperature, usually in a salt bath. Austempering temperatures shown in figure below.

- **SURFACE HARDENING**: SG iron are also flame or induction hardened. Pearlite type of SG irons are preferred for flame or induction hardening as time required for austenitizing is comparatively small. In the case pearlitic SG iron, tempering is carried out at 595-650°C for 1 hour plus 1 hour per 25 mm of section thickness to remove virtually all internal stresses before going in for flame or induction hardening.

- The possible applications of S.G Iron are very wide. The use of S.G Iron is suggested where improved properties are dictate a replacement of other material or where the use of S.G Iron will permit an improvement in the design.

- Some popular uses of S.G Iron for various engineering application are for – Support bracket for agricultural tractor, Tractor life arm, Check beam for lifting track, Mine cage guide brackets, Gear wheel and pinion blanks and brake drum, Machines worm steel, Flywheel, Thrust bearing, Frame for high speed diesel engine, Four throw crankshaft, etc.,
Spheroidal Graphite (SG) iron : Nodular cast iron

- Ferrite (White)
- Graphite (black)
- Bull's Eye
- Ferrite
- Pearlite (grey)

5 µm
As we discussed earlier that cementite is actually a metastable phase. There is a tendency for cementite to decompose into iron and carbon. This tendency to form free carbon is the basis for the manufacture of malleable cast iron.

The reaction of $\text{Fe}_3\text{C} \rightarrow 3\text{Fe} + \text{C}$ is favored by elevated temperatures, the existence of solid nonmetallic impurities, higher carbon contents, and the presence of elements that aid the decomposition of $\text{Fe}_3\text{C}$.

Categorized into 3 categories: Ferritic, Pearlitic, and Martensitic Malleable Cast Iron.

Ferritic malleable Irons require a two stage annealing cycle. First: converts primary carbides to temper Carbon.

Second: converts Carbon dissolved in Austenite at the first-stage annealing temperature to temper Carbon and Ferrite. Consists of temper Carbon in a matrix of Ferrite. Contain a slight amount of controlled Iron.

Pearlitic: 1st stage identical to that of Ferrite. Casting is slowly cooled to approx $870^\circ\text{C}$. When the combined Carbon content of the Austenite is reduced to about .75% the castings are air cooled. Usually air blasted to avoid the formation of ferrite around the temper Carbon particles. Then, the castings are tempered to specified time.
Stage I

A: Low T structure (Ferrite + Pearlite + Martensite) \(\rightarrow\) \((\gamma + \text{Cementite})\)

B: Graphite nucleation at \(\gamma /\text{Cementite}\) interface
\(\text{(rate of nucleation increased by } C, Si\text{)}\)
\((Si \downarrow \text{solubility of } C \text{ in } \gamma \Rightarrow \uparrow \text{driving force for growth of Graphite})\)

C: Cementite dissolves \(\rightarrow\) C joining growing Graphite plates

- \((940-960)\, ^\circ C\) (Above eutectoid temperature)
- Competed when all Cementite \(\rightarrow\) Graphite

Time for Graphitization in Stage I

Spacing between Cementite and Graphite \(\rightarrow\)
\(\downarrow \text{spacing} \Rightarrow \downarrow \text{time (obtained by faster cooling of liquid)}\)

Addition of Alloying elements
\(\rightarrow\) which increase the nucleation rate of Graphite temper nodules

Si \(\uparrow \Rightarrow t \downarrow\)
Stage II

- (720-730)°C (Below eutectoid temperature)
- After complete graphitization in Stage I → Further Graphitization

- Slow cool to the lower temperature such that \( \gamma \) does not form Cementite
- C diffuses through \( \gamma \) to Graphite temper nodules
  
  (called *Ferritizing Anneal*)
- *Full* Anneal in Ferrite + Graphite two phase region
- *Partial Anneal* (Insufficient time in Stage II Graphitization)
  \( \gamma \rightarrow \) Ferrite is partial and the remaining \( \gamma \) transforms to Pearlite
  \( \Rightarrow \gamma \rightarrow \) Pearlite + Ferrite + Graphite
- If quench after Stage I \( \Rightarrow \gamma \rightarrow \) Martensite (+ *Retained Austenite*(RA))
  
  (*Graphite temper nodules are present in a matrix of Martensite and RA*)

\[
\text{Fe}_3\text{C (WCI) } \xrightarrow{>48\text{ hrs}} \xrightarrow{2\text{ stage heat treatment}} \text{ Graphite Temper Nodules (Malleable Iron)}
\]
Malleable Cast Iron

Pearlitic Matrix

Ferrite (White)

Graphite (black)

Pearlite (grey)

Partially Malleabilized Iron → Incomplete Ferritizing Anneal

Ferritic Matrix

Ferrite (White)

Graphite (black)

10 µm

Fully Malleabilized Iron → Complete Ferritizing Anneal
A relatively recent addition to the family of cast irons is compacted graphite (CGI).

Microstructurally, the graphite in CGI alloys has a worm-like (or vermicular) shape; a typical CGI microstructure. In a sense, this microstructure is intermediate between that of gray iron and ductile iron and, in fact, some of the graphite (less than 20%) may be as nodules.

The chemistries of CGIs are more complex than for the other cast iron types; compositions of Mg, Ce and other additives must be controlled so as to produce a microstructure that consists of the worm-like graphite particles, while at the same time limiting the degree of graphite nodularity, and preventing the formation of graphite flakes. Furthermore, depending on heat treatment, the matrix phase will be pearlite and/or ferrite.

CGI are now being used in a number of important applications – these include: diesel engine blocks, exhaust manifolds, gearbox housings, brake discs for high speed trains and flywheels.
Cr, Mn, Si, Ni, Al

The range of microstructures

Beneficial effect on many properties

- High temperature oxidation resistance
- Corrosion resistance in acidic environments
- Wear/abration resistance

Alloy Cast Irons

- Graphite bearing
- Graphite free
- Excellent resistance to oxidation at high temperatures
- High Cr Cast Irons are of 3 types:
  - 12-28% Cr ➤ matrix of Martensite + dispersed carbide
  - 29-34% Cr ➤ matrix of Ferrite + dispersion of alloy carbides
    \[\text{[(Cr,Fe)_{23}C_6, (Cr,Fe)_7C_3]}\]
  - 15-30% Cr + 10-15% Ni ➤ stable γ + carbides \[\text{[(Cr,Fe)_{23}C_6, (Cr,Fe)_7C_3]}\]
  - Ni stabilizes Austenite structure

Chromium addition (12-35 wt %)

29.3% Cr, 2.95% C
Stabilizes Austenitic structure

↑ Graphitization (suppresses the formation of carbides)

(Cr counteracts this tendency of Ni for graphitization)

↓ Carbon content in Eutectic

Moves nose of TTT diagram to higher times ⇒ easy formation of Martensite

Carbide formation in presence of Cr increases the hardness of the eutectic structure → Ni Hard Cast Irons (4%Ni, 2-8% Cr, 2.8% C)

Good abrasion resistance

Needles of Martensite

Transformation sequence

- Crystallization of primary γ
- Eutectic liquid → γ + alloy carbide
- γ → Martensite
Ni Resist Iron: 15-30% Ni + small amount of Cr:

- Austenitic Dendrites + Graphite plates/flakes + interdendritic carbides due to presence of Cr
- Resistant to oxidation (used in chemical processing plants, sea water, oil handling operations…)

Graphite plates

Dendrites of $\gamma$
Silal Iron (trade name): Alloy CI with 5% Si

- Si allows solidification to occur over larger temperature range → promotes graphitization
- Forms surface film of iron silicate → resistant to acid corrosion
Chilled Cast Iron

- Chilled –iron castings are made by casting the molten metal against a metal chiller, resulting in a surface of white cast iron. This hard, abrasion-resistant white iron surface or case is backed up by a softer gray iron core.

- This case-core structure is obtained by careful control of the overall alloy composition and adjustment of the cooling rate.

Mottled Cast Iron

- Solidifying at a rate with extremes between those for chilled and gray irons, thus exhibiting micro structural and metallurgical characteristics of both

High-Alloy Graphitic Irons

- Produced with microstructures consisting of both flake and nodule structures. Mainly utilized for applications requiring a combination of high strength and corrosion resistance.
Graphite flake - $G_f$
Graphite nodules - $G_n$
Graphite rosettes - $G_r$
Heat treatment of selected Steels

Avala Lava Kumar : D.K.Mishra : Dr.S.K.Badjena
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla -768018
*E-mail : lavakumar.vssut@gmail.com
Stainless Steels

Stainless Steels are a large group of special alloys developed primarily to withstand corrosion. These steels contain chromium in excess of 12% by weight which imparts “stainless” characteristics to iron alloys.

Classification:

- **AISI Grades of stainless steels**

<table>
<thead>
<tr>
<th>Series Designation</th>
<th>Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>2xx</td>
<td>Chromium-Nickel-Manganese; Nonhardenable, Austenitic, Nonmagnetic</td>
</tr>
<tr>
<td>3xx</td>
<td>Chromium-Nickel; Nonhardenable, Austenitic, Nonmagnetic</td>
</tr>
<tr>
<td>4xx</td>
<td>Chromium; Hardenable, Martensitic, Magnetic</td>
</tr>
<tr>
<td>4xx</td>
<td>Chromium; Nonhardenable, Ferritic, Magnetic</td>
</tr>
<tr>
<td>5xx</td>
<td>Chromium; Low chromium; Heat-Resisting</td>
</tr>
</tbody>
</table>
Martensitic Stainless Steels

- These are primarily straight chromium steels with 11.5 to 18% Cr, 0.15% C, 1.25% Mn, and 1%Si.
- Common examples are 403, 410, 416, 420, 440A, 501 & 502 (AISI grades).
- Used for turbine blades and corrosion resistant applications

**Heat Treatment**

- Process Annealing $\rightarrow$ 650 - 760$^\circ$C, $\uparrow$ ductility and machinability
- Austenitizing $\rightarrow$ 925 - 1065$^\circ$C followed by oil quenching or air cooling, $\uparrow$ corrosion resistance and strength

Microstructure of annealed 416 stainless steel etched with Vilella’s reagent

Microstructure of hardened type 403 stainless steel etched with 4% picral-HCl
These are chrome-nickel (3xx type) or chrome-nickel-manganese (2xx type) alloys.
Total content of Ni and Cr is at least 23%.
Difficult to machine but can be improved by addition of selenium or sulfur.
Best high temperature strength and scaling resistance. Hence shows best corrosion resistance.
Used in chemical industry and for household and sanitary fittings.

**Heat Treatment**

- Cold working causes work hardening but hot working can easily be done.
- Annealing at high temperatures → Recrystallization and carbide solution
- Solution treatment → Dissolution of chromium carbides

Microstructure of annealed type 316L austenitic stainless steel etched in 20% HCl, 2% NH4FHF, 0.8% PMP
Ferritic Stainless Steels

- These are primarily straight chromium steels with 14 to 27% Cr. Carbon is restricted both to maintain high toughness and ductility and to prevent austenite formation (As carbon expands the gamma loop).
- These steels can be cold formed easily and hence are used for deep drawn parts such as vessels for food and chemical industries and for architectural and automotive trim.

**Heat Treatment**

- Can be cold or hot worked.
- Annealing → 760 - 966°C, Recrystallization of cold-worked structures → achieves maximum softness, ductility and corrosion resistance.

![Single-phase microstructure of an annealed ferritic stainless steel](image)

Microstructure of annealed ferritic stainless steel containing 26% Cr and 1% Mo, etched electrolytically in 60% HNO$_3$-H$_2$O
Precipitation Hardened Stainless Steels

- Contains Mo, Nb, Ti or Al in addition to basic composition. Ni content is generally less to reduce the stability of austenite.
- Common Grades are: 630/17-4 PH (17% Cr, 4%), 631/17-7 PH, 15-5 PH etc.
- Provides high strength and toughness while maintaining the corrosion resistance of stainless steels. Also shows excellent elevated-temperature performance and are widely used in the aerospace industry.
- Strengthening is accomplished by the precipitation of intermetallic compounds such as Ni₃Al in austenitic or ductile low-carbon martensitic matrices.

Heat Treatment

- These steels are usually solution – annealed followed by air cooling with the resultant transformation of austenite to martensite. After forming ageing (480-620 °C) is carried out to cause precipitation effect.
- More is the ageing temperature, better is the ductility, toughness and resistance to stress corrosion.

Microstructure of 17-4PH alloy solution treated at 1038 °C and aged at 495 °C

Fine, disc-shaped γ’ precipitates

Microstructure of an aged austenitic precipitation-hardening stainless steel

Tempered Martensite
Duplex stainless steels by design have nearly balanced amounts of ferrite and austenite.
Compositions of duplex stainless steels range from 17 to 30% Cr and 3 to 13% Ni. Molybdenum, a ferrite stabilizer, is also typically present.
Shows higher strength and better resistance to stress corrosion. Decrease in ductility at low temperature is compensated by increased rates of strain hardening due to strain-induced transformation of austenite to martensite.
Used in petrochemical industry (for handling wet an dry CO₂, sour gas and oil products), heat exchanges (welded tubing), chemical, industries etc.

Heat Treatment

- Thermomechanical processing is accomplished in the two-phase ferrite austenite fields.
- Amounts of ferrite and austenite formed during hot working or annealing are a function of temperature. Higher temperatures produce larger amounts of ferrite. Hence, hot working temperatures must be kept between 1000 - 1200°C.
Tool steel refers to a variety of carbon and alloy steels that are particularly well-suited to be made into tools. Characteristics include high hardness, resistance to abrasion (excellent wear), an ability to hold a cutting edge, resistance to deformation at elevated temperatures (red-hardness). Tool steel are generally used in a heat-treated state.

<table>
<thead>
<tr>
<th>Defining property</th>
<th>AISI-SAE grade</th>
<th>Significant characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-hardening</td>
<td>W</td>
<td></td>
</tr>
<tr>
<td>Cold-working</td>
<td>O</td>
<td>Oil-hardening</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>Air-hardening; medium alloy</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>High carbon; high chromium</td>
</tr>
<tr>
<td>Shock resisting</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>High speed</td>
<td>T</td>
<td>Tungsten base</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>Molybdenum base</td>
</tr>
<tr>
<td>Hot-working</td>
<td>H</td>
<td>H1-H19: chromium base</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H20-H39: tungsten base</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H40-H59: molybdenum base</td>
</tr>
<tr>
<td>Plastic mold</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>Special purpose</td>
<td>L</td>
<td>Low alloy</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>Carbon tungsten</td>
</tr>
</tbody>
</table>
Tool Steels and their uses

- **Shock resisting tool steels** → Intended for applications requiring toughness and resistance to shock-loading such as hammers, chisels, punches, driver bits and others.

- **Water hardening tool steels** → Shallow hardened and relatively low resistance to softening. They are suitable for woodworking tools, hand-metal cutting tools such as taps and reamers and cutlery.

**Steels for Room Temperature Use (Classified according to their quenching media)**

- **Water hardened grades (W)** → Plain carbon steels with 0.6-1.0 %C. These have a low hardenability, ie., martensite only to a depth of 0.5 in. V can be added (forms V₄C₃) to improve the hardness and wear resistance of these steels.

- **Shock resistant grades (S)** → Contain small amounts of Cr or Mo and are quenched in oil. They have lower C contents (0.5%) to improve impact strength.

- **Oil hardened grades (O)** → Small percentages of Cr and W with 0.9 %C. They have medium hardness and are used to short run cold forming dies.

- **Air hardening grades (A)** → Greater amounts of Cr and Mo and 1 %C. Used for complicated shapes and thread rolling. Mo and W are relatively expensive so they are only added in small amounts to give much improved hardenability.

- **High carbon, high Cr grades (D grade)** → 12 %Cr and 1.5-2.25 %C are extremely wear resistant and used for long run dies and for gauges. Chromium is a relatively low cost addition for increasing hardenability with the excess Cr, Cr₂₃C₆ is also formed, which improves wear resistance.
Tool Steels and their uses

- Chromium hot working steels (H grades) → 5-7% Cr, 0.4-1.0% V, 1.5-7.0% W, 1.5% Mo, 0.35% C. Medium hot working for Mg and Al extrusion die-casting dies.
- Tungsten hot working steels (H) → 9.5-12% W, 3.5-12.0% Cr, 0.35% C. Hot working, extrusion and forging dies for brass, nickel and steel.
- Tungsten high speed steel (T) → 12-18% W, 4.0% Cr, 1-5% V, 0.7-1.5% C. Original high speed (HS) cutting steel with excellent HT wear resistance.
- Molybdenum HS steel (M) → 3.5-8.0% Mo, 1.5-6.0% W, 4.0% Cr, 1-5% V, 5% Co, 0.8-1.5% C. Used for 85% of US cutting steels before the advent of ceramic cutting tools.

Heat Treatment Processes

Schematic diagram of tool steel processing up to the final hardening heat treatment
Steels possessing high elastic limit, toughness and fatigue strength are suitable for manufacturing springs.

Depending on the service conditions, a number of steels can be used for making springs.

These desirable properties of spring can be achieved firstly by a higher carbon content or with suitable alloying elements, and secondly by heat treatment. Steel springs are used in hard, high strength condition. To attain these properties springs are hardened and tempered.

High carbon steels are the cheapest among all the grades of spring steels. These steels are used in either hardened and tempered condition or in patented and cold-drawn conditions.

**Heat Treatment Processes**

Heat Treatment Cycle for Spring Steel Treatment
The Oxford English Dictionary defines a bearing as a part of a machine that allows one part to rotate or move in contact with another part with as little friction as possible.

Additional functions include the transmission of loads and enabling the accurate location of components. A bearing may have to sustain severe static as well as cyclic loads while serving reliably in difficult environments.

Steels are well-suited in this context, and in their many forms, represent the material of choice in the manufacture of bearings.

Definitions of directions. The over-rolling direction is that in which the contact point between the ball and raceway moves, relative to the inner ring. Notice that the circumferential section is normal to the circumferential direction. The axial and radial sections would similarly be on planes which are normal to the respective axial and radial directions. The contact angle is important in bearing design.

Metallurgical and engineering requirements which are necessary features of bearing steels

- Hardness
- Strength
- Fatigue: rolling contact, axial loading, crack growth
- Toughness
- Hydrogen resistance
- Ductility
- Corrosion resistance
- Reliability
- Hardenability
- Cleanliness
- Ability to manufacture: machining, forming, forging, grinding, heat-treatments, dimensional control, tolerance to variations
- Through life cost
EFFECT OF RETAINED AUSTENITE: A quenched high-carbon chromium bearing steel contains retained austenite in a range of several % to 15%, though this percentage can vary depending on the heating temperature before quenching. Because retained austenite is essentially a soft, unstable structure, it has been believed that too much retained austenite in a bearing steel material will cause the material to be less hard and more wear-prone as well as lead to greater deformation from aging (in other words, poorer dimensional stability). Therefore, people believed that a lower retained austenite content is favorable.

CARBONITRIDING PROCESS: In carbonitriding process, propane or butane is fired to generate reformed carburizing gas into which 5-15% of ammonia gas is added, thereby in the so formed atmosphere, C and N are allowed to simultaneously enter and get diffused in a bearing steel material.

Nitrogen diffused in the surface layer stabilizes retained austenite. Consequently, the amount of retained austenite is greater after quenching, and, at the same time, the solution of nitrogen helps enhance resistance to temper softening, thereby the rolling contact fatigue life of bearing steel is extended.

CRYSTAL GRAIN REFINEMENT PROCESS: As described above, the technologies for longer bearing life so far attempted use effects of either retained austenite or nitrogen-derived enhanced resistance to temper softening. In addition to these longer bearing life-endowing material factors, a new technology has been developed since the year 2000, wherein the new technology features adoption of a novel longer bearing life-endowing factor that is based on crystal grain refining technique.
**Heat treatment cycles for selected bearing steels**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Treatment</th>
<th>Pre-heat/time</th>
<th>Austenitization</th>
<th>Warm oil quenching (O.Q.)</th>
<th>Cryogenic quench</th>
<th>Tempering step. (T.S.)</th>
<th># of T.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>52100</td>
<td>1</td>
<td>...</td>
<td>1550 °F (843 °C)/30 min</td>
<td>120-130 °F (49-55 °C)</td>
<td>−120 °F</td>
<td>325 °F (163 °C)</td>
<td>2</td>
</tr>
<tr>
<td>52100</td>
<td>2</td>
<td>...</td>
<td>1550 °F (843 °C)/30 min</td>
<td>O.Q.</td>
<td>(−49 °C)/1 HR</td>
<td>325 °F (163 °C)</td>
<td>2</td>
</tr>
<tr>
<td>52100</td>
<td>3</td>
<td>...</td>
<td>1650 °F (899 °C)/30 min</td>
<td>O.Q.</td>
<td>...</td>
<td>325 °F (163 °C)</td>
<td>2</td>
</tr>
<tr>
<td>52100</td>
<td>4</td>
<td>...</td>
<td>1650 °F (899 °C)/30 min</td>
<td>O.Q.</td>
<td>...</td>
<td>275 °F (135 °C)</td>
<td>2</td>
</tr>
<tr>
<td>440C</td>
<td>1</td>
<td>1550 °F (843 °C)/30 min</td>
<td>1950 °F (1065 °C)/15 min</td>
<td>120-130 °F</td>
<td>−120 °F</td>
<td>350 °F (177 °C)</td>
<td>2</td>
</tr>
<tr>
<td>440C</td>
<td>2</td>
<td>1550 °F (843 °C)/30 min</td>
<td>1950 °F (1065 °C)/15 min</td>
<td>O.Q.</td>
<td>(−49 °C)/1 HR</td>
<td>350 °F (177 °C)</td>
<td>2</td>
</tr>
<tr>
<td>440C</td>
<td>3</td>
<td>1550 °F (843 °C)/30 min</td>
<td>2050 °F (1121 °C)/15 min</td>
<td>O.Q.</td>
<td>...</td>
<td>350 °F (177 °C)</td>
<td>2</td>
</tr>
<tr>
<td>440C</td>
<td>4</td>
<td>1550 °F (843 °C)/30 min</td>
<td>2050 °F (1121 °C)/15 min</td>
<td>O.Q.</td>
<td>...</td>
<td>275 °F (135 °C)</td>
<td>2</td>
</tr>
<tr>
<td>REX20</td>
<td>1</td>
<td>1550 °F (843 °C)/30 min</td>
<td>2175 °F (1190 °C)/15 min</td>
<td>120-130 °F</td>
<td>−120 °F</td>
<td>1000 °F (537 °C)</td>
<td>3</td>
</tr>
<tr>
<td>REX20</td>
<td>2</td>
<td>1550 °F (843 °C)/30 min</td>
<td>2175 °F (1190 °C)/15 min</td>
<td>O.Q.</td>
<td>(−49 °C)/1 HR</td>
<td>1000 °F (537 °C)</td>
<td>3</td>
</tr>
<tr>
<td>REX20</td>
<td>3</td>
<td>1550 °F (843 °C)/30 min</td>
<td>2220 °F (1215 °C)/15 min</td>
<td>O.Q.</td>
<td>...</td>
<td>1000 °F (537 °C)</td>
<td>3</td>
</tr>
<tr>
<td>REX20</td>
<td>4</td>
<td>1550 °F (843 °C)/30 min</td>
<td>2220 °F (1215 °C)/15 min</td>
<td>O.Q.</td>
<td>...</td>
<td>800 °F (427 °C)</td>
<td>3</td>
</tr>
<tr>
<td>CRU80</td>
<td>1</td>
<td>1550 °F (843 °C)/30 min</td>
<td>2100 °F (1149 °C)/15 min</td>
<td>120-130 °F</td>
<td>−120 °F</td>
<td>975 °F (524 °C)</td>
<td>3</td>
</tr>
<tr>
<td>CRU80</td>
<td>2</td>
<td>1550 °F (843 °C)/30 min</td>
<td>2100 °F (1149 °C)/15 min</td>
<td>O.Q.</td>
<td>(−49 °C)/1 HR</td>
<td>975 °F (524 °C)</td>
<td>3</td>
</tr>
<tr>
<td>CRU80</td>
<td>3</td>
<td>1550 °F (843 °C)/30 min</td>
<td>2175 °F (1190 °C)/15 min</td>
<td>O.Q.</td>
<td>...</td>
<td>975 °F (524 °C)</td>
<td>3</td>
</tr>
<tr>
<td>CRU80</td>
<td>4</td>
<td>1550 °F (843 °C)/30 min</td>
<td>2175 °F (1190 °C)/15 min</td>
<td>O.Q.</td>
<td>...</td>
<td>500 °F (260 °C)</td>
<td>3</td>
</tr>
</tbody>
</table>
Maraging Steels are ultrahigh strength steels based on Fe-Ni system. They derive their excellent properties due to combination of two solid state reactions: **MAR + AGEING**

⇒ Meaning, Martensitic transformation in Fe-Ni system and its subsequent ageing.

Fe-Ni martensite serves as an excellent host for a number of alloying elements which strengthen the steel on subsequent ageing.

### Excellent Mechanical Properties

1. High strength and high strength-to-weight ratio.
2. High plane strain fracture toughness.
3. High notch toughness
4. Maintains high strength up to at least 350°C.

### Good Processing and Fabrication Characteristics

1. Very good Hot and cold formability.
2. Work-hardening rates are low.
3. Excellent weldability, either in the annealed or aged condition.
4. Good machinability.

### Simple Heat Treatment

1. No quenching required. Softened and solution treated by air cooling from 820-900°C.
2. Hardened and strengthened by ageing at 450-500°C.
3. No decarburization effects
4. Dimensional changes during age hardening are very small – possible to finish machine before hardening.
5. Can be surface hardened by nitriding.
Austenite (γ) ↔ Martensite (α) transformation in Fe-Ni systems depend on Ni content

- Fe-Ni transformation diagram developed by John & Pumphrey
- Gilbert & Owen established that at least 18% Ni was essential to favour martensitic transformation in Fe-Ni system
- At lower concentration of Ni, because of higher temperature, thermodynamic conditions do not favour diffusion less transformation and α - ferrite is formed

- The nature of transformation, nevertheless, also depends on other alloying elements and interstitials.
- Blocky type of martensite has been found to occur over a wide range of Nickel (10-25%).
- In Maraging Steels, on solution treatment, the austenite transforms to blocky martensite having bcc crystal structure irrespective of cooling rate.
- Microstructure produced by annealing 1 hr at 800⁰C; 100% bcc phase (Figure a)
- Microstructure produced by Annealing 1 hr at 1240⁰C; 100% bcc phase. (Figure b)
Maraging Steels: Martensitic Transformation

Microstructure produced by annealing 1 hr at 800°C; 100% bcc phase.

Microstructure produced by annealing 1 hr at 1240°C; 100% bcc phase.
Presence of large hysteresis gap between α ↔ γ transformation on cooling and heating has made it possible to reheat transformed 'α' to a sufficiently higher temperature for aging.

On aging rapid increase in hardness and other mechanical properties takes place.

The optimum temperature and time to get best combination of strength, toughness in 18 Ni-Co-Mo type Maraging steels have been found to be 480°C in 3-4 hrs.

Fe-Ni Martensite serves as an excellent host for a number of alloying elements, which on ageing results in precipitation of Intermetallics as second phase particles in the soft α matrix.

Effect of maraging steel on hardness of 18% Ni steel. Initially annealed at 815°C.
These fine particles act as obstacles to dislocation movement and are responsible for increase in strength.

It is generally agreed that precipitation stages involved in these type of steels are;

a. Uniformly precipitated Mo-rich zones in under aged condition
   
   (<450°C and smaller duration)

b. Metastable Ni₃Mo as primary precipitate at temperature as one
   
   (>450°C for shorter period)

c. Ni₃Ti/σ-Fe Ti as Secondary precipitate

d. Ni₃Ti and stable Fe₂Mo on longer aging at 480°C

e. Stable Fe₂Mo coarse precipitate and reversed austenite in over aged condition.
One of the major attractive feature of maraging steels is their simple heat treatment. The alloys are normally solution treated at 820°C.

Solution annealing at 820°C is sufficient to give complete recrystallisation of hot worked structures and ensures fully austenitic phase from which martensite can be formed on cooling.

Soaking for 1 hr. for every 25mm thick section is employed. Air-cooling from the solution annealing temperature is adequate to transform austenite to fully martensitic structure throughout the cross-section.

The above also implies that there is no hardenability band in this type of alloys. The high strength properties are developed in relatively short time on ageing at 480°C, the standard ageing time being 3-4 hrs.

The over ageing tendency at this temperature is very slow even after 100 hrs. of ageing.

Since the steel contains very low carbon there is no decarburisation in these steels while heat treating.

Maraging steels components can be finish machined in soft annealed condition and subsequently age-hardened.

Mechanism of maraging steel is such that minimum dimensional changes are ensured.

Absence of retained austenite further ensures that there is no dimensional change in service. During maraging treatment, a very small uniform contraction occurs.
A general description of HSLA steel is as that containing:
1. low carbon (0.03–0.25%) content to obtain good toughness, formability, and weldability,
2. one or more of the strong carbide-forming microalloying elements (MAEs) (e.g., V, Nb, or Ti),
3. a group of solid solution strengthening elements (e.g., Mn up to 2.0% and Si), and
4. one or more of the additional MAEs (e.g., Ca, Zr) and the rare earth elements, particularly Ce and La, for sulfide inclusion shape control and increasing toughness.

In many other HSLA steels, small amounts of Ni, Cr, Cu, and particularly Mo are also present, which increase atmospheric corrosion resistance and hardenability.

A very fine ferrite grain structure in the final product produced by a combination of controlled rolling and controlled cooling with an optimum utilization of microalloying additions, in HSLA steels, is an important factor in simultaneously increasing strength and toughness and decreasing the ductile–brittle transition temperature (to as low as -70°C).

Carbides (NbC, VC, TiC), nitrides (TiN, NbN, AlN), and carbo-nitrides (e.g., V(C,N), Nb(C,N), (Nb,V) CN, (Nb,Ti) CN) are the dispersed second-phase particles that act as grain size refiners or dispersive strengthening phases in HSLA steels.

HSLA steels are successfully used as ship, plate, bar, structural sections, and forged bar products, and find applications in several diverse fields such as oil and gas pipelines; in the automotive, agricultural, and pressure vessel industries, in offshore structures and platforms and in the constructions of crane, bridges, buildings, ship buildings, railroad, tank cars, and power transmission and TV towers.
Classification of HSLA steels

Weathering steels

- Steels containing ~0.1% C, 0.2–0.5% Cu, 0.5–1.0% Mn, 0.05–0.15% P, 0.15–0.90% Si, and sometimes containing Cr and Ni, exhibiting superior atmospheric corrosion resistance. Typical applications include railroad cars, bridges, and unpainted buildings.

Control-rolled steels

- Steels designated to develop a highly deformed austenite structure by hot rolling (according to a predetermined rolling schedule) that will transform to a very fine equiaxed ferrite structure on cooling.

Pearlite-reduced steels

- Steels strengthened by very fine-grained ferrite and precipitation hardening but with low carbon content, and therefore exhibiting little or no pearlite in the microstructure.

Dual-Phase steels

- Steel comprising essentially fine dispersion of hard strong martensite but sometimes also retained austenite or even bainite in a soft and fine-grained ferrite matrix. The volume function of martensite is about 20–30%. Steels are characterized by continuous yielding (i.e., no yield point elongation), low yield stress (the YS/UTS ratio being around 0.50), high UTS, superior formability, and rapid initial work-hardening rate. Additionally, they possess greater resistance to onset of necking (i.e., plastic instability) in the uniaxial sheet material forming process to provide large uniform strain.
**Micro alloyed steels**

- Conventional HSLA steels containing V, Ti, or Nb, as defined above. They exhibit discontinuous yielding behavior.

**Acicular Ferrite steels**

- Very low-carbon (typically 0.03–0.06% ) steels with enough hardenability (by Mn, Mo, Nb, and B additions) to transform on cooling to a very fine, high-strength acicular ferrite structure rather than the usual polygonal ferrite structure. In addition to high strength and good toughness, these steels have continuous yielding behavior.

**Low carbon bainite steels**

- Steels are strengthened by bainite, with very fine grains and precipitations. They contain 0.02–0.2% C, 0.6–1.6% Mn, 0.3–0.6% Mo, and MAEs (such as V, Nb, Ti, and B), usually containing 0.4–0.7% Cr. The yield strength of these steels is higher than 490 MPa, with good toughness.

**Low carbon martensite steels**

- Steels are strengthened by martensite with high hardenability (by addition of Mo, Mn, Cr, Nb, and B) and fine grains (by Nb addition). These steels contain 0.05–0.25% C, 1.5–2.0% Mn, 0.20–0.50 Mo, and MAEs (such as Nb, Ti, V, and B). Some steels containing small amounts of Ni, Cr, and Cu, after rolling or forging, and directly quenching and tempering attain a low-carbon martensite structure with high yield strength (760–1100 MPa), high toughness (CVN 50–130J), and superior fatigue strength.
Dual – Phase (DP) steels were developed in the mid-seventies in order to satisfy the increasing needs of automotive industry for new high strength steels, which combine significant weight reduction improved crash performance, while keeping the manufacturing costs at affordable levels.

Duel-phase steels are characterized by a microstructure consisting of a fine dispersion of hard martensite particles in a continuous, soft, ductile ferrite matrix. The term ‘dual-phase’ refers to the presence of essentially two phases, ferrite and martensite, in the microstructure, although small amount of bainite, pearlite and retained austenite may also be present.

Irrespective of the chemical composition of the alloy, the simplest way to obtain a dual phase ferritic-martensitic steel is intercritical annealing of a ferritic-pearlitic microstructure in the $\alpha + \gamma$ two phase field. Followed by a sufficiently rapid cooling to enable the austenite to martensite transformation.

Three basic approaches exist for the commercial production of dual phase steels

a) The as-hot-rolled, where the dual phase microstructure is developed during the conventional hot-rolling cycle by careful control of chemistry and processing conditions.

b) The continuous annealing approach, where hot-or cold rolled steel strip is uncoiled and annealed intercritically to produce the desired microstructure.

c) The batch- annealing, where hot or cold-rolled material is annealed in the coiled condition.
Dual Phase Steels

- Box or batch annealing was mainly considered for economical and practical reasons by steel makers where continuous facilities were not available.
- Dual-phase steels could be obtained by means of batch annealing in the intercritical region for approximately 3h to ensure homogeneity, followed by very slow cooling.
- Due to extremely low cooling rates, much higher alloying contents were necessary to achieve the desired hardenability (i.e., 2.5% Mn, 1.5% Si, 1.0% Cr).
- On the other hand, dual-phase steel production in the hot strip mill demands precise control of the $\gamma \rightarrow \alpha$ transformation, because the transformation starts from single phase austenite.
- The determination of an accurate CCT diagram via dilatometry, where the influences of alloying elements, heat treatment conditions and desired properties are integrated, is of great importance for the success of process.
- The critical point is the “correction” of the CCT diagram to include the presence of strain in austenite (to simulate real process conditions).
- The use of continuous annealing lines (CAL) offers the advantages of high production rates, better uniformity of the steel properties and, furthermore, the possibility of using lower alloyed steels (having lean chemistry).
- In continuous annealing lines three types of cooling are utilized, (a) water – quenched, (b) ges-jet cooling and (c) air cooling. The use of CAL equipped with water quenching facilities makes possible an easy and economical production of dual phase high strength steel.
- The basic heat cycle involves intercritical annealing and subsequent water quenching to form the ferritic – martensitic microstructure. If necessary (according to application), a tempering stage follows.
Dual Phase Steels

Figure: (a) Intercritical annealing, (b) Repeated heating cycles oscillating between the $\alpha+\gamma$ and $\gamma$ phase fields.

Figure: Production of dual phase steels by Intercritical annealing.
Heat Treatment of Common Nonferrous Alloys

Avala Lava Kumar : D.K.Mishra : Dr.S.K.Badjena
Department of Metallurgical & Materials Engineering (MME)
Veer Surendra Sai University of Technology (VSSUT), Burla -768018

*E-mail : lavakumar.vssut@gmail.com
Metallic materials, when considered in a broad sense, may be divided into two large groups, ferrous and non-ferrous. The ferrous materials are iron-based, and the non-ferrous materials have some element other than iron as the principal constituent. The bulk of the nonferrous materials is made up of the alloys of copper, aluminum, magnesium, nickel, tin, lead, titanium and zinc. Other nonferrous metals and alloys that are used to a lesser extent include cadmium, molybdenum, cobalt, zirconium, beryllium, tantalum, and the precious metals gold, silver and the platinum group.

→ This chapter will be concerned with the more important nonferrous metals and alloys. These are as follows.

- Copper and copper alloys (Bronze and Brass)
- Aluminum and aluminum alloys
- Titanium and Titanium alloys
- Superalloys (Mainly Ni-base)
Copper and Copper alloys
Classification

Copper and Copper Alloys

- Pure Cu
- Cu- alloys
  - Brasses
  - Cupronickel
  - Cast alloys
  - Deformable alloys

Classification

Deformable alloys Cast alloys

338
The properties of copper that are most important are high electrical and thermal conductivity, good corrosion resistance, machinability, strength, and easy fabrication.

Most of the copper that is used for electrical conductors contains over 99.9 percent copper and is identified as electrolytic tough-pitch copper (ETP) or oxygen-free high-conductivity copper (OFHC).

ETP copper contains from 0.02 to 0.05 percent oxygen, which is combined with copper as the compound cuprous oxide (Cu$_2$O). As cast, copper oxide and copper form an interdendritic mixture. After working and annealing, the interdendritic network is destroyed, and the strength is improved.

Oxygen-free copper is used in electronic tubes or similar applications because it makes a perfect seal to glass.

**Arsenical copper**: 0.3 % arsenic has improved resistance to special corrosive conditions.

**Free cutting copper**: 0.6 % tellurium excellent machining properties.

**Silver – bearing copper**: 7 to 30 oz/ton. Silver raises the Recrystallization temperature of copper, thus preventing softening during soldering of commutators.

Heat treatment processes which are relevant to copper and copper alloys include homogenizing, annealing and stress relieving.
In the case of pure copper, the heat treatment processes which is adopted is annealing.

The purpose of annealing is to achieve the original ductility and softness in cold-worked copper.

Pure copper is annealed at about 600ºC. After holding at this temperature for some time, copper is quenched in cold water.

Annealing temperature of copper is higher than its recrystallization temperature (270ºC).

Water quenching removes scale formation and gives clean surface of copper.

Annealing above 600ºC does not have any significant effect on copper except that grain coarsening occurs.

Grain coarsening is undesirable since it reduces ductility.
Brasses are essentially alloys of copper zinc. Some of these alloys have small amounts of other elements such as lead, tin, or aluminum.

The portion of the binary copper zinc phase diagram which is applicable to commercial alloys is shown in Fig.

The solubility of zinc in the alpha (\(\alpha\)) solid solution increases from 32.5 % at 910 °C to about 39 % at 455 °C.

Since copper is F.C.C, the \(\alpha\) solid solution is F.C.C the beta (\(\beta\)) phase is B.C.C electron compound and undergoes ordering, indicated by a dot-dash line, in the region of 455 to 470 °C.

On cooling in this temperature range the B.C.C \(\beta\) phase, with copper and zinc atoms randomly dispersed at lattice points, changes continuously to the ordered structure \(\beta'\), which is still B.C.C.
But with the copper atoms at the corners and zinc atoms at the centers of the unit cubes. The ordering reaction is so rapid that it cannot be retarded or prevented by quenching. The best combination of strength and ductility is obtained in 70Cu-30Zn brass.

The commercial brasses may be divided into two groups, brasses for cold working (α brasses) and brasses for hot working (α plus β brasses).

1. These contain 20-36 % Zn
2. It is common practice to stress relief anneal these brasses after severe cold working to prevent season cracking.
3. Season cracking or stress corrosion cracking is due to the high residual stresses left in the brass as a result of cold working.
4. Dezincification and Plug-type dezincification
5. Most widely used yellow α brasses are cartridge brass (70Cu-30Zn) and yellow brass (65Cu-35Zn)

1. These contain between 5 and 20 percent zinc.
2. The most common low zinc brasses are gliding metal (95Cu-5Zn), commercial, commercial bronze (90Cu-10Zn), red brass (85Cu-15Zn) and low brass (80Cu-20Zn).
These contain from 54 to 62% copper. And this alloy consist of two phases, \( \alpha \) and \( \beta' \). The \( \beta' \) phase is harder and more brittle at room temperature than \( \alpha \); therefore, these alloys are more difficult to cold work than the \( \alpha \) brasses.

At elevated temperatures the \( \beta \) phase becomes very plastic, and since most of these alloys may be heated into the single phase \( \beta \) region, they have excellent hot-working properties.

The most widely used \( \alpha+\beta' \) brass is *muntz metal* (60Cu-40Zn), which has high strength and excellent hot-working properties.

Muntz metal is used in condenser heads, perforated metal and architectural work.
Free-cutting brass (61.5Cu-35.5Zn-3Pb) has the best machinability of any brass combined with good mechanical and corrosion resistant properties.

Forging brass (60Cu-38Zn-2Pb) has the best hot working properties of any brass and is used for hot forgings, hardware and plumbing parts.

Architectural bronze (57Cu-40Zn-3Pb) has excellent forging and free matching properties.

Naval brass (60Cu-39.25Zn-0.75Sn), also known as tobin bronze, has increased resistance to salt water corrosion and is used for condenser plates, welding rod, propeller shafts, piston rods, and valve systems.

Manganese bronze (58.5Cu-39Zn-1.4Fe-1Sn-0.1Mn), really a high-zinc brass, has high strength combined with excellent wear resistance and is used for clutch disks, extruded shapes, forgings, pump rods, shafting rod, valve stems, and welding rod.

Cast brasses The previous discussion was concerned primarily with wrought brasses, which are mainly binary alloys of copper and zinc. The cast brasses are similar in name to the wrought brasses but usually contain appreciable amounts of other alloying elements. Tin may be present from 1 to 6 percent and lead from 1 to 10 percent; some alloys may contain iron, manganese, nickel and aluminium.
Like pure copper, brasses are also subjected to recrystallization annealing treatment after cold working.

By annealing above recrystallization temperature, the original degree of ductility and toughness can be restored in the cold-worked brass.

Annealing may be carried out by heating the cold-worked brass at a temperature between 650ºC and 700ºC, followed by cooling at any suitable rate.

Controlled atmosphere is often used while annealing to avoid excessive oxidation and discoloration of the surface of the brass.

A low temperature (300ºC) annealing heat treatment may be given to brass articles for about one hour to remove internal stresses.

Such treatment reduces the tendency for season cracking. By low temperature annealing, tensile strength is maintained within acceptable limits.
The term bronze was originally applied to the copper-tin alloys; however, the term is now used for any copper alloy, with the exception of copper-zinc alloys, that contains up to approximately 12% of the principle alloying element.

Bronze, as a name, conveys the idea of a higher-class alloy than brass, and it has been incorrectly applied to some alloys that are really special brasses.

Commercial bronzes are primarily alloys of copper and tin, aluminum, silicon, or beryllium. In addition, they may contain phosphorus, lead, zinc or nickel.

**Tin Bronzes**

These are generally referred to as *phosphor bronzes* since phosphorous is always present as a deoxidizer in casting.

The usual range of phosphorus content is between 0.01 and 0.5%, and of tin between 1 and 11 percent.

The copper-rich portion of the copper-tin alloy system is shown in next page. The $\beta$ phase forms as the result of a peritectic reaction at 798 °C.

At 586 °C, the $\beta$ phase undergoes a eutectoid reaction to form the eutectoid mixture ($\alpha+\gamma$). At 520°C, gamma ($\gamma$) also undergoes a eutectoid transformation to ($\alpha+\delta$).
The diagram also indicates the decomposition of the δ phase. This takes place by a eutectoid reaction at 350 °C forming (α+ε). This reaction is so sluggish that in commercial alloys, the epsilon (ε) phase is nonexistent.

The slope of the solvus line below 520 °C shows a considerable decrease in the solubility of tin in the α phase.

The precipitation of the δ and ε phase due to this change in solubility is slow that, for practical purposes, the solvus line is indicated by the vertical dotted line below 520 °C.

For this reason, slow cooled cast tin bronzes containing below 7% tin generally show only a single phase, the α solid solution.

There is some of the δ phase in most castings containing over 7 percent tin. The phosphor bronzes are characterized by high strength, toughness, high corrosion resistance and freedom for season cracking.
The copper-rich portion of the copper-silicon alloy system is shown in Fig. The solubility of silicon in the $\alpha$ phase is 5.3% at 850°C and decreases with temperature.

The eutectoid reaction at 555°C is very sluggish, so that commercial silicon bronzes, which generally contain less than 5% Si, are single phase alloys.

Silicon bronzes are the strongest of the work-hardenable copper alloys. They have mechanical properties comparable to those of mild steel and corrosion resistance comparable to that of copper.

They are used for tanks, pressure vessels, marine construction, and hydraulic pressure lines.
The maximum solubility of aluminum in the $\alpha$ solid solution is approximately 9.5% at 565ºC to form the ($\alpha+\gamma_2$) mixture.

Most commercial aluminum bronzes contain 4 and 11 percent aluminum. Those alloys containing up to 7.5% Al are generally single-phase alloys, while those containing between 7.5 and 11% aluminum are two phase alloys. Other elements such as iron, nickel, manganese, and silicon are frequently added to aluminum bronzes.

The single-phase aluminum bronzes show good cold working properties with good corrosion resistance to atmospheric and water attack.

The $\alpha+\beta$ aluminum bronzes are interesting because they can be heat treated to obtain structures similar to those in steel.
These are copper-nickel alloys that contain up to 30% nickel. The copper-nickel binary phase diagram shows complete solubility, so that all cupronickels are single-phase alloys.

They are not susceptible to heat treatment and may have their properties altered only by cold working.

The cupronickel alloys have high resistance to corrosion fatigue and also high resistance to the corrosive and erosive action of rapidly moving sea water.

They are widely used for condenser, distiller, evaporator and heat exchanger tubes for naval vessels and coastal power plants.
Heat Treatment of Bronzes

- As in the case of aluminium alloys, beryllium bronzes (Cu-Be alloys) respond to precipitation heat treatment. Other types of bronzes are not given any heat treatment except annealing at about 500°C.

- Beryllium bronzes contain 1.5-2.25% beryllium. The solid solubility of beryllium in copper increases with temperature from less than 1% at room temperature to more than 2% at 815°C.

- Due to decrease in solid solubility with decrease in temperature, coupled with the possibility of quenching super saturated solid solution and formation of precipitates with coherency, these alloys are amenable to precipitation heat treatment which greatly improves mechanical properties such as strength and hardness.

- Copper beryllium alloys are solutionized at 800°C for about half an hour, followed by quenching in water. They are aged at a temperature between 300-320°C for a period of 2-4 hours.

- Aging temperature precipitates second phase particles (γ-phase) uniformly in the matrix. With this process, the hardness of the order of 200-400 BHN can be attained, depending on aging time.

- Tensile strength and yield strength also increase. By suitable heat treatment and cold working, tensile strength as high as 1400 Mpa can be attained.
Aluminum alloys
“Where ever weight is the enemy
Where ever appearance matters
Where ever durability is required”

The answer is Aluminum & its alloys
Aluminum and its alloys possess many attractive characteristics including light weight, high thermal and electrical conductivities, a nonmagnetic nature, high reflectivity, high resistance to corrosion, reasonably high strength with good ductility and easy fabrication.

Nevertheless, probably the most important characteristic of aluminum is its low density, which is about one-third that of steels and copper alloys. Because of this, certain aluminum alloys have a better strength-to-weight ratio than high-strength steels.

Among the many alloying elements added to aluminum, the most widely used are copper, silicon, magnesium, zinc, and manganese.

These are used in various combinations, and in many cases they are used together with other additions to produce classes of age hardening, casting, and work hardening alloys.

Most casting alloys contain silicon, which improves the fluidity and mold-filling capacity of aluminum alloys and reduces their susceptibility to hot cracking and the formation of shrinkage cavities during solidification.

Work hardening alloys frequently contain Mn and Mg, which form a fine dispersion of intermetallic phases and/or impart solid-solution strengthening.

Basically Al alloys are two types Wrought alloys (Heat treatable and Non heat treatable) and Cast alloys.
Principle groups of aluminium alloys

Al - Zn - Mg - Cu
Age-Hardening alloys
Al-Cu
Al-Cu-Mg
Al-Mg-Si
Al-Zn-Mg
Al-Zn-Mg-Cu
Casting alloys
Al-Si
Al-Si-Cu
Al-Mg
Al-Mn
Work Hardening alloys
## Aluminium alloy designation system

<table>
<thead>
<tr>
<th>ALLOY GROUP</th>
<th>MAJOR ALLOYING ELEMENTS</th>
<th>EXAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA 1XXX</td>
<td>Min. 90% pure Al.</td>
<td>AA 1050</td>
</tr>
<tr>
<td>AA 2xxx</td>
<td>Copper</td>
<td>AA 2014, AA 2024</td>
</tr>
<tr>
<td>AA 3XXX</td>
<td>Manganese</td>
<td>AA 3003</td>
</tr>
<tr>
<td>AA 4XXX</td>
<td>Silicon</td>
<td>AA 4030</td>
</tr>
<tr>
<td>AA 5XXX</td>
<td>Magnesium</td>
<td>AA 5083</td>
</tr>
<tr>
<td>AA 6XXX</td>
<td>Magnesium+Silicon</td>
<td>AA 6061</td>
</tr>
<tr>
<td>AA 7XXX</td>
<td>Zinc</td>
<td>AA 7075, AA 7175</td>
</tr>
<tr>
<td>AA 8XXX</td>
<td>Others</td>
<td>AA 8020</td>
</tr>
</tbody>
</table>

### WROUGHT ALLOYS
<table>
<thead>
<tr>
<th>Temper Designation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>As fabricated</td>
</tr>
<tr>
<td>O</td>
<td>Annealed</td>
</tr>
<tr>
<td>H</td>
<td>Strain hardened</td>
</tr>
<tr>
<td>H1</td>
<td>Strain hardened only</td>
</tr>
<tr>
<td>H2</td>
<td>Strain hardened and then partially annealed</td>
</tr>
<tr>
<td>H3</td>
<td>Strain hardened and stabilized</td>
</tr>
<tr>
<td>T</td>
<td>Thermally treated with or without supplementary strain hardening</td>
</tr>
<tr>
<td>T1</td>
<td>Cooled from elevated temperature shaping process and naturally aged</td>
</tr>
<tr>
<td>T2</td>
<td>Cooled from hot working temperature + cold work + natural aging</td>
</tr>
<tr>
<td>T3</td>
<td>Solution heat treated + water quenched + cold worked + natural aging</td>
</tr>
<tr>
<td>T4</td>
<td>Solution heat treated + water quenched + natural aging</td>
</tr>
<tr>
<td>T5</td>
<td>Cooled from elevated temperature shaping process and artificially aged</td>
</tr>
<tr>
<td>T6</td>
<td>Solution heat treated + water quenched + artificial aging</td>
</tr>
<tr>
<td>T7</td>
<td>Solution heat treated + water quenched + stabilized</td>
</tr>
<tr>
<td>T8</td>
<td>Solution heat treated + water quenched + cold worked + artificially aged</td>
</tr>
<tr>
<td>T9</td>
<td>Solution heat treated + water quenched + artificially aged + cold worked</td>
</tr>
<tr>
<td>T10</td>
<td>Cooled from elevated temperature shaping process + artificially aged + cold worked</td>
</tr>
</tbody>
</table>
The most important heat treating process for non-ferrous alloys is *age hardening*, or *precipitation hardening*.

In order to apply this heat treatment, the equilibrium diagram must show partial solid solubility, and the slope of the solvus line must be such that there is greater solubility at a higher temperature than at a lower temperature.

The purpose of precipitation hardening treatment is to improve strength of the materials. It can explained by with respect to dislocations.

The presence of dislocation weakens the crystal → easy plastic deformation

Putting hindrance to dislocation motion increases the strength of the crystal

Fine precipitates dispersed in the matrix provide such an impediment.

For example: Strength of Al → 100 MPa
Strength of Duralumin (Al + 4% Cu + other alloying elements) → 500 Mpa

Two stages are generally required in heat treatment to produce age hardening:

- Solution treatment
- Aging
Precipitation Hardening

\[ \text{Sloping Solvus line} \Rightarrow \text{high } T \rightarrow \text{high solubility} \]
\[ \text{low } T \rightarrow \text{low solubility} \]

of Cu in Al

Al rich end of the Al-Cu phase diagram
Slow equilibrium cooling gives rise to coarse θ precipitates which is not good in impeding dislocation motion.*
To obtain a fine distribution of precipitates the cycle $A \rightarrow B \rightarrow C$ is used.

Solution treating at high temperature, then quenching (second phase is in solid solution) $\rightarrow$ Cycle $A$ and $B$

- **A**  Heat (to $550^{\circ}C$) $\rightarrow$ solid solution $\alpha$

- **B**  Quench (to RT) $\rightarrow$  
  supersaturated solution
  Increased vacancy concentration

Ageing at room temperature or slightly higher temperature (Precipitation of second phase, giving strengthening effect) $\rightarrow$ Cycle $C$

- **C**  Age (*reheat* to $200^{\circ}C$) $\rightarrow$ fine precipitates

*Note: Treatments $A$, $B$, $C$ are for the same composition*
Precipitation Hardening

- Overaged
- Underaged
- Peak-aged

Dispersion of fine precipitates (closely spaced)
Coarsening of precipitates with increased interparticle spacing

Region of solid solution strengthening (no precipitation hardening)
Region of precipitation hardening (but little/some solid solution strengthening)

Higher temperature ⇒ less time of aging to obtain peak hardness
Lower temperature ⇒ increased peak hardness
⇒ optimization between time and hardness required
Precipitation Hardening

Hardness $\rightarrow 180^\circ C$ Peak-aged

Log$(t) \rightarrow$ Particle radius $(r) \rightarrow$ CRSS Increase $\rightarrow 2^{1/r} \propto 1/r$

Particle shearing $\propto r^{-2}$

Particle By-pass

Section of GP zone parallel to (200) plane

$r = f(t)$
A complex set of events are happening parallely/sequentially during the aging process → These are shown schematically in the figure ⇒

Increasing size of precipitates with increasing interparticle (inter-precipitate) spacing

Interface goes from coherent to semi-coherent to incoherent

Precipitate goes from GP zone → \( \theta'' \) → \( \theta' \) → \( \theta \)
Cu rich zones fully coherent with the matrix → low interfacial energy
(Equilibrium \( \theta \) phase has a complex tetragonal crystal structure which has incoherent interfaces)
Zones minimize their strain energy by choosing disc-shape \( \perp \) to the elastically soft \(<100>\) directions in the FCC matrix
The driving force \((\Delta G_v - \Delta G_s)\) is less but the barrier to nucleation is much less \((\Delta G^*)\)
2 atomic layers thick, 10nm in diameter with a spacing of ~10nm
The zones seem to be homogenously nucleated (excess vacancies seem to play an important role in their nucleation)
Due to large surface to volume ratio the fine precipitates have a tendency to coarsen → small precipitates dissolve and large precipitates grow
Coarsening
\( \Rightarrow \) ↓ in number of precipitate
\( \Rightarrow \) ↑ in interparticle (inter-precipitate) spacing
\( \Rightarrow \) reduced hindrance to dislocation motion \((\tau_{\text{max}} = Gb/L)\)
Precipitation Hardening

Distorted FCC
Unitcell composition
\( \text{Al}_6\text{Cu}_2 = \text{Al}_3\text{Cu} \)

Become incoherent as ppt. grows

\( (001)_{\theta} \| (001)_{\alpha} \)
\( [100]_{\theta} \| [100]_{\alpha} \)

\( \text{Unitcell composition} \)
\( \text{Al}_4\text{Cu}_2 = \text{Al}_2\text{Cu} \)

Tetragonal

Body Centered Tetragonal

\( \text{Unitcell composition} \)
\( \text{Al}_8\text{Cu}_4 = \text{Al}_2\text{Cu} \)

Structure and morphology of \( \theta'' \), \( \theta' \) and \( \theta \) in Al–Cu (\( \bigcirc \) Al, \( \bullet \) Cu).
Schematic diagram showing the lowering of the Gibbs free energy of the system on sequential transformation:

GP zones → θ'' → θ' → θ
The activation barrier for precipitation of equilibrium ($\theta$) phase is large. But, the free energy benefit in each step is small compared to the overall single step process.
At higher temperatures the stable $\theta$ phase is produced directly. At slightly lower temperatures $\theta'$ is produced first. At even lower temperatures $\theta''$ is produced first. The normal artificial aging is usually done in this temperature range to give rise to GP zones first.
Precipitation Hardening

Phase Diagram

TTT Diagram

Stable solvus line

Metastable solvus lines

Aging sequence: \( \theta'' \rightarrow \theta' \rightarrow \theta \)

Aging sequence: \( \theta' \rightarrow \theta \)

Aging sequence: \( \text{GP} \rightarrow \theta'' \rightarrow \theta' \rightarrow \theta \)
In previous slide, we show the Al-rich portion of the Al-Cu phase diagram (schematically). From the phase diagram, it is clear that the Al with a few percent copper is cooled from high temperature leads to the formation of a microstructure in which the $\theta$ phase precipitates out of the supersaturated $\alpha$ matrix.

However, if an alloy of composition Al - 4 wt. %Cu is solutionised at say, 540°C, and the resultant phase is rapidly quenched to room temperature, the solid solution is largely retained; if this alloy is kept at room temperature (or at any temperature below 180°C), a metastable phase known as Guinier-Preston zones (GP zones) is formed.

Similarly, the aging treatment at other temperatures can produce other precipitates such as $\theta''$ and $\theta'$.

The solvus for these metastable phases is shown in Fig. Further, we also show the corresponding time-temperature-transformation curves for these metastable phase as well as the stable phase.

we already discussed the crystallography and interface structure of all these phases as well as the reasons for their formation.
## Precipitation Hardening

### Precipitation Sequence in some precipitation hardening systems

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Alloy</th>
<th>Precipitation Sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>Al-Ag</td>
<td>GPZ (spheres) → γ' (plates) → γ (Ag₂Al)</td>
</tr>
<tr>
<td></td>
<td>Al-Cu</td>
<td>GPZ (discs) → θ'' (discs) → θ' (plates) → θ (CuAl₂)</td>
</tr>
<tr>
<td></td>
<td>Al-Cu-Mg</td>
<td>GPZ (rods) → S' (laths) → S (CuMgAl₂) (laths)</td>
</tr>
<tr>
<td></td>
<td>Al-Zn-Mg</td>
<td>GPZ (spheres) → η' (plates) → η (MgZn₂) (plates or rods)</td>
</tr>
<tr>
<td></td>
<td>Al-Mg-Si</td>
<td>GPZ (rods) → β' (rods) → β (Mg₂Si) (plates)</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu-Be</td>
<td>GPZ (discs) → γ' → γ (CuBe)</td>
</tr>
<tr>
<td></td>
<td>Cu-Co</td>
<td>GPZ (spheres) → β (Co) (plates)</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe-C</td>
<td>ε-carbide (discs) → Fe₃C</td>
</tr>
<tr>
<td></td>
<td>Fe-N</td>
<td>α' (discs) → Fe₄N</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni-Cr-Ti-Al</td>
<td>γ' (cubes or spheres)</td>
</tr>
</tbody>
</table>
In low T aging (130°C)→ The aging curves have more detail than the single peak as discussed schematically before.

In low T aging (130°C)→ the full sequence of precipitation is observed (GPZ →θ'' → θ').

At high T aging (190°C)→ θ'' directly forms (i.e. the full precipitation sequence is not observed).

Peak hardness increases with increasing Cu%.

For the same Cu%, the peak hardness is lower for the 190°C aging treatment as compared to the 130°C aging treatment.

Peak hardness is achieved when the microstructure consists of a θ' or combination of (θ' + θ'').
The strengthening of a heat-treatable alloy by aging is not due merely to the presence of a precipitate. It is due to both the uniform distribution of a finely dispersed submicroscopic precipitate and the distortion of the lattice.

There are several theories of precipitation hardening, to explain in what manner precipitate particles harden the matrix or solvent lattice, the most useful theory is coherent lattice theory.

After solution treatment and quenching, the alloy is in a supersaturated condition, with the solute atoms distributed at random in the lattice structure (Fig A).

During an incubation period, the excess solute atoms tend to migrate to certain crystallographic planes, forming clusters or embryos of the precipitate.

During aging, these clusters form an intermediate crystal structure, or transitional lattice, maintaining registry (coherency) with the lattice structure of the matrix.

The excess phase will have different lattice parameters from those of the solvent, and as a result of the atom matching (coherency), there will be considerably distortion of the matrix (Fig B).

The distortion of the matrix extends over a larger volume than would be the case if the excess phase were a discrete particle. Eventually the equilibrium excess phase is formed with its own lattice structure (Fig C).
This causes a loss of coherency with the matrix and less distortion hardness and strength will decrease, and the alloy is ‘over-aged’. There will now be a boundary between the excess phase and the matrix so that the precipitated particle will be visible under the microscope.

Coherent Lattice Theory

Stages in the formation of an equilibrium precipitate
Consider an interface between two solid phases, $\alpha$ and $\theta$, arising when $\theta$ nucleates and grows in $\alpha$. The interface can be of various types:

**Coherent.** There is perfect alignment of the lattices.

**Coherent, with strain.** It is likely that a coherent interface will have some elastic strain. The strain energy increases with the size of the growing particle and there will be a transition to a semi coherent interface.
Solid-Solid Interfaces

Semi-coherent. The introduction of dislocations (defects in the way the crystal is organized) reduces the overall elastic strain, although they themselves contribute to the energy of the system.

Incoherent. There is no matching at the interface.
Microstructures of common aluminum alloys

- Al-Mg-Fe-Si
- Duralumin
- Al-Si

[Images of microstructures of various aluminum alloys]
The high corrosion resistance of aluminum is due to the self-protecting, thin, invisible oxide film that forms immediately on exposing surfaces to the atmosphere.

This film protects the metal from further corrosion. If the oxide film is removed, in many environments, a new film will form immediately and the metal remains fully protected.

In certain strongly acid or alkaline solutions, or in contact with moist corrosive materials that prevent access of oxygen to the aluminum surface, the protective film does not form readily. Therefore, the aluminum should be adequately protected or not used at all.

A relatively thick oxide coating on aluminum and aluminum alloys may be produced by placing the metal into an aqueous solution containing 15 to 25% sulfuric acid. This process, known as anodizing, produces a clear, transparent coating containing submicroscopic pores that are usually sealed before use to prevent absorption and staining. Sealing may be accomplished by suitable heating in hot water.

The corrosion resistance of Al-Cu alloys and Al-Zn alloys is satisfactory for most applications but is generally lower than that of the other aluminum alloys. Under certain corrosive conditions they are subject to intergranular corrosion.

Therefore, these alloys in the form of sheet are usually clad with a high-purity alloy such as commercial aluminum or a magnesium-silicon alloy.

The coating slabs are mechanically attached to the alloy core ingot, and the bonding is accomplished by hot rolling. The nominal cladding thickness per side is usually 1½ or 2½ percent of thickness of the base material.
Super alloys
**Material Requirements**

### Oxidation & Corrosion Resistance
- Should resist corrosive action of Na, K, V, Pb & S which make way from air and fuel
- Should possess Oxidation resistance

### Elevated Temperature Strength
- Components experience
  - Impingement of high pressure gases associated with High temp: High temperature Tensile test.
  - Long exposures at working temperatures under high stresses: Stress rupture strength

### Micro structural Stability
- Should retain the microstructure when exposed to working temperature: i.e. free of TCP phases μ,6, Laves

---

Objective

![Diagram showing material composition](image-url)
A SUPERALLOY is an alloy developed 20th century as a material for elevated temperature service, usually based on group VIII elements where relatively severe mechanical stressing is encountered and where surface stability frequently is required. The classification of super alloys as follows.

- Iron Base
- Cobalt Base
- Nickel Base and Nickel-Iron base

Temperature Limitations of Super alloys

<table>
<thead>
<tr>
<th></th>
<th>Merits</th>
<th>Demerits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Base</td>
<td>Temperature applications below 650°C</td>
<td>Poor Oxidation resistance</td>
</tr>
<tr>
<td>Cobalt Base</td>
<td>Temperature applications below 650°C</td>
<td>Poor Ductility</td>
</tr>
<tr>
<td>Nickel Base</td>
<td>Temperature applications up to 0.9 Tm</td>
<td>In equi-axed condition applications are limited 850°C</td>
</tr>
<tr>
<td>Nickel – Iron Base</td>
<td>Temperature applications up to 650°C</td>
<td>Loses strength beyond 650°C</td>
</tr>
</tbody>
</table>
Strengthening Mechanisms

Gamma Prime Strengthening

- Gamma Prime is an ordered inter-metallic compound having the chemical formula Ni$_3$ (Al, Ti). It has the following characteristics:
  - It has FCC crystal structure and exhibits long range order, up to its melting point. It is coherent with the nickel matrix.
  - It gets precipitated uniformly throughout the matrix by a two-step heat treatment.
  - It contributes to about 55 - 65% volume in Ni-base cast alloys. It is a ductile phase and imparts very good transverse ductility before fracture in directionally solidified condition.

Carbide Strengthening

- Three types of Carbides are possible. They are MC type form during solidification: Ex: TiC, HfC, TaC, NbC (Form on Inter and Transgranular sites), M$_6$C & M$_{23}$C$_6$, from the Carbon available due to the dissociation of MC Carbides on heat treatment: Ex: Mo$_6$C, Cr$_{23}$C$_6$ (Form on grain boundaries in discontinuous form).

Solid Solution Strengthening

- Alloying elements viz: Co, Al, Mo, W, Fe, Cr, Ti etc; form solid solutions in Ni-matrix. The potentiality of these elements in order: Al > W > Mo > Cr > Fe > Ti > Co.
Subjected to solution treatment and two stage Ageing treatment under Vacuum 10^{-3} \mu to attain maximum strength.

Objective: To take cast \gamma' (\gamma/ \gamma' eutectic + coarser \gamma') in the cast structure into \gamma solution and to precipitate as fine \gamma' uniformly throughout the \gamma matrix upon ageing at lower temperatures. Apart from this MC carbides go into the solution and become a source for ‘C’ to form M_6C, M_{23}C_6 at lower temperatures.

Solutioning Treatment:
- Step I: 1230 \pm 5^0 C for ½ hour (Homogenizing treatment)
- Step II: 1254 \pm 5^0 C for 3 hours
- Takes Cast \gamma' and M_6C, M_{23}C_6 into solution.

Ageing Treatment
- Step I: 1080 \pm 2^0 C for 4hrs / AC
  - Some amount of \gamma' precipitate out (Secondary \gamma')
  - M_6 C type carbide form along grain boundaries
- Step II: 870 \pm 2^0 C for 20 hrs / AC
  - Secondary \gamma' grows into cuboidal shape
  - Further precipitation of fine takes \gamma' place (Tertiary \gamma')
This bimodal $\gamma'$ (Secondary & Tertiary) uniformly distributes throughout the matrix and this increases the yield strength of the alloy up to $870^0\text{C}$ which is uncommon with any other alloy system.

Formation of $M_{23}C_6$ carbides in discontinuous form along grain boundaries HfC dissociated and becomes a source for Carbon. The liberated Hf partition $\gamma'$ and forms an envelop around Grain Boundary.

**Limitations**

- Incipient melting constituents limits solutionising temperatures.
- Full solutionizing of cast $\gamma'$ is not possible. Only 88% $\gamma'$ goes into solution.
- Incipient melting is Localized melting of low melting constituents viz., $\gamma'/\gamma'$ eutectic.
- On cooling solidifies and exhibits cast structure and becomes a weak point.
- Step I solution treatment diffuses these constituents to some extent.
- Elements such as Ta, Hf, Ti increases $\gamma'$ solvus and decreases incipient melting point. Cobalt increases incipient melting and decreases $\gamma'$ solvus temperature.
Microstructural characteristics

Microstructural Study of Directionally Solidified Ni-based Super Alloy CM247LC

As cast SEM structure showing as cast optical microstructures showing 15% eutectic in average.

Non uniform precipitation of γ′.

Solutionized optical micrograph showing 9% eutectic in average.

Fully heat treated SEM structure showing 60% cubical γ′ precipitate.

Dendrite core

SDA

γ/γ′ eutectic

Cubical γ′

Precipitates
Titanium Alloys
Titanium alloys

- Titanium is named after titans of Greek mythology
- It has low density, high strength, good oxidation and corrosion resistance thus very good for industrial applications
- It undergoes an allotropic transformation at 882°C
- Exhibits a wide variety of microstructures depending upon the alloy chemistry, processing and heat treatment.
- Exhibits a broad range of phase transformations.
  - Transformations related to the α/β allotropic
  - Transformation due to precipitation reactions
- Precipitation reaction occurs due to formation of metastable transition phases and/or equilibrium that occur during the decomposition of the metastable α or β phase.
- The phase transformations and resultant microstructures in alloys based on ordered intermetallics Ti₃Al (α₂), Ti₂AlNb (‘ω’) and TiAl (γ), are similar to conventional titanium alloys in many aspects.
- Morphological changes due to recrystallization, spheroidisation can lead to more types of microstructures
- The central point in the evolution of microstructure is the α→β transformation temperature referred as β-transus temp. Specific temp. is a function of the alloy chemistry.
Ti-alloys heated above $\beta$-transus are in single phase $\beta$, on cooling through $\beta$-transus, $\beta$ can transform to various equilibrium or non-equilibrium phases depending on the rate of cooling and alloying content.

Fast cooling (OQ/WQ) $\beta$ phase can transform martensitically to $\alpha'$ (HCP) or $\alpha''$ (orthorhombic). On slower cooling $\beta$ can transform by nucleation and growth to Widmanstätten $\alpha$ phase (secondary $\alpha$).

The morphology of Widmanstätten $\alpha$ phase changes from a colony of similarly aligned laths to a basket weave arrangement with the increase in cooling rate or alloying content.

Pseudo binary schematic phase diagram of $a + b$ titanium alloys.

TTT curve of a typical $\alpha + \beta$ titanium alloys.
Lamellar structure becomes finer as cooling rate increases. On slower cooling α phase is also present at the prior β grain boundaries.

In addition to α, α’, α”, the microstructure may retain small amounts of β phase depending on the alloying content. The amount increases with the increase in solute content.

The α’ or α” martensite decomposes upon aging to precipitate fine β, which leads to increase in strength.

Precipitation of a₂ (Ti₃Al) in α-phase occurs on prolonged thermal exposures in some alloys.

Additional intermetallic phases like silicides may form upon aging martensite in some alloys.
In β stabilized alloys, the β phase may be retained completely as a metastable phase on fast cooling. However α phase can precipitate out at the grain boundaries and within the grains on slow cooling. The amount is a function of cooling rate and β-stabilizer content.

Athermal ω may form, in some compositions, in the β phase as fine precipitates. Undesirable phase as it causes severe embrittlement.

Microstructures resulting from S.T. above β phase are generally referred as transformed β or β heat-treated structure

Thermo-mechanical processing at temperatures in two phase α+β region has an important effect on α-phase morphology

Hot working below β-transus i.e in the α+β phase field results in recrystallization of α-phase and an equiaxed morphology (primary α)

The aspect ratio of primary α is determined by temp., strain rate and extent of hot working in the two phase region

The relative vol. fraction of primary α and transformed β can be controlled by solution treatment temperature in the two phase field and cooling rate from the solution treatment temperature.

The effect of cooling rate on the microstructure from a given S.T temperature is shown in next page.
Titanium alloys

Ti-6Al-4V, a + b heat treated showing a and transformed b microstructure. The volume fraction of a increases with decrease in cooling rate and also transformed b becomes coarser.
THANK YOU...!