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قسم الهندسة الميكانيكية

Course Handout

HEAT TREATMENTS

Intended for: 1^{ST} YEAR MASTER students

Materials Engineering

Edited by:

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Preface

The content of this course was chosen so as to be able to serve as a manual for materials engineering courses intended for 1st year master's students in accordance with the outline and guidelines of the mechanical engineering department.

Teaching objectives

- Implement the main heat treatments and the main techniques experimental for the study of structural transformations of metal alloys.
- Highlight changes in properties and valuation of materials obtained at the end of the treatments.
- Highlight the correlations between behaviors, treatments and structures.

Prerequisites: The target audience must have prior knowledge in: Thermodynamics (understanding of equilibrium and phase diagrams, thermochemistry), notions of mechanics. Metals and alloys.

The course content is presented in several themes subdivided into chapters:

Chapter 1. Thermal Equilibrium Diagram.

Chapter 2. Time-Temperature Transformation (TTT) diagram & Continuous Cooling Transformation (CCT) diagram.

Chapter 3. Classification of Metal Alloys.

Chapter 4. Heat Treatment Theory

Chapter 5. Classic industrial treatments (annealing and quenching,…..) & Thermochemical diffusion treatments (Carburizing heat, Nitriding etc.).

The hourly volume allocated to the course is 37h30min per semester in one lesson per week of 1h30 and a practical work of 1h. The evaluation of acquired knowledge is done in mode: Continuous assessment: 40%; Exam: 60%.

Depending on the means available in the establishment. manipulations are designed as an experimental project combining the material studied, the treatments, and the characterization.

The different manipulations address the following themes:

- The modification of the properties of alloys by heat treatment in the mass and the study of the hardening mechanisms of metal alloys.
- Predicting the mechanical characteristics of steels.
- The modification of the surface properties of materials.
- Cold deformation and the effects of annealing after work hardening.

Contents

Chapter 1. THERMAL EQUILIBRIUM DIAGRAM...

Chapter 3. CLASSIFICATION OF METAL ALLOYS..

Chapter 4. HEAT TREATMENT THEORY........

Chapter 5. HEAT TREATMENT PROCESSES........

Chapter 1

THERMAL EQUILIBRIUM DIAGRAM

1. Materials System

A material system refers to a definite amount of material or materials.

The components in a system refer to the smallest number or individual substances that must be listed to describe the chemical composition of the system. These may be elements (Pb, Sn, Fe, C, etc.) or compounds (H_2O, NaCl, etc.)

The phase in a system is described as either a pure metal, a solid solution or some form of intermediate compound so long as it is a single homogeneous substance. Similarly, a single element or compound can exist in different physical forms, eachone a separate phase. Thus, the chemical substance 'H_2O' can exist as ice, water or water vapour, each of these conditions constituting a '*phase*'.

Phase diagrams are graphs showing the phases present under selected conditions oftemperature, pressure, and composition when the system is in thermodynamicequilibrium.

1.1 One-component material systems (unary system)

The phases possible in a one component system are limited to liquid, solid, and gasstates (Figure 1.1). A phase diagram consists simply of a graph of pressure vs. temperature, with the phase regions indicated.

1.2. Two component material systems (binary system)

Materials with two components are called binary systems. They are commonly encountered in engineering materials (brass consisting of copper and zinc, carbon steel consisting of iron and carbon, etc.) The phase diagram of a binary material is customarily displayed in a temperature vs. composition format, with the pressure held fixed at atmospheric. There are many types of the binary system:

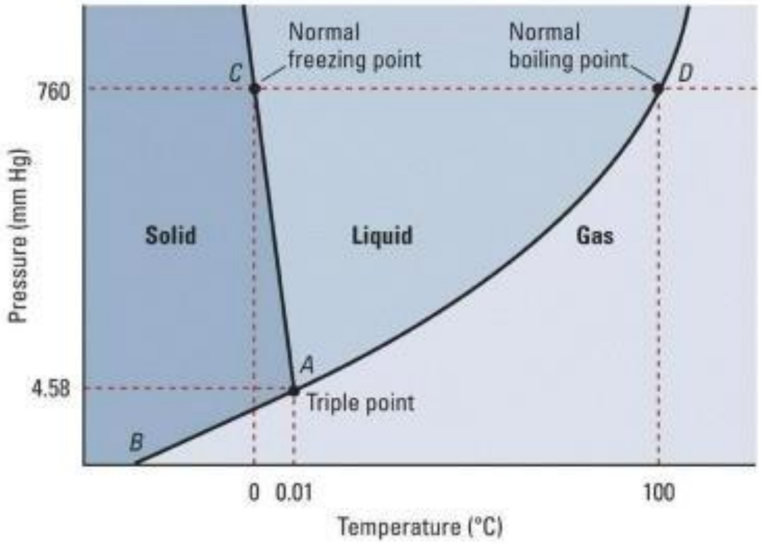


Figure 1.1. Phase diagram for a one-component system (water)

- ***Two-Components with Complete Solubility***: For a system having componentscompletely soluble in the solid state, the phase diagram is especially simple, since only one phase exists in the solid state. See Figure 1.2 for the phase diagram of the material.

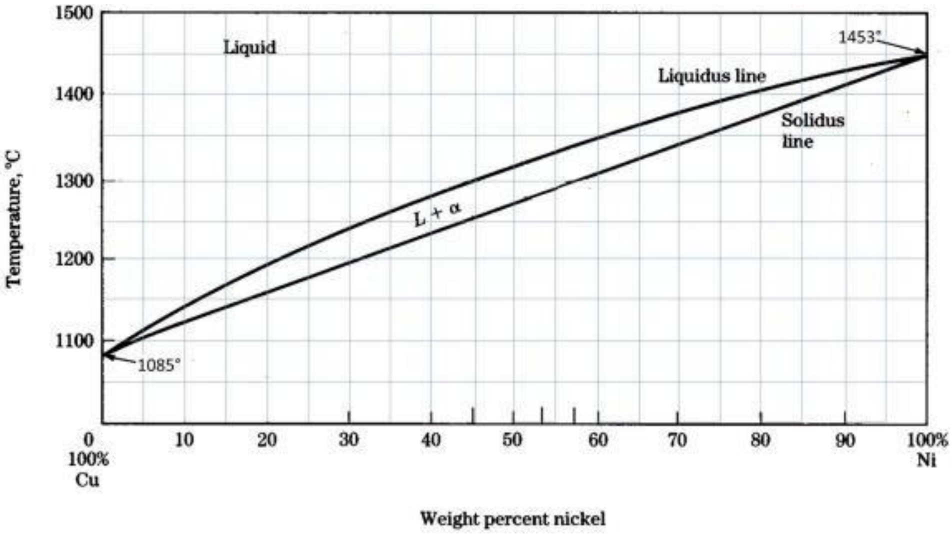


Figure 1.2. Components with complete solubility (Copper-Nickel System)

- ***Two-Components with Partial Solubility (Eutectic):*** For a binary system having components only partially soluble in the solid state, two solid phases will exist, andthe phase diagram is much more complex than Figure 1.3. A special case is an eutectic diagram shown in Figure 3. "*Eutectic*" means that when the two components are mixed, the melting point is lower than the melting temperatures of the two components separately. At point d, the eutectic reaction, L$\longrightarrow$ α + β occurs.

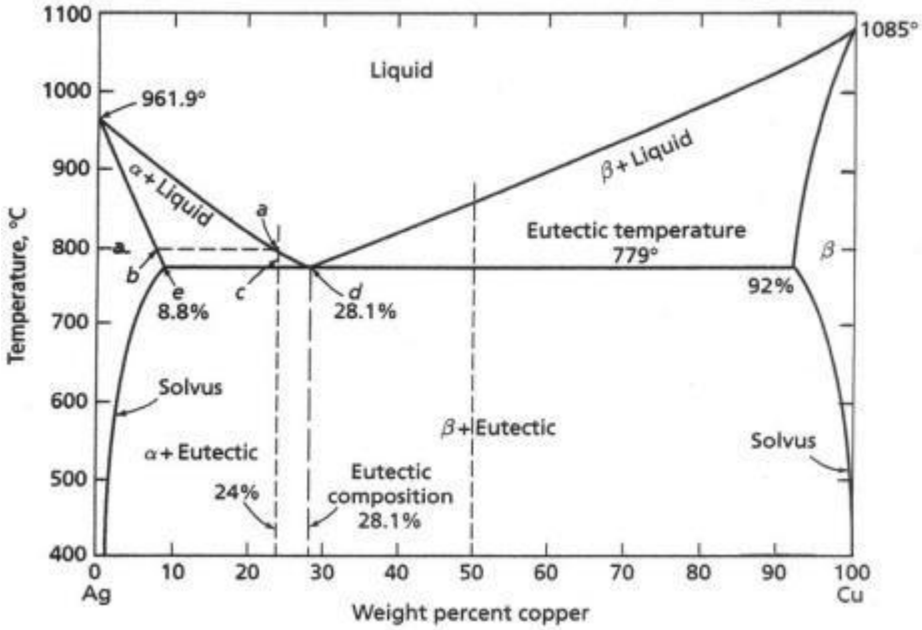


Figure 1.3. Two components with partial solubility (Silver Alloy Copper System)

- ***Two-Components with Partial Solubility (Eutectoid):*** When the liquid region is replaced by a third solid phase γ, we have the eutectoid reaction γ $\longrightarrow$α + β and associated phase diagram. Figure 1.4 shows such as phase diagram with both a Eutectic and Eutectoid point.

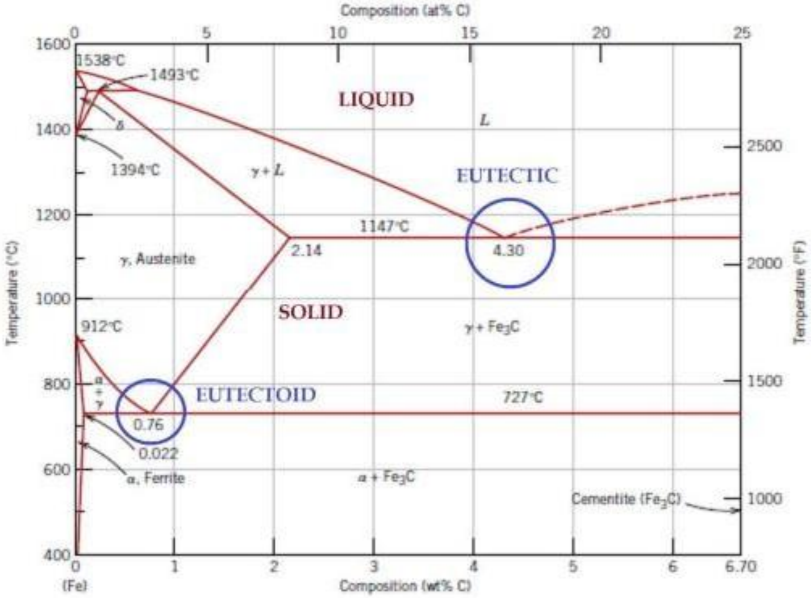


Figure 1.4. Two components with partial solubility (Iron Carbon System)

- ***Two-Components with Partial Solubility (Peritectic):*** For a binary system having components only partially soluble in the solid state, we may also have a phase diagram having a peritectic point P, where the reaction L + β → α occurs (Figure 1.5).

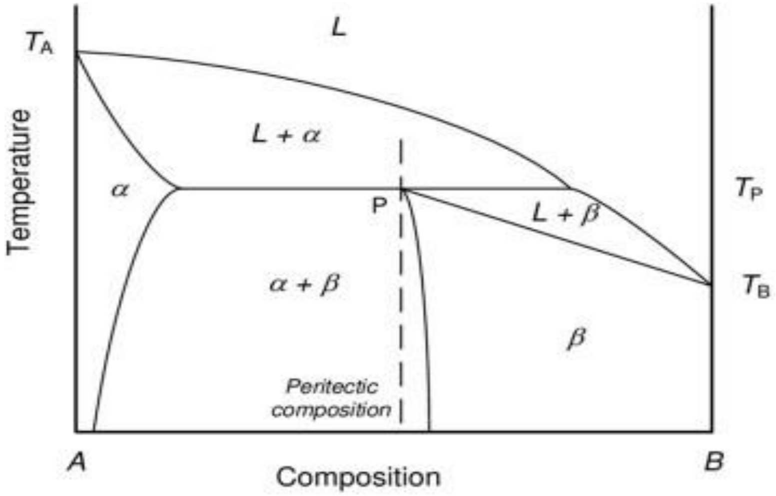


Figure 1.5. Two components with partial solubility. Peritectic-Reaction

- ***Two-Components with Partial Solubility (Peritectoid):*** If the liquid in the peritecticreaction is replaced by a third solid phase, γ, we have a peritectoid reaction α + γ → β. This is illustrated by Figure 1.6.

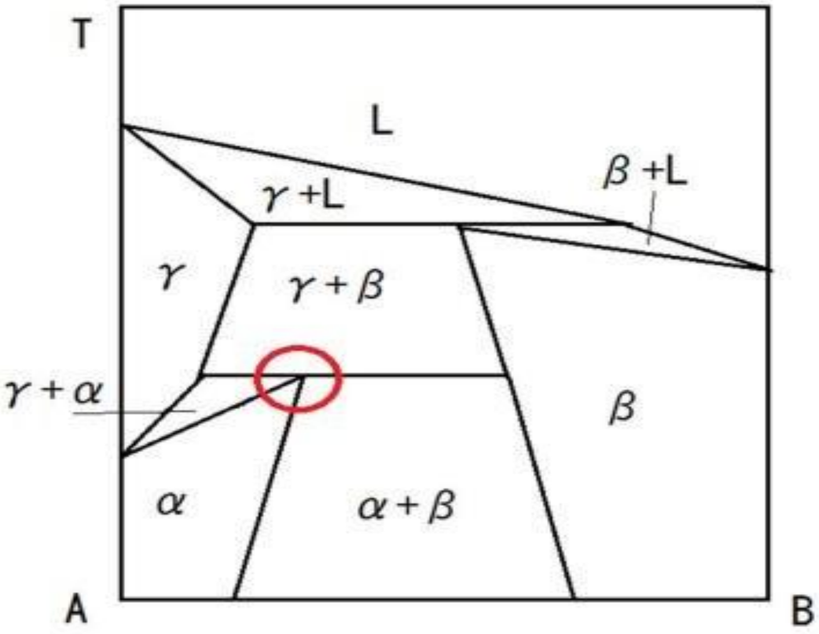
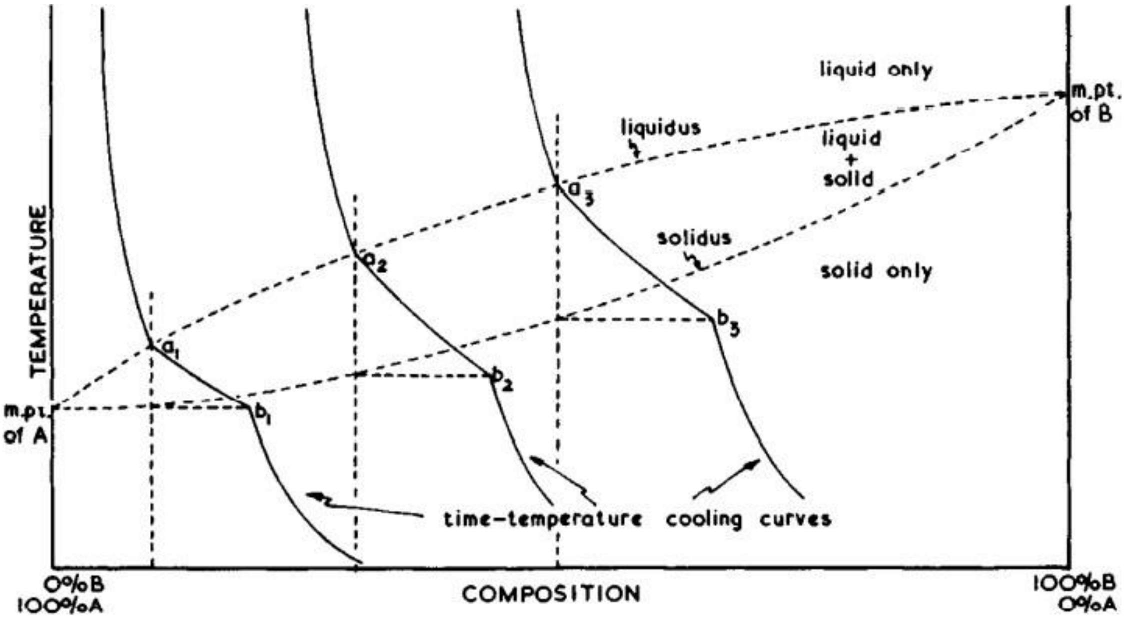


Figure 1.6. Two components with partial solubility- Peritectoid Reaction

2. Thermal Equilibrium Diagram

The thermal-equilibrium diagram is a chart which shows the relationship between the composition, temperature and structure of any alloy in a series. Moreover, the thermal equilibrium diagram is built based on cooling curves of the material.

A pure metal will complete its solidification without change of temperature, whilst an alloy will solidify over a range of temperature which will depend upon the composition of the alloy. Consider, for example, a number of alloys of different composition containing the two metals A and B which form a series of solid solutions (Figure 1.7).



Figurer 1.7. The construction of a simple equilibrium diagram of the solid solution type usingcooling curves of a series of alloys

For successive compositions containing diminishing amounts of the metal A, freezing starts at a_1, a_2, a_3, …, etc., and ends at b_1, b_2, b_3, …, etc. Thus, if we join allpoints of a_1, a_2, a_3, …, etc., we shall obtain a line called the ***liquidus***, indicating the temperature at which any given alloy in the series will commence to solidify. Similarly, if we join the points of b_1, b_2, b_3, etc., we have a line, called the ***solidus***, showing the temperature at which any alloy in the series will become completely solid. Hence the *liquidus can be defined as the line above which all indicated alloy compositions represent completely homogeneous liquids*, whilst *the solidus can be defined as the line below which all represented alloy compositions of A and B are completely solid*. For temperatures and compositions corresponding to the coordinates of points between the two lines both liquid solutions and solid solutionscan co-exist in equilibrium. Such a system as this occurs when the two metals are soluble in each other in all proportions in both the liquid and solid states, as in the case of copper and nickel or gold and silver.

3. Allotropic Changes in Iron

Iron in the solid state is known in two allotropic states. (*Allotropy is the phenomenonof an element having different crystal lattices depending on the particular temperature and pressure*), different crystal structures are shown in Figure 8.

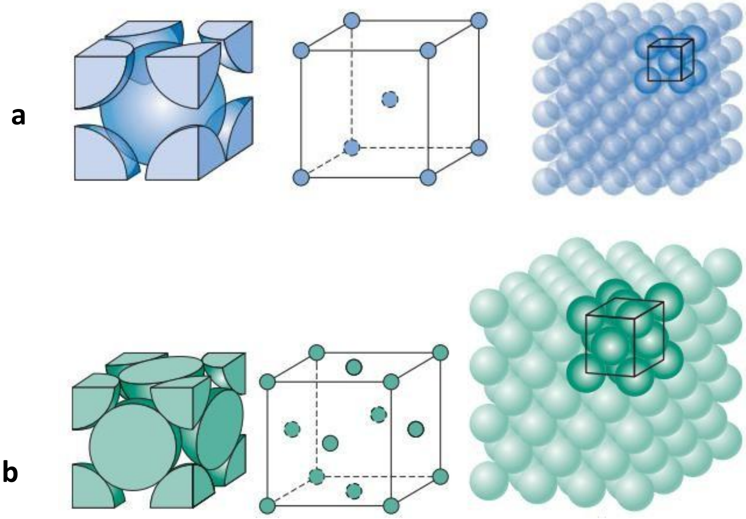


Figure 1.8. a. Body-centered cubic, and **b.** face-centered cubic crystal structures

Starting from low temperatures and up to 910 °C, iron possesses a body centered cubic (BCC) lattice and is called α-iron (α-Fe) as shown in Figure 1.9 and Figure 1.10. At 910 °C α-iron crystals turn into γ-iron crystals possessing a face-centered cubic (FCC) lattice. The γcrystals retain stability up to temperature of 1400 °C. Above this temperature they again acquire a bcc lattice and are usually called δ crystals. The δ crystals differ fromα crystals only in the temperature region of their existence. At low temperatures, α-Fe exhibits a strongly ferromagnetic character. When it is heated to about 770 °C, ferromagnetism vanishes. In accordance with the latest findings, this is because thelattice loses its ferromagnetic spin ordering. The state of iron above 770 °C is calledβ-Fe. The lattice of paramagnetic crystals is identical to the lattice of α crystals.

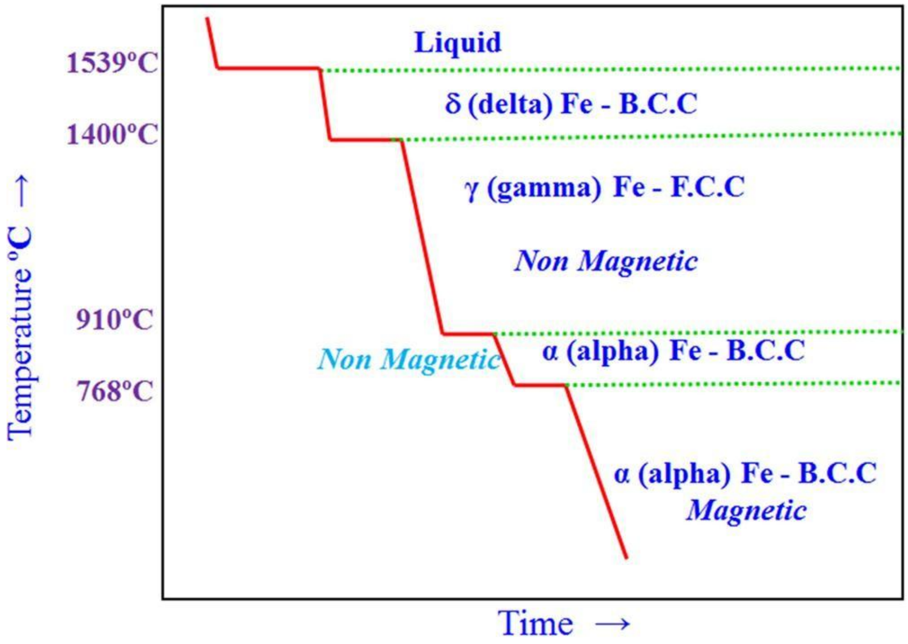


Figure 1.9. Cooling curve of iron

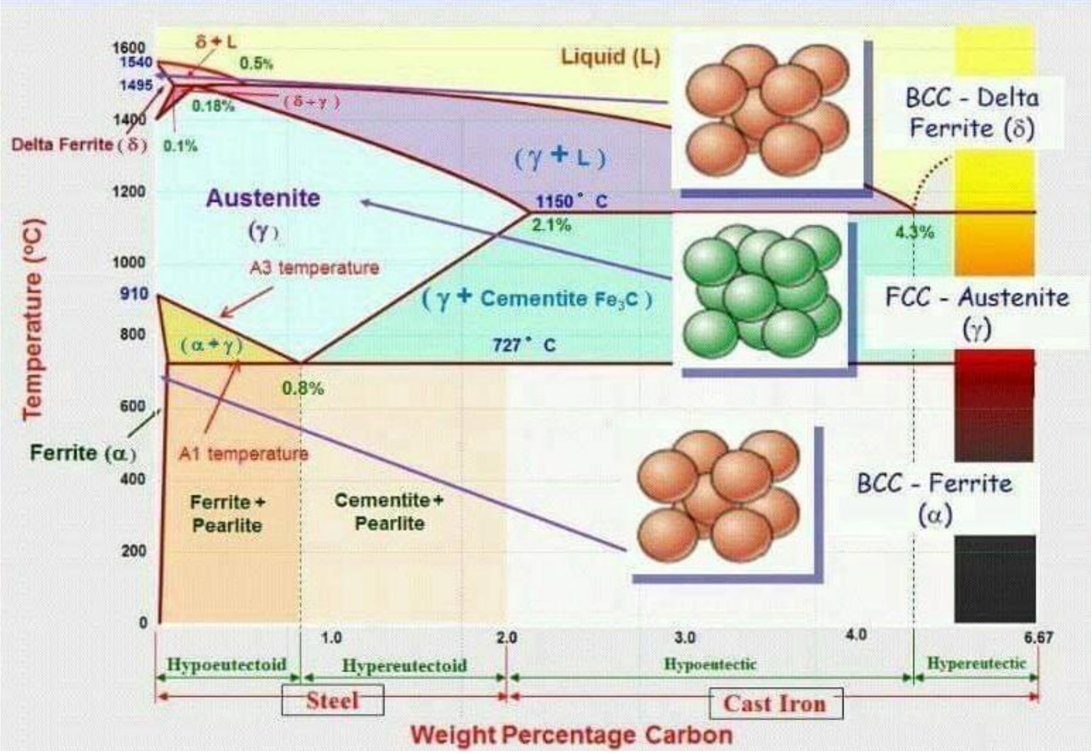


Figure 1.10. Iron-carbon phase diagram

The structure of iron-carbon alloys can contain either pure carbon (graphite) or a chemical compound (cementite) as the carbon-enriched component. Cementite is present even in relatively slowly cooled alloys: a long holding at elevated temperatures is required to decompose cementite to iron and graphite. For this reason, the iron–carbon diagram is usually treated as the iron-iron carbide diagram. The former is stable, whereas the latter is metastable. The iron-carbon diagram is shown in Figure 1.11(a) & (b). *Dashed lines stand for the stable Fe-C diagram, and solid linesdenote the metastable Fe–Fe_3C diagram.*

4. Fe-C binary system:

• The Fe-Fe_3C is characterized by five individual phases and four invariant reactions.

• Five phases that exist in the diagram are:

- α–ferrite (BCC) Fe-C solid solution,
- γ-austenite (FCC) Fe-C solid solution,
- δ-ferrite (BCC) Fe-C solid solution,
- Fe_3C (iron carbide) or cementite - an inter-metallic compound and
- liquid Fe-C solution.

• Four invariant reactions that cause transformations in the system are:

- peritectic reaction at 1495 ^{o}C and 0.16%C, δ-ferrite + L ↔ γ-iron (austenite)
- monotectic reaction 1495 ^{o}C and 0.51%C, L ↔ L + γ-iron (austenite)
- eutectic reaction at 1147 ^{o}C and 4.3 %C, L ↔ γ-iron + Fe_3C (cementite)
- eutectoid reaction at 723 ^{o}C and 0.8%C, γ-iron ↔ α–ferrite + Fe_3C (cementite)

• [ledeburite] Product phase of eutectic reaction is called ledeburite, while product from eutectoid reaction is called pearlite.

• During cooling to room temperature, ledeburite transforms into pearlite and cementite.

• At room temperature, after equilibrium cooling, Fe-C diagram consists of either α–ferrite, pearlite and/or cementite.

• Pearlite is actually not a single phase, but a micro-constituent having alternate thin layers of α–ferrite (~88%) and Fe3C, cementite (~12%).

• Steels with less than 0.8%C (mild steels up to 0.3%C, medium carbon steels with C between 0.3%-0.8% i.e. hypo-eutectoid Fe-C alloys) i.e. consists pro-eutectoid α–ferrite in addition to pearlite, while steels with carbon higher than 0.8% (high-carbon steels i.e. hyper-eutectoid Fe-C alloys) consists of pearlite and pro-eutectoid cementite.

- Phase transformations involving austenite i.e. processes those involve eutectoid reaction are of great importance in heat treatment of steels.

5. Iron-Carbon Equilibrium Diagram

In their simplest form, steels are alloys of Iron (Fe) and Carbon (C). The study of the constitution and structure of iron and steel start with the iron-carbon phase diagram. It is also the basis understanding of the heat treatment of steels.

The iron-carbon diagram (also called the iron-carbon phase or equilibrium diagram) is a graphic representation of the respective microstructure states depending on temperature (y axis) and carbon content (x axis). The actual iron-carbon diagram is far larger than the part shown here.

At this point we only consider the area of the steel with a carbon content up to 2% maximum. Iron with higher carbon concentration exists – at this point the partial diagram of cast iron would follow, but this is not of interest for our consideration here.

The melt essentially cools via the austenite to ferrite phases – i.e. from gamma to alpha mixed crystal. If this process is viewed from the viewpoint of the crystal structure, the carbon atoms attempt to move from the surfaces to the center of the crystal. But this position can only be taken by a single atom. The other carbon atoms are released and form cementite (Fe_3C).

The following phases are involved in the transformation, occurring with iron-carbon alloys:

L - Liquid solution of carbon in iron;

δ-ferrite – Solid solution of carbon in iron. Maximum concentration of carbon in δ-ferrite is 0.09% at 2719 ºF (1493ºC) – temperature of the peritectic transformation. The crystal structure of δ-ferrite is BCC (cubic body centered).

Austenite – interstitial solid solution of carbon in γ-iron. Austenite has FCC (cubic face centered) crystal structure, permitting high solubility of carbon – up to 2.06% at 2097 ºF (1147 ºC). Austenite does not exist below 1333 ºF (723ºC) and maximum carbon concentration at this temperature is 0.83%.

α-ferrite – solid solution of carbon in α-iron. α-ferrite has BCC crystal structure and low solubility of carbon – up to 0.025% at 1333 ºF (723ºC). α-ferrite exists at room temperature.

Cementite – iron carbide, intermetallic compound, having fixed composition Fe3C. Cementite is a hard and brittle substance, influencing on the properties of steels and cast irons.

Ferrite: contains hardly any carbon.

Ferrite + perlite: As the carbon concentration increases, cementite is released. This becomes a new microstructure constituent and forms a ferrite-perlite microstructure.

Perlite: As the carbon concentration increases further, the ferrite fraction reduces steadily. From a carbon concentration of 0.8…0.85 %, only perlite is left.

Perlite + cementite: If the carbon concentration continues to increase, cementite deposits on the grain boundaries of the perlite. If examined under a microscope, these thickened grain boundaries can be seen. Cementite is a very hard and brittle microstructure component. Therefore, in many steel grades the cementite separation must be prevented. This is done by fast cooling. If the formation of cementite is not prevented, material can spall under mechanical loads.

The important boundaries (the lines) separating phases have some universally used abbreviations:

- **A_1:** The upper limit of the ferrite / cementite phase field (horizontal line going through the eutectoid point).
- **A_2:** The temperature where iron loses its magnetism (so-called Curie temperature). Note that for pure iron this is still in the α-phase.
- **A_3:** The boundary between the γ austenite and the austenite/ ferrite field.
- **A_4:** The point in this case where α changes to δ at high temperatures.
- **A_{CM}:** The boundary between the γ austenite and the austenite / cementite field.

Phase compositions of the iron-carbon alloys at room temperature:

- **Hypoeutectoid steels** (carbon content from 0 to 0.83%) consist of primary (proeutectoid) ferrite (according to the curve A_3) and pearlite.
- **Eutectoid steel** (carbon content 0.83%) entirely consists of pearlite.
- **Hypereutectoid steels** (carbon content from 0.83 to 2.06%) consist of primary (proeutectoid)cementite (according to the curve ACM) and pearlite.
- **Cast irons** (carbon content from 2.06% to 4.3%) consist of proeutectoid cementite C_2 ejected from austenite according to the curve ACM, pearlite and transformed ledeburite (ledeburite in which austenite transformed to pearlite).

- ***The austenite- ferrite transformation***

Under equilibrium conditions, pro-eutectoid ferrite will form in iron-carbon alloys containing up to 0.8 per cent carbon. The reaction occurs at 910 ^{o}C in pure iron, but takes place between 910 ^{o}C and 723 ^{o}C in iron-carbon alloys. However, by quenching from the austenitic state to temperatures below the eutectoid temperature A_1, ferrite can be formed down to temperatures as low as 600 ^{o}C. There are pronounced morphological changes as the transformation temperature is lowered, which it should be emphasized apply in general to hypo-and hyper-eutectoid phases, although in each case there will be variations due to the precise crystallography of the phases involved. For example, the same principles apply to the formation of cementite from austenite, but it is not difficult to distinguish ferrite from cementite morphologically.

- ***The austenite-cementite transformation***

The Dube classification applies equally well to the various morphologies of cementite formed at progressively lower transformation temperatures. The initial development of grain boundary allotriomorphs is very similar to that of ferrite, and the growth of side plates or Widmanstaten cementite follows the same pattern. The cementite plates are more rigorously crystallographic in form, despite the fact that the orientation relationship with austenite is a more complex one. As in the case of ferrite, most of the side plates originate from grain boundary allotriomorphs, but in the cementite reaction more side plates nucleate at twin boundaries in austenite.

- ***The austenite-pearlite reaction***

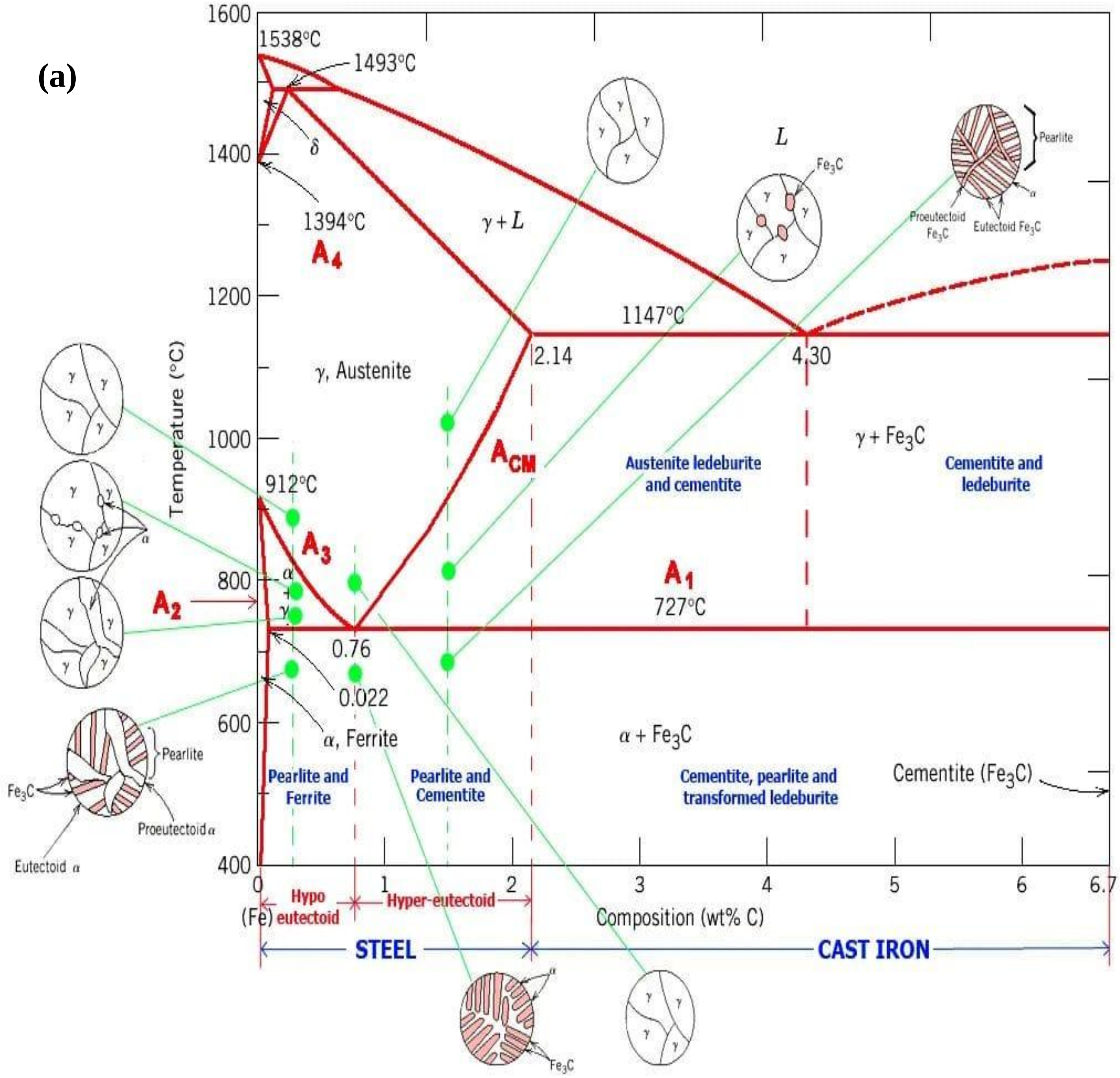
Pearlite is the most familiar micro structural feature in the whole science of metallography. It was discovered by Sorby over a century ago, who correctly assumed it to be a lamellar mixture of iron and iron carbide. Pearlite is a very common constituent of a wide variety of steels, where it provides a substantial contribution to strength. Lamellar eutectoid structures of this type are widespread in metallurgy, and frequently pearlite is used as a generic term to describe them.

These structures have much in common with the cellular precipitation reactions. Both types of reaction occur by nucleation and growth, and are, therefore, diffusion controlled. Pearlite nuclei occur on austenite grain boundaries, but it is clear that they can also be associated with both pro-eutectoid ferrite and cementite. In commercial steels, pearlite nodules can nucleate on inclusions.

It may be seen that the normal Iron carbon equilibrium diagram represents the metastable equilibrium between iron and iron carbide. Cementite is metastable as the true equilibrium is between iron and graphite. Although graphite occurs extensively in cast irons (2 to 4 wt per cent carbon), it is usually difficult to obtain this equilibrium phase in steels (0.03 to1.5 wt per cent carbon). Therefore, the metastable equilibrium between iron and iron carbide is normally considered, since it is relevant to the behavior of a variety of steels in practice.

On comparing austenite (gamma-iron) with ferrite (alpha-iron) it is noticed that solubility of carbon is more in austenite with a maximum value of just over 2 wt % at 1147^{O}C. This high solubility of carbon in austenite is extremely important in heat treatment, when solution treatment in the austenite followed by rapid quenching to room temperature allows formation of a supersaturated solid solution of carbon in iron. The ferrite phase is restricted with a maximum carbon solubility of 0.02 wt % at 723 ^{O}C. Since the carbon range available in common steels is from 0.05 to 1.5 wt %, ferrite is normally associated with cementite in one or other form. Similarly, the δ-phase is very restricted and is in the temperature range between 1390 and 1534 ^{O}C and disappears completely when the carbon content reaches 0.5wt %.

(a)



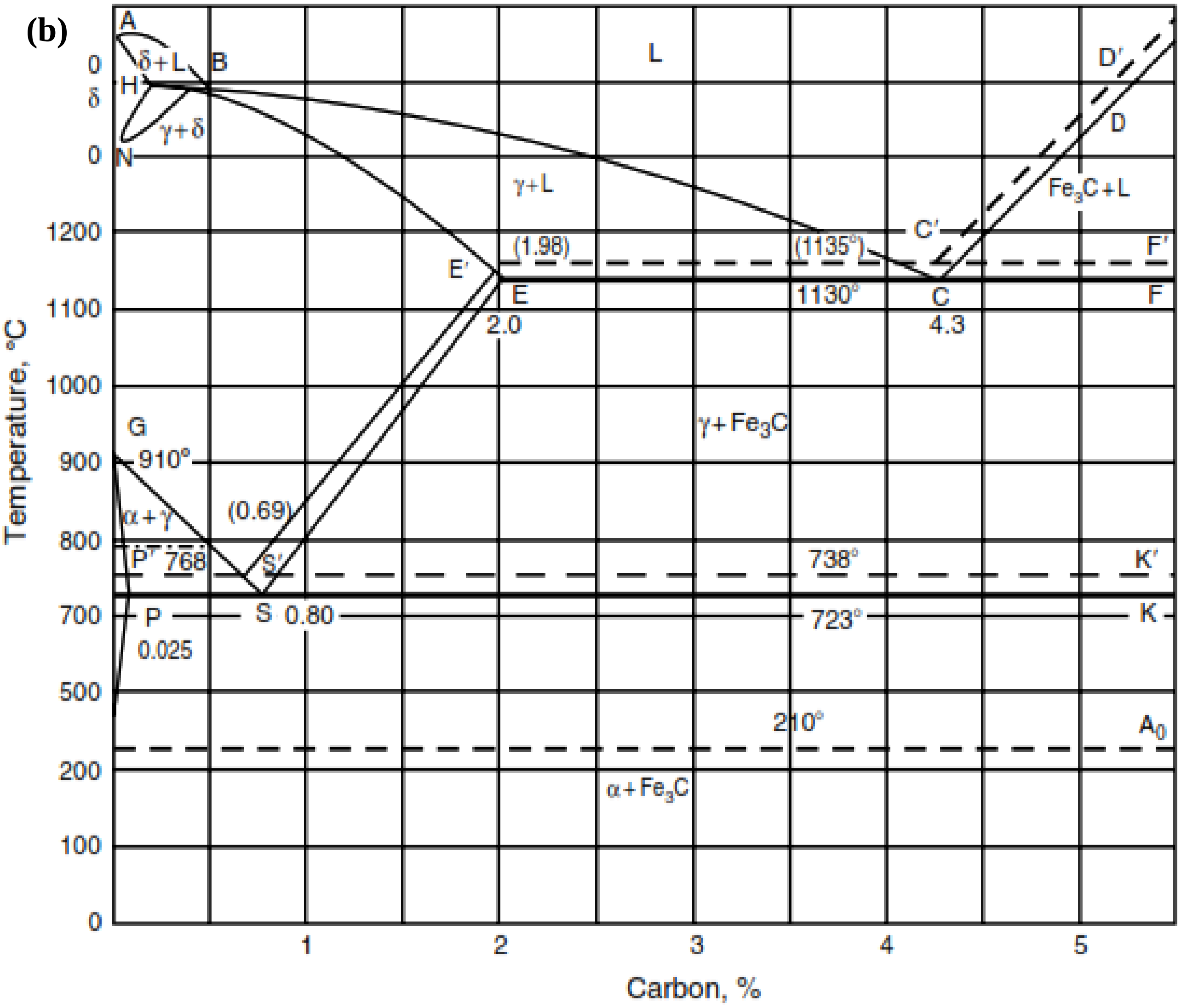


Figure 1.11. **(a) &(b)** Iron-carbon equilibrium diagram

Table 1. Summary of components of the Iron–Carbon System

Name	Definition
Ferrite	• Solid solution of carbon in α-iron, it is stable form of iron below 910 ℃ • The maximum solubility is 0.025% C at 723 (727) ℃ and it dissolvesonly 0.008% C at room temperature. • It is the softest structure that appears on the diagram
Austenite	• Solid solution of carbon in γ-iron, maximum solubility is 2.0 % C at 1130 °C. • High formability, most of heat treatments begin with this single phase. • It is normally not stable at room temperature. But, under certain conditions it ispossible to obtain austenite at room temperature
Cementite	• Iron carbide (Fe_3C), is very hard, brittle intermetallic compound ofiron and carbon, as Fe_3C, contains 6.67 % C. • It is the hardest structure that appears on the diagram, exact meltingpoint unknown. • Its crystal structure is orthorhombic
Ledeburite	• Eutectoid mixture of carbon solid solution in γ-iron with iron carbide, in other word it is the eutectic mixture of austenite and cementite. • It contains 4.3% C and is formed at 1130°C.

Bainite	- Mixture of ferrite and cementite formed by isothermal transformation of austenite under selected conditions.
Pearlite	- Eutectoid solid solution of carbon in α-iron with iron carbide which iscontaining 0.80%C and it is formed at 723 °C on very low slow cooling. - It is very fine plate like or lamellar mixture of ferrite and cementite.
Martensite	- It is a super saturated solid solution of carbon in ferrite. - It is formed when steel is cooled so rapidly that the change fromaustenite to pearlite is suppressed

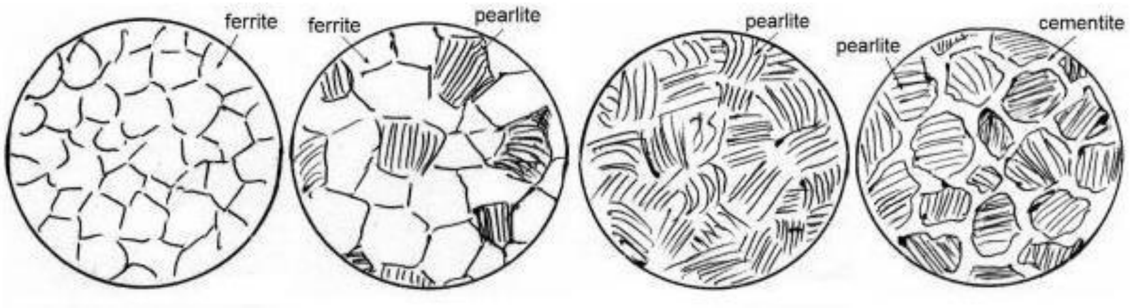


Figure 1.12. Microstructure of Components of the Iron–Carbon System

6. Main Reactions and Lines in Iron-Carbon Diagram

isothermal reactions(on cooling / heating): The diagram shows three reactions (on cooling / heating):

- ***Peritectic***: L + δ → γ at 1490 ℃
- ***Eutectic***: L → γ + Fe_3C at 1130 ℃ max solubility of carbon in ferrite is 0.025%
- ***Eutectoid***: γ → α + Fe_3C at 723 ℃ max. solubility of C in austenite is 2.11%

The diagram shows three horizontal lines which indicate

- First horizontal line is at 1490 °C, where peritectic reaction takes place:

  Liquid + δ ↔ austenite
- Second horizontal line is at 1130 °C, where eutectic reaction takes place:

  liquid ↔ austenite + cementite
- Third horizontal line is at 723 °C (Ac_1), where eutectoid reaction takesplace:

  austenite ↔ pearlite (mixture of ferrite & cementite)

Chapter 2

Time-Temperature Transformation (TTT) Diagram
&
Continuous Cooling Transformation (CCT) Diagram

2.1 Introduction

There are two main types of transformation diagram that are helpful in selecting the optimum steel and processing route to achieve a given set of properties. These are:

- **Time-Temperature Transformation (TTT) Diagram:** It measures the rate of transformation at a constant temperature. In other word, a sampleis austenitized and then cooled rapidly to a lower temperature and heldat that temperature whilst the rate of transformation is measured.Obviously, a large number of experiments are required to build up a complete TTT diagram.
- **Continuous Cooling Transformation (CCT) Diagram*:*** It measures the extent of transformation as a function of time for a continuously decreasing temperature. In other word, a sample is austenitized and thencooled at a predetermined rate and the degree of transformation is measured. Obviously, a large number of experiments are required to build up a complete CCT diagram.

2.1.1. T (Time) T (Temperature) T (Transformation) diagram

It is used to determine when transformations begin and end for an isothermal (constant temperature) heat treatment of a previously austenitized alloy, so this diagram is called ***Isothermal Transformation diagram***. When austenite is cooled slowly to a temperature below lower critical temperature (LCT i.e.,723 or 727°C), the structure that is formed is Pearlite. As the cooling rate increases, the pearlite transformation temperature gets lower. The microstructure of the material is significantly altered as the cooling rate increases. TTT diagram indicates when a specific transformation starts and ends and it also shows what percentage of transformation of austenite at a particular temperature is achieved. Cooling rates in the order of increasing severity are achieved by quenching from elevated temperatures as follows: furnace cooling, air cooling, oilquenching, liquid salts, water quenching, and brine. If these cooling curves are superimposed on the TTT diagram, the end product structure and the timerequired to complete the transformation may be found.

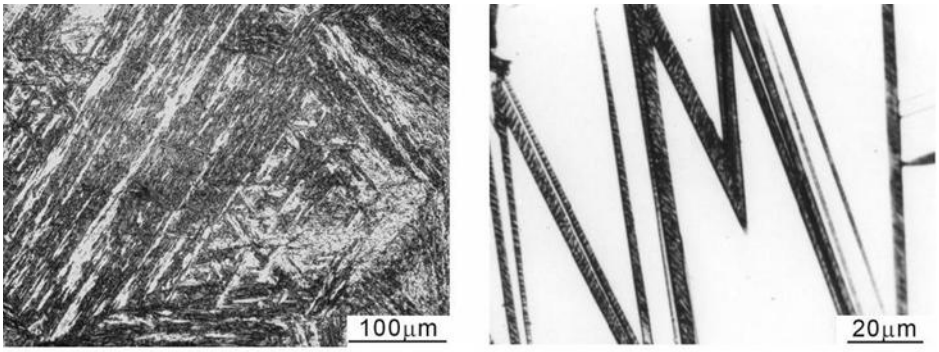
2.1.1.1 Factors Affecting T.T.T. Diagram

a. Carbon Content (wt%)

As the carbon content increases A_3 decreases. So, the incubation period for the austenite to pearlite increases i.e., the C curve moves to right. However, after 0.77wt%C any increase in carbon content, A_{cm} line goes up, i.e., austenite become less stable with respect to cementite precipitation. So, transformation to pearlite becomes faster. Therefore, C curve moves towards left after 0.77%C. Pearlite formation is preceded by ferrite in case of hypoeutectoid steel and by cementite in hypereutectoid steel.

For eutectoid steel bainitic transformation occurs at 250 to 550°C. At higher temperature it is upper bainite and at lower temperature it is lower bainite. Ascarbon increases the austenite to ferrite decomposition becomes increasinglydifficult. As bainitic transformation precedes by the nucleation of ferrite, therefore bainitic transformation range moves to higher timing and lower temperature. With increasing percentage of carbon, the amount of carbide in upper bainite increases and carbides become continuous phase. However, at lower percentage of carbon they are discrete particles and amount of carbide will be less in both types of bainites. For start and finish temperatures for bothtypes of bainites go down significantly with increasing amount of carbon. However, increasing carbon makes it easier to form lower bainite.

For eutectoid steel, martensite forms at around 230°C. From 230°C to room temperature martensite and retained austenite are seen. At room temperature about 6% retained austenite can be there along with martensite in eutectoid steel. At lower carbon percentage M_s goes up and at higher percentage it goesdown. Below 0.4%C there is no retained austenite at room temperature but retained austenite can go up to more than 30% if carbon percentage is more than 1.2%. Morphology of martensite also changes from lath at low percentage of carbon to plate at higher percentage of carbon (Figure 2.1). Plate formation is start at around 0.6%C. Therefore below 0.6% carbon only lath martensite can be seen, mixed morphologies are observed between 0.6%C to1%C and above 1% it is 100% plate martensite.



Lath Martensite
(Fe-9%Ni- 0.15%C)

Thin plate Martensite
(Fe-31%Ni- 0.23%C)

Figure 2.1 Changes in Morphology of Martensite

b. Alloying Elements

Almost all alloying elements (except, Al, Co, Si) increases the stability of super cooled austenite and retard 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 reduces the rate of allotropic change*. 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, T_i, 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.

The effect of alloying elements is less pronounced in bainitic region as the diffusion of only carbon takes place (either to neighbouring 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. Most alloying elements which are soluble in austenite lower M_s and M_f temperature except Al and Co. 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.

c. Grain Size of Austenite

Fine grain size shifts C curve towards left side because it helps for nucleation of ferrite, cementite and bainite. However, M_s is lowered by reduction in austenite grain size. Grain size of austenite affects the maximum plate or lathsize, i.e., larger the austenite size the greater plate size or lath size.

d. Heterogeneity of Austenite

Heterogeneous austenite increases transformation time range, start to finish offerritic, 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 agents for pearlite transformation.

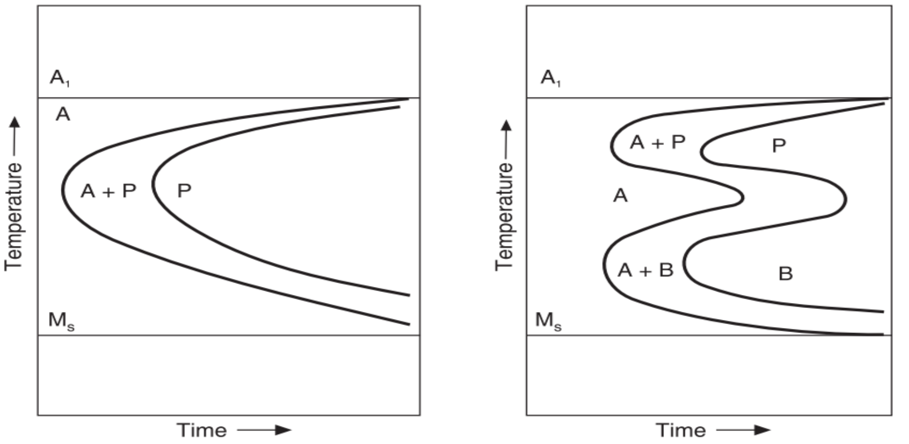
2.1.1.3 Effect of Alloying Elements on TTT Diagram

Almost all alloying elements, except cobalt, decrease both the tendency for and the rate of decomposition of austenite. The reason for this is obvious for austenite stabilizing elements. Ferrite stabilizers do the same job by forming carbides. Alloy carbides are more stable than cementite, and hence they retard the diffusion of carbon which in turn decrease the rate of decomposition of austenite. Strong carbide formers have more pronounced effect on the retardation of austenite decomposition than the weak carbide formers. Since pearlitic transformation involves diffusion of both carbon and metallic atoms, the effect of alloying elements is much more pronounced in pearlitic region. The effect is less pronounced in bainitic region as bainitic transformation involves diffusion of carbon atoms only. The TTT diagrams for alloy steels can broadly be classified into four types as shown in Figure 2.2.

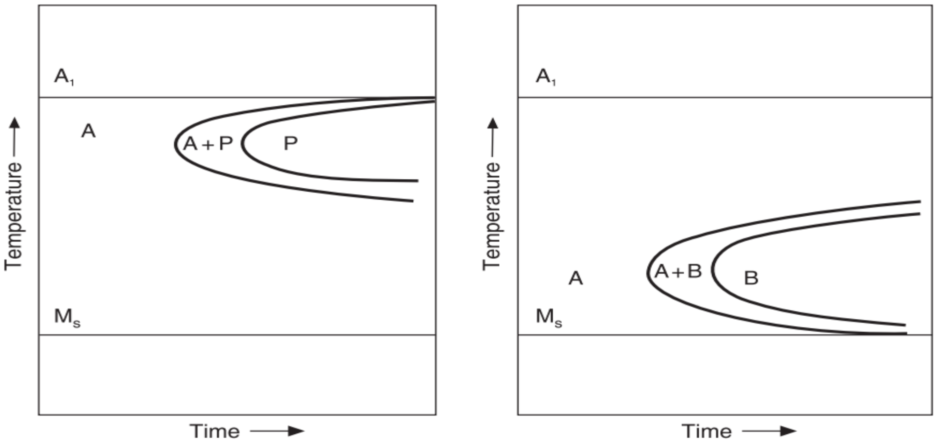
The first type of TTT diagram [Figure 2.2(a)] is similar to that of carbon steel. There is practically no difference in the pattern of austenite decomposition in the presence of non-carbide forming elements. However, in the presence of carbide forming elements, supercooled austenite decomposes to a mixture of ferrite and carbides rather than to an aggregate of ferrite and cementite.

The second type of TTT diagram [Figure 2.2(b)] differs from the remaining TTT diagrams as it consists of two minima with respect to the stability of austenite. The upper bay (at higher temperature) corresponds to the transformation of austenite to pearlite, whereas the lower bay corresponds to the transformation of austenite to bainite. Very few steels exhibit such a TTT diagram. The two types of TTT diagrams discussed above are, in general, observed for low alloy steels.

The third type of TTT diagram [Figure 2.2(c)] is peculiar in the sense that bainitic region is not present. This implies that bainite cannot be formed in such steels. Such a TTT diagram is obtained, in general, for high alloy steels, especially those in which the start of martensitic transformation temperature has been shifted to sub-zero region. In such steels, stable austenitic structure is obtained at room temperature. The fourth type of TTT diagram [Figure 2.2(d)] does not exhibit pearlitic bay. Here, under normal cooling conditions, either bainite or martensite is formed.



(a) with resemblance of plain carbon steel (b) with both pearlitic and bainitic bays



(c) without bainitic bay (d) without pearlitic bay

Figure 2.2 Various types of TTT diagrams for alloy steels.

2.1.2 Continuous Cooling Transformation

The TTT diagrams have gained great importance from heat treater's point of view. This is due to the simple reason that these diagrams are extremely useful as they give information about the hardening response of steels and the nature of transformed products of austenite at varying degrees of supercooling.

In practice, however, transformation during heat treatment occurs by continuous cooling, and not isothermally. Thus, TTT diagrams have limited applications. For most of the heat treatment processes, these diagrams are useful only qualitatively, and not quantitatively. A diagram, which can correlate transformation, temperature and time during continuous cooling, will be of real value to heat treaters. Continuous cooling transformation (CCT) diagrams can be obtained by a technique which is similar to that for TTT diagrams except that, in the case of CCT diagrams, points of start and end of austenitic transformation are recorded on continuous cooling. For the construction of CCT diagram for a eutectoid steel, a large number of small samples are heated above the lower critical temperature (A_1) to get a completely austenitic structure. From this temperature, specimens are cooled at a constant cooling rate, and points corresponding to start and finish of pearlite are determined. By repeating the same process at various cooling rates, different sets of start and end points for pearlitic transformation are obtained. On joining start and end points, two curves, similar to those in TTT curves, corresponding to start and end of transformation, are obtained. Thus, a CCT diagram is obtained. The CCT diagram for eutectoid steel is shown in Figure 2.3.

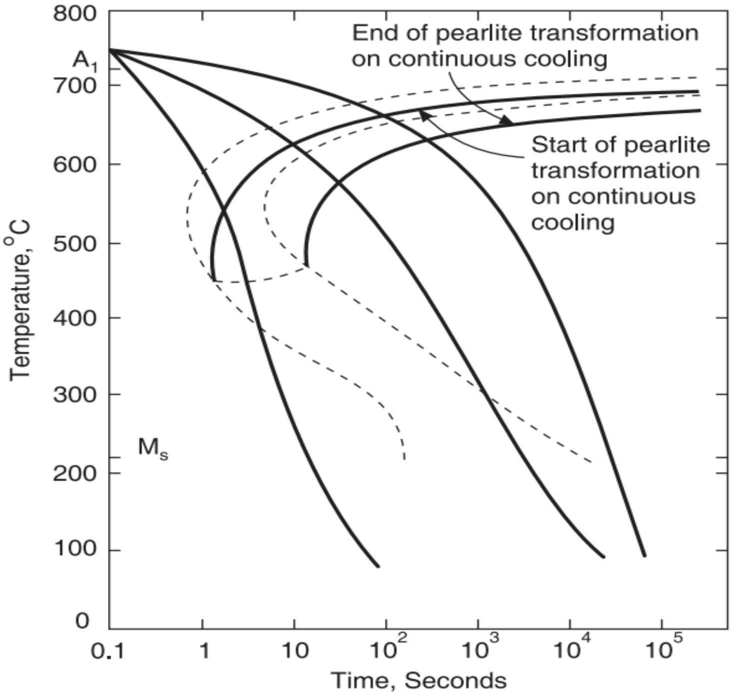


Figure 2.3 CCT diagram for eutectoid steel.

2.2. Pearlitic Transformation

Pearlite is an eutectoid mixture of two phases, namely, ferrite and cementite. The microstructure of pearlite is shown in Figure 2.4. It consists of alternate layers of ferrite and cementite. It is an important constituent of steel and is present in almost all the steels which have been slowly cooled. The mechanical properties of annealed or normalized hypoeutectoid steels mainly depend on this constituent. Pearlite is formed by cooling austenite of eutectoid composition just below the lower critical temperature. The pearlite, thus formed, consists of about 88 percent ferrite and 12 percent cementite. It is important to point out at this stage that in spite of the lamellar structure, ferrite is a continuous phase.

Figure 2.4 Microstructure showing lamellar nature of pearlite (×1200).

One of the most interesting features of austenite to pearlite transformation is that the transformation product (pearlite) consists of two entirely different phases. One phase, i.e. ferrite, has very low carbon content and for all practical purposes, it can be considered almost pure iron, whereas the second phase, i.e. cementite (Fe_3C), is an intermetallic compound of iron with 6.67 wt.% carbon. Such a transformation is possible only by the redistribution of carbon atoms of austenite on cooling. The redistribution takes place by diffusion of carbon atoms. Thus, the pearlitic transformation is essentially a diffusion-controlled phenomenon and proceeds by nucleation and growth mechanism.

Another aspect to be considered in this context is: Which one of the two phases (ferrite and cementite) nucleates first? The nucleus which is formed first is referred to as active nucleus for pearlitic transformation, provided it is present in the transformed product and has lattice orientation relationship with parent austenite. It has not been possible till date to specify with certainty as to which one of the two phases nucleates first. Also, there is no theory which can explain all the characteristics associated with pearlitic transformation such as lamellar nature, temperature dependence of interlamellar spacing and of kinetics of transformation and, finally, the effect of alloying elements on interlamellar spacing and on kinetics of transformation. However, it is a well-established fact that active nuclei for austenite to bainite transformation are ferrite crystals. Active nuclei for pearlitic transformation are generally taken to be cementite platelets. This assumption can explain the lamellar nature of pearlite. An orientation relationship between cementite and austenite has also been found, which confirms that cementite platelets are active nuclei for pearlitic transformation.

2.2.1 Mechanism of Transformation

The most widely accepted mechanism of pearlite formation is due to Mehl and his coworkers.

According to them, the active nucleus for austenite to pearlite transformation is cementite.

Some of the reasons in favour of their proposal are based on the following observations:

(i) Orientation relation between pearlitic ferrite and parent austenite is different from that of proeutectoid ferrite and parent austenite. Therefore, ferrite cannot be active nucleus. This is in contrast to bainitic transformation where ferrite has an orientation relation with parent austenite.

(ii) Formation of pearlite is affected by the presence of undissolved cementite particles whereas the presence of ferrite does not exhibit any such effect,

(iii) Proeutectoid cementite as well as pearlitic cementite platelets are, in general, parallel to a high index (or low atomic density) plane of austenite.

Many doubts have been raised about Mehl's hypothesis. The assertion that cementite is an active nucleus for the transformation was challenged. According to Smith's generalized hypothesis, "pearlitic ferrite as well as pearlitic cementite can have any orientation relationships with the parent austenite except for those which allow the formation of interfaces which are partially coherent with the parent austenite". Both cementite and ferrite can be active nucleus and, consequently, formation of pearlite can be initiated by either of the two. In general, ferrite will form first in hypoeutectoid steels and will then nucleate pearlite, whereas cementite will form first in hypereutectoid steels and then nucleate pearlite. The most popular model for the formation of pearlite has been proposed by F.C. Hull and R.F. Mehl. This model explains the lamellar nature of pearlite. Figure 2.5 shows the mode of formation of pearlite colony from austenite. According to the Hull-Mehl model, the cementite platelet is nucleated first at the austenitic grain boundaries. The diffusion of carbon atoms from the austenite surrounding the cementite platelet takes place, and thus the cementite platelet grows. The carbon diffusion results in lowering of carbon in austenite and, Consequently, austenite transforms to ferrite. The transformation of austenite to ferrite takes place only when the carbon content of austenite reaches some minimum critical value. Thus, ferrite nucleates at the interface of cementite and adjacent austenite and grows along the surface of the cementite plate. Since ferrite is almost carbon-free phase, the growth of ferrite is accompanied by the rejection of carbon. In this process of ferrite growth, the austenite adjacent to ferrite is enriched with carbon. The enrichment of austenite continues till a new platelet of cementite nucleates. Growth of this cementite platelet lowers the carbon content of the adjacent austenite and again ferrite is nucleated. Such a sequence of formation of cementite and ferrite continues, resulting in a lamellar structure.

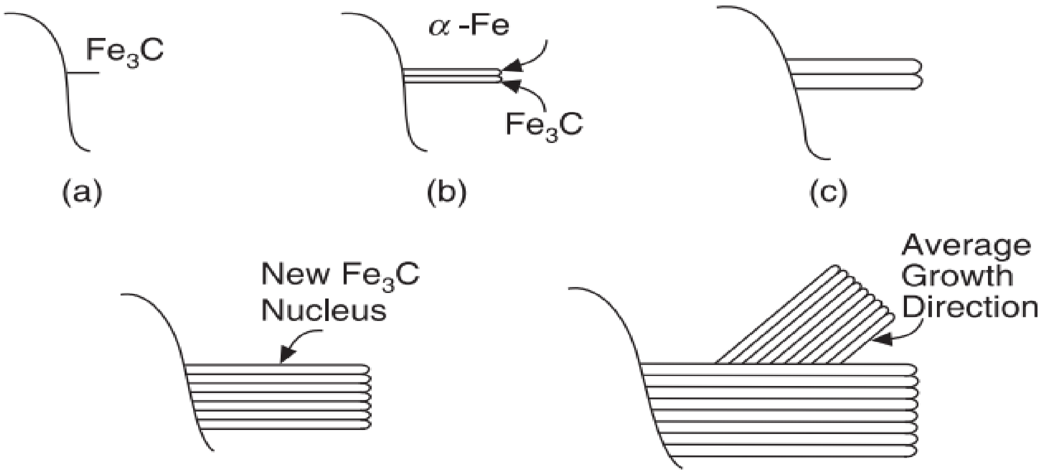


Figure 2.5 Successive stages in formation of pearlite from austenite.

New colonies of pearlite are also formed at the interfaces between the already formed colonies and the adjacent parent austenite. These colonies also grow in the same manner as already discussed. In this way, a pearlite colony grows by simultaneous edge-wise and sidewise growth by repeated nucleation. This process of nucleation of new colonies and growth of existing ones continues till the complete austenitic grain is consumed and converted into a pearlite nodule which is generally spherical in shape as pearlitic colonies are formed with almost equal growth rates along and perpendicular to the lamellae directions. During growth, a pearlitic colony may meet an adjacent pearlitic colony (colonies), and a common boundary results. Prior to formation of such a boundary, the growth rate for pearlitic colonies is constant and so the colonies are almost of the same size. Some parent austenite remains in between pearlite nodules which may grow by consuming such an austenite. With this final stage of pearlite growth, austenite to pearlite transformation is completed.

2.2.2 Kinetics of Transformation

At a lower critical temperature, the free energy of austenite is equal to the free energy of pearlite. Therefore, at this temperature, transformation of pearlite from austenite will be completed in infinite time. In other words, the austenite to pearlite transformation rate will be zero for all practical purposes at this temperature. It is therefore essential to undercool the austenite below the equilibrium (A_1) temperature. Below the lower critical temperature, the free energy of pearlite is lower than that of austenite and so the pearlite is thermodynamically stable. The lower the free energy of pearlite, the more is the stability of the pearlite. Free energy of pearlite will be less at lower temperatures, and hence the stability of pearlite can be increased by increasing the degree of supercooling or, in other words, by lowering the transformation temperature. This means that the rate of austenite to pearlite transformation increases with lowering of transformation temperature.

The decomposition of austenite to pearlite proceeds by the redistribution of carbon atoms of austenite into ferrite and cementite, and is essentially a diffusion-controlled process. The rate of diffusion of carbon atoms decreases exponentially with decreasing temperature. This implies that lower transformation temperature retards the rate of transformation. There may be a transformation temperature for which the diffusion rate for carbon atoms may be too small to result in the diffusion-controlled transformation. In general, for all practical purposes, the rate of carbon diffusion is negligible below 200°C. This means that undercooling affects the rate of transformation in two ways: On the one hand, increased degree of undercooling increases the transformation rate by providing a greater difference in free energies of austenite and pearlite (curve (b) of Figure 2.6). On the other hand, increased degree of undercooling reduces the transformation rate by lowering the rate of carbon diffusion (curve (a) of Figure 2.6). The combined effect is shown as curve (c) in Figure 2.6.

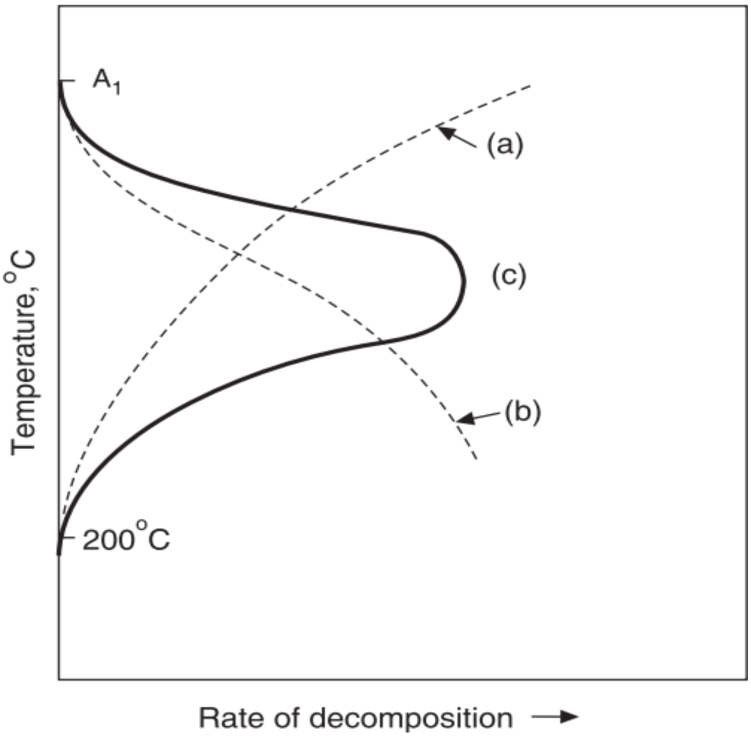


Figure 2.6 Effect of temperature on rate of transformation of austenite.

The austenite to pearlite transformation is completed by nucleation and growth mechanism. The rate of transformation is governed by both the rate of nucleation (N) and the rate of growth (G), which are in turn controlled by transformation temperature. The rate of nucleation is expressed as total numbers of nuclei appearing per unit time in a unit volume of untransformed austenite. Both the rate of nucleation and the rate of growth are zero at eutectoid temperature. They also tend to be zero below 200°C, as shown in Figure 2.7.

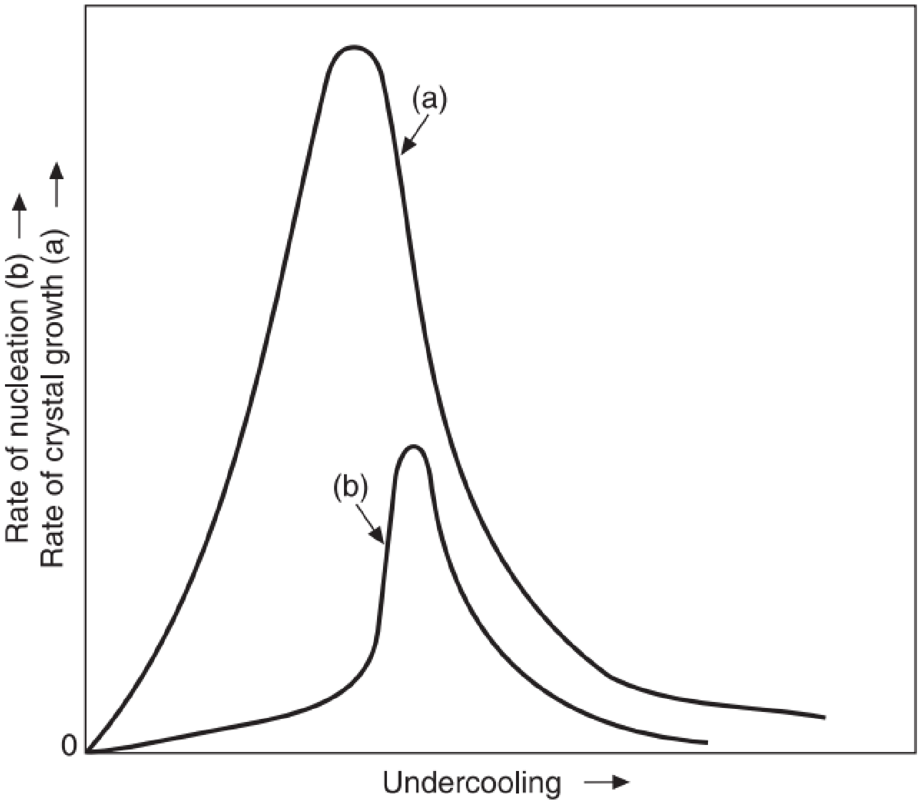


Figure 2.7 Effect of degree of undercooling on the rates of nucleation and growth.

2.2.3 Effect of Alloying Elements on Transformation

Transformation of austenite to pearlite in alloy steels is more complicated than in carbon steels. Almost all alloying elements, whether ferrite stabilizers or austenite stabilizers, except cobalt, lower both the rate of nucleation and the rate of growth. As compared to carbon, alloying elements diffuse very slowly. Carbon and alloying elements partition to ferrite and carbide phases on decomposition of austenite. The partitioning approaches equilibrium value at higher transformation temperatures, say, in the vicinity of eutectoid temperature. As transformation temperature decreases, the amount of carbon and alloying elements present in ferrite and carbide phases deviate from equilibrium partitioning. Stable carbides, in general, possess higher metal to carbon ratio. As the diffusion rate for metallic atom is much slower than carbon atom, the formation of stable carbides during pearlitic transformation will be feasible only at higher transformation temperatures.

2.2.4 Interlamellar Spacing

Interlamellar spacing of pearlite is of great significance as it affects the mechanical properties of steel. Interlamellar spacing is a function of transformation temperature alone, provided all other parameters are kept constant. This implies that interlamellar spacing can be assigned a definite value for a given transformation temperature. The lower the transformation temperature, the smaller is the interlamellar spacing. The smaller the interlamellar spacing, the stronger is the steel. Interlamellar spacing is less for both hypoeutectoid and hypereutectoid steels than for eutectoid steel. Alloying elements, except cobalt, increase the interlamellar spacing. The simple reason for this is that alloy steels transform at higher temperatures. This, in turn, increases interlamellar spacing. One of the interesting features of interlamellar spacing is that it is structure-insensitive in nature, i.e. it does not depend on austenitic grain size and the degree of homogeneity of the austenite.

2.3 Bainitic Transformation

The term bainite refers to a mixture of ferrite and carbide. This ferrite-carbide mixture has a basic difference with respect to pearlite. It is not lamellar in nature. Also, the distribution of carbides is on finer scale. Hence, higher magnifications than those required for resolution of pearlite are required in order to resolve the bainite which is formed within a specific temperature range. The upper limit of the range is just below the minimum temperature for pearlitic transformation which, in general, is below the nose of the TTT curve for a given steel. Thelower limit of the temperature range is above the M_s temperature, i.e. above the temperature at which martensite formation starts. For a eutectoid steel, bainite forms from the undercooled austenite in the temperature range of 200–500°C. Transformation of austenite to bainite occurs only below a definite temperature, known as Bs temperature. Only a few alloy steels exhibit the presence of sharp B_s, temperature. For such steels, two separate bays, one each for pearlite and bainite, exist. Austenite can be transformed into bainite either isothermally or by continuous cooling in such a case. Figure 2.8 shows the TTT curve for an alloy steel having separate pearlitic and bainitic bays. However, for carbon steels and most of the alloy steels, pearlitic and bainitic bays overlap, and austenite transforms to pearlite or martensite, depending on the cooling rate. In such steels, bainite cannot be produced by continuous cooling. It can be formed by cooling austenite at a sufficiently high rate so that its transformation to pearlite is suppressed. Austenite to bainite transformation completes at a definite temperature designated as B_f, the end temperature of bainitic transformation. Figure 2.8 illustrates the isothermal transformation to bainite.

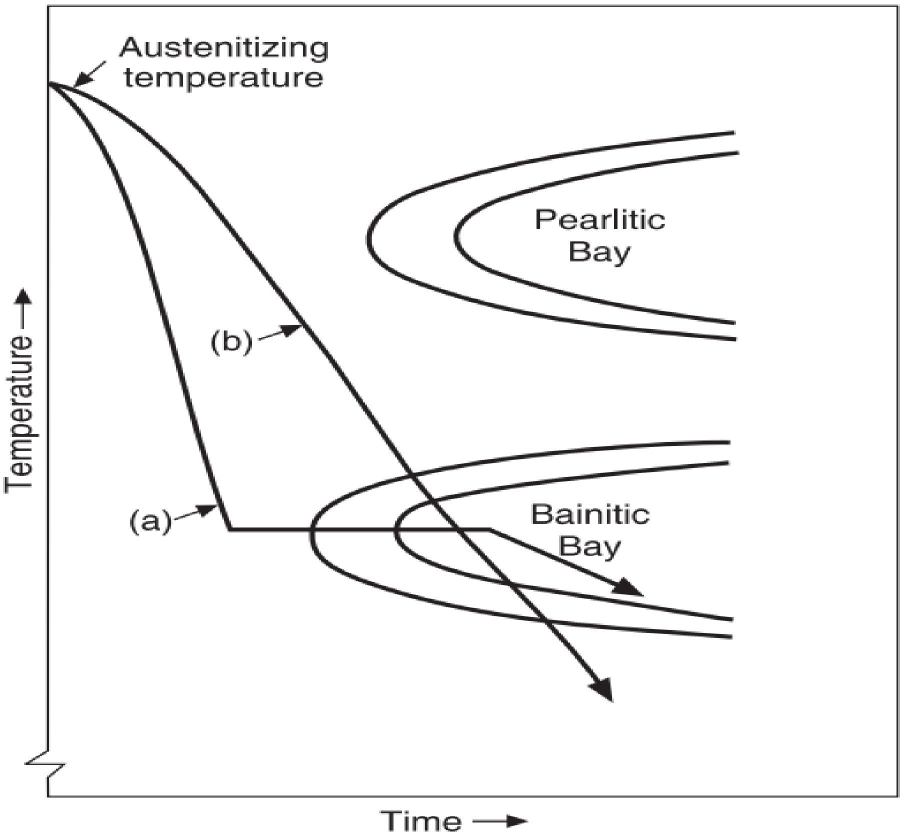


Figure 2.8 Formation of bainite by isothermal transformation of austenite.

2.3.1 Mechanism of Bainitic Transformation

The presence of incubation period for bainitic transformation implies that the transformation is diffusion controlled. However, formation of bainite starts at a temperature at which the diffusion of iron atoms is very slow (almost zero for all practical purposes), but the diffusion of carbon atoms is very important. No significant diffusion of metallic atoms (alloying elements) is possible at this temperature. This means that, in addition to diffusion, some other mechanism is also involved in bainitic transformation. It has been observed that the formation of bainite is always accompanied by surface distortion. This implies that shear processes are also involved in bainitic transformation. Thus, the bainitic transformation is complex by nature as both diffusions controlled and diffusion less (shear) processes are involved. It exhibits features common to both types of transformations. When austenite is undercooled below the B_s temperature, carbon atoms redistribute in the austenite by diffusion. This redistribution leads to the formation of regions with varying carbon concentrations in austenite. Some of these regions are enriched in carbon whereas others are depleted in carbon. Such a difference in carbon concentration will result in the development of stresses. The M_s (the start of martensitic transformation) temperature for austenitic regions with low carbon content lies in between the B_s and B_f temperatures. Here, low carbon austenitic regions transform to martensite (ferrite) by diffusion less (shear) process. It is important to note here that low carbon austenite, which transforms to ferrite by shear process, is itself produced by diffusion process. A portion of the carbon enriched austenitic regions does not transform on cooling from holding temperature to room temperature. Such a portion may transform partially to martensite. Thus, a characteristic feature of bainitic transformation is that it is never completed. A structure consisting of bainite and martensite or bainite and retained austenite is obtained. Precipitation of carbides may occur from the carbon enriched austenitic regions, depending on the degree of saturation. The carbon depleted austenitic regions thus obtained by the precipitation of carbides now transform to ferrite by shear mechanism. Such a condition is favourable in the upper region of the intermediate transformation temperature range. As ferrite has very low solubility for carbon, the transformed ferrite will be supersaturated with carbon. The degree of supersaturation increases with decrease in transformation temperature. As carbon diffusion is intensive in the bainitic transformation region, carbon may precipitate out from the supersaturated ferrite. This happens when the bainitic transformation proceeds in the lower region of the transformation range. Thus, in spite of the fact that mechanism of transformation for bainite is same over the entire temperature (B_s–B_f) range, various bainitic structures can be obtained within the bainitic temperature range, depending on the transformation temperature.

2.3.2 Bainitic Structures

The two typical structures of bainite are referred to as upper and lower bainites. The upper bainite is feathery, whereas the lower bainite is accicular in appearance. Figures 2.9 and 2.10 show the microstructures of upper and lower bainite, respectively. The names upper and lower bainites signify that the former is formed in the upper region and the latter in the lower region of the bainitic transformation temperature range. The microstructure of upper bainite consists of lath-shaped ferrite with precipitated carbides parallel to the needle axis. This structure differs considerably from that of lower bainite which consists of ferrite plates within which carbides have been precipitated at an angle to the major axis of the plate. The sequence of formation of upper and lower bainites is shown in Figures 2.11 and 2.12, respectively.

Figure 2.09 Microstructure of upper bainite (×500).

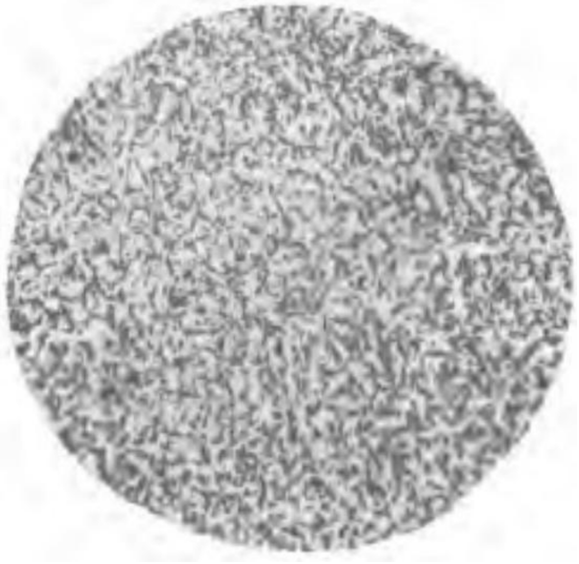


Figure 2.10 Microstructure of lower bainite (× 500).

Both upper and lower bainites are nucleated by ferrite, i.e. ferrite is an active nucleus for both. This ferrite is formed by the transformation of low carbon austenitic regions to ferrite, and is coherent with the parent austenite. The ferrite thus nucleated grows into bainitic plate on cooling to and holding at a temperature in the bainitic region. The bainite plate so formed is surrounded by austenite which is enriched in carbon. The diffusion of carbon is significant in bainitic transformation temperature range, and specially in the upper region of the range. Carbon diffusion takes place in the carbon enriched austenite surrounding the bainitic plate, giving rise to the formation of cementite (carbide) at the austenite-bainite interface. The formation of cementite results in the depletion of carbon from the austenite. Low carbon austenitic region thus obtained transforms to ferrite by the shear mechanism. In this way, the growth of the existing bainitic plates and nucleation of new bainitic plates proceed simultaneously. Therefore, the diffusion of carbon in carbon enriched austenite surrounding the bainitic plate is the most important (controlling) step in the formation of upper bainite. The transformation temperature has an important effect on the morphology of upper bainite. This change in the morphology of upper bainite is due to the sympathetic nucleation of ferrite laths. These laths are in intimate contact with each other. The formation of upper bainite is accompanied by multiple surface relief. It confirms that the upper bainite is formed by sympathetic nucleation. A number of lattice orientation relationships have been found between ferrite and precipitated cementite in the upper bainite. Majority of these relationships match with those existing in the tempered martensite. The lower bainite differs from the upper bainite with respect to the transformation temperature. The lower bainite is formed at the transformation temperature which lies within the lower region of the bainitic transformation temperature range. In contrast to the upper bainite, the diffusion of carbon in supersaturated ferrite (formed from low carbon austenite by shear mechanism) is the controlling step in the formation of lower bainite. Carbides are precipitated from supersaturated ferrite in the case of lower bainite. The nature of the precipitated carbide, in addition to being dependent on chemical composition of steel, is also a function of transformation temperature and transformation time. A lattice orientation relationship has also been observed between the bainitic ferrite and cementite in the lower bainite. This means that bainitic cementite has been precipitated out from the ferrite, and not from the austenite. The same fact has been confirmed by the presence of epsilon carbide in some alloy steels. Epsilon carbide cannot be precipitated from austenite. This is the reason why in lower bainite, carbides are formed at a definite angle to the major axis (generally growth direction) of the bainitic plate.

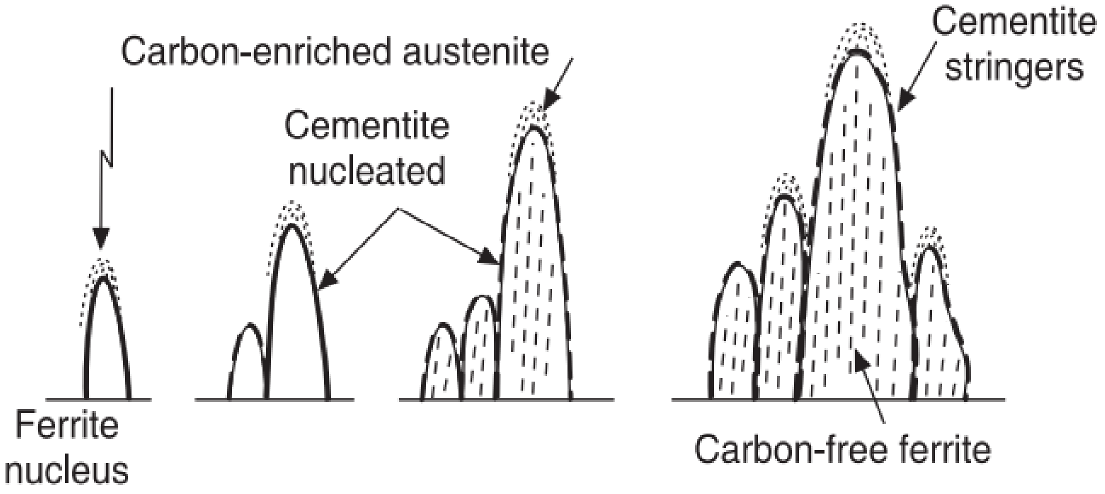


Figure 2.11 Stages in formation of upper bainite.

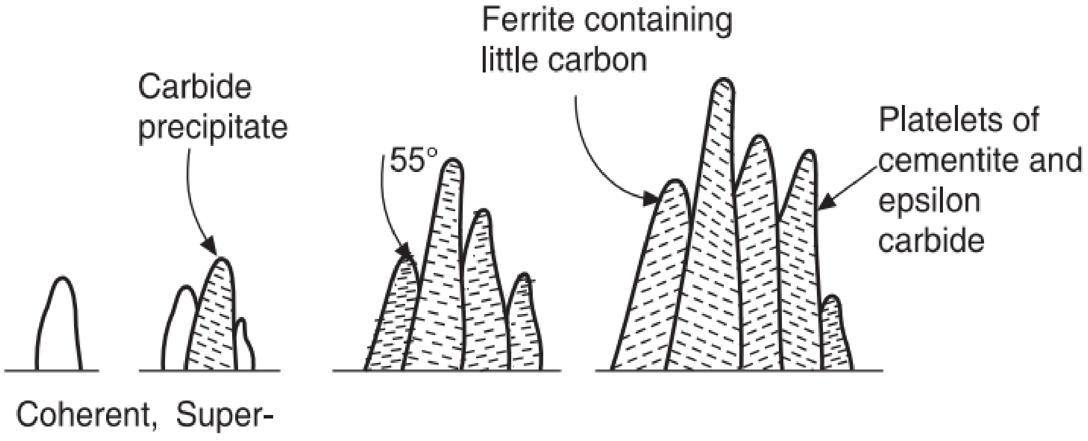


Figure 2.12 Stages in formation of lower bainite.

2.4 Martensite transformation

- Austenite transforms to martensite by rapid cooling from above eutectoid temperature to room temperature.
- Crystal structure of γ is (FCC) which transform to martensite (body centered tetragonal (BCT) involves collective motion of a lot of atoms.

Figure 2.13 shows the TTT diagram. The area on the left of the transformation curve represents the austenite region. Austenite is stable phase at temperatures above LCT but unstable below LCT. Left curve indicates the start of a transformation and right curve represents the finish of a transformation. The area between the two curves indicates the transformation of austenite to different types of crystal structures: austenite to pearlite, austenite to martensite, austenite to bainite transformation.

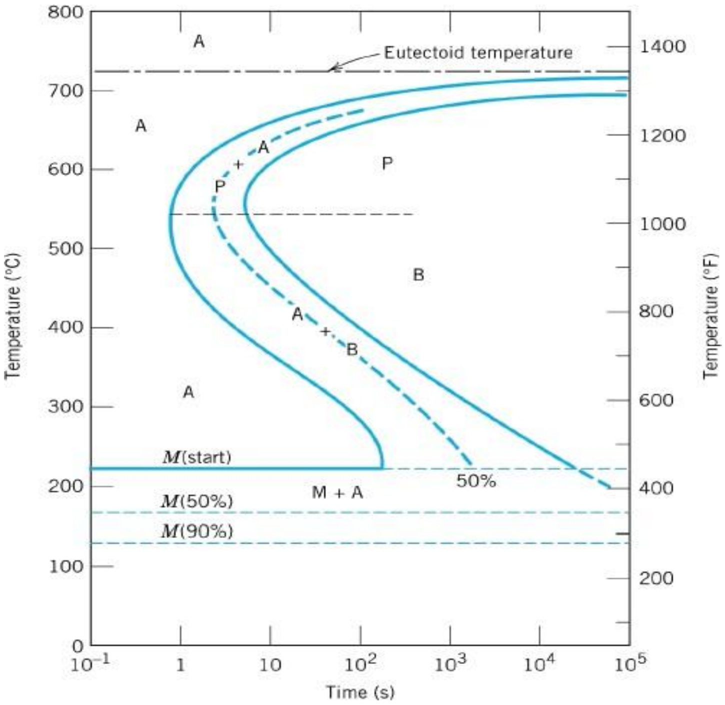


Figure 2.13 TTT diagram

Figure 2.14 show two rapid cooling rates represented by lines A and B. In this case line A will cause a higher distortion and higher internal stresses than thecooling rate B. The end product of both cooling rates will be martensite. Cooling rate B is also known as the ***critical cooling rate***, which is representedby a cooling curve that is tangent to the nose of the TTT diagram. *Critical cooling rate is defined as the lowest cooling rate which produces 100% martensite while minimizing the internal stresses and distortions.*

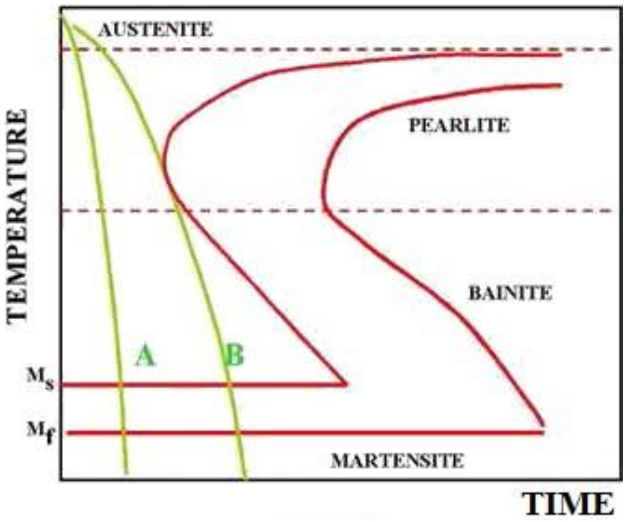


Figure 2.14 two rapid cooling rates represented by lines A and B

In Figure 2.15, a rapid quenching process is interrupted (horizontal line represents the interruption) by immersing the material in a molten salt bath and soaking at a constant temperature followed by another cooling process that passes through bainite region of TTT diagram. The end product is bainite,which is not as hard as martensite. As a result of cooling rate C; more dimensional stability, less distortion and less internal stresses are created.

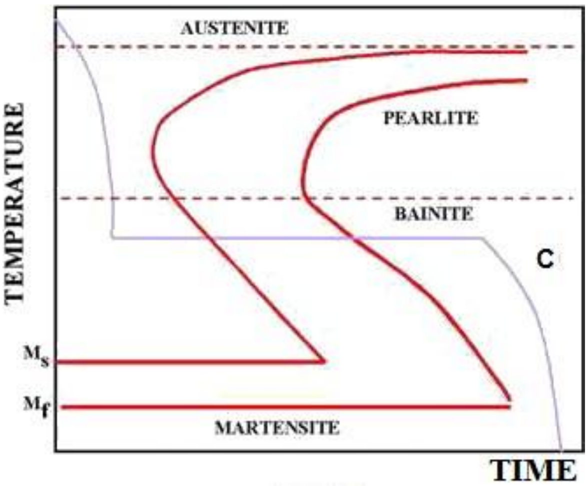


Figure 2.15 rapid quenching process is interrupted

In Figure 2.16 cooling line D represents a slow cooling process, such as furnacecooling. An example for this type of cooling is annealing process where all the austenite is allowed to transform to pearlite as a result of slow cooling.

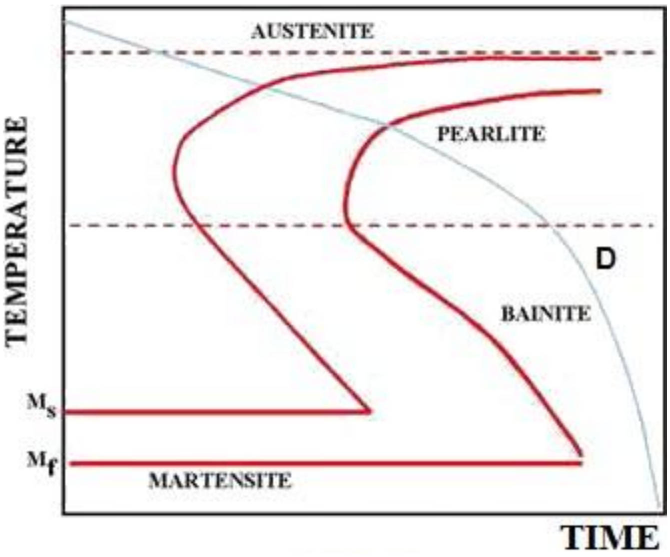


Figure 2.16 cooling line D: a slow cooling process

In Figure 2.17, cooling line E indicates a cooling rate which is not high enough to produce 100% martensite. This can be observed easily by looking at the TTT diagram. Since the cooling curve E is not tangent to the nose of the transformation diagram, austenite is transformed to 50% Pearlite (line E is tangent to 50% curve). Since line E leaves the transformation diagram at the martensite zone, the remaining 50% of the austenite will be transformed to martensite.

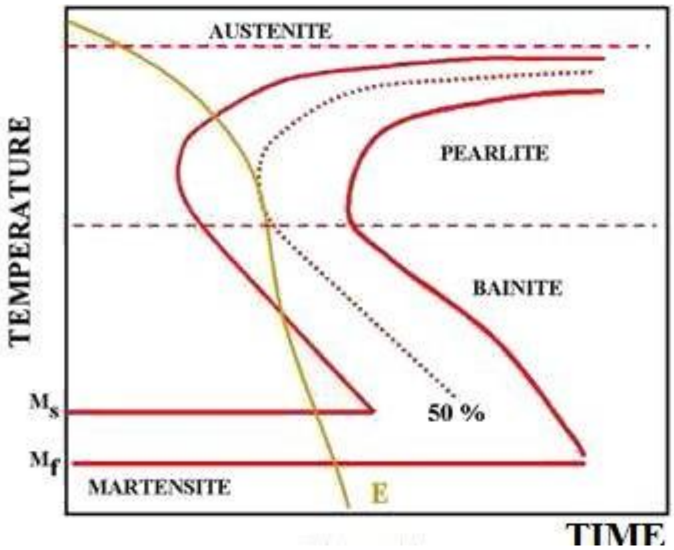


Figure 2.17 cooling line E: a cooling rate not high enough to produce 100% martensite

Chapter 3

CLASSIFICATION OF METAL ALLOYS

3.1. Classification of Metal Alloys

All metal alloys may be classified as ***ferrous*** or ***nonferrous*** alloys. A ferrous alloy has iron as its main element. An alloy is still considered ferrous even if it contains less than 50 percent iron, as long as it contains more iron than any other one metal. An alloy is nonferrous if it contains less iron than any other metal.

- ***Ferrous alloys*** are that contain iron as the base metal. The properties of ferrous alloys may be changed by adding various alloying elements. Ferrous alloys include steel, cast iron and the various steel alloys.
- ***Nonferrous alloys*** include a great many metals that are used mainly for metal plating or as alloying elements, such as tin, zinc, silver, gold, aluminum, magnesium, titanium, nickel and copper.

3.2 Classification of ferrous alloys:

Ferrous alloys include steel, cast iron and the various steel alloys, the only difference between iron and steel is the carbon content. Cast iron contains more than 2-percent carbon, while steel contains less than 2 percent. An alloy is a substance composed of two or more elements. Therefore, all steels are an alloy of iron and carbon, but the term “alloy steel” normally refers to a steel that also contains one or more other elements. For example, if the main alloying element is tungsten, the steel is a “tungsten steel” or “tungsten alloy.” If there is no alloying material, it is a “carbon steel.” Classification of ferrous alloys is shown in figure 3.1. Depending upon the carbon content and the reactions occurring in the iron-cementite phase diagram, the alloys of iron are broadly divided into two groups: steel and cast iron.

3.2.1. Steels

Steels are Iron-carbon alloys that may contain appreciable concentrations of other alloying elements; there are thousands of alloys that have different compositions and/ or heat treatments. The mechanical properties are sensitive to the content of carbon, which is normally less than 1.0 wt%. Some of the more common steels are classified according to carbon concentration into low, medium, and high-carbon steel (Figure 3.1). Subclasses also exist within each group according to the concentration of other alloying elements. Plain carbon steels contain only residual concentrations of impurities other than carbon and a little manganese.

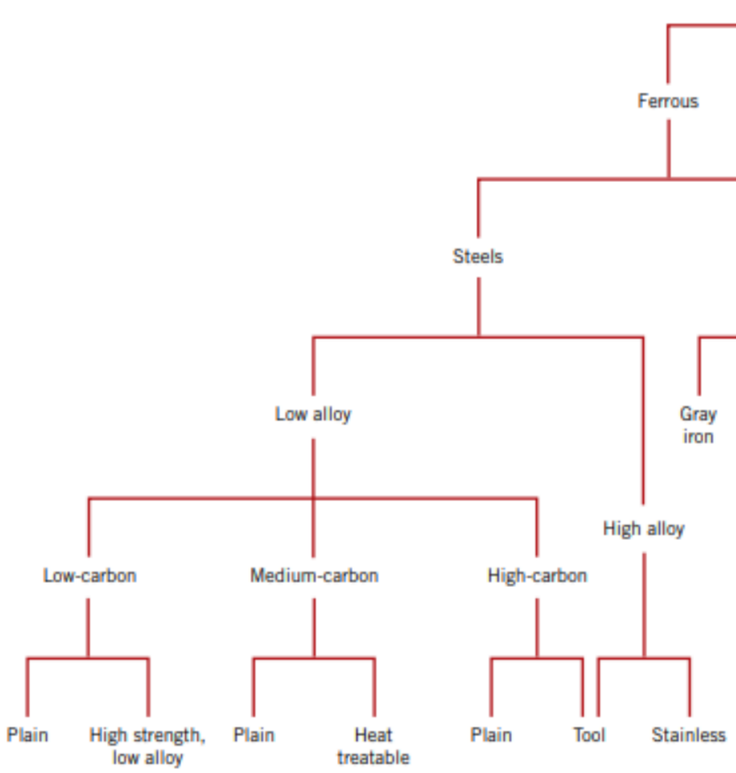


Figure 3.1. Classification of metal alloys, ferrous alloys

Steels with carbon content from 0.025 percent (point *P*) to 0.8 percent (point *S*) are called hypo-eutectoid steels. Steel with a carbon content of 0.8 percent is known as eutectoid steel. Steels with carbon content greater than 0.8 percent are called hypereutectoid steels.

3.2.1.1 Classification of Steels

In general, steels may be classified into two broad groups: plain carbon steel and alloy steels.

Plain carbon steel is that steel in which carbon is the main element which governs the properties of steel. Other elements which are associated in the steel are kept below a certain limit so that they do not influence properties of steel. On the other hand, alloy steels are those steels in which one or more elements are added to impart some peculiar characteristics. In such steels, carbon and alloying elements, contribute towards properties of steels.

Plain carbon steel and alloy steels can be further subdivided on the basis of various factors. Plain carbon steel can be further classified on the basis of carbon content, structure at room temperature at slow cooling, quality and application. It may be recalled that a steel having

0.8 percent carbon is called eutectoid steel and it has a completely pearlitic structure on slow cooling.

Hypoeutectoid steels contain proeutectoid ferrite and pearlite, while hypereutectoid steels contain proeutectoid cementite and pearlite. These divisions are not so precise for many reasons. So, for all practical purposes, these can be classified into low, medium and high carbon steel:

i. Low carbon steel up to 0.3% C
ii. Medium carbon steel from 0.3% C to 0.6% C
iii. High carbon steel from 0.6% C to 2.03% C

These constitute over 90% of the total steel production and in that the mild steels take the major share. Plain carbon steel may contain several other elements like Al, Mn, Si, P, S, and so on, but their individual contents are below the critical limits above which the properties of steel are significantly affected.

i. ***Low carbon steel*****s** are produced in the greatest quantities of all the different steels. These generally contain less than about 0.25 wt% C and are unresponsive to heat treatments intended to form martensite; strengthening is accomplished by cold work. Microstructures consist of ferrite and pearlite constituents. It is mainly used for sheets, strips, structural sections, case hardening, etc.
ii. ***Medium carbon steels*** have carbon contents between about 0.25 and 0.60 wt%. These alloys may be heat treated by austenitizing, quenching, and then tempering to improve their mechanical properties. Then, microstructures consist of tempered martensite it has good strength, toughness and its response to heat treatment is also good. It is mainly used for such applications as gear and connecting rods, laminated springs, and so on.
iii. ***High carbon steels*** have carbon contents between 0.60 and 1.4 wt%, are the hardest, strongest, and yet least ductile of the carbon steels. They are almost always used in a hardened and tempered condition it has good strength and is used as tool steel, prestressed concrete wire.

The quality of any steel, in general, depends on S and P contents, the degree of the oxidation and cleanliness. In the case of plain carbon steel, S and P are main factors which Iron control the quality of steel. A quality steel has S and P contents, each 0.04% max. Steel with content of these elements less than 0.025% is known as high quality steel. Steels having S and P between 0.04 percent and 0.06 percent are known as ordinary quality steels.

Plain carbon steels are used successfully where strength and other requirements are not absolutely essential. At ordinary temperature and in an atmosphere, which are not of a severely corroding nature, the performance of plain carbon steels is quite satisfactory. However, the relatively low hardenability of the plain carbon steels limits the strength that can be attained except in relatively small cross-sections. Following disadvantages limit the usefulness of plain carbon steels:

- (i) Low hardenability
- (ii) Major loss of hardness on tempering
- (iii) Low corrosion resistance and oxidation resistance
- (iv) Low strength at elevated temperature.

The most common and practical method of overcoming the deficiencies of the plain carbon steel is to employ alloy steels.

Alloy steels are those in which one or more elements are added to steel for enhancing further the prominent characteristics of the plain carbon steels or to ensure specific properties. These added elements are known as alloying elements. Based on their four features, alloy steels can be classified as follows:

- (i) Classification on the basis of the amount of alloying element:
  - (a) Low alloy steel in which the total alloying content is less than about 5 percent.
  - (b) Medium alloy steel in which the total alloying content is in the range of 5–10 percent.
  - (c) High alloy steels in which the total alloying content is above 10 percent.
- (ii) Classification on the basis of composition: Depending on the alloying elements, alloy steels are classified into nickel steels, chromium steels, Cr-Ni steel and Cr-Ni-Mo steels. They are classified according to the presence of various alloying elements.
- (iii) Classification on the basis of structure: Various structures such as martensite, austenite, or bainite constitute steels. Accordingly, they are called martensitic steel, austenitic steel, and so on.
- (iv) Classification on the basis of application; Corrosion resistant steel, heat resistant steel, magnetic steel, tool steel, electrical steel, etc.

Alloying elements are added with a view to impart a number of desirable properties in steels. Some of these properties are:

- (i) to increase hardenability, resistance to softening on tempering, resistance to corrosion and oxidation, and to increase resistance to abrasion;
- (ii) to improve high temperature properties; and

(iii) to achieve the desired constituents (e.g. stabilization of austenite at room temperature) and higher elastic ratio and endurance strength.

Alloy steels, however, are normally costly. They require more careful handling during manufacturing, heat treatment and mechanical working. Alloy steels have greater tendency for retention of austenite. The retained austenite decomposes at a later stage, leading to dimensional changes and introduction of internal stresses. Certain grades of alloy steels are also prone to temper brittleness.

3.2.1.2 Transformations in Hypo-eutectoid Steels

There are solid state transformations in these steels. They are the transformation of gamma iron to alpha iron and the decomposition of austenite. Line GS in the phase diagram shows the temperatures where transformation of austenite to ferrite starts. Below this line, ferrite is separated out of the austenite. The critical points that make up line GS are shown by Ar_3 (in cooling) and AC_3 (in heating). Line ES indicates the variation in the solubility of carbon in austenite with the temperature and, in cooling, corresponds to the temperature at which separation of cementite from austenite starts. Point S is called the eutectoid point and here the degree of freedom is zero. When point S (0.8% C) is reached during cooling, the austenite decomposes to 100 percent lamellar pearlite at 723°C. Pearlite is a eutectoid mixture of two phases: ferrite and cementite. The critical point where austenite decomposes to pearlite is denoted by Ar_1 (in cooling) and Ac_1 (in heating). The line PQ shows the variation in solubility of carbon in alpha iron with the temperature and, in cooling, corresponds to starting of precipitation of surplus cementite out of ferrite.

The limiting composition for getting pearlite is 0.025 percent carbon. With carbon content less than this amount, no pearlite will be formed. The alloy will contain only ferrite grains. Steels containing carbon between 0.025 percent to 0.8 percent would contain varying amount of ferrite and pearlite and their relative proportions depend on carbon content. Let us take the case of heating up to austenitic region followed by slow cooling of component X_1 containing 0.4 percent carbon [Figure 3.2(a)]. In the austenitic range, this alloy consists of a uniform interstitial solid solution. Each grain contains 0.4 percent carbon dissolved in the interstitial spaces of the FCC iron lattice structure.

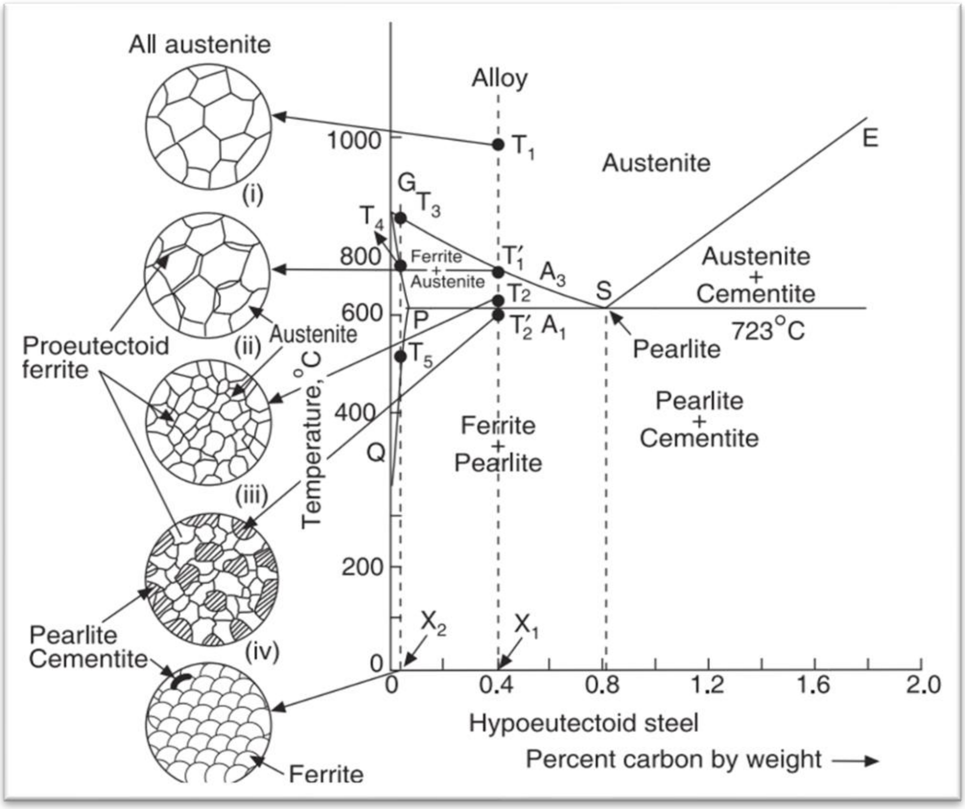


Figure 3.2(a) Part of iron-cementite phase diagram showing microstructural changes during the slow cooling of 0.4% carbon steel and steel containing less than 0.025% carbon.

Upon slow cooling, nothing happens until the line GS is crossed at temperature T'_1 where component X_1 cuts the GS line. Proeutectoid α-ferrite starts separating out along line GP, and the composition of austenite moves along line GS. Therefore, at temperature T'_1 ferrite begins to form at the austenite grain boundaries. Since ferrite can dissolve very little amount of carbon, in those areas that are changing to ferrite the carbon must come out of solution before the atoms rearrange themselves to BCC structure. The carbon which comes out of solution is dissolved in the remaining austenite, so that, as cooling progresses and the amount of ferrite increases and the remaining austenite becomes richer in carbon. PS line is the eutectoid-temperature line (723°C) and is the lowest temperature at which FCC iron can exist under equilibrium conditions. Just above the PS line (T_2), the microstructure consists of austenite and proeutectoid ferrite. At the eutectoid temperature, the remaining austenite, of the total material which contains 0.8 percent carbon decomposes to pearlite by the eutectoid reaction. Thus,

$$\underset{(0.8\%\ \text{C})}{\text{Austenite}} \xrightleftharpoons[\text{Heating}]{\text{Cooling}} \underbrace{\underset{(0.025\%\ \text{C})}{\text{Ferrite}} + \underset{(6.67\%\ \text{C})}{\text{Cementite}}}_{\text{Pearlite}}$$

Only austenite transforms to pearlite at eutectoid temperature. Therefore, when the reaction is complete at temperature T'_2, the microstructure will consist of pearlite and ferrite.

The eutectoid decomposition of austenite takes place at a constant temperature of 723°C, because at this point the degree of freedom is zero. (F = C – P + l = 2 – 3 + 1 = 0, where F is the degree of freedom, C is the number of components and P is the number of phases.) Figure 3.2(b) Part of iron-cementite phase diagram showing microstructural changes during the slow cooling of 1.2% carbon steel and 0.8% carbon steel.

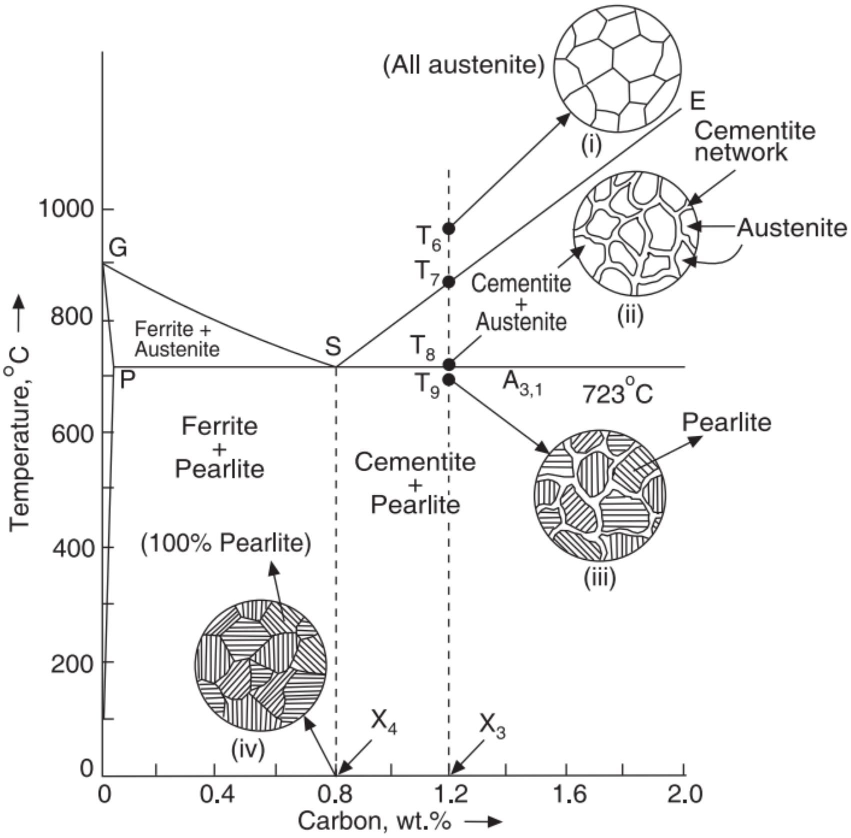


Figure 3.2(b) Part of iron-cementite phase diagram showing microstructural changes during the slow cooling of 1.2% carbon steel and 0.8% carbon steel.

3.2.1.3 Transformations in a Steel Containing Less Than 0.025% Carbon

another steel of composition X_2 (see Figure 3.2(a)). In this steel, carbon content is less than 0.025 percent. This alloy begins to transform to a at T_3 °C and transformation is completed at T_4 °C. No change in this structure occurs between T_4 °C and T_5 °C. At T_5 °C, the vertical composition cuts the solvus line PQ. Excess carbon, thus rejected, separates out as Fe_3C. Hence, the microstructure is predominantly (ferrite) a with small amount of Fe_3C. If the cooling rate is higher than the equilibrium rate, then enough time is not available for cementite to separate, and the microstructure is 100 percent ferrite. The ferrite is supersaturated as its carbon content is higher than the one according to the solvus line of the equilibrium diagram.

3.2.1.4 Transformations in Hypereutectoid steels

Consider a steel X_3, containing 1.2 percent carbon [Figure 3.2(b)]. The phase present in the steel in the austenitic condition is FCC iron with carbon forming interstitial solid solution. The composition is uniform throughout each grain. As the temperature is lowered from T_6, phase transformation starts at temperature T_7 which is the point of intersection of vertical line at X_3 and the line ES. At this temperature, austenite is fully saturated with carbon. As the temperature is lowered below T_7 (for example T_8) solubility of carbon in austenite starts moving along ES. The excess carbon comes out in the form of proeutectoid cementite. This cementite is precipitated primarily along the grain boundaries. This leads to formation of grain boundary network of cementite in the hypereutectoid steel. As the steel attains the eutectoid temperature (A_3), eutectoid transformation takes place in the austenite and pearlite is formed. Below A_3 (for example, T_9) the microstructure consists of pearlite with network of cementite.

3.2.1.5 Transformations in Eutectoid Steel

Let us consider a steel containing 0.8 percent carbon [X_4 in Figure 3.3(b)]. On cooling at eutectoid point S (723°C), all austenite will transform into 100 percent pearlite. So, the microstructure at room temperature will reveal alternate layers of ferrite and cementite, called Figures 3.3(a), (b) and (c) shows the microstructures of hypoeutectoid, eutectoid, and hypereutectoid steels.

(a) Hypoeutectoid (ferrite + pearlite), ×500

(b) Eutectoid steel (pearlite), ×1000

(c) Hypereutectoid steel (pearlite with network of cementite), ×500.

Figure 3.3 Microstructures of steels.

3.2.2. Cast Iron

Cast Iron is the name applied to a family of high-carbon content Fe-C alloys, specifically, those containing more than 2.14 wt. % C. Generally, most cast irons fall within the 3.0 to 4.2 wt. % range. Many contain silicon. Many cast irons are strong, but also brittle. As such, they find uses as small cylinder blocks, cylinder heads, pistons, clutch plates, transmission cases, diesel engine casting. There are four types of cast irons: gray, nodular, white, and malleable. Cast irons melt between ~ 1150°C and 1300°C; since this range is lower than for steels, they are easier to melt and cast than steels. Cast irons consists of varying amounts of ferrite, cementite (Fe_3C), and graphite (C). In most cast irons, the carbon-rich phase is graphite, not cementite. Cementite (Fe_3C) is a metastable compound, and under some circumstances it can be made to decompose to form a ferrite and graphite, according to the following reaction:

$$Fe_3C \rightarrow 3Fe\ (\alpha) + C\ (\text{graphite})$$

3.2.2.a Gray Iron

The carbon and silicon contents of gray cast irons vary between 2.5 and 4.0 wt% and 1.0 and 3.0 wt%, respectively. For most of these cast irons, the graphite exists in the form of flakes (similar to corn flakes), which are normally surrounded by an a-ferrite or pearlite matrix; the microstructure of a typical gray iron is shown in Figure 3.4. Because of these graphite flakes, a fractured surface takes on a gray appearance hence its name.

Mechanically, gray iron is comparatively weak and brittle in tension as a consequence of its microstructure; the tips of the 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.

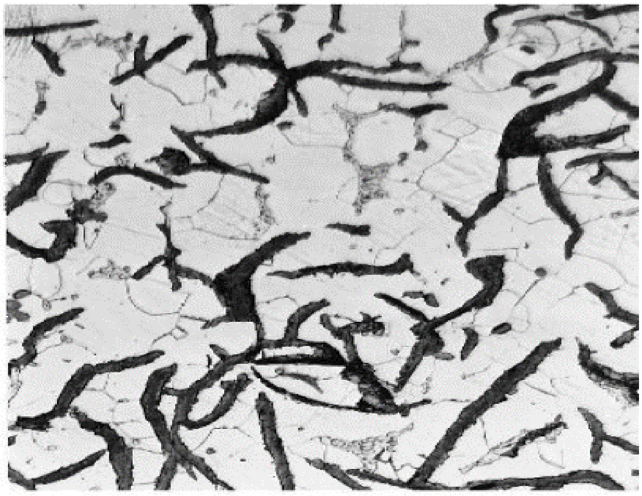


Figure 3.4 Gray cast iron structure

3.2.2.b Ductile (or Nodular) Iron

The nodular cast iron (figure 3.5) contains 2.5 to 4.0 wt. % C, 1.0 to 3.0 wt. % Si, plus Mg &/or Ce. The Mg &/or Ce cause the flakes to spherodize (hence nodular). Graphite is dispersed throughout a ferrite or pearlite matrix in the form of *spheres or nodules*. The graphite nodules have no sharp features; therefore, the resulting material is much more ductile than gray iron.

The mechanical properties of nodular iron are similar to steel. Nodular iron is frequently used in valves, crankshafts, gears, and other automotive components. Typical applications for this material include valves, pump bodies, crankshafts, gears, and other automotive and machine components.

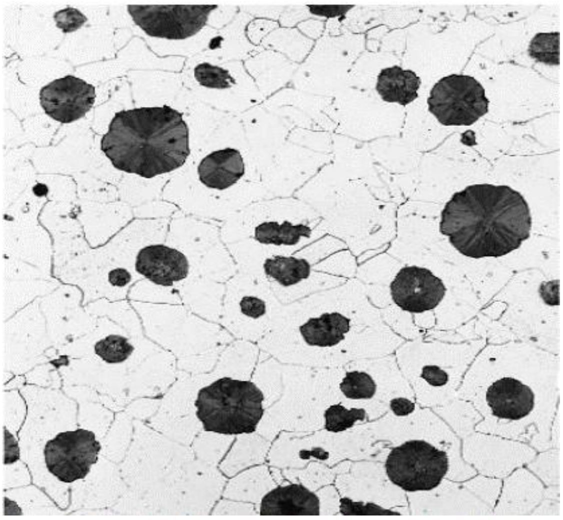


Figure 3.5 Nodular cast iron structure

3.2.2.c White Iron and Malleable Iron

White iron (figure 3.6) contains 2.5 to 4.0 wt. % C and less than 1.0 wt. % Si. Because of the low Si content, the carbon forms Fe_3C instead of graphite. Cementite is dispersed throughout pearlite (ferrite + cementite) matrix. White iron contains a considerable volume fraction of cementite (Fe_3C), a hard and brittle compound. Because of the amount of cementite, white iron is extremely hard and extremely brittle. Limited usage - mainly applications requiring hardness and wear resistance (such a roller in rolling mills). Also used as a precursor to malleable iron.

Figure 3.6 White cast iron structure

3.2.2.d Malleable Cast Iron:

Malleable iron (figure 3.7) (just like white iron) contains 2.5 to 4.0 wt. % C *and less than 1.0 wt. % Si.* Unlike white iron, the C exists in the form of graphite instead of cementite. Graphite rosettes are dispersed throughout a *ferrite (or pearlite)* matrix. Malleable iron is produced by *heating white iron in order to decompose the cementite into graphite*. The graphite forms clusters, similar to nodular iron. Reduction in the amount of cementite causes the material to become relatively ductile (or malleable). Used in connecting rods, transmission gears, differential cases, flanges, pipe fittings.

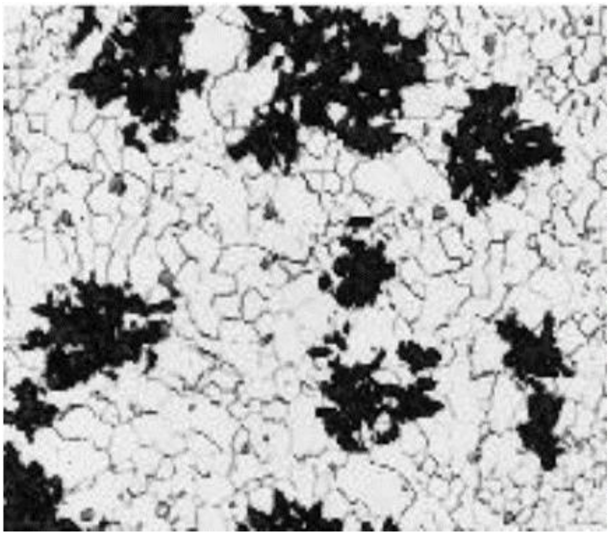


Figure 3.7 Malleable Cast Iron structure

3.2.2.e Compacted Graphite Iron

A relatively recent addition to the family of cast irons is compacted graphite iron (abbreviated CGI). As with gray, ductile, and malleable irons, carbon exists as graphite, whose formation is promoted by the presence of silicon, (figure 3.8). Silicon content ranges between 1.7 and 3.0 wt%, whereas carbon concentration is normally between 3.1 and 4.0 wt%.

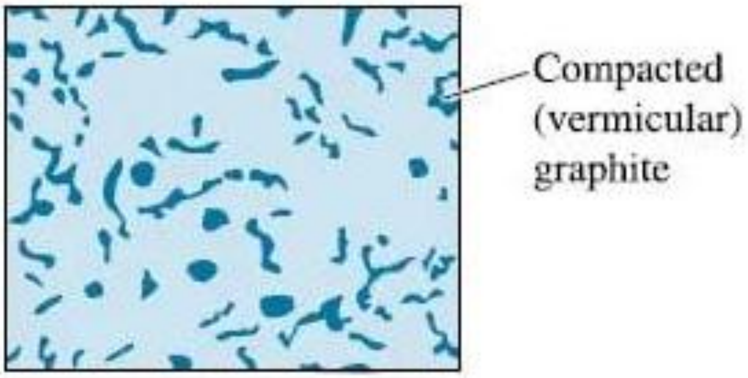


Figure 3.8 Optical micrograph of Compacted graphite iron

Based on the Fe-Fe_3C phase diagram, cast irons can be classified into three groups: eutectic, hypoeutectic, and hypereutectic cast irons. Eutectic cast iron contains 4.3 percent carbon.

3.2.2.1 Transformations in Hypoeutectic Cast Iron

In this case, a structure just below 1147°C consists of proeutectic austenite and ledeburite (eutectic mixture consisting of austenite and cementite). On further cooling in the temperature range 1147°C–723°C, excess carbon comes out as cementite from proeutectic and eutectic austenite. Therefore, at the eutectoid temperature, both eutectic and proeutectic austenite would contain 0.8 percent carbon and would decompose by the eutectoid reaction to pearlite. Hence, the final microstructure would be the same as the high temperature microstructure, except that wherever austenite was present, pearlite would now be present.

3.2.2.2 Transformations in Hypereutectic Cast Iron

In this case the structure just below 1147°C consists of proeutectic cementite and ledeburite. On further cooling in the temperature range 1147°C–723°C, excess carbon comes out as cementite from the eutectic austenite. Proeutectic cementite will remain as such since it does not undergo any further change on cooling. Austenite from eutectic rejects excess carbon as cementite. At 723°C, the austenite contains 0.8 percent carbon. At 723°C, eutectic austenite transforms into pearlite. Thus, the final microstructure will reveal proeutectic cementite present as plate and transformed eutectic consisting of pearlite plus cementite.

3.2.2.3 Transformations in Eutectic Cast Iron

Eutectic cast iron solidifies at 1147°C. In the temperature range 1147°C–723°C the solid alloy consists of ledeburite eutectic, i.e. austenite and cementite. As the temperature decreases, the solubility of carbon in -iron decreases, as indicated by the cementite line. Consequently, excess carbon is rejected from austenite and comes out in the form of cementite. On further cooling, proeutectoid cementite separates out of the austenite, and at 723°C austenite containing 0.8 percent carbon transforms to pearlite by eutectoid reaction.

The microstructure of eutectic cast iron at room temperature is identical to that at the high temperature structure. However, there is a distinct difference. In place of austenite, the transformed product, namely, pearlite, will be observed. The cementite that separates out on cooling the alloy between 1147°C and 723°C joins the existing cementite. The eutectic structure consisting of austenite and cementite can be visualized as forming alternate layers of the two phases. Therefore, the final structure will be transformed ledeburite.

The reactions during transformations in eutectic cast iron, on cooling, are as follows:

$$\underset{(4.3\%\ \mathrm{C})}{\mathrm{L(liquid)}} \xrightarrow[1147^\circ\mathrm{C}]{\text{Cooling}} \underset{(2.03\%\ \mathrm{C})}{\gamma} + \underset{(6.67\%\ \mathrm{C})}{\mathrm{Fe_3C}}$$

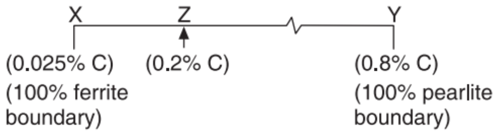
$$\underset{(0.8\%\ \mathrm{C})}{\gamma} \xrightarrow[723^\circ\mathrm{C}]{\text{Cooling}} \underset{(0.025\%\ \mathrm{C})}{\alpha} + \underset{(6.67\%\ \mathrm{C})}{\mathrm{Fe_3C}}$$

Figures 3.9 (a), (b) and (c) show the microstructures of hypoeutectic, eutectic and hypereutectic cast irons.

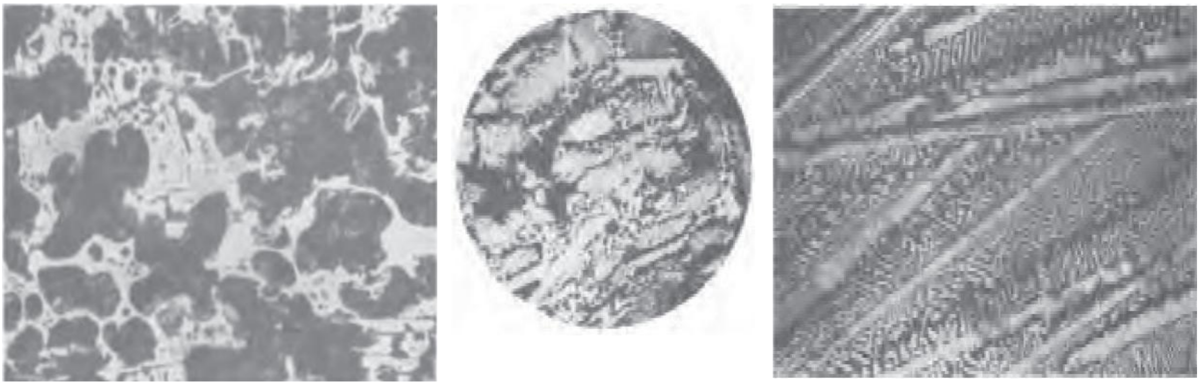
❖ Lever Rule

With the help of this rule, the relative amount of the coexisting phases or microconstituents at a particular temperature can be worked out. We now give four examples of this.

EXAMPLE 1**:** The relative amount of ferrite and pearlite in 0.2 percent carbon steel can be found with the help of this rule, as in the following representation.



Here, YX is the lever arm. Fulcrum is at point Z. The fraction of α in the 0.2 percent carbon steel is given by the ratio of the lever arm length on the other side of the fulcrum, i.e. YZ to the total length of the lever arm (XY).



(a) Hypoeutectic cast iron (ledeburite + pearlite + cementite), ×200

(b) Eutectic cast iron (ledeburite), ×100

(c) Hypereutectic cast iron (ledeburite + primary cementite), ×200

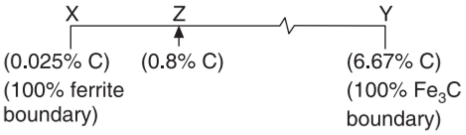
Figure 3.9 Microstructures of cast irons.

Thus,

$$\text{percent } \alpha = \frac{YZ}{XY} \times 100 = \frac{0.8 - 0.2}{0.8 - 0.025} \times 100 = 77.4\%$$

$$\text{percent pearlite} = \frac{ZX}{XY} = \frac{0.2 - 0.025}{0.8 - 0.025} \times 100 = 22.6\%$$

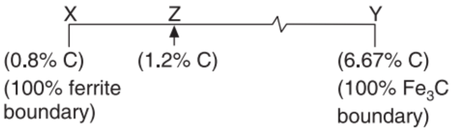
EXAMPLE 2: The relative amount of ferrite and cementite in a steel containing 0.8 percent carbon can be worked out as follows:



$$\text{percent ferrite} = \frac{6.67 - 0.8}{6.67 - 0.025} \times 100 = 88.34\%$$

$$\text{percent cementite} = \frac{0.8 - 0.025}{6.67 - 0.025} \times 100 = 11.66\%$$

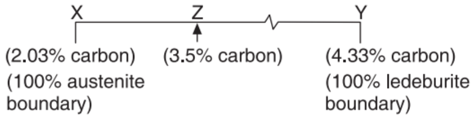
EXAMPLE 3: The relative amount of proeutectoid cementite and pearlite in a steel containing 1.2% carbon can be calculated as follows:



$$\text{percent pearlite} = \frac{6.67 - 1.2}{6.67 - 0.8} \times 100 = 93.2\%$$

$$\text{percent cementite} = \frac{1.2 - 0.8}{6.67 - 0.8} \times 100 = 6.8\%$$

EXAMPLE 4: The relative amount of austenite and liquid in cast iron containing 3.5 percent carbon at eutectic temperature can be estimated as follows:



$$\text{percent proeutectic austenite} = \frac{4.33 - 3.5}{4.33 - 2.03} \times 100 = 36.1$$

$$\text{percent ledeburite} = \frac{3.5 - 2.03}{4.33 - 2.03} \times 100 = 63.9$$

3.2.2.4 Iron-Graphite Phase Diagram

The process by which the stable phase, namely graphite, is formed in cast iron (or steel) is known as graphitization. At all temperatures, the following reaction takes place:

$$\mathrm{Fe_3C} \xrightarrow{\text{Cooling}} 3\mathrm{Fe} + \mathrm{C}\ (\text{graphite})$$

At low temperatures, however, the reaction occurs so slowly that Fe3C remains as such. At higher temperatures, the graphitization of the iron carbide occurs. In the presence of silicon, graphitization becomes faster. Aluminium and nickel, which are also graphitizers, form additional centres for crystallization of graphite flakes. So, the stable phase, graphite, forms either by separating out of the liquid (or solid) solution, or as a result of decomposition of metastable cementite.

Figure 3.10 is an iron-graphite phase diagram. As the liquid alloy (say having 3.2% C) cools to 1153°C, dendrites of austenite phase starts forming in the liquid. At 1153°C the liquid reaches eutectic composition and solidifies as a eutectic mixture of austenite and graphite. This is called primary stage of graphitization. Upon subsequent slow cooling, additional graphite forms from the austenite and eutectoid graphite is formed in the temperature interval from 738°C to 723°C.

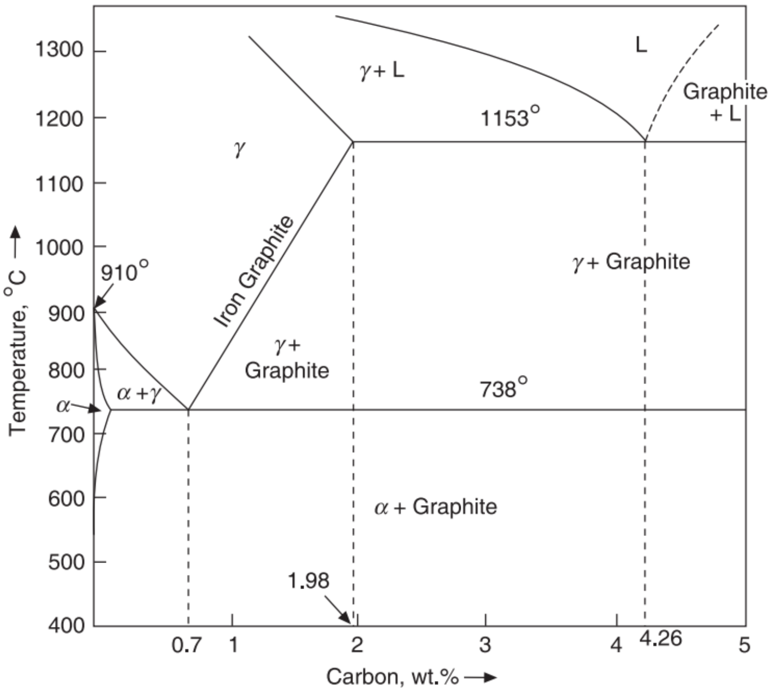


Figure 3.10 Iron-graphite phase diagram.

Separation of secondary graphite from the austenite is called the inter-mediate stage of graphitization. Formation of eutectoid graphite, as well as the decomposition of eutectoid cementite into graphite and ferrite, is called the secondary stage of graphitization. A major amount of graphite precipitates during the primary stage of graphitization. While during intermediate and secondary stage of graphitization, the additional graphite merely adds to the pre-existing graphite flakes and increases its size. If austenite is supercooled below 723°C, it decomposes with the separation of a ferrite-cementite mixture. The prolonged heating at high temperatures of cast iron containing carbon in combined form also leads to graphitization, i.e. decomposition of cementite into graphite and ferrite at temperature below 738°C, or into graphite and austenite at higher temperature. Composition and cooling rate are two factors which determine the type of structure formed on cooling of cast iron. Rapid cooling inhibits precipitation of graphite partially or completely and promotes formation of cementite. If liquid cast iron is supercooled below 1147°C, cementite is precipitated. The precipitation of graphite from the liquid phase is possible only at very slow cooling rates, i.e. when the degree of supercooling does not exceed 5°C.

Since a cast iron containing coarse graphite flakes has low strength, various methods are used to improve the graphite distribution. Finer graphite tends to form when the alloy is superheated just before casting. A finer flake size can also be produced by adding inoculants like ferrosilicon and calcium-silicon in very small amounts which promote graphitization. Graphite nodules, rather than graphite flakes, will form if the molten alloy is treated with magnesium or cerium. This results in formation of spheroidal graphite (SG) cast iron. The rapid cooling prevents graphitization of cementite in white cast iron, but if the casting is reheated to about 875°C and held there for long time, then graphite is slowly produced in the form of temper carbon. This is called malleable cast iron.

3.3. Nonferrous Alloys

Steel and other ferrous alloys are consumed in exceedingly large quantities because they have such a wide range of mechanical properties, may be fabricated with relative ease, and are economical to produce. However, they have some limitations like (1) a relatively high density, (2) a comparatively low electrical conductivity, and (3) an inherent susceptibility to corrosion in some common environments. Thus, for many applications it is advantageous or even necessary to use other alloys that have more suitable property combinations. Alloy systems are classified either according to the base metal or according to some specific characteristic that a group of alloys share as shown in Figure 3.11.

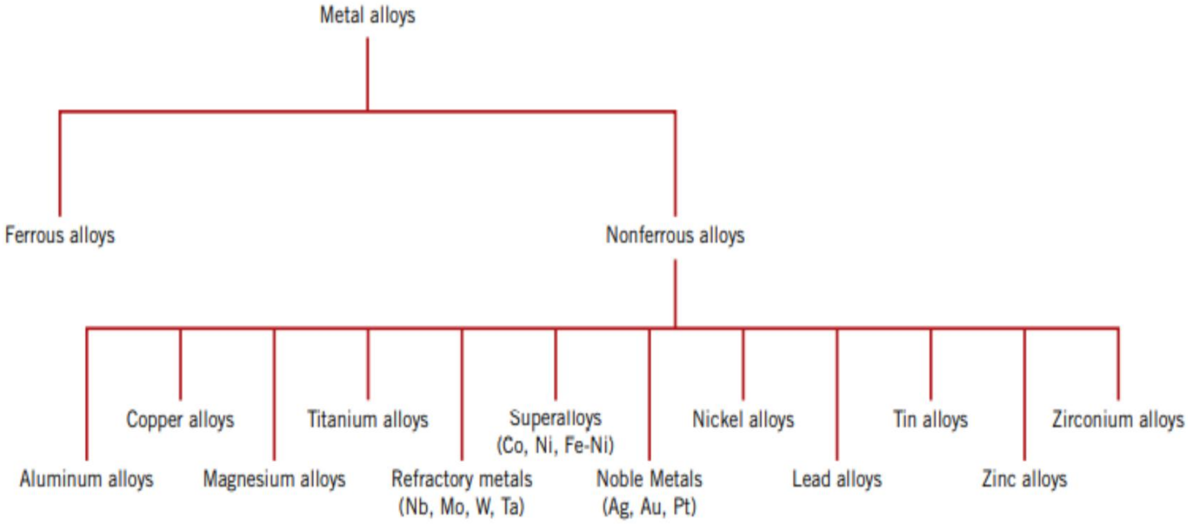


Figure 3.11 Classification of metal alloys, nonferrous alloys

Chapter 4

HEAT TREATMENT THEORY

4.1. Heat Treatment Theory

Heat treatment can be defined as a process or combination of processes that involving heating and cooling of metal/alloy in solid state to obtain desirable conditions like stress relieve and improve properties like machinability and ductility.

Why Use Heat Treating?

The most common reasons metals undergo heat treatment are to improve their strength, hardness, toughness, ductility and corrosion resistance. In simple Terms….

- Soften a part that is too hard.
- Harden a part that is not hard enough.
- Put hard skin on parts that are soft put hard skin on parts that are soft.
- Make good magnets out of ordinary material.
- Make selective property changes within parts

The various types of heat-treating processes are similar because they all involve the heating and cooling of metals; they differ in the heating temperatures and the cooling rates used and the final results. The heat treatment of ferrous metals is annealing, normalizing, hardening, and tempering. Whereas, the nonferrous metals can be annealed, but never tempered, normalized, or case-hardened. Successful heat treatment requires close control over all factors affecting the heating and cooling of a metal. This control is possible only when proper equipment is available. The furnace must be of the proper size and type and controlled, so the temperatures are kept within prescribed limits for each operation. Even the furnace atmosphere affects the condition of the metal being heat-treated. The furnace atmosphere consists of the gases that circulate throughout the heating chamber and surround the metal, as it is being heated. In an electric furnace, the atmosphere is either air or a controlled mixture of gases.

4.2. Definition of Heat Treatment

Heat treatment is the process of heating and cooling metals to change their microstructure and to bring out the physical and mechanical characteristics that make metals more desirable. Heat treatment is an operation or combination of operations involving heating at a specific rate, soaking at a temperature for a period of time and cooling at some specified rate. The aim is to obtain a desired microstructure to achieve certain predetermined properties (physical, mechanical, magnetic or electrical).

Surface hardening is the process of hardening the surface of a metal object while allowing the metal deeper underneath to remain soft, thus forming a thin layer of harder metal (called the "case") at the surface. For example, components like turbine shaft, gears, spindle, automotive components and axle need to have a hard surface but a soft core.

4.3. Main Purposes of Heat Treatment

- to increase strength, harness 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 machineability **(full annealing and normalising)**
- to improve cutting properties of tool steels **(hardening and tempering)**
- to improve surface properties **(surface hardening, corrosion resistance-stabilising treatment and high temperature resistance-precipitation hardening, surface treatment)**
- to improve electrical properties **(recrystallisation, tempering, age hardening)**
- to improve magnetic properties (hardening, phase transformation) Fe-cementite metastable phase diagram (Figure 4.1) consists of phases liquid iron(L), δ ferrite, γ or austenite, α-ferrite and Fe_3C or cementite and phase mixture of pearlite (interpenetrating bi-crystals of α ferrite and cementite) (P) and ledeburite (mixture of austenite and cementite) (LB). Solid phases/phase mixtures are described here.

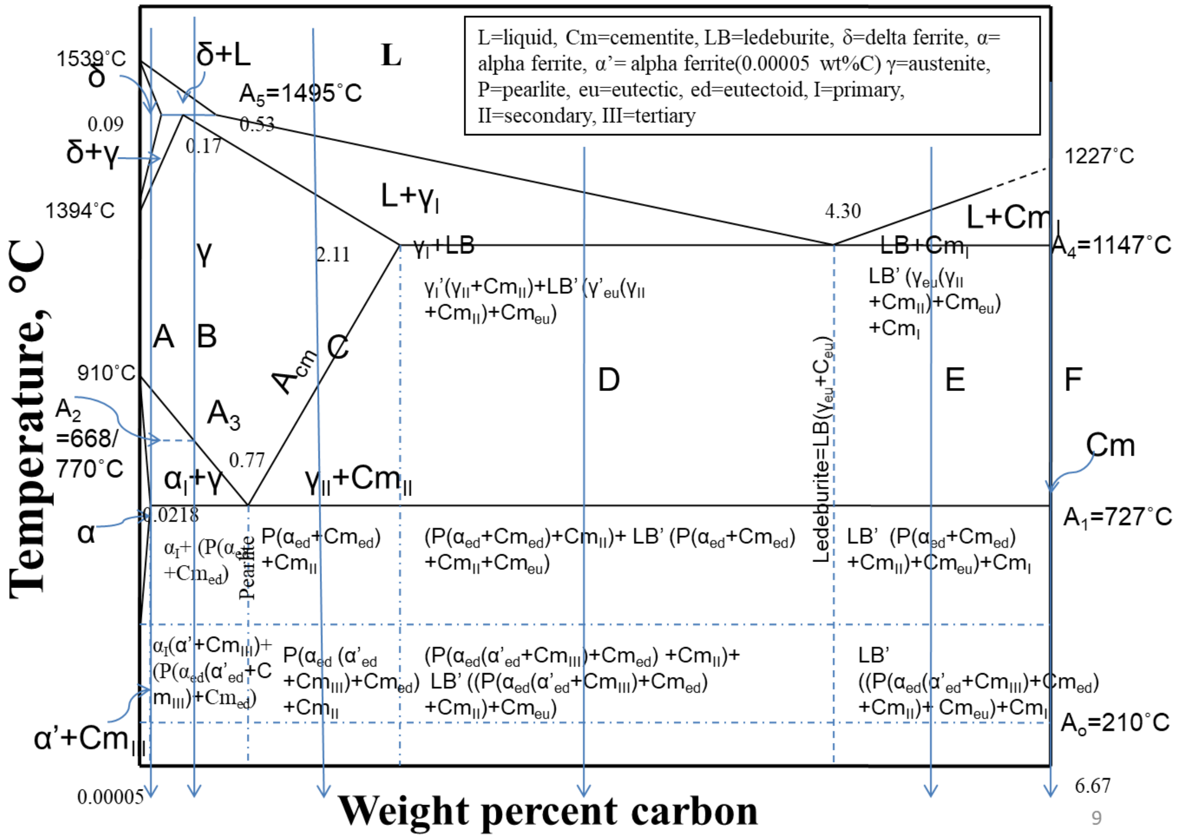


Figure 4.1 Fe-cementite metastable phase diagram

There are a number of factors of paramount importance which are to be considered when heat treating a metal or alloy. Some of them are the temperature up to which the metal/alloy is heated, the length of time that the metal/alloy is held at the elevated temperature, the rate of cooling, and the atmosphere surrounding the metal/alloy when it is heated.

Any heat treatment process can be represented graphically with temperature and time as coordinates. Figure 4.1 describes the simplest possible heat treatment cycle in which the metal/alloy is heated, held at the elevated temperature for some time, and then cooled to room temperature.

4.4 Heat Treatment Process Variables

Heat treatment temperature, holding time, and rate of heating and cooling are some of the parameters which affect the heat treatment processes, and are commonly referred to as *heat treatment process variables* (figure 4.2). The required magnitude of these variables depends on the chemical composition, size and shape of the object and the final properties desired in the metal/ alloy.

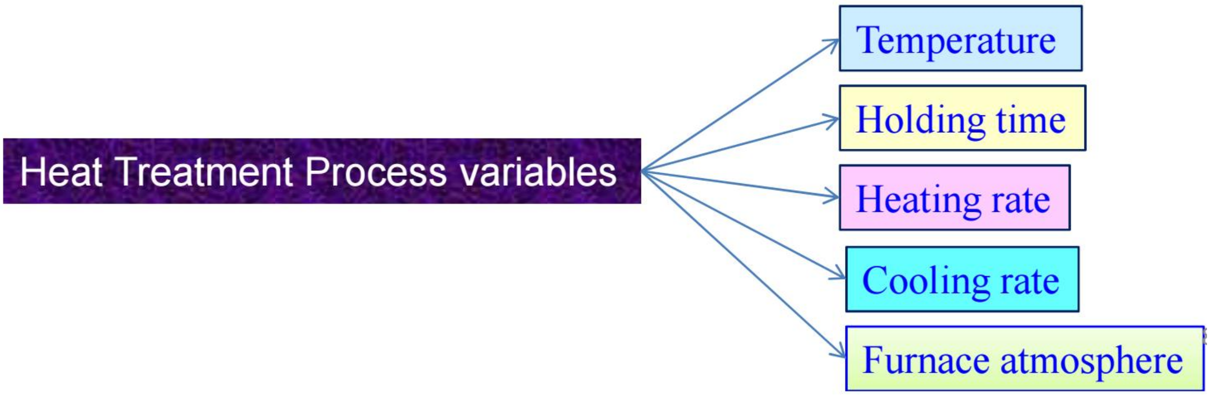


Figure 4.2 Heat treatment process variables

In general, the object to be heat treated is put into a heat treatment furnace at room temperature. This furnace is then heated up to a pre-decided temperature. The average rate of heating is the total increment in temperature divided by the total time taken. The rate of heating can also be calculated for various stages by considering appropriate ranges of temperature. In practice, however, the rate of heating is not constant throughout the complete temperature interval.

In order to minimize the problem of oxidation or grain growth, two heat treatment furnaces are employed. In one furnace, the object is heated to a temperature up to which there is no appreciable oxidation or grain growth. The object is then transferred to the second furnace maintained at heat treatment temperature. This practice reduces the total time of holding near the higher heat treatment temperature and thus the above-mentioned problems are reduced.

In addition to the mode of heating up to heat treatment temperature, the rate of heating is also of significance. The heating rate depends on the size and shape of the object and the thermal conductivity of the alloy. Fortunately, almost all metallic alloys have good thermal conductivity and thus, in general, this parameter plays only a marginal role. However, for some alloys such as stainless steels, thermal conductivity is an important factor while arriving at the rate heating. The larger the size of the object, the lower shall be the rate of heating. It avoids development of internal stresses due to thermal gradient. Secondly, low heating rates ensure homogeneity of the structure and reduce holding time at heat treatment temperature.

Complicated shapes, sharp cornered objects, and objects with variable sections are also heated slowly. Some alloys, such as high carbon steels and austenitic stainless steels, are also subjected to slow heating rates. Smaller sized and simple shaped objects can be heated with higher heating rates and homogeneity of the structure can be ensured in such cases by increasing the holding time. Also, for the alloys which are prone to oxidation at high temperatures of heat treatment, faster rates of heating are recommended at high temperature range.

Heat treatment temperature is governed mainly by chemical composition of the alloy, prior heat treatment, if any, and the final properties required. For example, for supercritical heat treatments, steel is heated above the upper critical temperature. This temperature is also known as austenitizing temperature, and can be determined, for carbon steels, by the iron-cementite phase diagram. For carbon steels, this temperature decreases first with increasing carbon content up to eutectoid composition and again rises with increasing carbon content.
Theoretically, at this temperature, steel should be fully austenitic with the smallest grain size. With rapid heating, actual austenitizing temperature is raised as compared to the theoretical value obtained from iron-cementite phase diagram, whereas in practice, this temperature is lowered on fast cooling. Hence, during heat treatment practice, temperatures which are slightly higher than the temperature determined from the phase diagram are employed. The austenite formed on heating near (just/slightly above) the equilibrium temperature is inhomogeneous in nature. In the case of alloy steels, some alloying elements or their compounds do not dissolve or diffuse with ease. Such steels require higher heating temperatures for homogenization of austenite. Iron carbide, in general, dissolves readily in gamma-iron as compared to carbides of strong carbide-forming elements.

Once the heat treatment temperature is decided, holding time is generally provided at a rate of 2 to 3 minutes per millimeter of section thickness. For an object with variable section thickness values, the holding time is determined on the basis of the thickest section. As already mentioned, objects which are heated up with high heating rates require longer holding time. Heat treatment temperature and holding time are somewhat related in the sense that an increased heat treatment temperature results in reduction of holding time. Similarly, lowering of heat treatment temperature demands an increase in holding time. High alloy steels and alloys, heavily enriched with alloying elements, are kept for more time at heat treatment temperature than plain carbon steels and thinly enriched alloys. In such cases, holding time may be increased by 25 to 40 percent.

As far as cooling from heat treatment temperature is concerned, the mode of cooling as well as the rate of cooling are governed by those factors which control the heating mode and rate, as already discussed. Heavy sections, complicated shapes, objects with variable section thickness, and highly enriched alloys are cooled slowly. Extremely slow cooling results in the development of a structure as is evident from the equilibrium phase diagram. The size, shape, distribution and relative proportions of microconstituents can be controlled over a wide range by varying the cooling rates. Up to a certain limit, higher cooling rate results in a structure which should exist according to the equilibrium diagram. By increasing the cooling rates beyond this limit, structures that are produced will consist of either non-equilibrium products or the high temperature phase(s) retained by sudden quenching.

Ranges of temperature where Annealing, Normalizing and Spheroidization treatment are carried out for hypo- and hyper-eutectoid steels. Whereas Normalizing Heat Treatment process is heating a steel above the critical temperature, holding for a period of time long enough for transformation to occur, and air cooling.

4.5. Stages of Heat Treatment

The basic heat-treating methods are: hardening, case hardening, annealing, normalizing, and tempering. Each of the above methods, when applied, produces different results and all the Heat-treating methods are similar. The parameters in which they differ from each other are the heating temperatures, the cooling rates used and the final results. To achieve the desired results, control over the heating and cooling of a metal is very much necessary. This control is possible only when the proper equipment is available. But all the methods have three basic stages to be performed. They are as follows:

- Heating
- Soaking, and
- Cooling or Quenching

The various types of heat-treating processes are somewhat similar because they all involve the heating, soaking and cooling (Fig.4); they differ in the heating temperatures, soaking time and the cooling rates used and the final results.

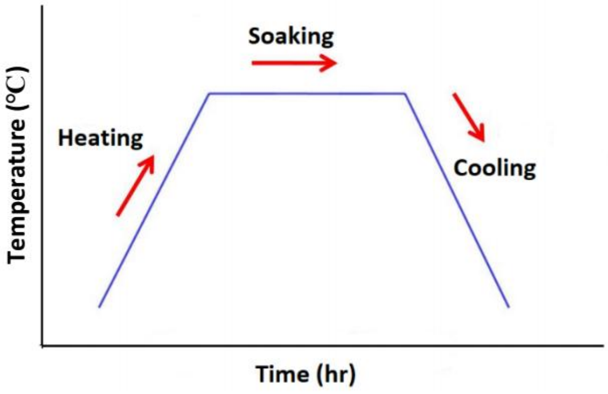


Figure 4.3 Stage of heat treatment

4.5.1 Heating Stage

Heating is the first stage in any Heat Treatment process. In this stage the metals are subjected to heating at required temperatures. The main concern in this stage is to maintain the temperatures at a uniform rate. If the temperatures are not maintained uniformly, uneven heating of the metal happens and the desired characteristics are not obtained. Usually an electric – furnace or a fuel – fired furnace is used for the heating process. Metals both Ferrous and Non-Ferrous react differently to various temperatures and change their crystalline structure when they are subjected to heat at specific temperatures.

- **Factors influencing Heating process**

The heating of the metals is influenced by many factors, and if proper control of the factors is not taken care of, it may hamper the heating process and may alter the desired results. The common factors that influence the heating process are mentioned below:

- ***Conductivity***

The conductivity of a metal greatly influences the process of the heating. Based on the heat conductivity of the metal, the temperature of the furnace is adjusted. A low-heat conductive metal needs higher temperatures to get heated and vice-versa.

- ***Heating Rate***

The heating rate depends on different Heat treatment methods. For parts which need to be hardened, the rate of heating should be slow, whereas for stress removal, the heating rate is high.

- ***Type of Furnace***

An electric – furnace has a controlled atmosphere of gases, whereas a fuel –fired furnace has a mixture of different gases like, Carbon monoxide, carbon dioxide, hydrogen, nitrogen, oxygen, water vapor etc. which are a result of the combustion of the fuel. These gases may alter the chemical composition of the metals or the parts that are being heated. Therefore, decision about the type of furnace that should be used influences the heating process.

- ***Material thickness.***

The size and cross section of the parts influence the heating process. Parts which are small in size can be heated quickly, whereas parts having large cross –section need slower rate of heating, so that the interiors of the parts also get heated up. The main objective is to maintain a uniform temperature all over the body of the part to avoid warping or cracking.

4.5.2 Soaking (Holding) Stage

After the metal is heated to proper temperature, it is held at that temperature until the desired internal structural changes take place. This process is called ***soaking***. Soaking is the second stage of the Heat treatment process. In this stage the metal which is heated to the specified temperature, is held at the same temperature for some time, to obtain the desired characteristics in the metal. This time period is usually referred to as ***Soaking Period***. When the metal is soaked in that particular temperature for a specified period of time, the molecular structure and the mechanical properties gets changed, and the desired results are obtained. The soaking periods of different metals depends on the following parameters:

- The type of the metal.
- Desired characteristics.
- Material thickness.

Preheating is a process that is employed as a part of the soaking stage. In this process the metals are preheated to a particular temperature which is below the required temperature. And after soaking the metal in the preheated temperature for some time, the metal is then heated to the final temperature and soaked in that temperature. The main objective of Preheating is to reduce the risk of cracking and wrapping of the metal parts. Ferrous metals are usually preheated; nonferrous metals do not require preheating.

For example, assume an intricate part needs to be heated to 815 °C for hardening. This part could be slowly heated to 316°C, soaked at this temperature, then heated slowly to 649 °C, and then soaked at that temperature. Following the final preheat, the part should then be heated quickly to the hardening temperature of 815°C.

4.5.3 Cooling Stage

After the metal has been soaked, it must be returned to room temperature to complete the heat-treating process. Cooling is the third and the final stage of the Heat Treatment process. After soaking of the metal in the specified temperature is done, the metal is finally cooled. This stage of the Heat Treatment is very crucial because, the final results i.e., the desired characteristics of the metal are obtained here. The mechanical and the structural properties of the metal can be altered according to the requirements in this stage. The cooling of the metal parts can be done in two ways. The metal can be left aside for slow cooling, or a cooling medium can be used for rapid cooling, which may be a liquid, a gas or a combination of both. Usually, the cooling rate decides the desired properties of the metal, and the cooling rate depends on the cooling medium. Therefore, the choice of a cooling medium has to be decided based on the requirements or the desired characteristics. Quenching is a method of cooling the metal parts.

It is associated with rapid cooling of the metals using a cooling medium usually with liquids like water, oil, brine etc. Quenching and the cooling medium used in it, depends on the method of Heat Treatment employed. For example, metals which require slower cooling rates are quenched in oils, and which require higher cooling rates are usually quenched in water and brine solution. Nonferrous metals are normally quenched in water.

Chapter 5

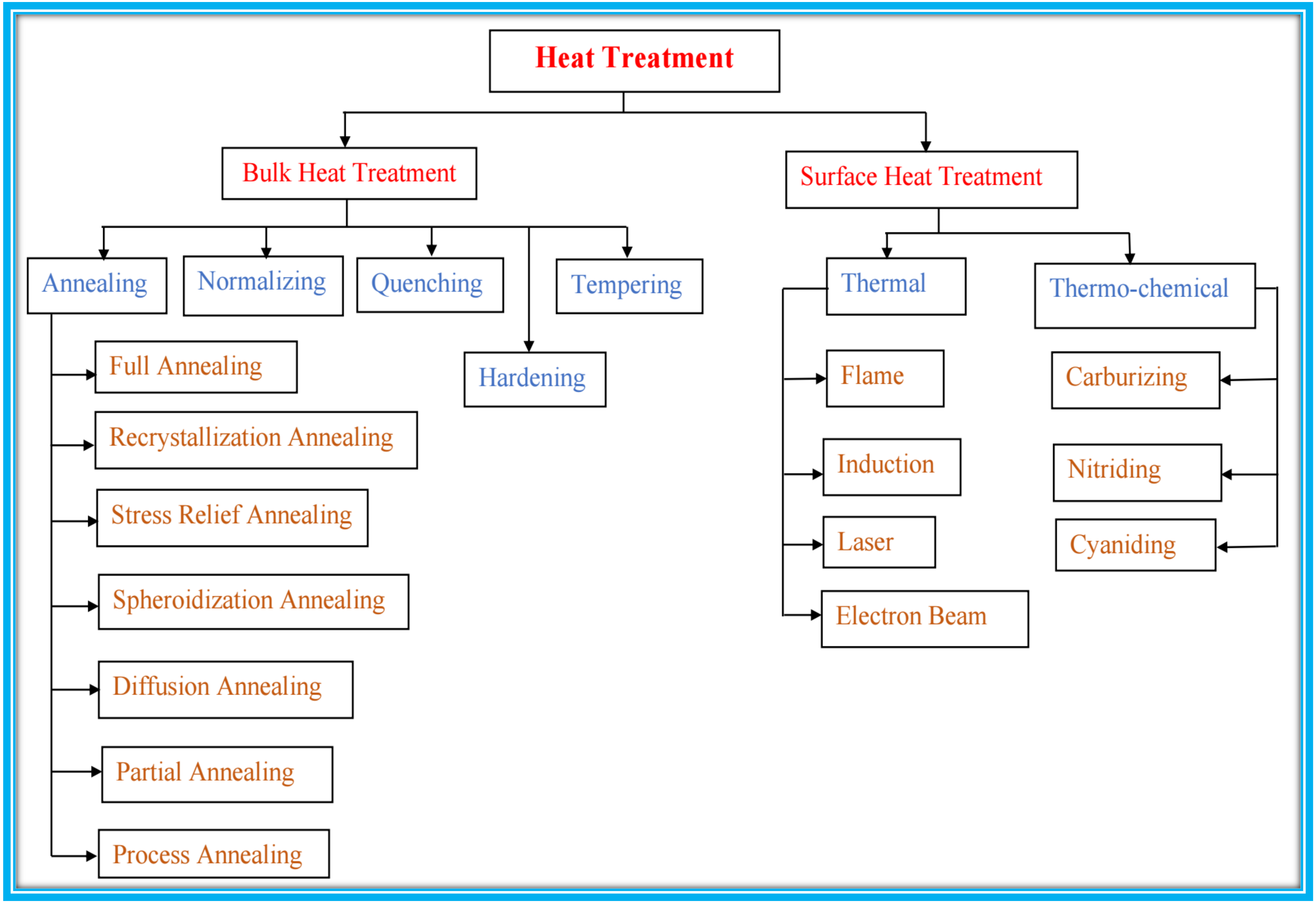
HEAT TREATMENT PROCESSES

In order to understand the complete mechanism of heat treatment it is essential to know the internal structure, phase transformation, etc. fully. However, a brief review of heat treatment processes is given below.

5.1. Classification of Heat Treatment Processes

There are four basic types of heat treatment in use today: annealing, normalizing, hardening, and tempering. The following sections describe the techniques used in each process and show how they relate to Steelworkers. Various heat treatment processes can be classified as follows:

- Annealing.
- Normalizing.
- Quenching or Hardening.
- Tempering.


Heat Treatment
Bulk Heat Treatment
Surface Heat Treatment
Annealing
Normalizing
Quenching
Hardening
Tempering
Full Annealing
Recrystallization Annealing
Stress Relief Annealing
Spheroidization Annealing
Diffusion Annealing
Partial Annealing
Process Annealing
Thermal
Thermo-chemical
Flame
Induction
Laser
Electron Beam
Carburizing
Nitriding
Cyaniding

5.2 Normalizing

Normalizing is similar to full annealing, except steel is generally cooled in still air. It is a heat-treating process that is often considered from both thermal and microstructural standpoints. In the thermal sense, normalizing is an austenitizing heating cycle followed by cooling in still or slightly agitated air, see Figure 5.1. Typically, the alloy is heated to a temperature about 55 °C above the upper critical line of the iron -iron carbide phase diagram, as shown in Figure 5.2; that is, above A_3 for hypoeutectoid steels and above A_{cm} for hypereutectoid steels. To be properly classed as a normalizing treatment, the heating portion of the process must produce a homogeneous austenitic phase prior to cooling.

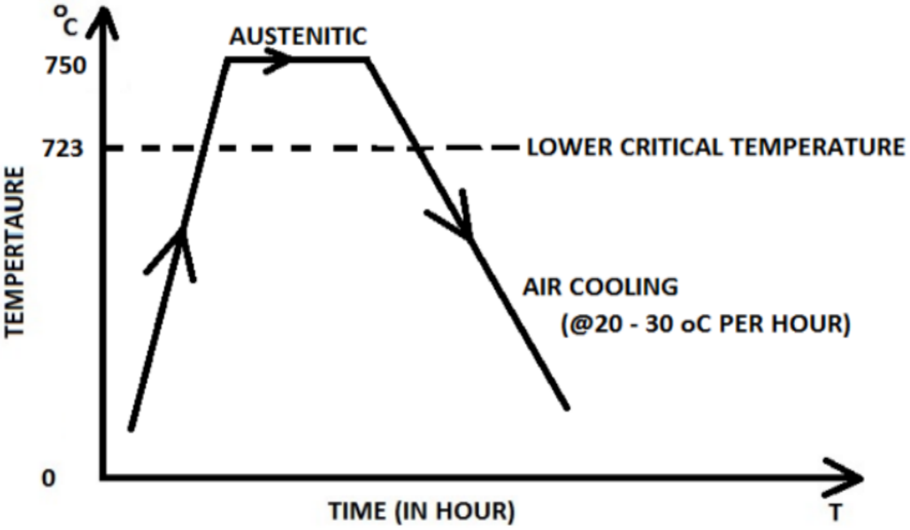


Figure 5.1. Normalizing stages of steel

Normalizing is also frequently thought of in terms of microstructure. The areas of the microstructure that contain about 0.77% C, are pearlitic (lamellae of ferrite and Fe_3C). The areas that are low in carbon are ferritic. In hypereutectoid steels, proeutectoid iron carbide first forms along austenite grain boundaries. This transformation continues until the carbon level in the austenite reaches approximately 0.8%, at which time a eutectoid reaction begins as indicated by the formation of pearlite. Air-hardening steels are excluded from the class of normalized steels because they do not exhibit the normal pearlitic microstructure that characterizes normalized steels.

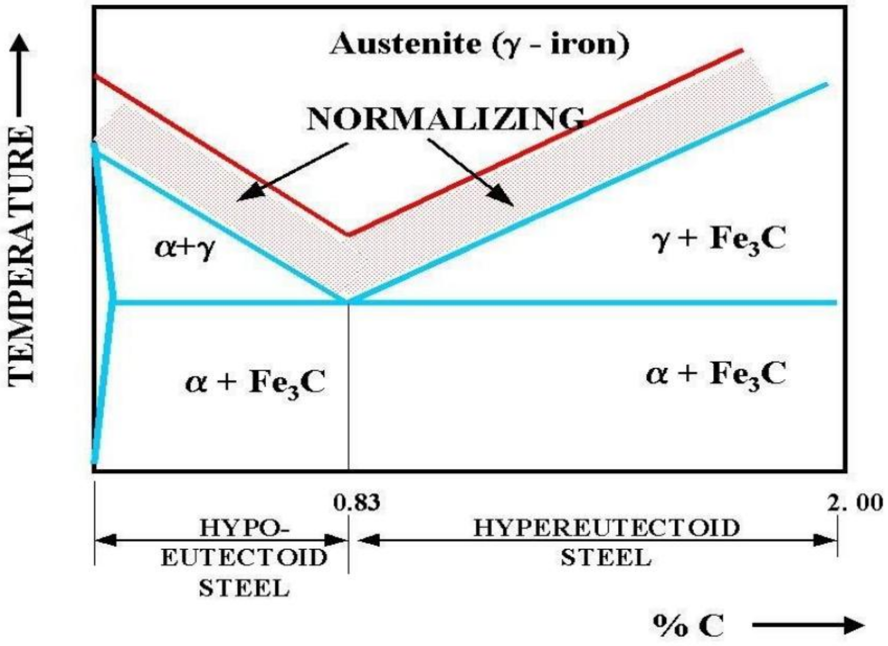


Figure 5.2. Normalizing temperatures of hypo-and-hypereutectoid steel

5.2.1. Applications and Purposes of Normalizing

A broad range of ferrous products can be normalized. All of the standard low-carbon, medium-carbon, and high carbon wrought steels can be normalized, as well as many castings. Many steel weldments are normalized to refine the structure within the weld-affected area. Austenitic steels, stainless steels, and maraging steels either cannot be normalized or are not usually normalized. Normalizing may be done for the following purposes:

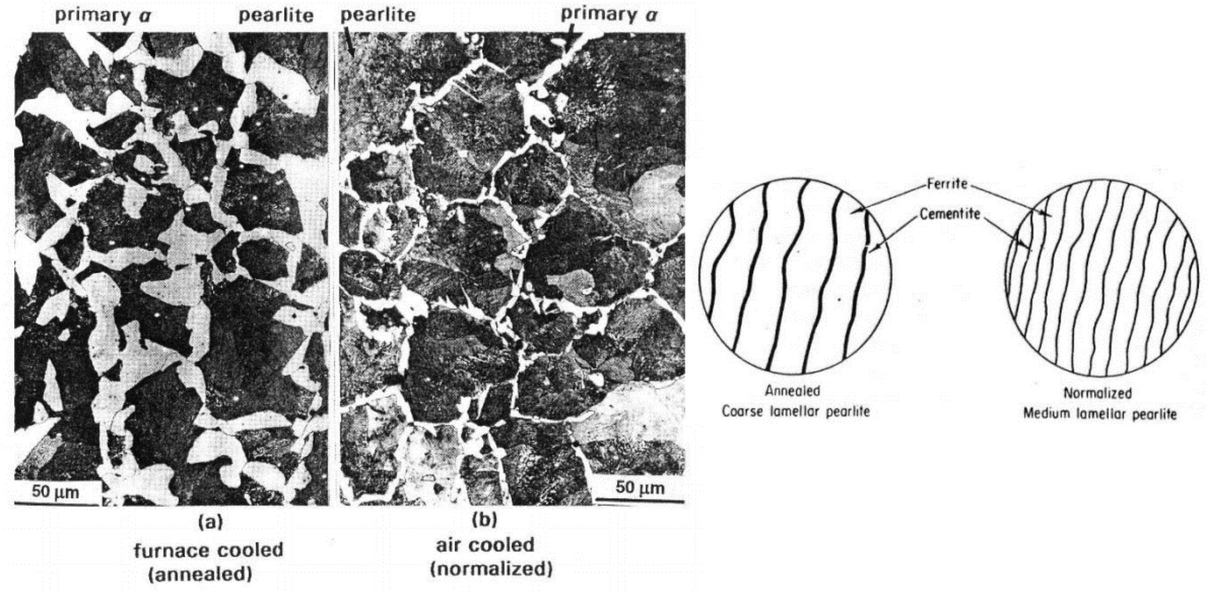
- To produce a harder and stronger steel than full annealing.
- To improve machinability.
- To modify and/or refine the grain structure.
- To obtain a relatively good ductility without reducing the hardness and strength.
- Improve dimensional stability.
- Produce a homogeneous microstructure.
- Provide a more consistent response when hardening or case hardening.
- Produce isotropic mechanical properties.

5.2.2. Comparing Normalizing with Annealing Heat Treatment

There are many differences and similarities between annealing and normalizing:

- The metal is heated to a higher temperature and then removed from the furnace for air cooling in normalizing rather than furnace cooling in annealing.

- In normalizing, the cooling rate is slower than that of a quench-and-temper operation but faster than that used in annealing.
- As a result of this intermediate cooling rate, the parts will possess a hardness and strength somewhat greater than if annealed.
- Fully annealed parts are uniform in softness (and machinability) throughout the entire part; since the entire part is exposed to the controlled furnace cooling. In the case of the normalized part, depending on the part geometry, the cooling is non-uniform resulting in non-uniform material properties across the part.
- Internal stresses are more in normalizing as compared to annealing.
- Grain size obtained in normalizing is finer than in annealing (Figure 3).
- Normalizing is a cheaper and less time-consuming process.



(a)
furnace cooled
(annealed)

(b)
air cooled
(normalized)

Figure 5.3. Microstructure differences between normalized and full-annealed steel

5.2.3. Effect of Normalizing and Full annealing on Mechanical Properties of Steel

- ***Tensile and Yield Strength***

Normalizing and annealing do not show a significant difference on the tensile and yield strength of the low carbon steels, but the normalized high carbon steels present much higher tensile and yield strength than those that are annealed, as shown in Figure 5.4.

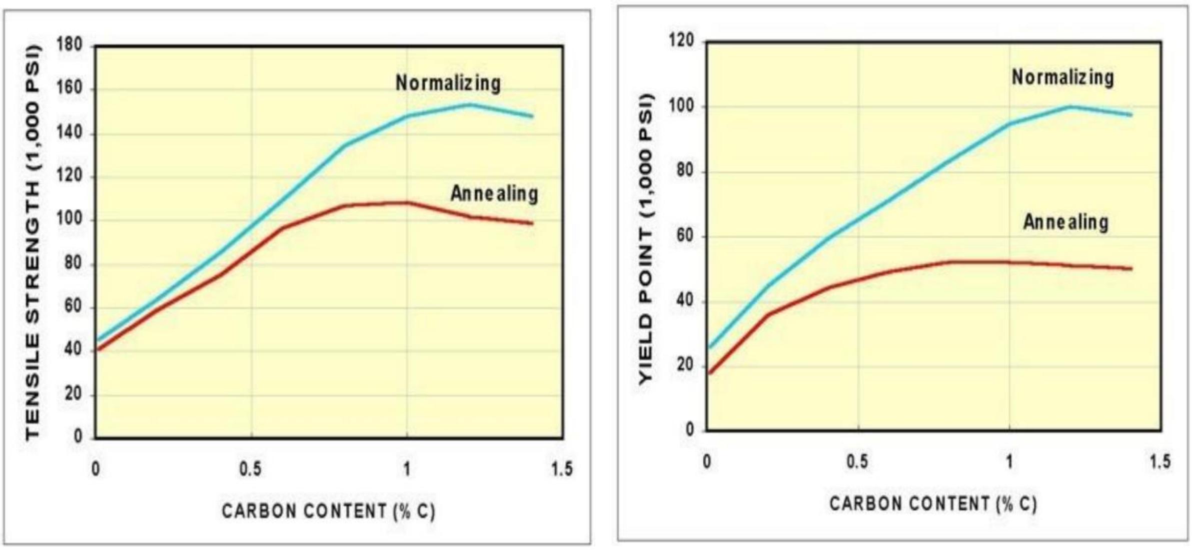


Figure 5.4. Effect of normalizing and full annealing on tensile and yield strength

- ***Elongation Percent***

Annealing and normalizing do not present a significant difference on the ductility of low carbon steels. As the carbon content increases, annealing maintains the elongation around 20%. whereas, the elongation of the normalized high carbon steels drops to 1 to 2 % level as shown in Figure 5.5.

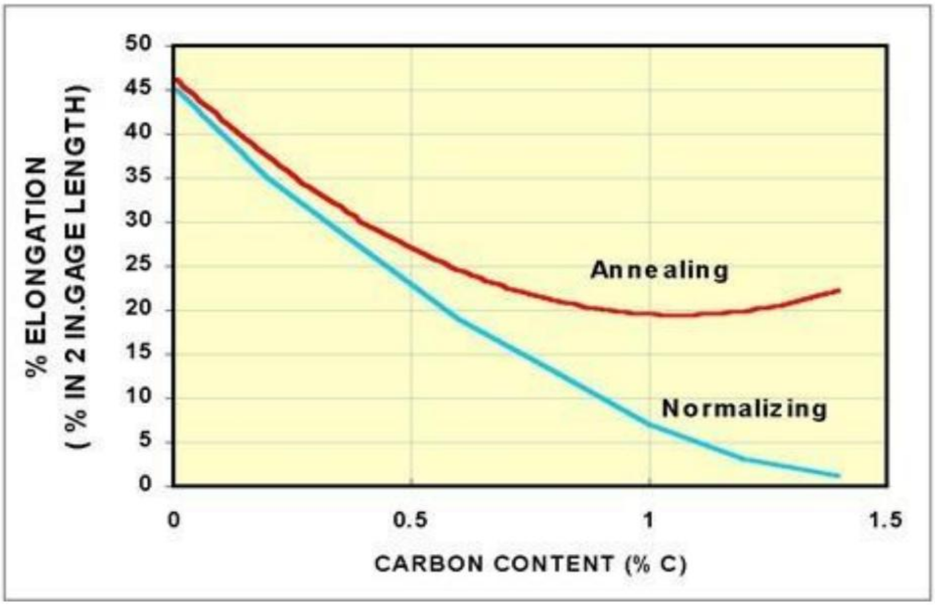


Figure 5.5. Effect of normalizing and full annealing on elongation percent of steel

- ***Hardness***

Low and medium carbon steels can maintain similar hardness levels when normalized or annealed. However, when high carbon steels are normalized, they maintain higher levels of hardness than those that are annealed, see Figure 5.6.

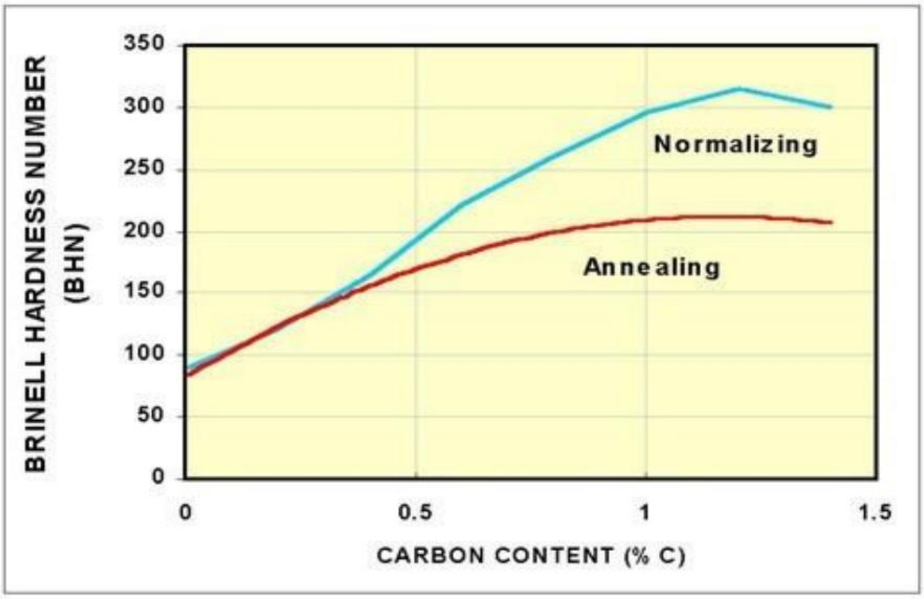
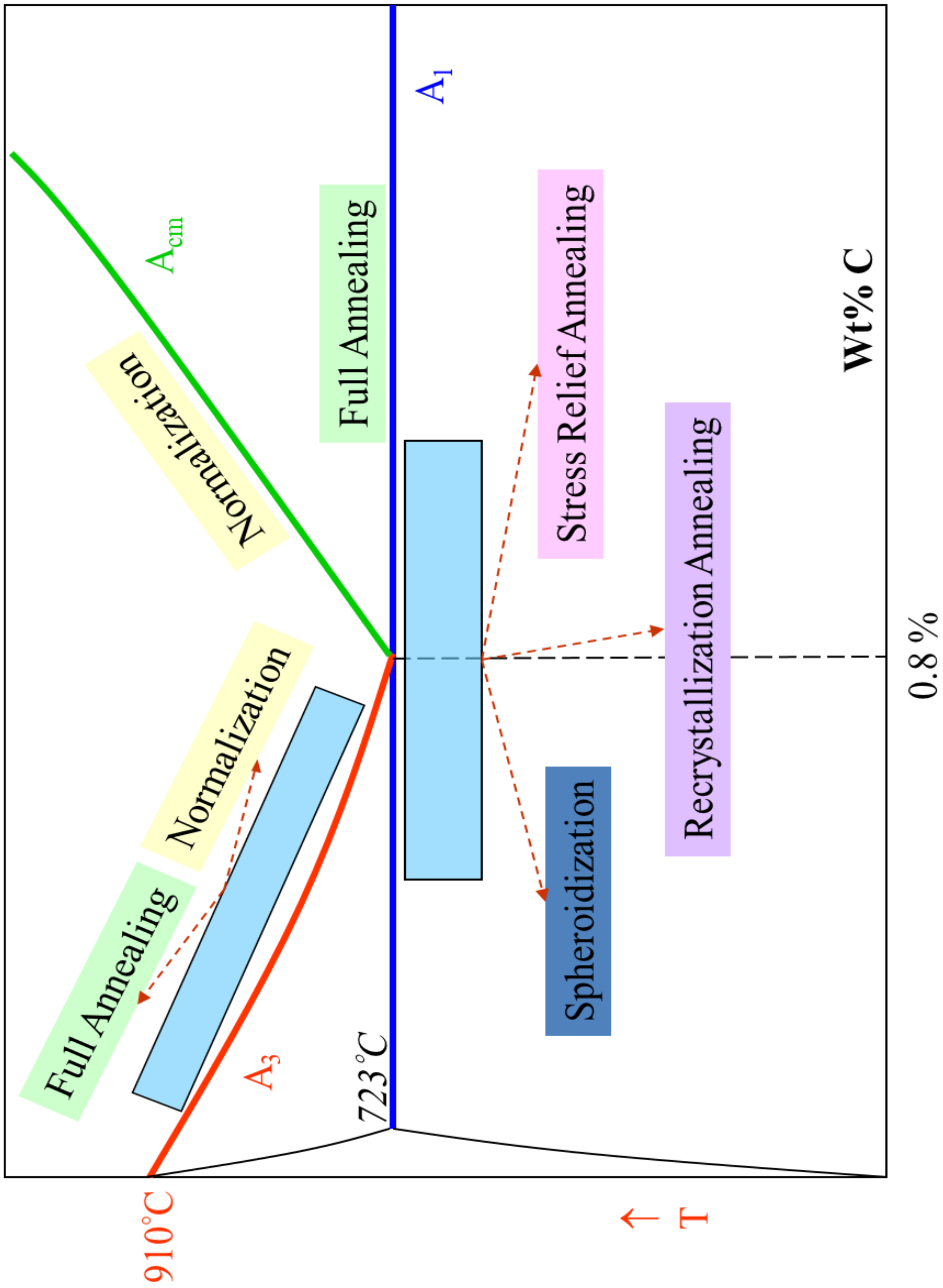


Figure 5.6. Effect of normalizing and full annealing on hardness of steel

5.3 Annealing

Figure 5.7. Annealing temperatures for carbon steel



Annealing is a heat treatment process which involves heating the steel above A_3 (for hypo-eutectoid steels) and A_1 (for hyper-eutectoid steels) with control heating rate (149-175 °C/hr), then soaking (holding) at this temperature; the soaking period depends on the chemical analysis of the metal and the mass of the part, and finally furnace cooling to obtain coarse pearlite. Heating stage should be not above the A_{cm} to avoid a continuous network of proeutectoid cementite along grain boundaries that produced path for crack propagation (Figure 5.7).

Annealing is indeed one of the most important heat treatment processes. The internal structure of the metal gets stabilized through this process. This heat treatment is given to the metal so as to achieve one on more of the following objectives:

- To refine the grains and provide homogenous structure.
- To relieve internal stresses set up during earlier operations.
- To soften the metal and, thus, improve its machinability.
- To effect changes in some mechanical, electrical and magnetic properties.
- To prepare steel for further treatment or processing.
- To drive out gases trapped during casting.
- To produce desired macro structure.

5.3.1 Annealing stages

- **Stress relief (recovery):**

A relatively low temperature process of reducing internal mechanical stresses, caused by cold-work (Figure 5.8-a), casting or welding. During this process atoms move to more stable positions in the crystal lattice (Figure 5.8-b). Vacancies and interstitial defects are eliminated and some dislocations are annihilated. Recovery heat treatment is used mainly for preventing stress-corrosion cracking and decreasing distortions, caused by internal stresses.

- **Recrystallization:**

Alteration of the grain structure of the metal. If the alloy reaches particular temperature (recrystallization or annealing temperature) new grains start to grow from the nuclei formed in the cold worked metal (Figure 5.8-c). The new grains absorb imperfections and distortions caused by cold deformation. The grains are equiaxed and independent to the old grain structure. The annealing temperature and the new grains size are dependent on the degree of cold-work which has been conducted. The more the cold-work degree, the lower the annealing temperature and the fine recrystallization grain structure. Low degrees of cold-work (less than 5%) may cause formation of large grains.

- **Grain growth:**

Growth of the new grains at the expense of their neighbors, occurring at temperature, above the recrystallization temperature. This process results in coarsening grain structure and is undesirable (Figure 5.8-d).

5.3.2 Classification of Annealing Heat Treatment

Annealing heat treatment can be classified based on temperature used, phase transformation (Figure 5.8) takes place and their specific purposes to many types. Some of these types are in the following section:

- Heating to required temperature, which is defined according to the objective of the annealing.
- Soaking at the required temperature by leaving the heat-treated material for soaking of half hour for every 25 mm thickness.
- Cooling step is done slowly inside the furnace by switch off the furnace after the soaking. This will achieve about 50-100 °C/hr cooling rates.

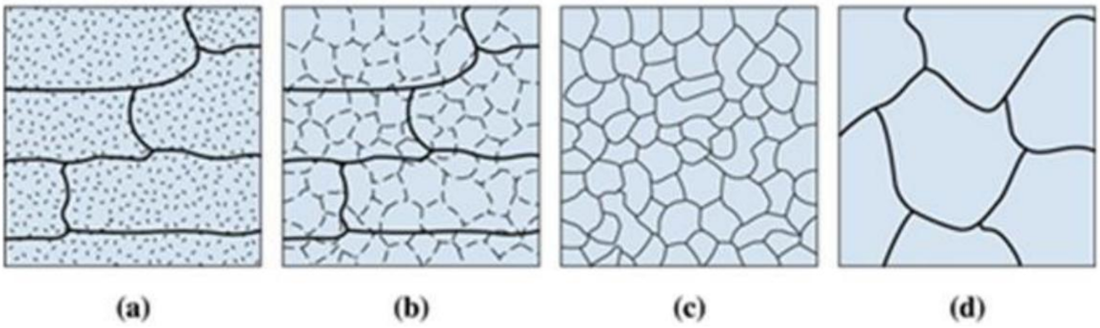


Figure 5.8 Effect of annealing temperature on the microstructure of cold-worked metals; (a) cold-worked, (b) after recovery, (c) after recrystallization, and (d) after grain growth.

Different type of annealing processes can be classified as follows:

1. Full annealing.
2. Process annealing.
3. Spheroidization annealing.
4. Diffusion annealing.
5. Isothermal annealing.

5.3.2-1. Full Annealing

The main objectives of this type of annealing are to soften the metal, relieve its stresses and refine its grain structure. It is also known as high temperature annealing. The heating temperature range of the full annealing is shown in the given figure as the following:

- For hypoeutectoid steel: $T = A_3 + (20\text{-}40)$ °C
- For hypereutectoid steel: $T = A_{1,3} + (20\text{-}40)$ °C

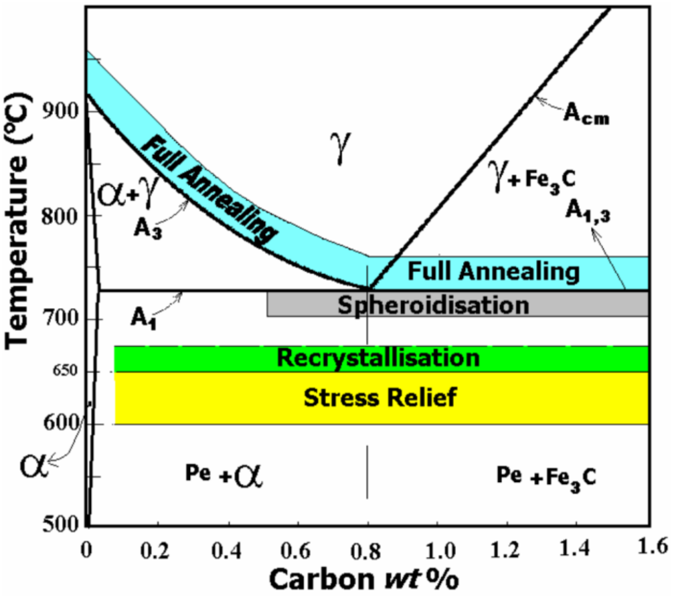
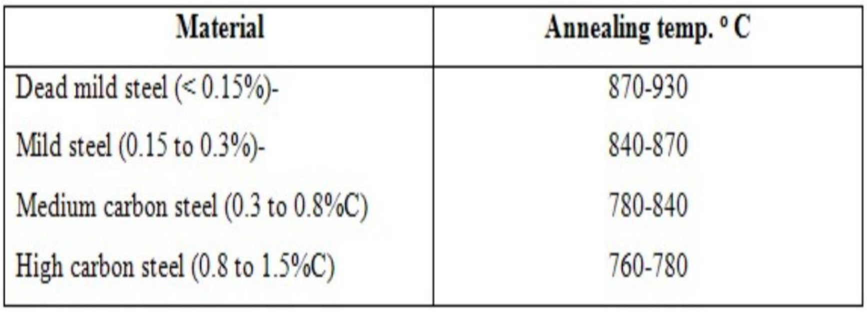


Figure 5.9 Heating temperature range of the full annealing

In this process complete phase recrystallisation takes place and, therefore, all imperfections of the previous structure are wiped out. This involves heating of steel to a temperature about 30^{o} to 50^{o} above the higher critical point for hypoeutectoid steels, and by the same amount above the lower critical point for hypereutectoid steels, holding it at that temperature for sufficient time to allow the internal changes to take place and then cooling slowly. The steel gets softened by this process, together with an appreciable amount of increase in its ductility and toughness.

Table 1. Annealing temperatures for carbon steels



Material	Annealing temp. ° C
Dead mild steel (< 0.15%)-	870-930
Mild steel (0.15 to 0.3%)-	840-870
Medium carbon steel (0.3 to 0.8%C)	780-840
High carbon steel (0.8 to 1.5%C)	760-780

Cooling is done by allowing approximately 3 to 4 minutes time at elevated temperatures per mm thickness of the largest section. High temperature cooling is usually done in the furnace itself by lowering of temperature at the rate of 10 to 30^{o}C below the lower critical temperature.

The specimen is then air cooled down to the room temperature. This process makes a course pearlitic structure which is quite soft and ductile. An alternate method of cooling after soaking is to embed the metal in a non-conducting material like sand, lime, mica, ash, etc

This result in the formation of fine grains of austenite that transform into relatively fine grains of ferrite and pearlite or pearlite and cementite (depending upon the carbon content) as the steel is slowly cooled to room temperature, usually in the furnace.

Ferrite, which then begins to precipitate in accordance with the equilibrium diagram, deposits first at the grain boundaries of the austenite. The remainder of the ferrite is then precipitated along certain crystallographic planes within the lattice of the austenite. This gives rise to a directional precipitation of the ferrite and plate, as shown in Figure 5.10 representing typically what is known as a ***Widmanstätten structure***.

Widmanstätten structure describes a ferrite morphology in the form of side plates or laths and grows into austenite grains. This structure may be expected to exhibit a coarse structure in view of the extent to which they are overheated during their passage through the upper atmosphere. The mesh-like arrangement of ferrite in the Widmanstätten structure tends to isolate the stronger pearlite into separate patches, so that strength, and more particularly toughness, are impaired. The main characteristics of such a structure are, therefore, weakness and brittleness, and steps must be taken to remove it either by heat-treatment or by mechanical working. Hot working will effectively break up this coarse as-cast structure and replace it by a fine-grained material, but in this instance, we are concerned with retaining the actual shape of the casting. Heat-treatment must therefore be used to affect the necessary refinement of grain. This operation needs a very specific controlling on the heat temperature of annealing because if any fault occurs, it will make some undesired phases in the steel such as:

- ***Over heating:***

  Overheating during annealing, or heating for too long a period in the austenitic range, will obviously cause grain growth of the newly formed austenite crystals, leading to a structure almost as bad as the original Widmanstätten structure. For this reason, the requisite annealing temperature should not be exceeded, and the alloy should remain in the austenitic range only for as long as is necessary to make it completely austenitic. In fact, alloys are sometimes air-cooled to about 650°C and then cooled more slowly to room temperature, by returning to a furnace to prevent stresses due to rapid cooling from being set up.

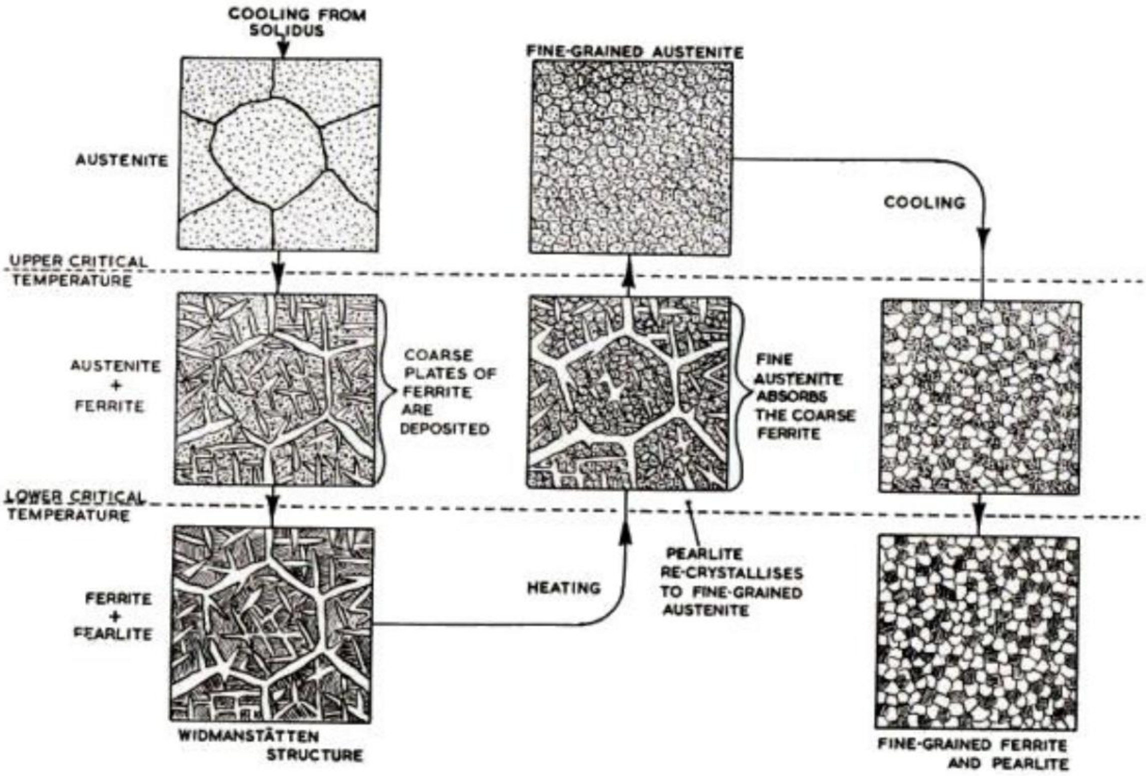


Figure 5.10. Formation and elimination of Widmanstätten structure

- **Burning (Excessive over heating):**

Excessive overheating will probably cause oxidation, or "burning", of the surface, and the penetration by oxide films of the crystal boundaries following decarburization of the surface. Such damage cannot be repaired by heat-treatment, and the alloys can only be scrapped. To prevent "burning", alloys are often annealed in cast-iron boxes into which they are packed with lime, sand, cast-iron turnings or carbonaceous material according to the carbon content of the alloys.

- **Purpose of full annealing**
  - Relieving internal stresses.
  - Reducing hardness and increase ductility.
  - Refining of grain size.
  - Homogenizing chemical composition.
  - Improving machinability of material.
  - Making steel suitable for undergoing other heat treatment processes like hardening, normalizing etc.

5.3.2.2. *Diffusion Annealing*

The purpose of diffusion annealing is to remove the heterogeneity in the chemical composition of steel ingots and heavy castings This process is mainly used before applying full annealing to steel castings. This type of annealing is usually carried out in the range of austinite at a temperature of 1100-1300°C, where diffusion occurs and grains are homogenized. The metal piece being treated is held at the diffusion temperature for a short time to allow complete diffusion and then cooled down to between 800°C to 850°C by keeping it inside the shut off furnace for a period of about 6 to 8 hours. Then it is removed from the furnace and cooled in air down to the room temperature. Then full annealing is performed.

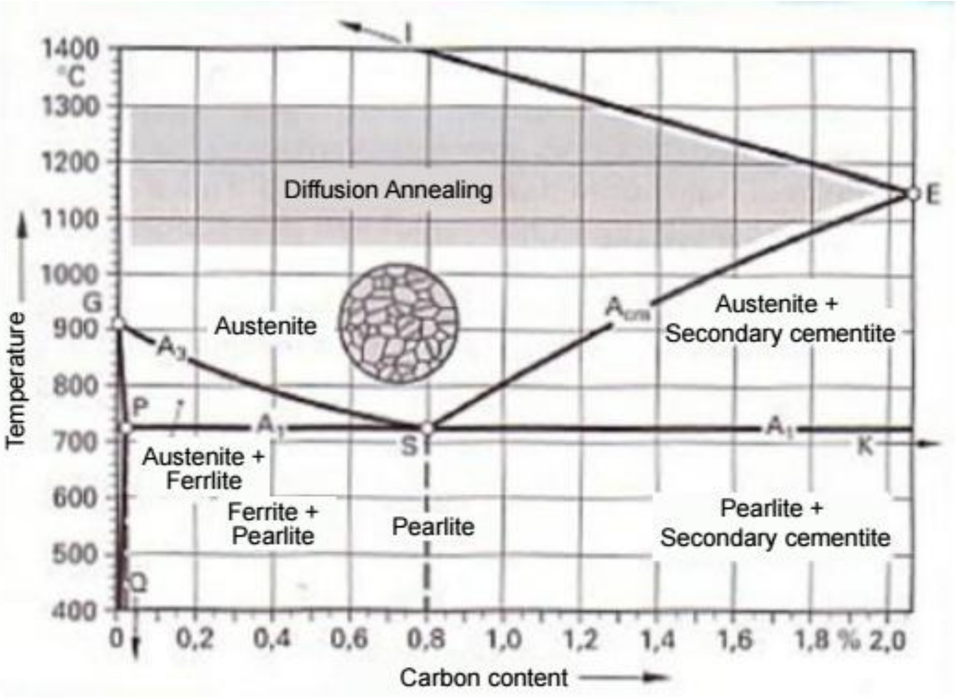


Figure 5.11 Heating temperature range of the diffusion annealing

This process, also known as homogenizing annealing, is employed to remove any structural non-uniformity like dendrites, columnar grains and chemical inhomogeneity which promote brittleness and reduce ductility and toughness of steel. Diffusion annealing can be used primarily to smooth out a difference in the content of alloying elements, the difference being due to the inter-crystal liquation. This shows up as smearing (deformation) of dendrites with an increase in temperature and heating time. Differences in microhardness are eliminated simultaneously. Some average hardness is obtained. The success of diffusion annealing largely depends on the steel purity and liquation. This type of annealing is usually used to improve properties of medium-purity steels.

5.3.2.3. *Spheroidizing Annealing*

It is long soaking time heating just below the eutectoid temperature of the 727 °C (below A_1 and $A_{1,3}$) by about 25-30°C. This will produce soft spheroid structure that could be needed in subsequent forming operations. It is usually performed for plain carbon steel of more than 0.45wt%. The heating temperature range and the plain carbon steel composition that used by this process are shown in the given figure 5.12.

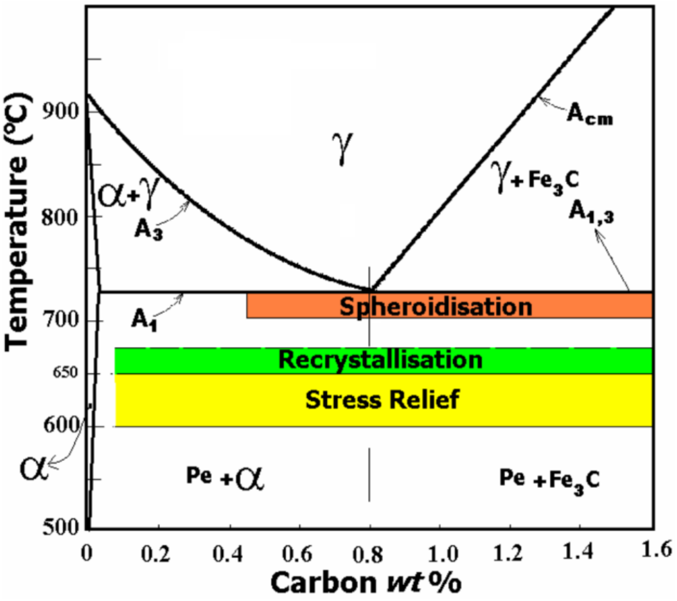


Figure 5.12 Heating temperature range of the Spheroidizing annealing

The main purpose of spheroidized annealing is to produce a structure of steel which consists of globules or well dispersed spheroids of cementite in ferrite matrix. The Spheroidizing temperature is between 650 and 700°C, just below the lower critical temperature. Since the temperature involved are sub-critical no phase changes take place. Spheroidization is an annealing process used for high carbon steels (Carbon > 0.5%) that will be machined or cold formed subsequently. This is done by one of the following ways:

a) Heat the part to a temperature just below the lower critical temperature (A_1). Hold the temperature for a prolonged time and follow by fairly slow cooling. Or;

b) Cycle heating for multiple times between temperatures which are slightly above and slightly below the 723 ºC line, say for example between 700 and 750 ºC and slow cool. Or;

c) For tool and alloy steels heat to 750 to 800 ºC and hold for several hours followed by slow cooling.

All these methods result in a structure in which all the cementite is in the form of small globules (spheroids) dispersed throughout the ferrite matrix. This structure allows for improved machining in continuous cutting operations such as lathes and screw machines. Spheroidization also improves resistance to abrasion. Figure 5.13 shows the formation of Spheroidized cementite.

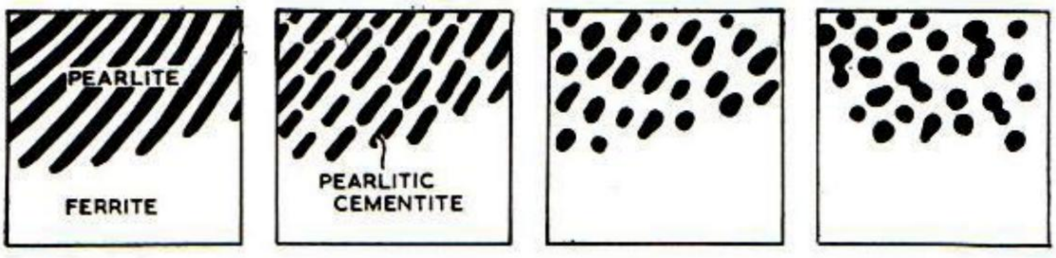


Figure 5.13. Spheroidization annealing of pearlitic-cementite

5.3.2.4. Partial Annealing

Partial annealing, also known as inter-critical annealing or incomplete annealing, is a process in which steel is heated between A_1 and A_{cm} and is followed by slow cooling. Hypereutectoid steels are subjected to this treatment. The resultant microstructure consists of fine pearlite and cementite instead of coarse pearlite and a network of cementite at grain boundaries. As low temperatures are involved in this process, it is less expensive than full annealing. Whereas, hypoeutectoid steels are subjected to this treatment to improve machinability. However, steels with coarse structure of ferrite and pearlite are not suitable for this treatment. This is because only a considerable amount of ferrite remains untransformed, and only a part of it along with pearlite transforms to austenite. This coarse or acicular untransformed ferrite results in poor mechanical properties.

5.3.2.5. Recrystallization Annealing

It is used to eliminate residual and internal stresses and create new grains that will be coarse grains. This process will lead to increase the ductility and the workability. As shown in the figure 5.14. Heating temperature for recrystallisation is about 650-670 °C to eliminate strain hardening. This makes further reshaping possible.

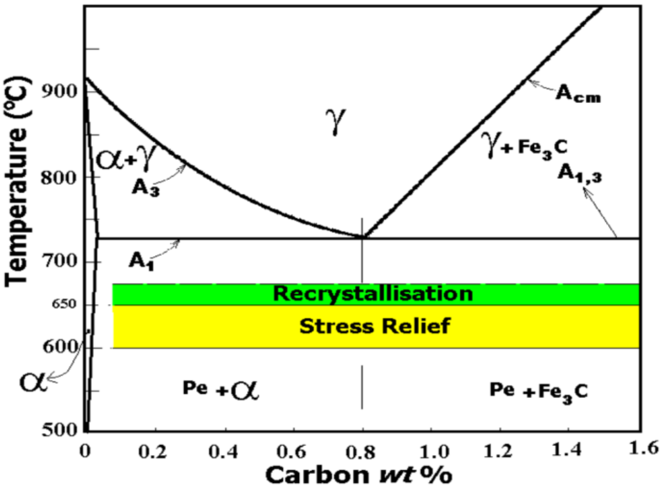


Figure 5.14 Heating temperature range of the recrystallization annealing

The recrystallization annealing consists of heating steel above the recrystallization temperature, holding at this temperature and cooling thereafter. It is used to treat work-hardened parts made out of low-carbon steels (< 0.25% Carbon). This allows the parts to be soft enough to undergo further cold working without fracturing. Recrystallization temperature (**T_r**) is given by:

$$\mathbf{T_r = (0.3\text{-}0.5)\,T_m}$$

There are no phase change takes place and the final structure consists of strain-free, equiaxed grains of fine ferrite produced at the expense of deformed elongated ferrite grains (see figure 5.14). It would produce very coarse grains if the steel has undergone critical amount of deformation. In such cases, full annealing is preferred.

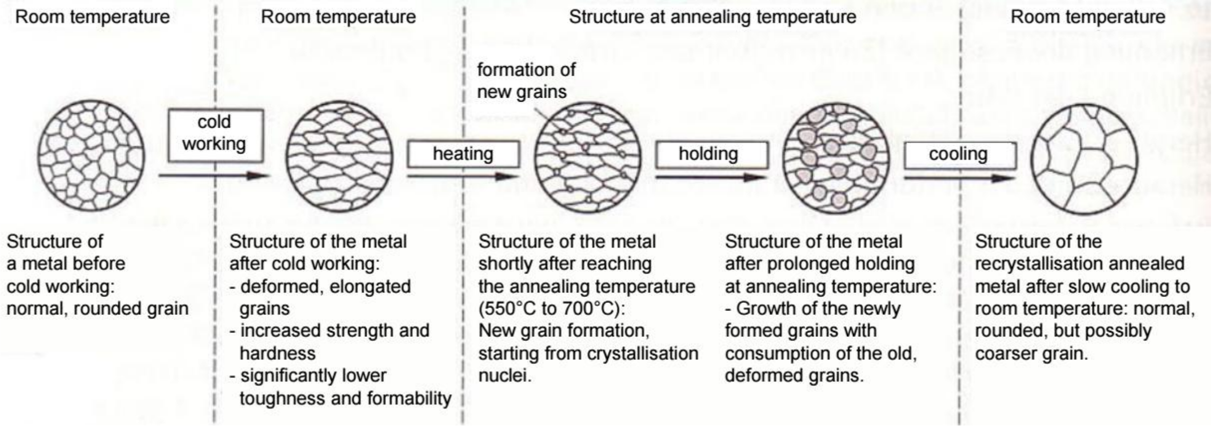


Figure 5.15 Processes of the recrystallization annealing

5.3.2.6. Stress-Relief Annealing

It is also called “**process annealing**, **inter-stage annealing** and **subcritical annealing**”, it is often used for softening cold worked low carbon steel or mild steel. In a mild steel ferrite makes up about 90 % of the structure, and the recrystallization temperature of cold worked ferrite is only about 500 °C. Annealing of cold worked mild steel in the temperature range 550-600 °C will result in complete recrystallization of ferrite, although the cold worked pearlite will be largely unaffected.

When the cold-work of mild steels is achieved, for example in the drawing of wire, stress-relief annealing becomes necessary to soften the metal so that further drawing operations can be carried out. Such annealing is carried out at about 650 °C. Since this temperature is well above the recrystallization temperature of 500 °C.

It is used to eliminate and/or minimize stresses arising from plastic deformation during machining or forming processes. Stress relief annealing allows these stresses to relax. Annealing temperatures are relatively low so that useful effects of cold working are not eliminated. The figure 5.16 shows that heating temperature for the stress relief annealing is between 625-650°C.

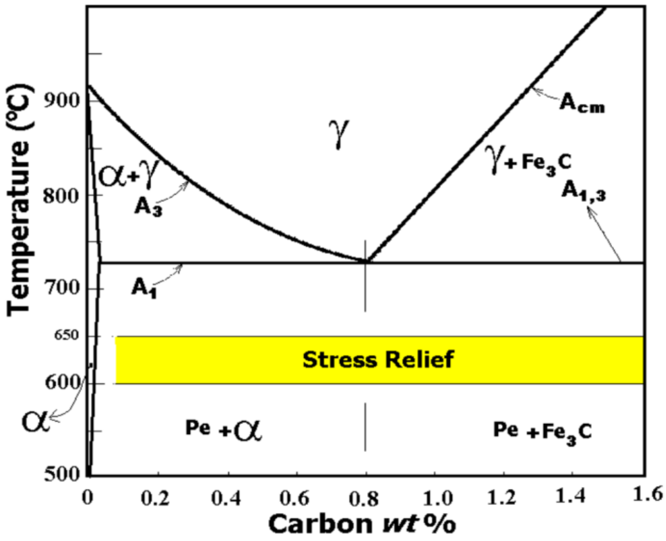


Figure 5.16 Heating temperature range of the Stress-relief annealing

Stress-relief heat treating is the uniform heating of a structure or portion to a suitable temperature below the transformation range (A_1) for this reason, although recrystallization is promoted, there is no phase change and the ferrite and cementite remain present in the structure throughout the process. After heating, the holding for a predetermined period of time must take place, followed by uniform cooling. Care must be taken to ensure uniform cooling, particularly when a component is composed of variable section sizes. If the rate of cooling is not constant and uniform, new residual stresses can result that are equal to or greater than those that the heat-treating process was intended to relieve. Process annealing is generally carried out in either batch-type or continuous furnaces, usually with an inert atmosphere of burnt coal gas.

The main differences between various kinds of annealing processes based on the temperature and final structure are summarized in Figure 5.17.

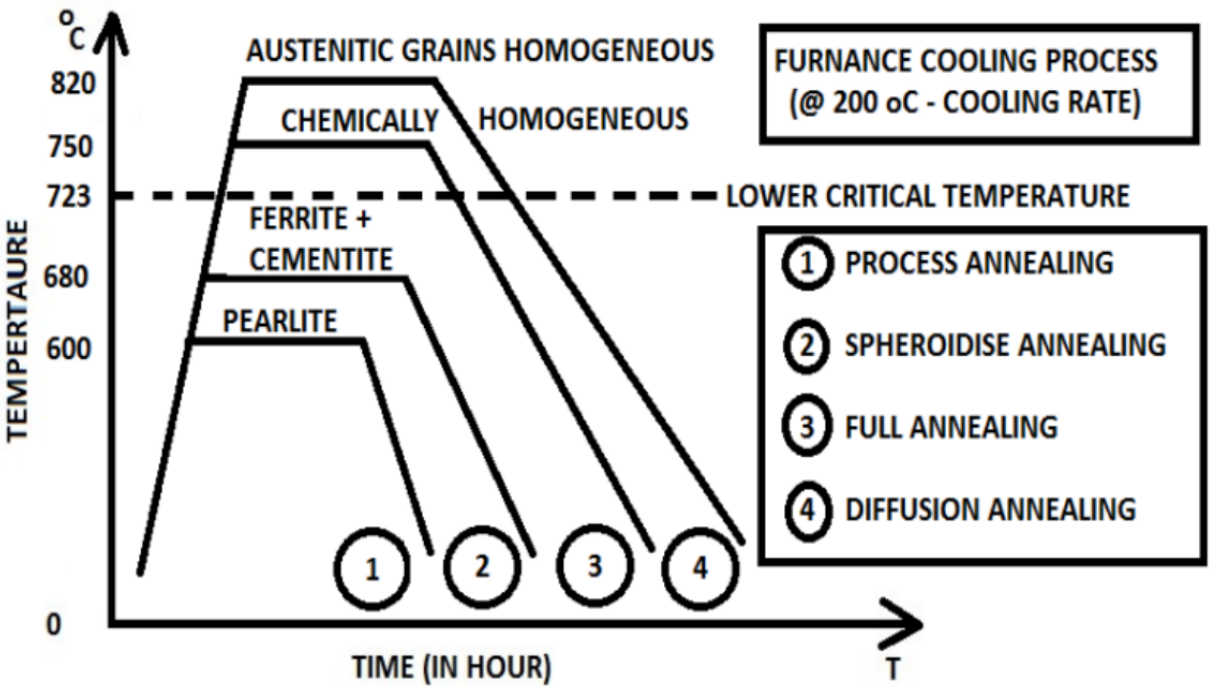


Figure 5.17 Sketch diagram of different annealing processes

5.4. Quenching or Hardening

5.4.1. Introduction

Quenching refers to the process of rapidly cooling from the austenitizing or solid solution temperature, typically from within the range of 815 to 870°C, at such a rate that a martensite is formed (see Figure 5.18). In this state, steels are characterized by the greatest hardness. In normal quenching, to provide fast cooling rate during quenching, various cooling media and methods are employed. Water, oil, or gas can serve as the cooling medium. A certain amount of austenite is retained during quenching even in steels with a relatively small content of carbon. For this reason, it is impossible to impart the maximum hardness to an alloy. Since austenite is stable at room temperature and passes to martensite at lower temperatures, steels undergo a ***subzero treatment.*** *Under this treatment quenching is continued and steels with a high content of retained austenite are immersed in liquid air or quenching mixtures whose temperature is below room temperature.*

For surface quenching (*if it is necessary to harden only the surface layer to a preset depth*), special quenching heating regimes are used. The surface of the product is fully heated, while the core is cold and remains unquenched on subsequent rapid cooling. The selection of steel for surface quenching must be governed by the sensitivity of the metal to quick heating and cooling. For this reason, the carbon concentration is limited to 0.7%. Otherwise, cracks are formed. Among the main quenching defects are excessive holding and overheating. They show up as enlargement of martensite needles and coarse-grain fracture. This leads to a high brittleness of quenched products and the formation of cracks. Cracks often form at the boundaries of initial austenite grains. A low quenching temperature or too short a holding time at the given temperature causes incomplete quenching. In this case, a quenched metal is insufficiently hard.

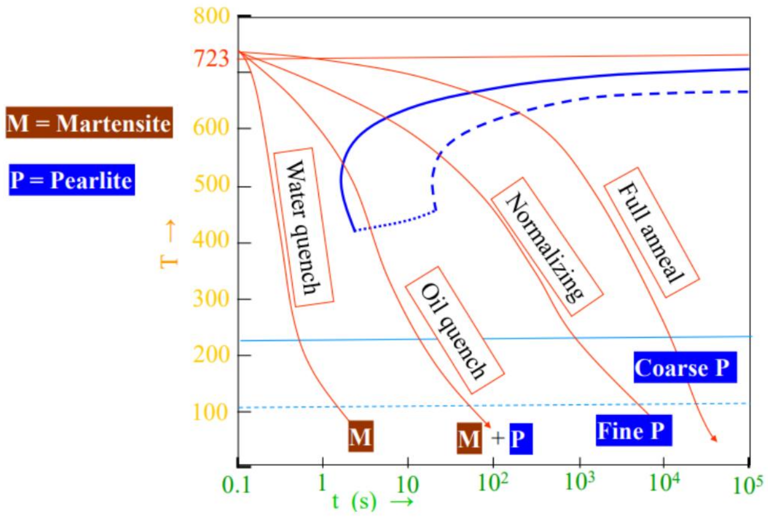


Figure 5.18. Microstructure changes of steel with heat treatment type

5.4.2. Effect of Quenching Mediums

Quenching medium has the profound effect on the final phase of the material. Quenching medium is directly related to the rate of the cooling of the material**.** Some of the widely employed quenching media are water, aqueous solutions, oils (mineral, vegetable and even animal oils), molten salts and air.

The selection of a quenchant medium depends on the:

(i) hardenability of the particular alloy,
(ii) the section thickness and shape involved,
(iii) the cooling rates needed to achieve the desired microstructure.

The most common quenchant media are either liquids or gases. The liquid quenchants commonly used include:

- Oil that may contain a variety of additives
- Cold water
- Aqueous polymer solutions
- Water that may contain salt or caustic additives (brine solution)

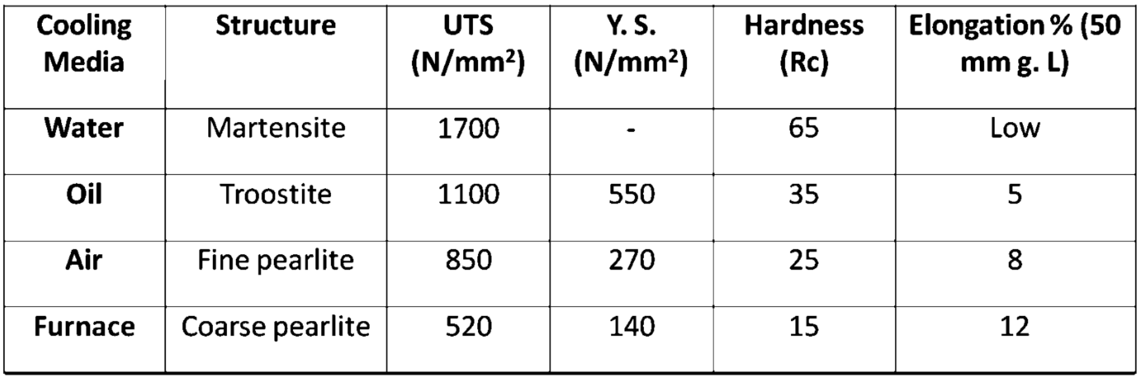
The most common gaseous quenchants are inert gases including helium, argon, and nitrogen. These quenchants are sometimes used after austenitizing in a vacuum. The ability of a quenchant to harden steel depends on the cooling characteristics of the quenching medium. Quenching effectiveness is dependent on:

(a) the steel composition,
(b) type of quenchant, and
(c) the quenchant use conditions.

The design of the quenching system and the thoroughness with which the system is maintained also contribute to the success of the process.

- Just the drastic water quench generates a fully martensite structure.
- Although quenched in oil the austenite converts into suitably fine pearlite.
- Accurate pearlite also results if the austenised eutectoid steel is air-cooled.
- Though, if allowed to cool in furnace coarse pearlite is appearance.

Table 5.1 Quenchant media properties



Cooling Media	Structure	UTS (N/mm^2)	Y. S. (N/mm^2)	Hardness (Rc)	Elongation % (50 mm g. L)
Water	Martensite	1700	-	65	Low
Oil	Troostite	1100	550	35	5
Air	Fine pearlite	850	270	25	8
Furnace	Coarse pearlite	520	140	15	12

5.4.2.a Effect of Quenching Medium (Water)

Water has maximum cooling rate amongst all common quenchants except few aqueous solutions. It is very cheap and easily disposed off compared to other quenchants. Hence water is used for carbon steels (see Figure 5.19), alloy steels and non-ferrous alloys. The layer if scale formed on the surface during heating is also broken by water quenching, thus eliminating an additional process of surface cooling.

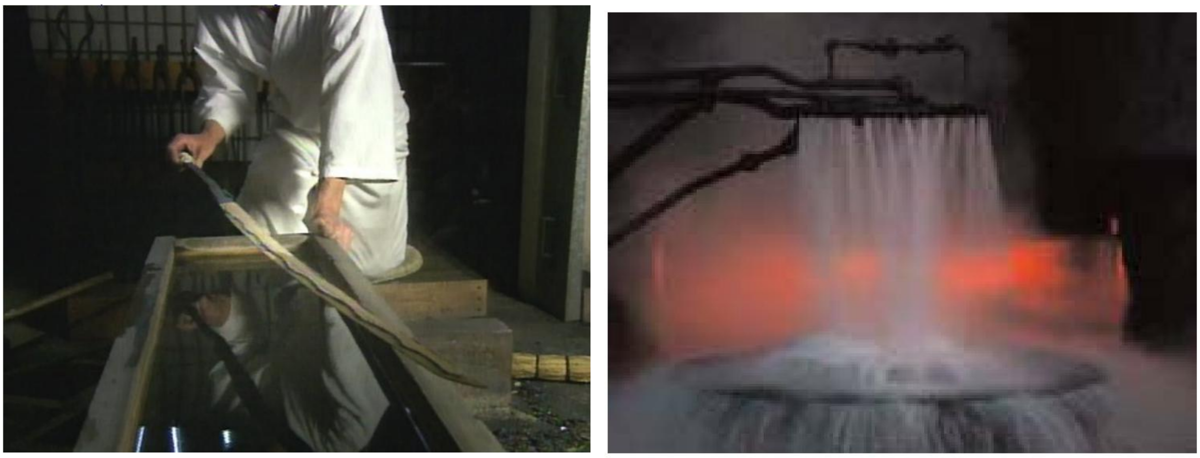


Figure 5.19 Quenching Medium (Water)

5.4.2.b Effect of Quenching Medium (OIL)

Most of the Oils used as quenchants are mineral oils (see Figure 5.20). These are in general paraffin based and do not possess any fatty oils. Quenching in oil provides slower cooling rates as compared to those achieved by water quenching. The slower cooling rate reduces the possibility of hardening defects. The temperature difference between core and the case of work piece is less for oil quenching than for water quenching.

Figure 5.20 Quenching Medium (OIL)

5.4.2.c Effect of Quenching Medium (AIR)

Many alloy steels are capable of getting hardened by cooling either in still air or in a blast of air (see Figure 5.21). Such steels are popularly known as air hardening steels. These steels are almost free from distortion problem. However, the problem of oxidation during cooling (quenching) may be encountered in practice. Many grades of tool steels are subjected to air hardening.

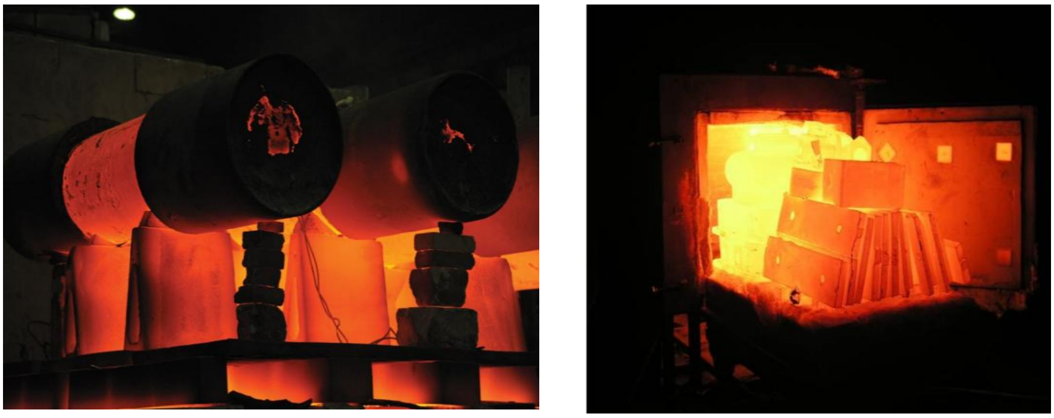


Figure 5.21 Quenching Medium (Air)

5.4.3. Quenching Techniques

The rate of heat extraction by a quenching medium and the way it is used substantially affects quenchant performance. Variations in quenching practices have resulted in the assignment of specific names to some quenching techniques:

- Direct quenching
- Time quenching
- Selective quenching
- Spray quenching
- Fog quenching
- Interrupted quenching

5.4.3.1. 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.

5.4.3.2. Time quenching

It is used when the cooling rate of the part being quenched needs to be abruptly changed during the cooling cycle. The change in cooling rate may consist of either an increase or a decrease in the cooling rate depending on which is needed to attain desired results. The usual practice is to lower the temperature of the part by quenching in a medium with high heat removal characteristics (for example, water) until the part has cooled below the nose of the time-temperature- transformation (TTT) curve, and then to transfer the part to a second medium (for example, oil), so that it cools more slowly through the martensite formation range. In some applications, the second medium may be air or an inert gas. Time quenching is most often used to minimize distortion, cracking, and dimensional changes.

5.4.3.3. Selective quenching

It is desirable for certain areas of a part to be relatively unaffected by the quenching medium. This can be accomplished by insulating an area to be more slowly cooled so the quenchant contacts only those areas of the part that are to be rapidly cooled.

5.4.3.4. 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.

5.4.3.5. Fog quenching

It utilizes a fine fog or mist of liquid droplets in a gas carrier as the cooling agent. Although similar to spray quenching, fog quenching produces lower cooling rates because of the relatively low liquid content of the stream.

5.4.3.6. Interrupted quenching

Interrupted quenching consists of rapidly quenching steel from the austenitizing temperature to a temperature above the Ms temperature (starting temperature of forming martensite), 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; ***marquenching***, ***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 martempering oils.

- ***Marquenching***

It 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 workpiece, and then removing it from the bath before transformation into bainite (it is mixture of ferrite and cementite formed by isothermal transformation of austenite under selected conditions) begins. The martensite structure formed during marquenching is the same as after direct quenching; however, residual stresses are minimized owing to the more homogeneous temperature distribution throughout the part and slower cooling rate during martensite formation.

- ***Austempering***

It is similar to marquenching in that the steel is rapidly quenched from the austenitizing temperature to a temperature above Ms but differs in that the workpiece is held at temperature for sufficient time to allow an isothermal transformation into bainite. Martensite formed during direct quenching and marquenching is often tempered, because tempered martensite exhibits a more homogeneous elemental distribution and improved toughness and strength.

- ***Isothermal annealing***

It differs from marquenching 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.

- 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

5.4. Hardening

Hardening and Hardness are two very different things. One is a process of heat treatment and other is an extrinsic property of a material. Hardening is a heat treatment process in which steel is rapidly cooled from austenitising temperature. As a result of hardening, the hardness and wear resistance of steel are improved.

5.4.1 *Procedure for Hardening*

The high hardness developed by this process is due to the phase transformation accompanying rapid cooling. Rapid cooling results in the transformation of austenite at considerably low temperature into non-equilibrium products. The main aim of the hardening process is to make steel hard. In this process, steel is heated 30° – 40°C above the upper critical temperature A_{C3} e; holding it at this temperature for a considerable period; quenching (sudden cooling) in water, oil/molten salt solution. This is done to develop hardness to resist wear and to improve strength, elasticity, ductility and toughness and to enable it to cut other metals (to make it suitable for cutting tools). It is the opposite process of annealing.

The heating operation is required form the purpose of transforming the ferrite and pearlite for hypo eutectoid steels and pearlite and cementite for hyper eutectoid steels into austenite. A rapid cooling forms the hardened temperature causes austenite to be transformed into martensite which is very hard and brittle. 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**.

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 socking 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 hardening process, the steel is heated above its critical temperature range. It is held at that temperature for a definite period. The steel is then rapidly cooled in a medium of quenching.

The quenching medium is selected according to the degree of hardness desired. The air, water, brine, oils, and molten salts are used as quenching mediums. A thin section such knife blades are cooled in the air. Water is a widely used medium but it results in the formation of bubbles on the surface of the metal. Hence brine solution is used to prevent this. Oil is used when there is a risk of distortion on cracks and is suitable for alloy steels. The molten salts are used to cool thin sections to obtain crack-free and impact-resistant products.

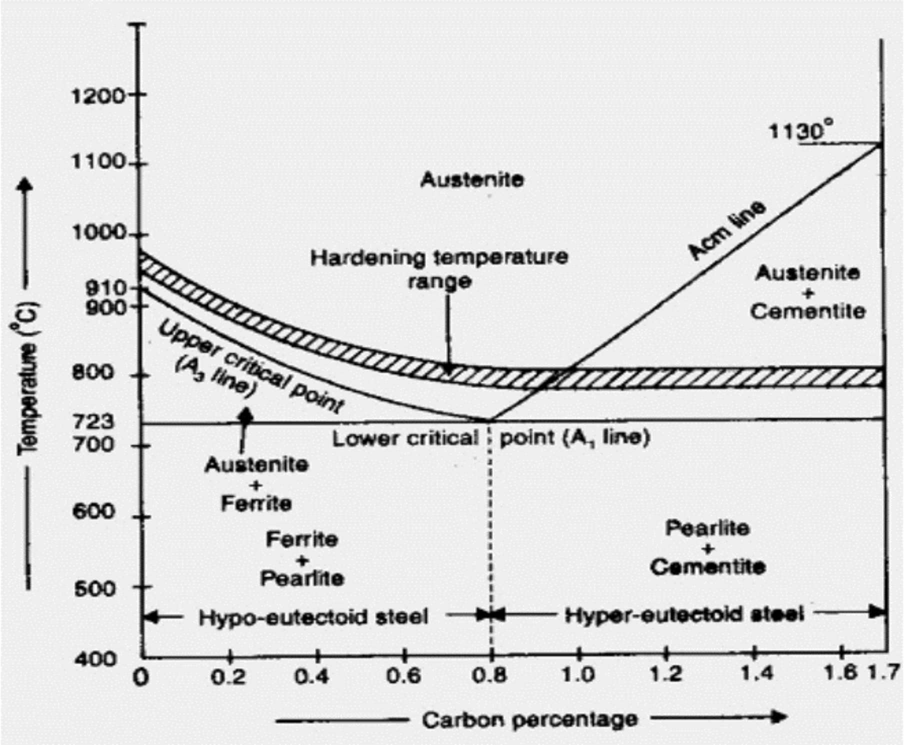


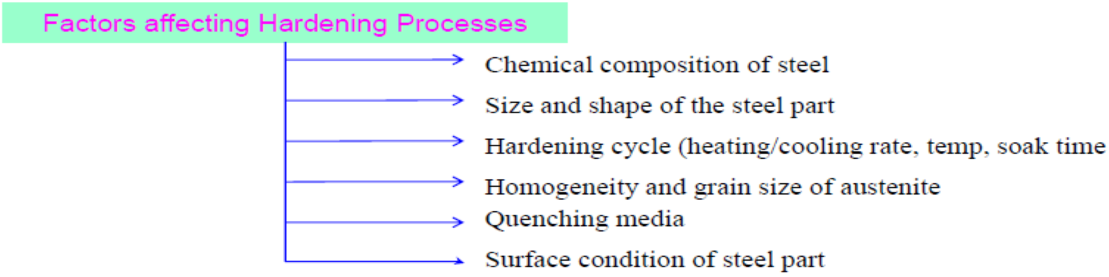
Figure 5.22. Hardening process

5.4.2 Purpose of Hardening

- increases the hardness of steel.
- To resist to wear
- Allows the steel to cut other metals

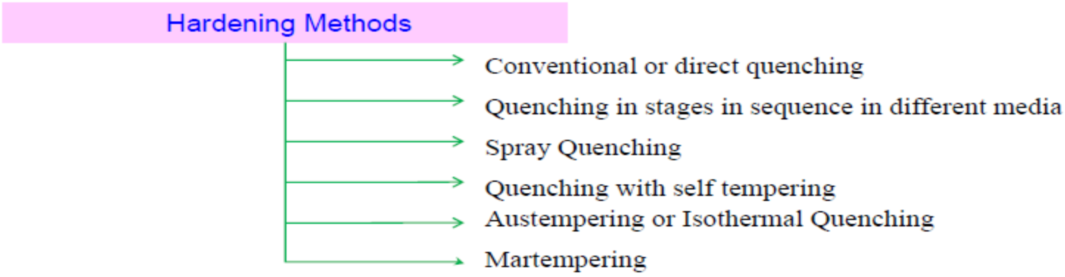
*5.4.*3 Application of Hardening

It is applied for hand hammers, center punches, taps, dies, milling cutters, knife blades, and gears.



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

5.4.4 Hardenability:

- It is an index of the depth to which the martensite can be formed in a given steel as a result of a given hardening treatment.
- The term Hardenability is used to measure the depth of hardness achieved i.e. martensite introduced into the steel section by quenching the steel from austenite state.
- The responsibility of a steel to a given hardening treatment is indicated by the property known as Hardenability.
- Greater the depth of hardness below the surface, higher will be the Hardenability of steel.
- Hardenability of steel depends on composition of steel, method of quenching and section of steel.
- The addition of alloying elements in steel decreases the critical cooling rate. Thus, the Hardenability of alloy steels is more than that of the carbon steels.
- The larger section shows lower Hardenability because of their increase mass results in a lower overall rate of cooling.

5.4.5 Jominy End Quench Test

- The Jominy test involves heating a standard test piece of diameter 25 mm and length 100mm to the austenite state, fixing it to a frame in a vertical position and then quenching the lower end by means of a jet of water (Figure 5.23).
- The most simple and convenient method of determining the Hardenability is the Jominy End Quench Test.
- The mode of quenching results in different rate of cooling along the length of the test piece.

- After a quenching, a flat of 0.38 mm deep is ground along one side of the test price, and hardness measurements are made along the length of the test piece.
- A bar of steel having good Hardenability shows higher hardness readings for greater distance from the quenched end.

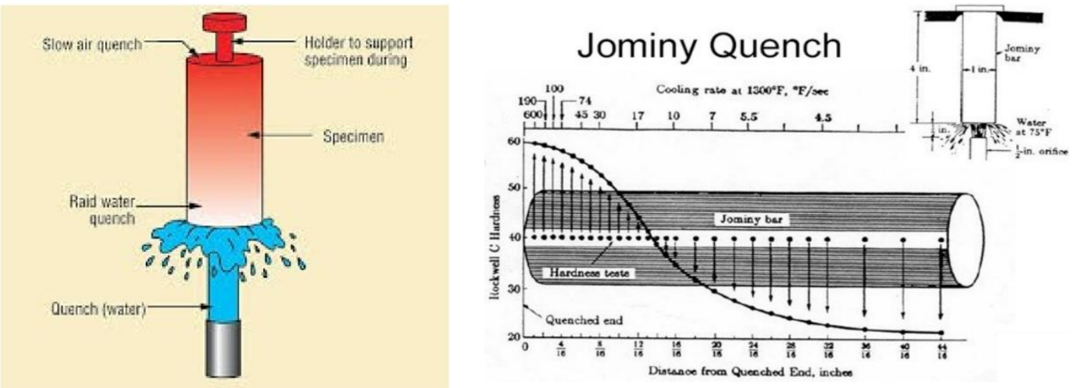


Figure 5.23 Jominy End Quench Test

5.5. Tempering

5.5.1. Introduction

Tempering of steel is a process in which previously hardened or normalized steel is usually heated to a temperature below the lower critical temperature and cooled at a suitable rate, primarily to increase ductility and toughness, but also to increase the grain size of the matrix. Steels are tempered by reheating after hardening to obtain specific values of mechanical properties and also to relieve quenching stresses and to ensure dimensional stability. Tempering usually follows quenching from above the upper critical temperature; however, tempering is also used to relieve the stresses and reduce the hardness developed during welding and relieve stresses induced by forming and machining.

Tempering process of heat treating, which is used to increase the toughness of iron-based alloys. Tempering is usually performed after quenching, to reduce some of the excess hardness, and is done by heating the metal to some temperature below the critical point for a certain period of time, then allowing it to cool in still air.

Between 66 and 148 °C ⟷ internal stresses, decrease in brittleness
148 to 205 °C ⟷ internal stresses, reduction in hardness
260 to 340 °C ⟷ decrease in ductility and an increase in brittleness "tempered martensite embrittlement" tool steel
370 to 540 °C ⟷ toughness is desired at the expense of strength

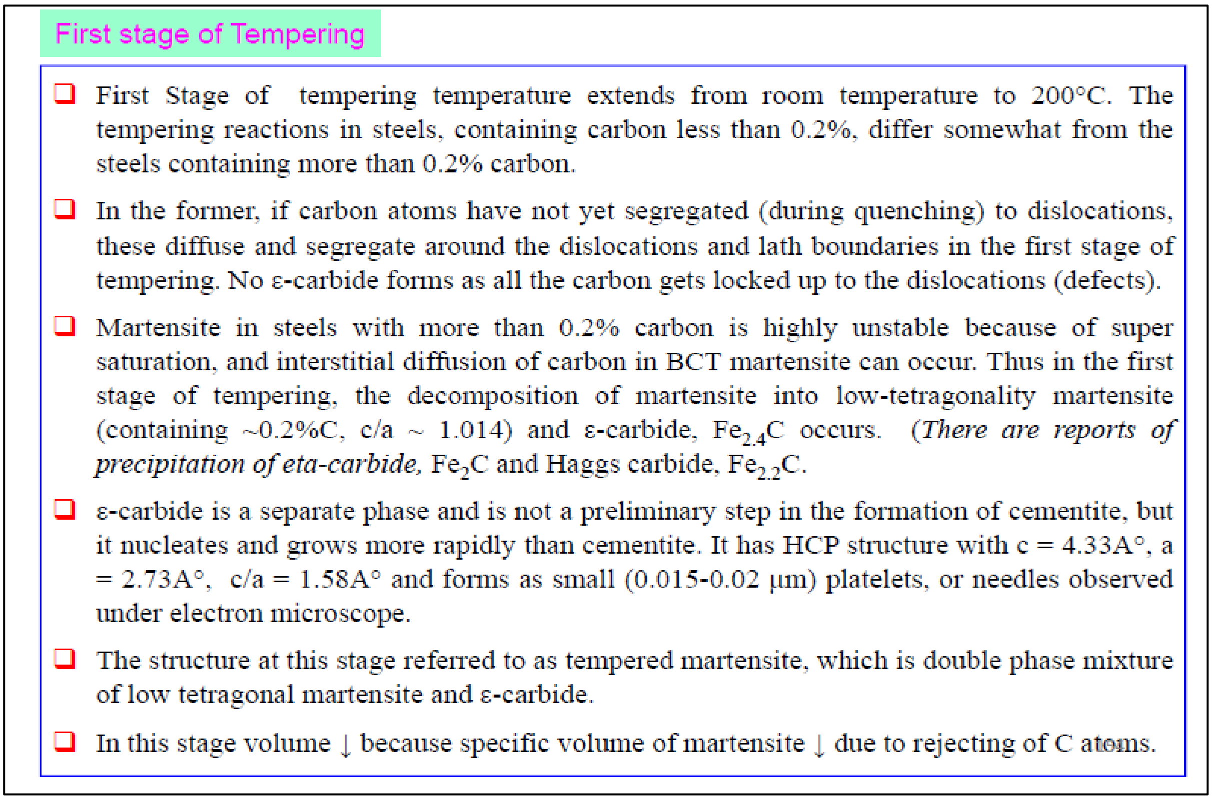
540 to 600 °C ⟷ Excellent toughness

In quenched steels that its microstructure consisting essentially of martensite, the iron lattice is strained by the carbon atoms, producing the high hardness of quenched steels. Upon heating, the carbon atoms diffuse and react in a series of distinct steps that eventually form Fe_3C or alloying elements carbide in a ferrite matrix of gradually decreasing stress level. *The properties of the tempered steel are primarily determined by the size, shape, composition, and distribution of the carbides that form, with a relatively minor contribution from solid-solution hardening of the ferrite*. These changes in microstructure usually decrease hardness, tensile strength, and yield strength but increase ductility and toughness.

Under certain conditions, hardness may remain unaffected by tempering or may even be increased as a result of it. For example, tempering hardened steel at very low tempering temperatures may cause no change in hardness but may achieve a desired increase in yield strength. Also, those alloy steels that contain one or more of the carbide-forming elements (chromium, molybdenum, vanadium, and tungsten) are capable of secondary hardening; that is, they may become somewhat harder as a result of tempering.

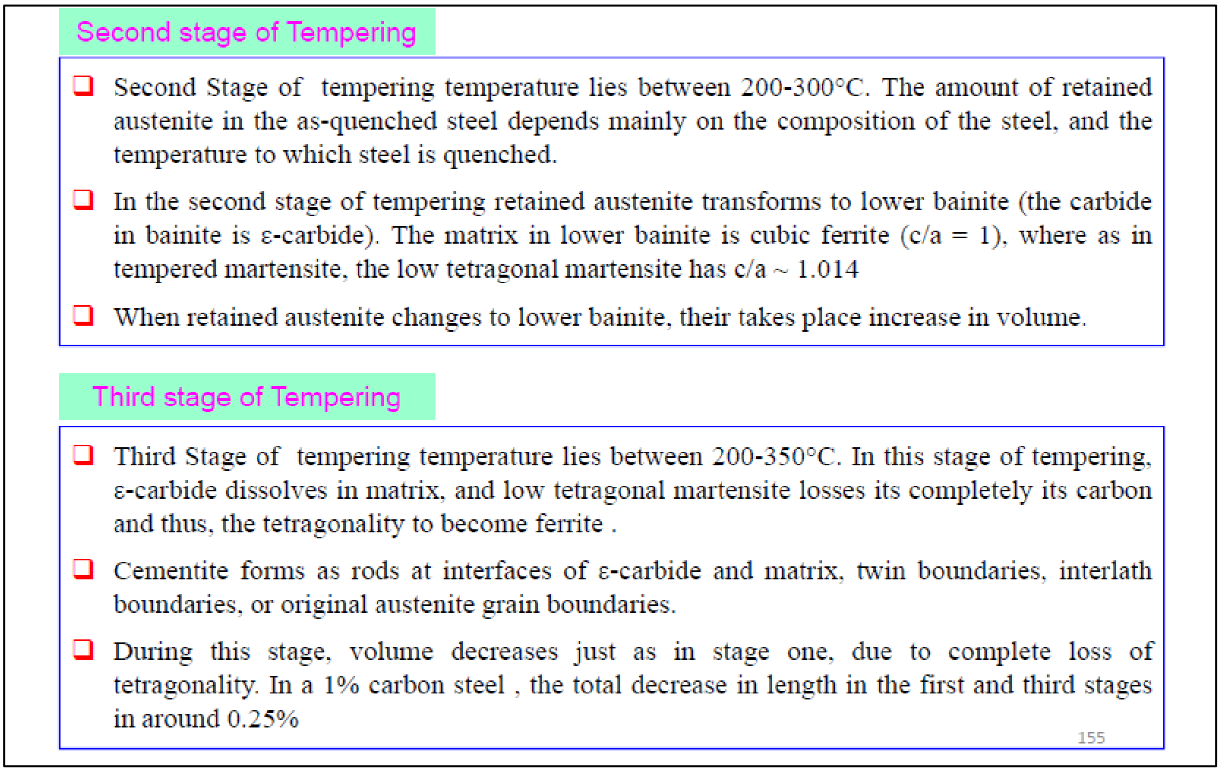
5.5.2. Structural Changes

There are three distinct stages of tempering, even though the temperature ranges overlap:



First stage of Tempering

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

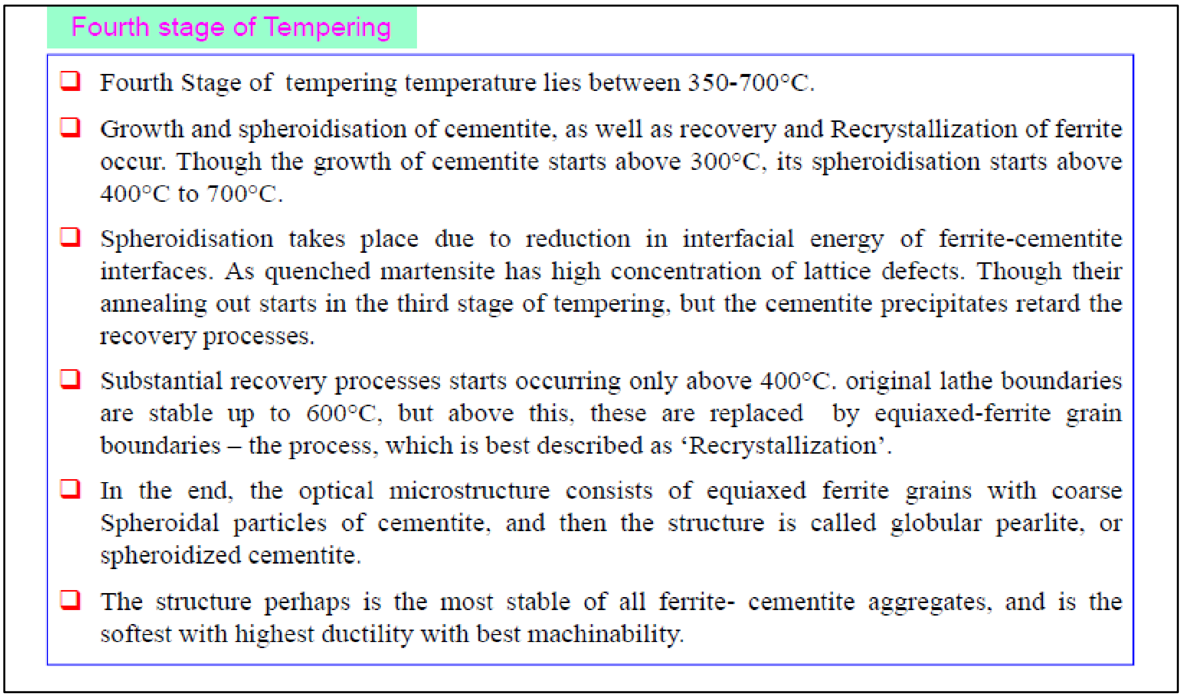


Second stage of Tempering

- ❑ 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 ε-carbide). The matrix in lower bainite is cubic ferrite (c/a = 1), where as in tempered martensite, the low tetragonal martensite has c/a ~ 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, ε-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 ε-carbide and matrix, twin boundaries, interlath boundaries, or original austenite grain boundaries.
- ❑ During this stage, volume decreases just as in stage one, due to complete loss of tetragonality. In a 1% carbon steel , the total decrease in length in the first and third stages in around 0.25%



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.

It has been found that stage I of tempering is often preceded by the redistribution of carbon atoms, called auto-tempering or quench tempering, during quenching and/or holding at room temperature. Other structural changes take place because of carbon atom rearrangement preceding the classical stage I of tempering.

5.5.3. Dimensional Changes

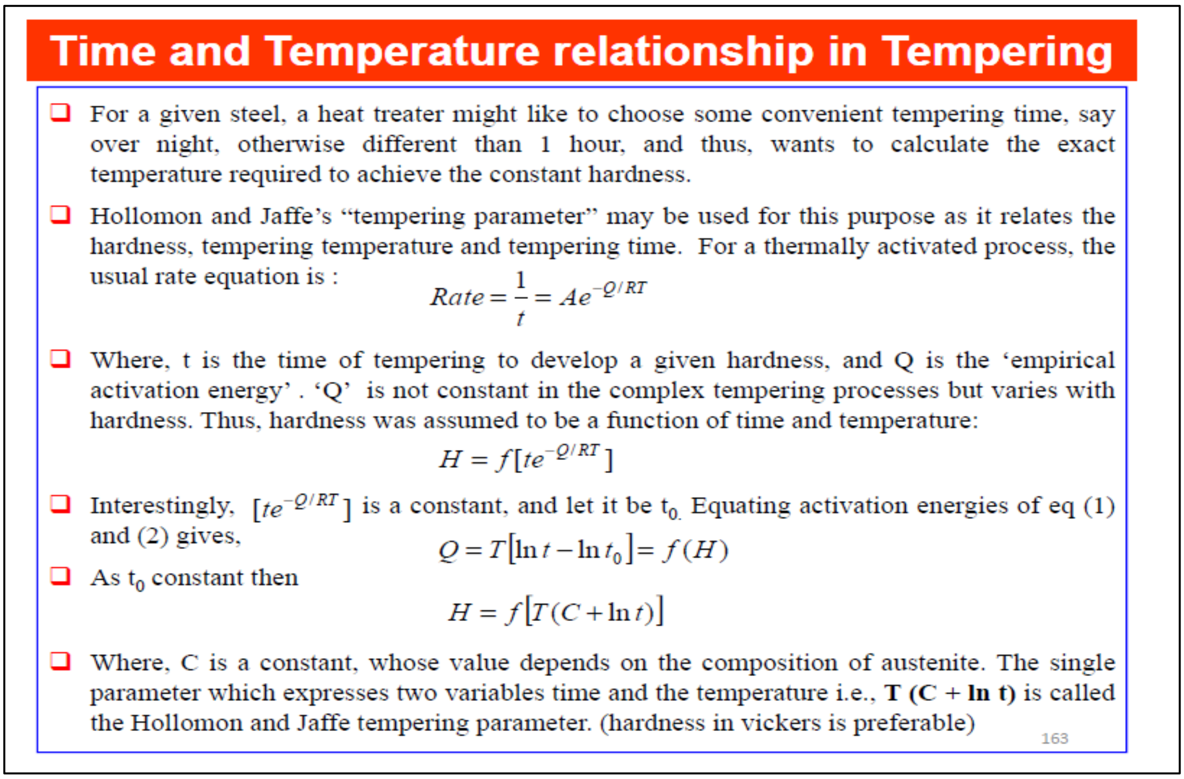
Martensite transformation is associated with an increase in volume. During tempering, martensite (is a super saturated solid solution of carbon in in ferrite) decomposes into a mixture of ferrite and cementite with a resultant decrease in volume as tempering temperature increases. Because a 100% martensitic structure after quenching cannot always be assumed, volume may not continuously decrease with increasing tempering temperature.

The retained austenite in plain carbon steels and low-alloy steels transforms to bainite with an increase in volume, in stage II of tempering. When certain alloy steels are tempered, a precipitation of finely distributed alloy carbides occurs, along with an increase in hardness, called secondary hardness, and an increase in volume. With the precipitation of alloy carbides, the ***M_s* temperature** (*temperature at which martensite starts to form from austenite upon cooling*) of the retained austenite will increase and transform to martensite during cooling from the tempering temperature.

5.5.4. Principal Variables

The nature of structural changes in tempering depends on

- The temperature and time of tempering
- the content of carbon in the steel



Time and Temperature relationship in Tempering

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

$$Rate = \frac{1}{t} = Ae^{-Q/RT}$$

- 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

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

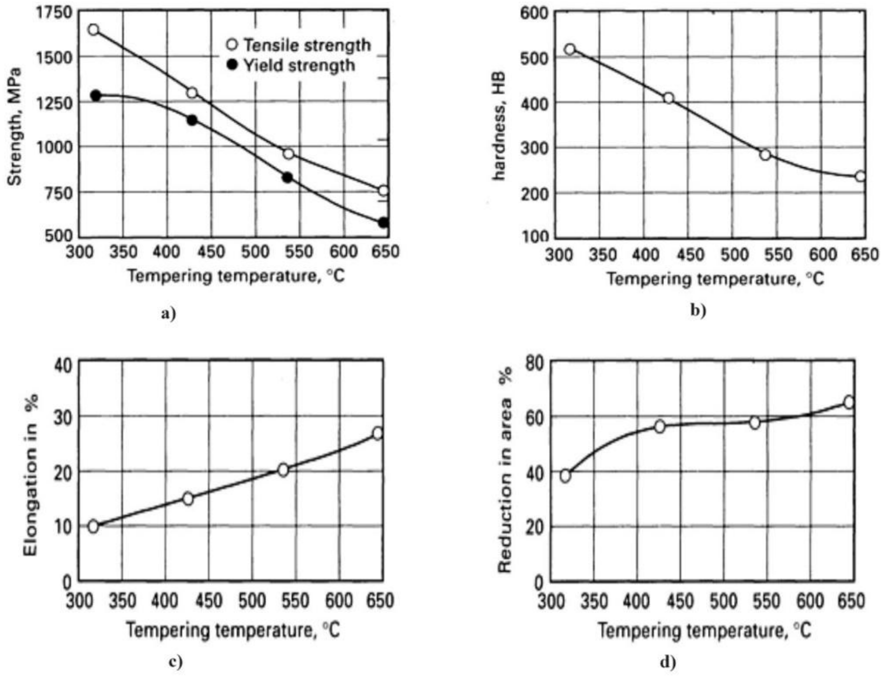
- Where, C is a constant, whose value depends on the composition of austenite. The single parameter which expresses two variables time and the temperature i.e., **T (C + ln t)** is called the Hollomon and Jaffe tempering parameter. (hardness in vickers is preferable)

Variables associated with tempering that affect the microstructure and the mechanical properties of tempered steel include:

- Tempering temperature
- Time at temperature
- Cooling rate from the tempering temperature

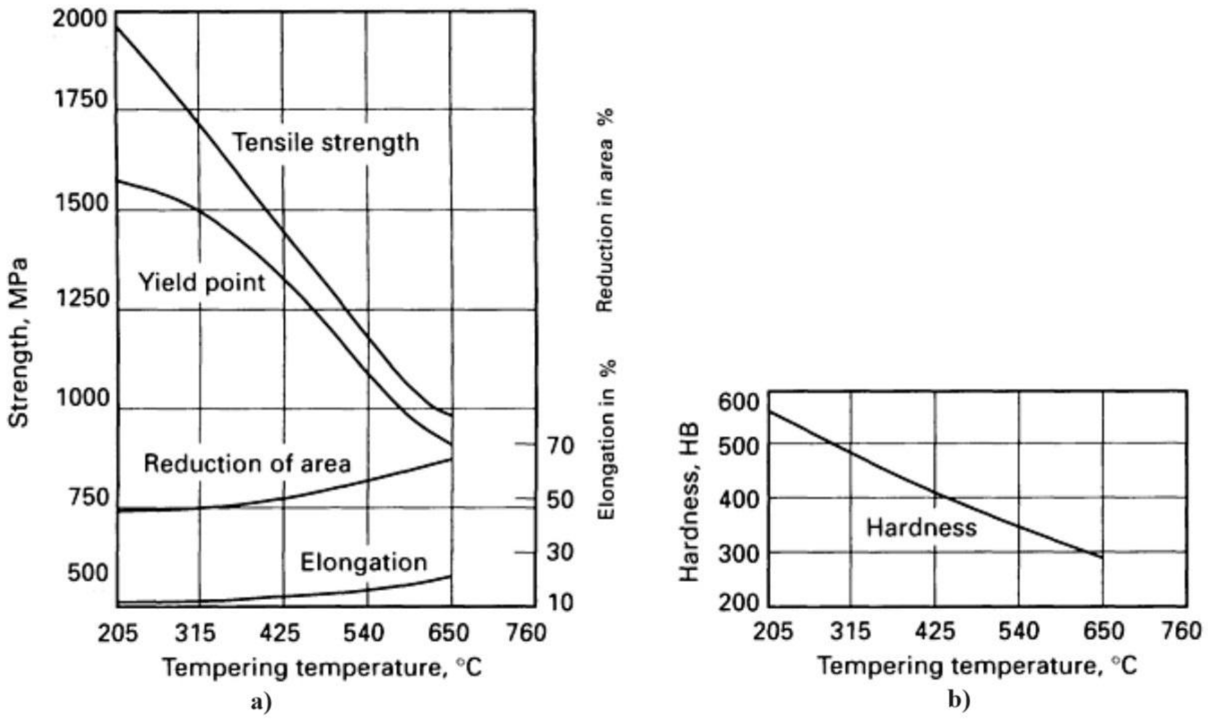
5.5.4.1 Tempering temperature*:*

Figures 5-24 show the effect of tempering temperature on tensile and yield strengths, hardness, elongation, and reduction in area, of a plain carbon steel (AISI 1050), respectively, held at temperature for 1 h. It can be seen that both room temperature hardness and strength decrease as the tempering temperature is increased. Ductility at ambient temperatures, measured by either elongation or reduction in area, increases with tempering temperature.



Figures 5.24. Effect of tempering temperature on mechanical properties of carbon steel

Most medium-alloy steels exhibit a response to tempering similar to that of carbon steels. For 4340 steel the change in tensile and yield strengths, elongation, and reduction in area with tempering temperature is shown in Figure 5.25 (a), while the change in hardness is shown in Figure 5.25 (b).



Figures 5.25 a) & b). Effect of tempering temperature on mechanical properties of medium alloy steels

Toughness varies with tempering temperature for most steels, as shown in Figure 5.26. Tempering at temperatures from 260 to 320°C decreases impact energy to a value below that obtained at about 150°C. Above 320°C, impact energy again increases with increasing tempering temperature. Both plain carbon and alloy steels respond to tempering in this manner.

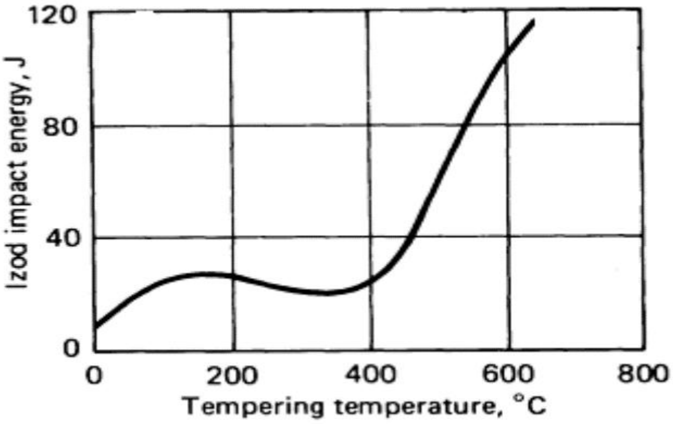
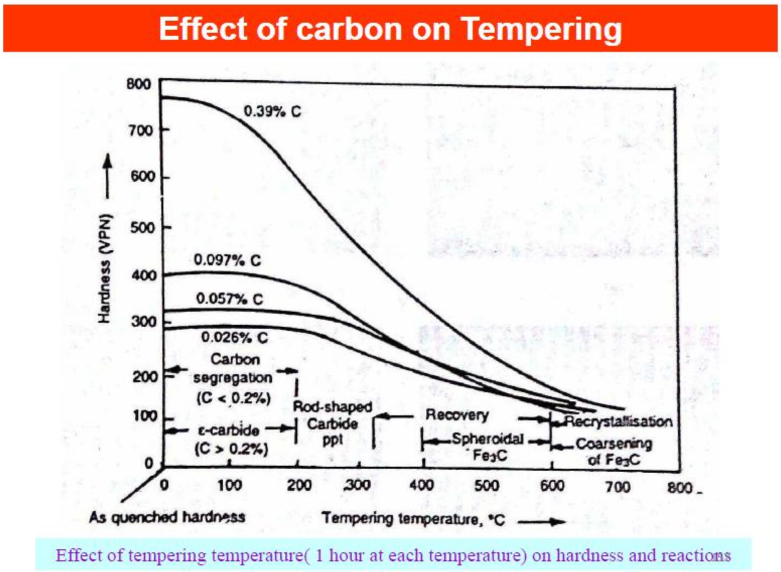


Figure 5.26. Effect of tempering temperature on toughness of carbon and alloy steels


Effect of carbon on Tempering

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

Figure 5.27. effect of carbon in tempering process

5.5.4.2 Tempering Time:

The diffusion of carbon and alloying elements that necessary for the formation of carbides is temperature and time dependent. The effect of tempering time on the hardness of a 0.82% C steel tempered at various temperatures is shown in Figure 5.28. The changes in hardness are approximately linear over a large portion of the time range when the time is presented on a logarithmic scale. Rapid changes in room-temperature hardness occur at the start of tempering in times less than 10 s. Less rapid, but still large, changes in hardness occur in times from 1 to 10 min, and smaller changes occur in times from 1 to 2 h. For consistency and less dependency on variations in time, components generally are tempered for 1 to 2 h.

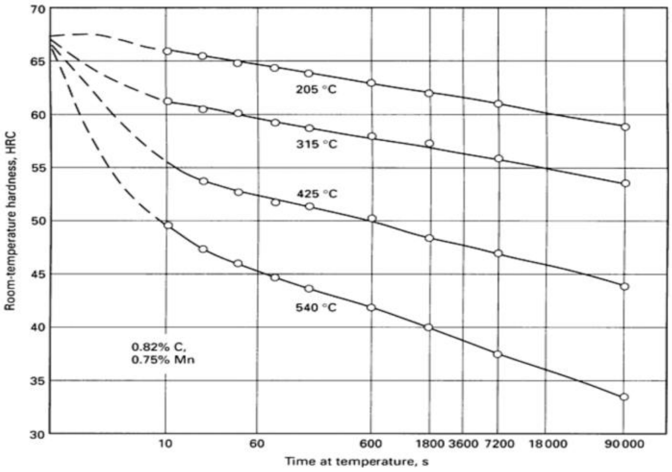


Figure 5.28. Effect of tempering time on hardness of carbon steel

5.5.4.3 Cooling Rate:

Another factor that can affect the properties of steel is the cooling rate from the tempering temperature. Although tensile properties are not affected by cooling rate, toughness can be decreased if the steel is cooled slowly through the temperature range from 375 to 575 °C, especially in steels that contain carbide-forming elements.

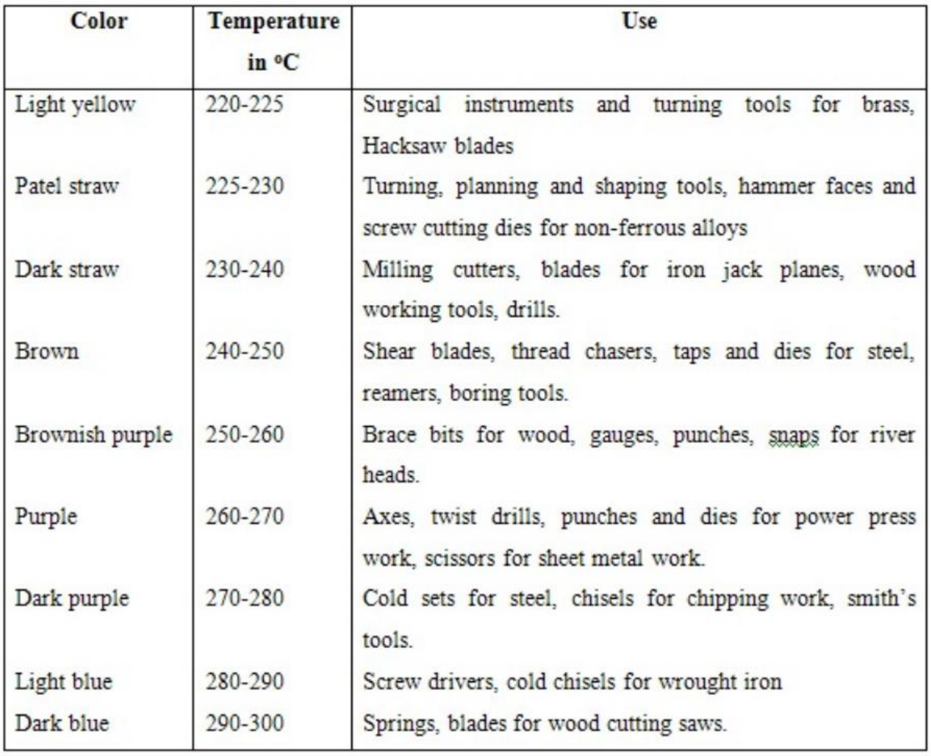
5.5.5 Types of tempering

On the basis of the ranges of temperatures to which the components are reheated for tempering, the tempering procedures are classified as follows:

5.5.5.a. Low temperature tempering

This treatment results in reduction of internal stresses and improvement in toughness and ductility without any appreciable loss in hardness. The heating range for this type of tempering is from 150^{o}C to 250^{o}C. The different colors appearing on the surface of the metal are indicative of the approximate temperature attained by it. Carbon tool steels, low alloy tool steels, case carburized and surface hardened parts, measuring tools, etc. are tempered by this method. Approximate temperatures, corresponding colors and the tools for whose tempering they are used are given in following table 2.

Table .2 Approximate tempering temperatures and temper colours for tools



Color	Temperature in °C	Use
Light yellow	220-225	Surgical instruments and turning tools for brass, Hacksaw blades
Patel straw	225-230	Turning, planning and shaping tools, hammer faces and screw cutting dies for non-ferrous alloys
Dark straw	230-240	Milling cutters, blades for iron jack planes, wood working tools, drills.
Brown	240-250	Shear blades, thread chasers, taps and dies for steel, reamers, boring tools.
Brownish purple	250-260	Brace bits for wood, gauges, punches, snaps for river heads.
Purple	260-270	Axes, twist drills, punches and dies for power press work, scissors for sheet metal work.
Dark purple	270-280	Cold sets for steel, chisels for chipping work, smith's tools.
Light blue	280-290	Screw drivers, cold chisels for wrought iron
Dark blue	290-300	Springs, blades for wood cutting saws.

5.5.5.b. Medium temperature tempering

This process involves reheating the component to a temperature range between 350°C to 450°C, holding at that temperature for sufficient time and then cooling it to room temperature. This method of tempering is used to increase the toughness of steel but reduces the hardness. It also increases the ductility and decreases the strength. It is mainly used for articles where a high yield strength, coupled with toughness, is a major requirement and subjected to impact loading, like coils and springs, hammers, chisels, etc.

5.5.5.c. High temperature tempering

The process involves reheating the hardened steel to a temperature between 500°C to 650°C, holding it there for a certain time and then cooling it down to the room temperature. This process enables the steel attaining high ductility while retaining enough hardness. This provides a microstructure which carries a useful combination of good strength and toughness with complete elimination of internal stresses. E.g., Crankshafts, connecting rods and gears

5.5.6 Tempering bath

Mainly following three types of tempering baths are used for tempering of steel parts and cutting tools:

- **Lead bath:**

Lead or lead alloy bath may be used for tempering steel parts. The parts are preheated and then immersed in the bath, which is already heated to the tempering temperature. Once the parts reach the tempering temperature they are taken out and cooled to attain the required temper.

- **Oil bath:**

Oil baths can be employed for various temperature ranges. Mineral oils are commonly used for these baths. Light oil baths are used for temperatures up to 230^{o}C only. Heavy oil baths can be used for heating range from 343^{o}C to 370^{o}C for oil heating the bath temperature is first raised to the required tempering range and then partially heated component is immersed in it. If the temperature of the bath falls below the required level both the bath and the immersed component can be heated together to the tempering temperature. After the component has reached the required temperature, it is removed and immersed in a tank of caustic soda, followed by quenching in a hot water bath.

- **Salt bath:**

Salt baths, carrying liquid nitrates or nitrates plus nitrites, are used for higher temperatures. The salts used for these baths are generally chlorides and fluorides. These baths are very widely used for tempering of high-speed steels. They can be used for temperature range up to 540^{o}C to 600^{o}C from efficiency and economy points of view salt bath cannot be used below 173^{o}C.

5.5.7 Tempering of alloy steels

❑ 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.

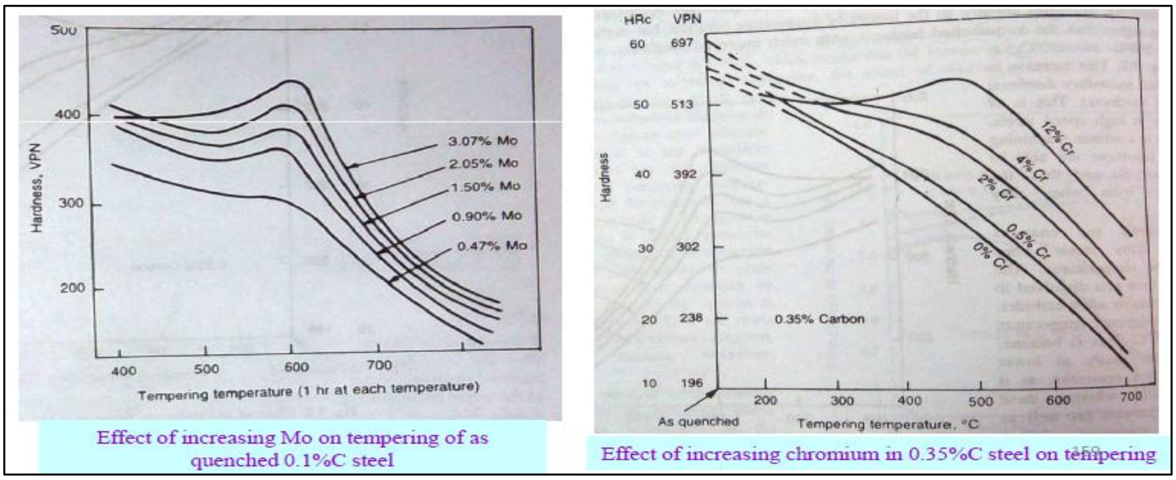
❑ Some elements, that are not found in carbides, but are present as solid solution in ferrite, are Al, Cu, Si, P, Ni, and Zr. Some elements arranged in order of increasing tendency to form carbides are Mn, Cr, W, Mo, V and Ti. These carbide forming elements retard most effectively the rate of softening 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 Mo on tempering of as quenched 0.1%C steel

Effect of increasing chromium in 0.35%C steel on tempering

Figure 5.29 Effect of alloys in tempering

❑ Element, such as, silicon dissolves in s-carbide to stabilize it. Steels with 1-2% silicon have s-carbide present even after tempering at 400°C, which means that the formation of cementite is delayed considerably, and thus, resisting the softening. Otherwise, the effect of silicon is essentially due to solid solution strengthening.

❑ Nickel has a small, but constant effect on tempered hardness at all temperatures due to solid solution strengthening as it is not a carbide former.

❑ Manganese has little effect on softening at low tempering temperatures, but at high temperatures, has a strong effect on due to its faster diffusion then, and thus, it resists cementite coarsening as it is present in cementite as $(Fe, Mn)_3C$.

❑ Martensite in plain carbon steels losses its tetragonality by 300°C, but the tetragonality is seen at 450°C, or even at 500°C if the steels have elements like Cr, W, Mo, Ti, V and Si.

❑ The basic cause of steep softening in carbon steels on tempering above 400°C, is the coagulation of the cementite particles. Alloying elements notably Si, Cr, Mo, V, when present in steels, retard the coalescence and the coarsening of cementite particles., resulting in enhanced hardening over and above the solid solution hardening effect.

❑ Elements like Cr, Si, Mo, or W delay coarsening to temperature range of 500-550°C. up to tempering temperature 500°C, the carbides formed are of iron with proportional alloying elements in it, but above 500°C, alloying elements can form their own carbides and thus. coarse cementite particles are replaced by fine dispersion of more stable alloy carbides.

- ***Tempering of alloy steels: Secondary Hardening***

❑ In alloy steels, having larger amounts of strong carbide forming elements like Mo, Ti, V, Nb, W, Cr etc., and 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 V4C3, Mo2C, W2C (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.

5.6. Thermochemical treatments of steel

The name thermochemical treatment is given to the surface saturation of the steel in this or that element (for example: carbon, nitrogen, aluminum, chromium etc.), by its diffusion in the atomic state from an external environment brought to a high temperature, that is to say, in case even higher surface hardness and ductility are required at an even larger core, thermochemical treatments are used. All treatments thermal to be considered take place without change in chemical composition. While thermochemical treatments are carried out with a change in the chemical composition of a certain thickness of the surface layer. Besides this the change of the chemical composition of the surface layer which takes place in the solid state is not possible than by diffusion. To enrich the surface layer of one metal with atoms of another metallic element, we must create conditions on the surface of the metal which must ensure the transport of these atoms from this surface or towards this surface. The problem to enrich the surface layer of a metal A with another metal B, requires that certain conditions must be met. First of all, it is necessary that metal B must be soluble in metal A in the solid state, that is to say, there is formation of mixed crystals. Then you have to that the atoms dissolved in mixed crystals must change places and it will depend on the type of element B, only elements with low atoms radius, can take an interstitial position and have high mobility in the network, even at low temperatures. At room temperature for example, hydrogen can weakly diffuse, forming mixed insertion crystals. Elements that form mixed substitution crystals diffuse with difficulty and require temperatures above the recrystallization temperature. For example, the diffusion of aluminum and chromium is much more difficult than that of elements such that: C, N. Generally, diffusion increases with increasing temperature. The diffusion power of an element is characterized by its diffusion coefficient and depends mainly temperature:

$$D = D_0 \,.\, e^{\frac{-Q}{R.T}}$$

- D: diffusion coefficient.
- D_0: frequency factor (depends on the material).
- Q: diffusion activation energy of the element considered.
- R: gas constant.
- T: absolute temperature.

Diffusion is therefore ensured by the penetration of the B atom into the surface peripheral of the atom A. The simplest case, to imagine, is that of the immersion of steel in an easily meltable metal bath. In certain cases, there is transfer (diffusion) of atoms of the added element not only at the surface layer, but also deep in the metal, when there is saturation of the surface layer.

In general, there are no pure materials, but in the form of an alloy, for example steel which is an alloy of iron and carbon and other elements. In the case of a system with several components, several layers are formed, in which are formed during the diffusion, several phases with each other. Thermochemical treatment consists of heat a room to the given temperature in a solid, liquid or gaseous medium, which easily releases the diffusion element in the atomic state, to be maintained at this temperature, then cool it. So, unlike a heat treatment, a treatment thermochemical changes not only the structure of the steel, but also the composition chemical surface layers, which makes it possible to modify within wider limits its properties.

A thermochemical treatment has three basic stages:

1. Process whose headquarters is the external environment and which ensures the release of the diffusing element in the atomic state.
2. Contact of the diffusing element atoms with the surface of the steel part and formation of chemical bonds with iron atoms (absorption).
3. Penetration of the saturating element deep into the base metal, i.e., diffusion. Saturation with carbon or nitrogen, which form solid solutions with iron insertion, makes the diffusion faster than the saturation of metals which form solid alternative solutions.

Penetration depth depends on temperature and the saturation duration, as well as the concentration of the diffusing element on the surface. Figure 5.30 shows that the diffused layer as a function of the duration of the phenomenon, at the temperature considered, is most often determined by a parabolic relationship. Therefore, over time the rate of increase in layer thickness does not stops decreasing.

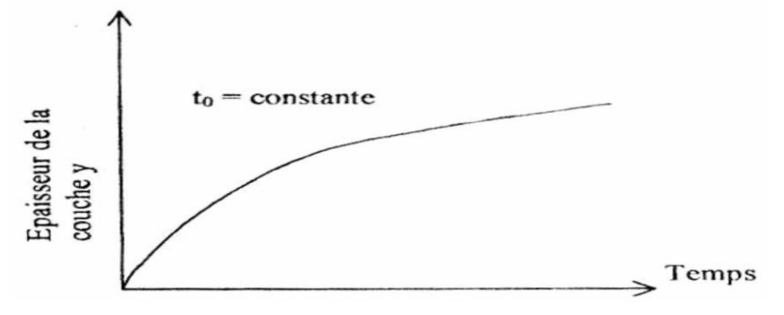


Figure 5.30

Figure 5.31 shows us the thickness of the diffused touch, all conditions being equal moreover, is all the greater as the concentration, of the diffusing element at the metal surface is lower.

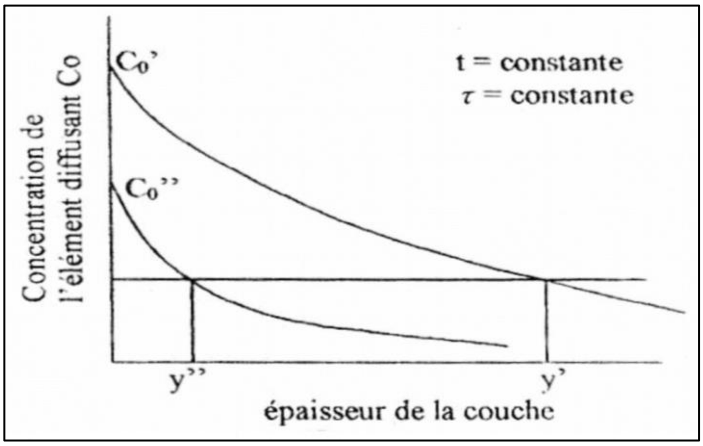


Figure 5.31

The depth of the diffuse layer formed, during the given duration, increases strongly depending on the process temperature (**Figure 5.32**).

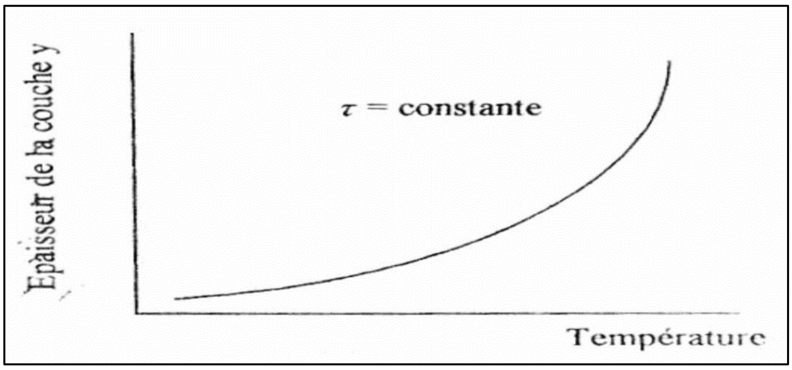


Figure 5.32

Chemical heat treatment is the process used to achieve different properties in core and steel components. There are situations in which the requirement is such that the outer surface should be hard and wear resistant and the inner core more ductile and tougher. Such a combination of properties ensures that the component has sufficient wear resistance to give long service life and at the same time has sufficient toughness to withstand shock loads. Such combination can basically be achieved by two different methods. The first method is known as thermochemical treatment because the surface composition of the steel changes by diffusion of carbon and/or nitrogen (as in carburizing and nitriding) and sometimes by other elements. The second method involves phase transformation by rapid heating and cooling of the outer surface (flame hardening, induction hardening and electron beam and laser hardening). The aim of both methods is the same.

5.6.1 CARBURIZING

This is the most widely used process for surface hardening of steels. It is carried out on low carbon steels which contain from 0.10% to 0.25% carbon and are known as carburizing steels.

Examples of such steel grades are AISI 1018, 1117, 4023, 4118, 5015 and 8620. Generally, carburizing is carried out in the temperature range 900–930°C, and the surface layer is enriched with carbon up to 0.7–0.9 percent. In this process, carbon is diffused into steel by heating above the transformation temperature and holding the steel in contact with a carbonaceous material which may be a solid medium, a liquid or a gas. Under such conditions, carbon is absorbed in solid solution in austenite. As the solubility of carbon is more in austenitic state than in ferritic state, fully austenitic state is essential for carburizing. The surface hardness depends on the relationship of hardness (VPN) with carbon content which differs slightly for different grades of steels, as shown in Figure 5.33. Carburizing can be divided into three categories according to the carbonaceous material used: pack carburizing, liquid carburizing, and gas carburizing, which we now discuss.

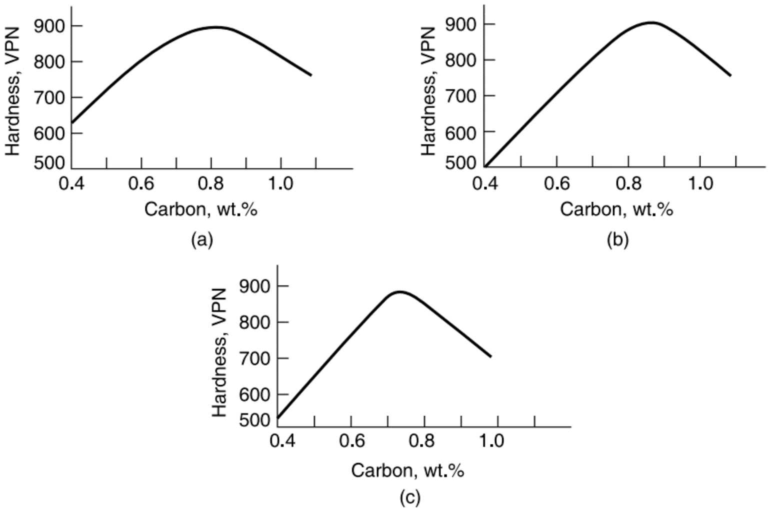


Figure 5.33 Relationship between hardness and carbon content for carburized steels in quenched condition. (a) plain carbon steel (En 32). (b) C-Mn steel (En 201). (c) Ni-Cr steel (En 351).

5.6.1.1 Pack Carburizing

This method of carburizing is also known as solid carburizing. It is the oldest method of carburizing steel components. In this process, steel components to be heat treated are packed with 80 percent granular coal and 20 percent $BaCO_3$ as energizer in heat resistant boxes and heated at 930°C in furnace for a specific period of time which depends on the case depth required (see Figure 5.33).

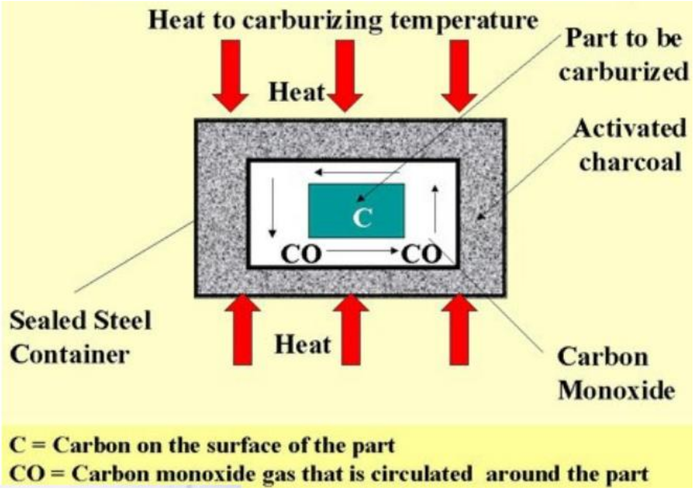


Figure 5.34 Pack Carburizing Process

Such a high temperature in furnace helps in absorption of carbon at the outer layer. The following reactions take place:

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

$$BaCO_3 \rightarrow BaO + CO_2$$
$$CO_2 + C \rightarrow 2CO$$

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

$$2CO + Fe \rightarrow Fe(C) + CO_2$$

(iii) Diffusion of carbon into steel.

(iv) CO_2 formed in step (ii) reacts with “C” in the coal:

$$CO_2 + C \rightleftharpoons 2CO$$

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:

$$\text{Case depth} = k\sqrt{t}$$

where *k* is a constant.

Generally, carburizing time varies from 6 hours to 8 hours, and case depth obtained varies from 1 mm to 2 mm. In this process, the results depend on the quality of coal. So, there is some element of uncertainty. Here, temperature and case depth control are less than in liquid and gas carburizing.

5.6.1.2 Liquid Carburizing

Liquid carburizing 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 process are named according to their carbon potential activity. Besides sodium or potassium cyanide, the bath contains (i) sodium and potassium chlorides, and (ii) barium chloride which acts as an activator.

The reactions in cyanide salt bath are as follows:

$$BaCl_2 + 2NaCN \rightarrow Ba(CN)_2 + 2NaCl$$
$$Ba(CN)_2 + Fe \rightarrow Fe(C) + BaCN_2$$

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 (0.08 mm thick). However, extensive safety precautions are required to avoid explosions.

5.6.1.3 Gas Carburizing

This is the most widely used method of carburizing. It is carried out in retort type, sealed quench type, or continuous pusher type furnaces. These furnaces are either gas fired or are heated electrically. Gas carburizing temperature varies from 870°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 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. Carbon potential is computed by measuring the dew point or carbon dioxide, by infra-red absorptiometry or oxygen, by an electrolytic potential technique using a zirconia probe.

During gas carburizing, the following reactions take place:

$$\begin{aligned} &\text{(i)}\quad C_3H_8 \rightarrow 2CH_4 + C \text{ (cracking of hydrocarbon)}\\ &\text{(ii)}\quad CH_4 + Fe \rightarrow Fe(C) + 2H_2\\ &\text{(iii)}\quad CH_4 + CO_2 \rightarrow 2CO + 2H_2\\ &\text{(iv)}\quad 2CO + Fe \rightarrow Fe(C) + CO_2 \end{aligned}$$

Carburizing occurs mainly due to conversion of CO to CO2 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 O2 are also present due to the following reactions:

$$\begin{gathered} 2CO_2 \rightarrow 2CO + O_2\\ CO_2 + Fe \rightarrow Fe(C) + O_2 \end{gathered}$$

Average concentrations of CO_2, H_2O, and O_2 are 0.2 percent, 0.5 percent, 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 the process. Small and medium industries cannot afford to have such high investment for this process. Therefore, these industries produce carburizing atmosphere in situ by supplying liquid hydrocarbons into the furnace above 700°C. The carbon potential is controlled by regulating liquid flow rates.

5.6.2 Vacuum Carburizing

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. The quantity of the gaseous hydrocarbon which is introduced into the furnace depends on the size of the article to be heat treated, the area of the surfaces to be carburized, the depth of the case desired, and the concentration of carbon to be introduced. As compared to conventional atmosphere carburizing, only about 1 percent of the volume of gaseous hydrocarbon is required for an identical case carburization.

As soon as the hydrocarbon in gaseous form comes in contact with the surface of the job, it cracks. As a result, a very thin layer of extremely fine carbon is deposited on the surface. This carbon is immediately absorbed by the steel till saturation is attained. The process continues till sufficient carbon is absorbed and the required case depth is formed. The inflow of gas is then stopped and the excess gas is removed by vacuum pumps. 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. Currently, the most popular batch type of vacuum carburizing furnace in use is a two-chamber unit, incorporating an oil quenching system in conjunction with a cooling zone. Figure 5.35 gives the relationship between carburizing time and case depth for vacuum carburizing.

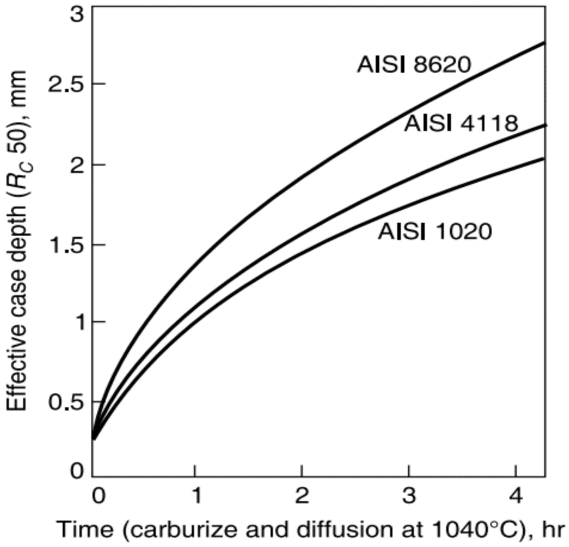


Figure 5.35 Total carburizing time and case depth for various carbon and alloy steels (all values were established on as-quenched samples).

Metallographic studies of cases produced by vacuum carburizing have shown that they are almost free from oxides, microcracks and decarburization.

Vacuum carburizing is basically an energy saving process. Vacuum carburizing cycles are shorter than conventional carburizing cycles. Other factors responsible for saving of energy are as follows:

(i) Since heating is carried out by radiation, there is improved efficiency due to the presence of vacuum.

(ii) Heat zones occupy less volume.

(iii) It is not necessary to keep the furnace on throughout the process. It can be heated and cooled rapidly as and when required.

(iv) Absence of atmosphere.

(v) The quantity of gas required is only about 1 percent of the requirement in conventional processes.

The main limitation of the vacuum carburizing process is that only batch type units are available at present. Also, there is a limitation on the size of the work-piece due to the limited size of vacuum furnace.

5.6.3 Post-Carburizing Heat Treatments

While carburizing at 900–930°C, overheating may occur both in the core and the outer case of the steel due to the prolonged nature of operations. This may cause grain coarsening throughout the cross-section. Therefore, in most of the cases, the steels require specific treatment after carburizing. 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% carbon). (Network of carbide imparts brittleness to the case.)

In cases where steel is inherently fine grained (e.g. Al-killed), the work-piece is heated above A_{c1} temperature and directly quenched. If the steel is coarse grained throughout the cross-section, then double heat treatment may be required to improve the properties of the case and core. In such cases the steel is first heated above A_{c3} (900°C) temperature and normalized to refine the grain size in the core. The additional advantage of this step is that the carbide network also dissolves on heating and does not appear after quenching. The second step of heat treatment consists of heating the work above Ac1 temperature (760–780°C), followed by quenching.

By the second heat treatment, refining and hardening of case are achieved. On quenching, the austenite transforms to martensite at the surface of steel. The core does not harden during second heat treatment and remains fine grained and tough. These heat treatment cycles are shown in Figure 5.36 and their characteristic effects described in Table 5.1.

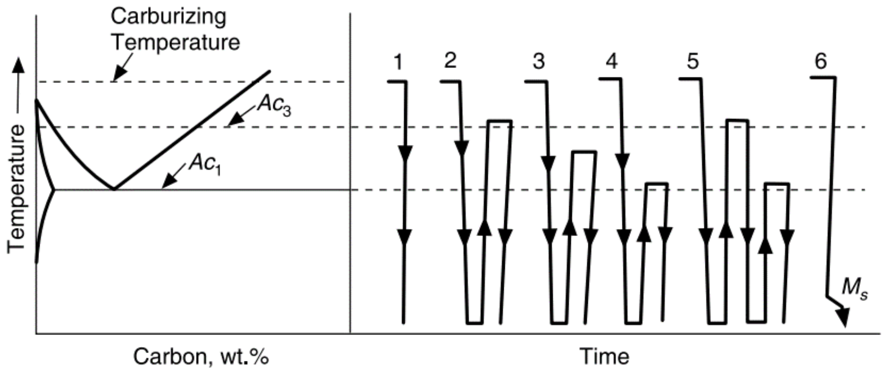
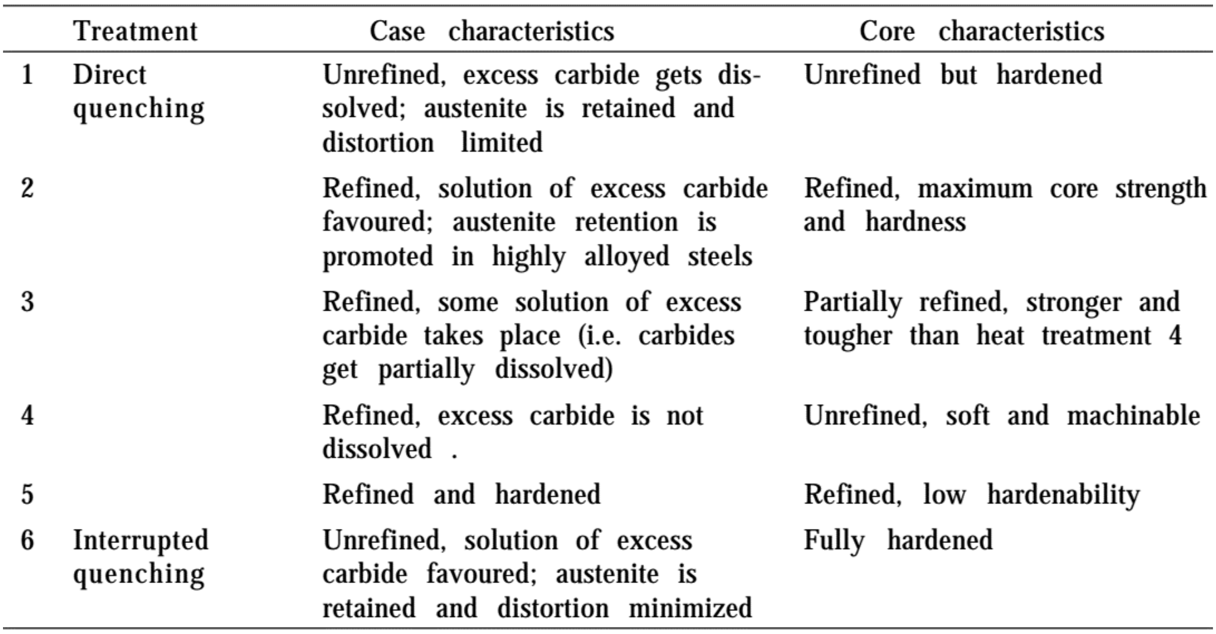


Figure 5.36 Schematic representation of post-carburizing treatments subsequent to carburizing and the case and core characteristics obtained.

Table 5.1 Effect of Various Post-carburizing Heat Treatments on the Characteristics of Case and Core



	Treatment	Case characteristics	Core characteristics
1	Direct quenching	Unrefined, excess carbide gets dissolved; austenite is retained and distortion limited	Unrefined but hardened
2		Refined, solution of excess carbide favoured; austenite retention is promoted in highly alloyed steels	Refined, maximum core strength and hardness
3		Refined, some solution of excess carbide takes place (i.e. carbides get partially dissolved)	Partially refined, stronger and tougher than heat treatment 4
4		Refined, excess carbide is not dissolved .	Unrefined, soft and machinable
5		Refined and hardened	Refined, low hardenability
6	Interrupted quenching	Unrefined, solution of excess carbide favoured; austenite is retained and distortion minimized	Fully hardened

A procedure has been devised to obtain maximum case hardness and very fine grain size.

The heat treatment cycle for this is shown in Figure 5.37. The steps involved are as follows:

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 austenitizing by induction beating just above A_{c3} temperature, followed by oil quenching.

Step 4: Final step consists of tempering at about 180°C.

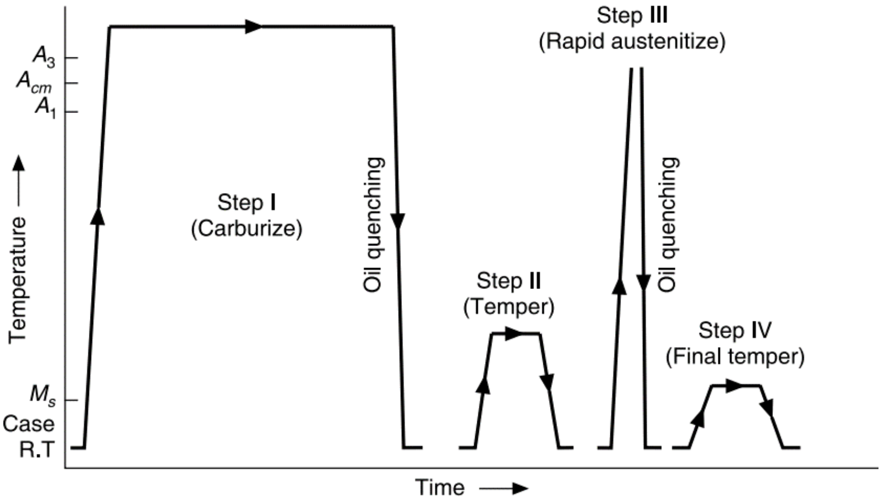


Figure 5.37 Recommended heat treatment cycle for maximizing case hardness along with grain refinement.

This four-step treatment gives maximum case hardness (around 900 DPH) with very fine grained case and core.

In fact, in all cases the final operation in the heat treatment of carburized parts is tempering at about 160–180°C. When high alloy steels are case hardened, problem arises due to retention of austenite. This sharply reduces the hardness. A sub-zero treatment may be given to such steels to convert retained austenite into martensite.

5.6.4 Cyaniding and Carbonitriding

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.

Cyaniding is carried out in a liquid bath of NaCN. If the process is carried out in a gaseous atmosphere, it is called carbonitriding.

5.6.4.1 Cyaniding

In this process, the parts to be heat treated are immersed in a liquid bath (at 800–960°C) of NaCN with the concentration varying between 25% and 90%. The measured amount of air is passed through the molten bath. NaCN reacts with the oxygen in the air and is oxidized. The basic reactions in the bath are:

$$2\text{NaCN} + \text{O}_2 \rightarrow 2\text{NaCNO}$$
$$2\text{NaCNO} + \text{O}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO} + 2\text{N}$$
$$2\text{CO} \rightarrow \text{CO}_2 + \text{C}$$

Carbon and nitrogen so formed in atomic form diffuse into the steel and give thin wear resistant layer of the carbonitride e-phase. Usually, this process requires 30–90 minutes for completion. For obtaining case depth from 0.5 mm to 2 mm, the process is carried out at higher temperature (950°C) in a bath containing 8% NaCN, 82% BaCl2 and 10% NaCl. This process takes 1.5–6 hours for completion. For case depth from 0.13 mm to 0.35 mm, the bath is maintained at 850°C with the following concentration:

$$\begin{aligned} \text{NaCN} &= 30\% \\ \text{NaCl} &= 35\% \\ \text{Na}_2\text{CO}_3 &= 35\% \end{aligned}$$

(Soda ash)

The higher the temperature at a given cyanide level, the higher is the percentage of carbon diffusion (up to 0.8–1.2% C) into the surface of steel as compared to nitrogen (0.2–0.3%). After cyaniding, the pieces are taken out and are quenched in water or oil. For thick sections, mineral oil is preferred for quenching. The final operation is low temperature tempering. After heat treatment, the case has a hardness of 850 VHN. This process is less time consuming. Because of the high heat transfer coefficient in liquid bath and uniform bath temperature, distortion of pieces is less. This 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.

5.6.4.2 Carbonitriding

This process is specifically used for improving wear resistance of mild, plain carbon or very low alloy steels.

Carbonitriding is carried out at lower temperatures (in the range 800–870°C) in a gas mixture consisting of a carburizing gas and ammonia. A typical gas mixture contains about 15% NH_3, 5% CH_4 and 80% neutral carrier gas. Carbon and nitrogen are diffused at the same time into the surface of the steel in the austenitic-ferritic condition and gives case thickness of the order of 0.05–0.75 mm. Nitrogen is more effective in increasing hardenability of the case as compared to carbon. Nitrogen content of the steel depends on ammonia content and temperature.

After carbonitriding, quenching is done in oil to avoid cracking. This is followed by tempering at 150–180°C. Heat treatment produces a case having a hardness of 850 VHN.

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.

5.6.5 Nitriding

Nitriding is most effective for those alloy steels which contain stable nitride forming elements such as aluminium, chromium, molybdenum, vanadium and tungsten. Examples of popular medium-carbon alloy steels which are used for nitriding are: 708A37 and 817A40 to B5970: Part 2. The typical composition of such steel is 0.1–0.5% C, 0.75–1.25% Al, 1–1.5% Cr, and

0.2% Mo. Nitriding is carried out in a ferritic region below 590°C. So, there is no phase change after nitriding (Figure 5.38). Before nitriding, proper heat treatment should be given to steel components (hardening by heating to 930°C and quenching in oil, then tempering at 650°C) to develop bainitic structure, which increases the strength and toughness of the core. All machining and grinding operations are finished before nitriding. The portions which are not to be nitrided are covered by thin coating of tin deposited by electrolysis. The coating checks diffusion of nitrogen due to its surface tension. Anhydrous ammonia gas is passed into the furnace at about 550°C, where it dissociates into nascent nitrogen and hydrogen. Thus,

$$2NH_3 \rightarrow 2[N]_{Fe} + 3H_2$$

The treatment time varies from 21 hours to 100 hours. Actually, it depends on the desired case depth and size of the steel parts. After nitriding, the steel part is allowed to cool in furnace itself in the presence of ammonia. The furnace container is made of heat resisting alloy steel. The time required for a case depth of 0.5 mm is about 100 hours.

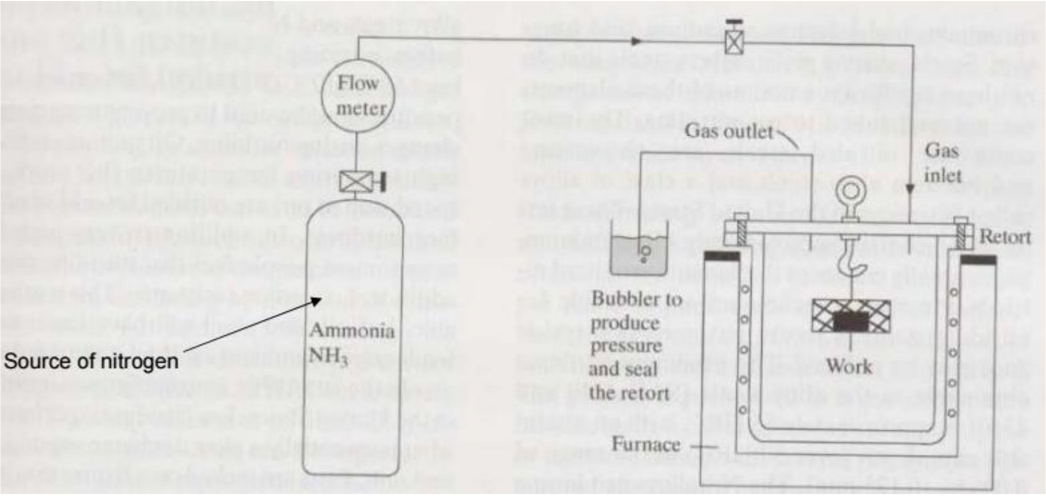


Figure 5.38 Shematic of gaz nitriding system.

The hardness achieved at the surface of steel varies from 900 VHN to 1100 VHN. The hard layer so formed imparts good wear resistance, hot hardness and corrosion resistance. During nitriding process, a white layer of Fe_4N (γ' nitride) and Fe_2N (ε nitride) form on the outer layer of surface. This layer is problematic as it is very brittle and tends to crack. Formation of this layer is caused by high nitrogen potential. So, this can be avoided by keeping nitrogen potential at the desired level. White layer should be removed from component by mechanical polishing or by boost diffusion techniques.

There are two ways by which white layer can be totally suppressed.

(a) Floe process or double-stage nitriding, where a white layer is first produced and then decomposed.

The first stage is carried out between 495 and 525°C for 15–20 hours with around 20% dissociated ammonia to achieve faster growth of nitrided case. The second stage is done between 550 and 565°C with 75–80% dissociated ammonia (atmosphere of low nitrogen potential). The iron nitrides formed in first stage dissociate, so that white layer reduces from 0.05 mm to 0.01 mm, or even gets eliminated. Elimination of white layer means case depth is increased by that thickness. Higher nitriding temperatures in the second stage lower case hardness, increase case depth.

The decomposition of the white layer takes place by means of three fundamental processes:

(i) Diffusion of nitrogen out of the white layer into the vacuum of the ion nitriding vessel.

(ii) Diffusion of nitrogen from the white layer into the diffusion layer.

(iii) Sputtering of the white layer by bombardment with inert ions.

The first two processes cause a decomposition of the white layer by a phase transformation of the nitrogen depleted iron nitride g back to the a(N)-ferrite. The third process results in a reduction of the white layer by a removal of material from the surface. All three processes at the same time contribute to the reduction of the white layer during the second stage. However, the part each process plays varies according to the size of the voltage or the temperature of the work piece.

(b) Ion Nitriding Process or Plasma Nitriding which is described in the following section.

5.6.6 Plasma Nitriding (Ion Nitriding)

Plasma nitriding is also known as ion nitriding process. In this process the steel component to be nitrided acts as cathode (Figure 5.39), the component is heated by electrical heaters to 370 to 650°C. This heating operation is followed by switching on supply of a gas mixture of hydrogen and nitrogen at 1–10 torr. Sufficiently high DC voltage (500–1000 V) is applied between the cathode (component) and anode to form plasma. Current flows between two electrodes and the mixture of hydrogen and nitrogen gas gets ionized. When the part to be treated is subjected to this ionized discharge, the nitrogen ions that are formed bombard the surfaces of the component (cathode) with considerable energy. Part of this energy heats the cathode and allows diffusion of nascent nitrogen inwards from nitrides. The remaining part of energy is used for displacing the secondary electrons from the cathode surface. These secondary electrons gain energy from the applied voltage (potential). Bombarded ions clean the surface, heat the component and gives nascent nitrogen. A glow envelops the component and nitriding starts. Nitrided case depth depends on current temperature and time of nitriding. After ion-nitriding, the component is cooled in atmosphere of N_2 gas. For successful plasma nitriding. the glow-discharge current density is to be maintained between 0.5 × 10–3 and 3 × 10–3 amperes/cm^2 by appropriately controlling the glow discharge voltage. Once glow is established, it envelops the part completely and then plasma nitriding takes place. The anode is kept cool by circulating water around it.

Since, in this process, the diffusion of nitrogen can be controlled, it is possible to get a pure diffusion layer without any trace of white layer. That is why, this process is especially suitable for machine components which, in addition to wear, are subjected to high impact, rolling, bending, or twisting stresses. This method is suitable for a wide range of steels starting right from low-alloy steels, nitriding steels, and tool steels and upto the most highly alloyed steels. lon nitriding is carried out after completing all the machining operations according to the need and type of steels. Components to be nitrided by this process are cleaned and degreased to ensure that blocking of the nitriding action does not occur. This process is characterized by uniform build-up of nitrided cases which are hard but still ductile and core hardness is retained. No dimensional changes of work-piece take place. The process is completely non-toxic and environmentally clean. It is a low energy consumption and single step operation.

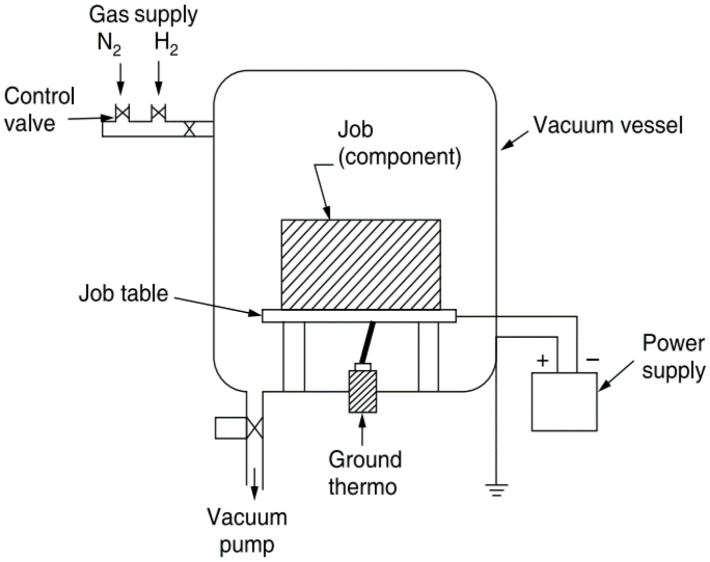


Figure 5.39 Plasma nitriding process.

Plasma nitriding is mainly used for ferrous components such as valves, camshafts and piston rods in the mechanical engineering and automotive industries. Other applications are cutting tools or large forming dies. Cast iron parts, such as pump and gear houses, can also be nitrided.

Advantages of plasma nitriding include complex shapes and geometries and components of different sizes can be nitrided. The process provides excellent dimensional stability with no distortion. Steels sensitive to tempering can be nitrided at comparatively low treatment temperatures. The white layer formation is very slow. Even after a longer processing time it remains almost constant at 6 mm. The degree of control of the process allows full exploitation of the non-brittle layer. The fatigue properties of the plasma-nitrided components are markedly improved. Mechanical masking is a feature of the plasma nitriding process. Such a mask can be made of mild sheet, which would be fitted at a distance of approximately 0.5 mm from the area to be masked. These masks have almost indefinite life and can be fitted easily. Since plasma-nitriding can be carried out at lower temperatures, cold work steels can be successfully plasma nitrided to get high absolute wear resistance.

However, the process suffers from some limitations like equipment is complex and needs closer control by skilled workers. The parameters are to be controlled strictly. Equipment cost is high. Different sized and shaped parts cannot be plasma-nitrided together. Moreover, the process that is to be adopted for nitriding of deep surfaces is complex. The rate of growth of case is slow as compared to that formed during salt bath nitriding. Initial investment cost is also high. No quenching facility is available for obtaining better fatigue strength for components made out of unalloyed steels. But besides having these limitations, the process is very attractive because of advantages which score more in comparison to limitations of the process.

5.6.7 Salt Bath Nitrocarburizing

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 mm is about 1½ hours for low carbon unalloyed steels. Reactions that take place in the bath are as follows:

$$\begin{aligned} 4NCO^- &\rightarrow CO_3 + CO + 2N + 2CN \\ XFe + N &\rightarrow FexN \\ 2CN^- + O_2 &\rightarrow 2NCO^- \text{ (regeneration of } CN^-) \\ 3CO_3 + \text{regenerator} &\rightarrow 6NCO^- + XH_2O \text{ (regeneration of } CO_3^-) \end{aligned}$$

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.

Nitrocarburizing is widely applied in manufacturing of machine components and tools, since improved surface hardness, fatigue strength and corrosion resistance at elevated temperatures are achieved at minimal distortion. Thus, the service life of a part is significantly extended. Moreover, corrosion non-resistant steel grades attain a rather fair corrosion resistance due to compound zone.

Its field of application includes gears and pinion shafts, plastic injection molding screws and barrels, piston rings, aluminium extrusion dies, forging and forming dies, spindles for grinding machines, gun barrels, springs, crankshafts and camshafts and other wear components.

The main advantage of nitrocarburizing over other means of surface hardening is the low process temperature. Components can often be nitrided in the fully hardened and tempered condition without the core properties being adversely affected. An additional advantage of the low temperature process is the low risk of distortion. Moreover, the parts can be machined to final dimensions and do not need costly finishing work such as grinding or straightening after nitrocarburizing. Carbonitride layer has good resistance to adhesive wear.

Limitation of the process is that the typical treated layers are very thin and nitrocarburizing atmospheres/salts are difficult to handle safely.

5.6.8 Boronizing

Boronizing is one of the recent methods of surface hardening, which may be applied to any ferrous material but is generally adopted for carbon steels and tool steels. Both pack and gaseous techniques can be applied for surface hardening. 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 additions of activators and diluents at 900–1000°C. Boron diffuses inwards and iron borides (FeB and Fe_2B) layers are formed. On the outer surface, FeB phase forms, while in the interior, Fe2B phase is formed. FeB phase is more brittle and is not desirable. Higher temperatures, longer treatment times and high alloy steels favour the formation of FeB phase. The boride layers are very hard. The hardness of boride layers produced on carbon steels exceeds that of hard chrome electroplate, hardened tool steels and tungsten carbide. 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 with the layer depth being matched to the intended application:

- Thick layers (up to 0.127 mm)—for abrasive wear.
- Thin layers (up to 0.025 mm)—for adhesive wear and friction reduction.

The treatment time required for a case depth of 0.15 mm is 6 hours at about 900°C. In this process, treatment temperature is very high, and hence hardening of components before boronizing is not required. Only in the case of tool steels after boronizing, hardening and tempering are required to have the desired mechanical properties.

High hardness can be achieved on steel alloys which is retained up to subcritical temperatures (i.e., 650°C). Heat treatable materials can be fully hardened after boronizing to optimize performance. Boronizing can increase the resistance of low alloy steel to acids such as sulphuric, phosphoric and hydrochloric acids. Boronized austenitic stainless steel has excellent resistance to hydrochloric acid. Boronizing can be selectively applied to only the area that requires hardening. Boronized layer can be polished to a high finish. It can be uniformly applied to irregular shapes.

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.

However, due to wear benefits provided by the boronized layer, combined with the broad range of compatible substrates and the cost-effective nature of the process, boronizing is used successfully for general wear resistance of carbon steel components. Additionally, due to its temperature and wear resistance, boronizing is also a good choice for certain tooling applications like in hot forging dies, wire drawing dies, extrusion dies, straightening rolls, ingot molds, etc. It is also used for general components including nozzles, plungers, gears, shafts, and rollers. Oil and gas components (production tubing, valve components, valve fittings, metal seals, coal/oil burner nozzles, etc.) also employ this technique. Other miscellaneous application includes turbine components, pump impellers, ball valves and seats, shaft protection sleeve, and guide bars.

5.6.9 Chromizing

Like boronizing process, chromizing is also used for surface hardening of both carbon and tool steels. There are two 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 percent chromium or ferro chrome (with carbon content not exceeding 0.1%), 0.2 percent ammonium iodide, and 39 percent 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 is 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. If necessary, the work-piece can be heat treated after diffusion coating. The structure of the chromized layer is formed of mixed carbides of chromium, characterized by hardness and abrasive resistance.

Soft chromizing

On steel, with low carbon content (< 0.35%), a chromium carbide layer cannot be formed. Instead, a chromium diffusion layer builds up during the chromizing process which can reach up to 200 mm 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.

5.7 Surface hardening

Those surface hardening processes are discussed in which there is no change in the chemistry of the surface of steel component to be surface hardened. These processes are flame hardening, induction hardening, laser hardening and electron beam hardening.

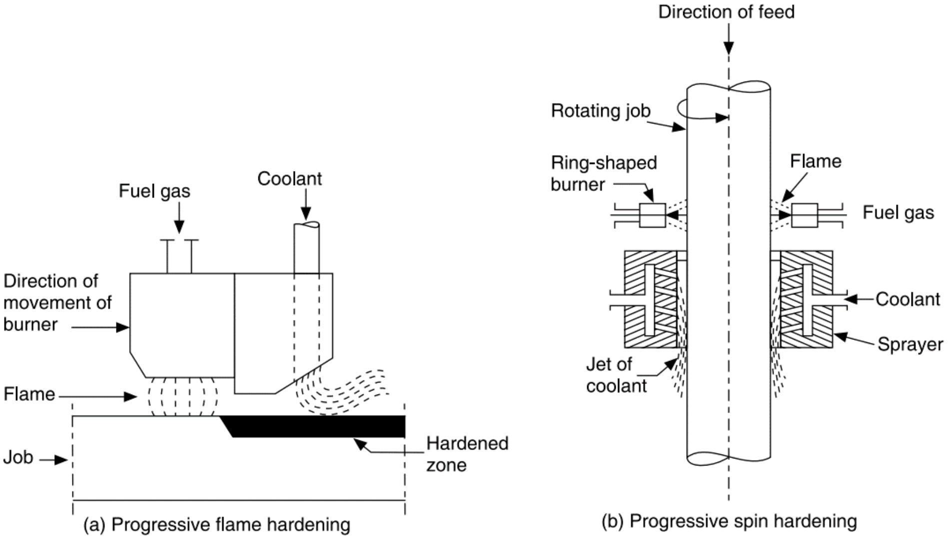
5.7.1 Flame hardening

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. Such a treatment does not appreciably reduce the hardness at the surface. Hardness in flame hardened steel is due to martensitic and lower bainitic structure.

Overheating of work-piece should be avoided, otherwise, there is danger of cracking after quenching and excessive grain growth in the region just below the hardened surface. The carbon content required for flame hardening steels varies from 0.3 percent to 0.6 percent. High carbon steels can also be hardened by this process, but greater care is required to avoid cracking. Normally, case depth up to 3 mm can be achieved. A high rate of heating is essential for thin cases with proper adjustment of timing of application of flame. For good quality, strict control of heating time and fuel and oxygen consumption is essential.

There are four different methods which are used in general for flame hardening: (i) stationary, (ii) progressive, (iii) spinning, and (iv) progressive-spinning.

In the first, both burner and work-piece are stationary. Progressive hardening is carried out by using a burner combined with a water spray, as shown in Figure 5.40(a). In this case, the burner moves over the large stationary work-piece. This is followed by quenching. In the spinning method, the work-piece is rotated, while the burner remains stationary. After heating, the flame is removed and quenching is carried out by a water jet. In the progressive-spinning method, the burner moves over a rotating work-piece [see Figure 5.40(b)]. In all the cases, rapid quenching is carried out after heating. There is little scaling, decarburization, or distortion in flame hardening. Since the heating and cooling are very fast, the core remains unaffected.



(a) Progressive flame hardening

(b) Progressive spin hardening

Figure 5.40 Schematic diagram illustrating two principles,

5.7.2 Induction Hardening

Induction hardening may be used for local surface heat treatment. Generally, it is used to surface harden crank shafts, cam shafts, gears, crank pins and axles. In this process, heating of the component is achieved by electromagnetic induction. A conductor (coil) carries an alternating current of high frequency which is then induced in the enclosed steel part placed within the magnetic field of the coil. As a result, induction heating takes place. The heat so generated affects only the outer surface of the steel component due to skin effect. The degree of flow of current on the outer surface of a component depends on the frequency, resistivity and permeability of the component. For a given material, the last two factors depend on temperature.

The depth to which the current, penetrates and raises the temperature is given by the following relation for steel components:

$$\text{In cold state (at } 20^\circ\text{C)},\ d_{20} = 20/\sqrt{f} \tag{5.1}$$

$$\text{In hot state (at } 800^\circ\text{C)},\ d_{800} = 500/\sqrt{f} \tag{5.2}$$

where *d* is the depth (mm) to which current flows and f is the frequency of current carried by the coil. This frequency is expressed in hertz. This relationship shows that the depth of hardening decreases with increase in frequency. In addition to direct heating of the skin by induced current, there is also some heating of the core due to conduction of heat. Hence, the overall depth of heating is greater than that given by Eqs. (5.1) and (5.2). Accordingly, the overall depth of penetration of heat (d_0, in mm) at 800°C is given by the relation

$$(d_0)_{800} = d_{800} + d_c \tag{5.3}$$

where d_c (mm) is the depth of penetration of heat due to conduction and is given by the relation:

$$d_c = 0.2\sqrt{t} \tag{5.4}$$

where *t* is the heating time (seconds).

In induction hardening, the component is heated usually for a few seconds only. Immediately after heating, the surface is quenched by a jet of cold water. Due to quenching, a martensitic structure is formed, which makes the outer surface hard and wear resistant. Figure 5.41 shows the operation of induction hardening. In hardening, temperature for plain carbon steel is about 760°C. For alloy steels, higher hardening temperatures are required. For example, for Cr-Mo steels the hardening temperature is about 800°C.

A striking feature of induction hardening (which is true of other surface hardening processes also) is that in this process the original toughness and ductility remain unaffected even after heat treatment.

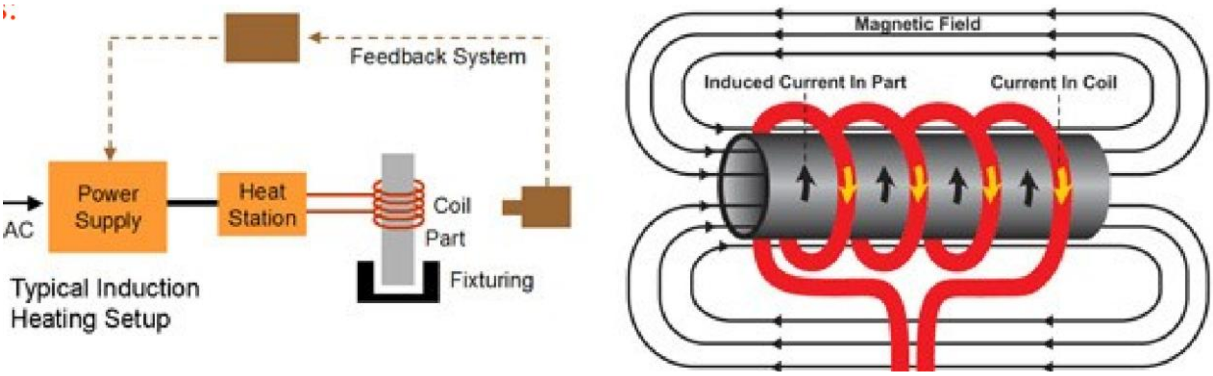
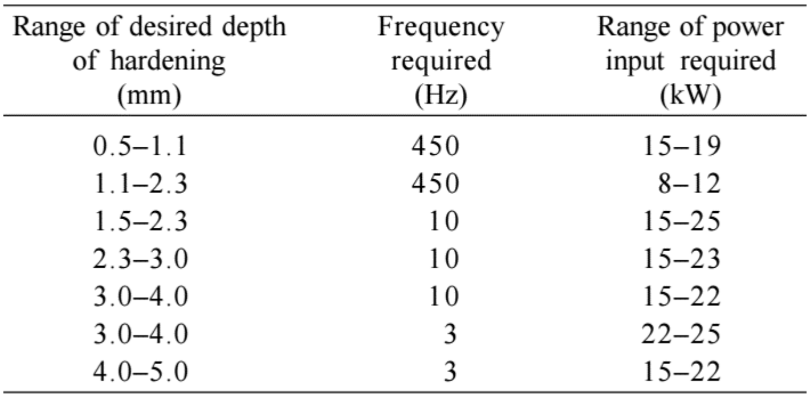


Figure 5.41 Diagrammatic representation of induction hardening process.

Table 9.1 gives the process conditions for induction hardening of steels.

Table 5.2 Process Conditions for Induction Heating of Steels



Range of desired depth of hardening (mm)	Frequency required (Hz)	Range of power input required (kW)
0.5–1.1	450	15–19
1.1–2.3	450	8–12
1.5–2.3	10	15–25
2.3–3.0	10	15–23
3.0–4.0	10	15–22
3.0–4.0	3	22–25
4.0–5.0	3	15–22

5.7.3 Electron Beam 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 process. The work-piece is kept in vacuum at 0.06 m bar pressure. Electron beam is focused on the work-piece to heat the surface. In the beginning, energy input is kept high. With time, power input is reduced as the component gets heated up. This is done to avoid melting. Normally, case depth up to 0.75 mm can be achieved by this method. A mini-computer is used to control voltage, current, beam, dwell time and focus.

5.7.4 Laser Hardening

Laser beams are also used for surface hardening treatment. Since these have very high intensity, they may melt the work-piece when they are used at such high intensity. Therefore, a lens is used to reduce the intensity by producing a defocused spot or scans from 1–25 mm wide. A laser beam of 1 kW produces a circular spot whose diameter may vary from 0.50 mm to 0.25 mm. Industrial lasers up to 20 kW are now available. Case depth of about 0.75 mm is obtained by self-quenching. The depth of hardening is governed by both time and energy density. In laser hardening process, less time is required than in induction and flame hardening processes, and the effect of heat on the surrounding surface is less, thus leading to less distortion. Some heat patterns are shown in Figure 5.42. No separate quenching media are required since quench is effected by the mass of the surrounding unheated portion. The microstructure of laser-heated steel consists of bainite + ferrite at the surface of the heated spot and pearlite and ferrite in the interior.

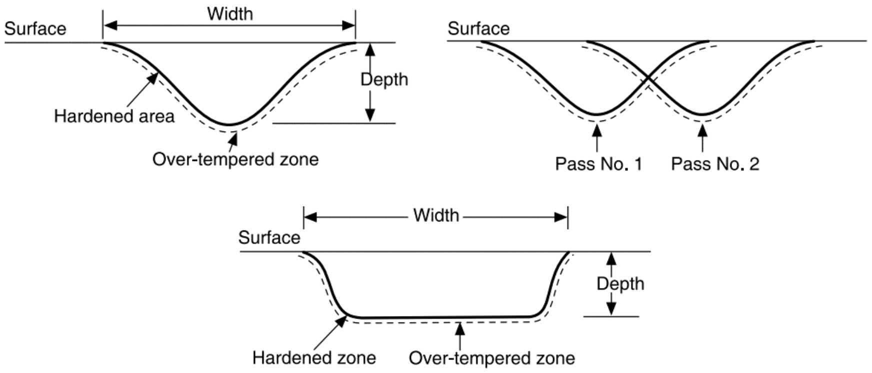


Figure 5.42 Heat effects of three different beam optics, viz. defocused beam, single pass; defocused beam, overlapping passes; and oscillating beam, single pass employed in laser heat treatment

The relationship between depth of hardening and power is as follows:

$$Y = -0.11 + \frac{3.02P}{(D_b\, V)^{1/2}} \qquad (5.5)$$

where

Y = case depth (mm)

P = laser power (W)

D_b = incident beam diameter (mm)

V = traverse speed (mm/s)

However, experimental data show scattering. At a constant value of $P/(D_bV)^{1/2}$ case depth may vary by a factor of 2.

In many countries, the industrial scale application of laser, heat treatment has already commenced. Rapid progress in this area has been achieved because of the availability of high-power CO_2 lasers and advanced cost-effective laser production techniques. The main advantages of laser heat treatment are as follows:

(i) It is possible to achieve high production rates since light has no inertia and, consequently, it is possible to obtain high processing speeds with rapid stopping and starting.

(ii) Input distortion is quite low because specific energy is very low.

(iii) It is possible to give localized treatment with this process.

(iv) No external quenching is needed. At times external quenching may be adopted for such small parts which have insufficient mass for self-quenching.

(v) There is hardly any contamination during surface hardening treatment.

(vi) It is possible to control the process with the help of a computer.

(vii) Those areas which are difficult to be treated by conventional methods can be easily treated with this technique.

(viii) It is not necessary to carry out any final machining operation subsequent to hardening.

Laser heat treatment is best suited for steel and cast irons. During laser heating, heat transfer takes place by inverse Bremsstrahlung effect, i.e. by interaction of laser beam with the free electrons of the substrate. As a result, the energy state of the electrons of the conduction band is raised.

For successful laser heat treatment, it is necessary that the temperature of the zone which is being hardened must reach closer to the austenitizing range. Further, between the heating and cooling cycles, the substrate must be maintained at the austenitizing temperature for sufficiently long time to ensure adequate diffusion of carbon. Also, there should be enough mass so that the cooling rate achieved by self-quenching is greater than the critical cooling rate required for martensite transformation.

While considering laser heat treatment, it is necessary to apply the same metallurgical concepts as in the case of other conventional heat-treating processes. However, there are some basic differences between the laser heat treatment process and other conventional processes. Some of these are as follows:

(i) It is possible to harden low carbon steel with relative ease due to extremely rapid heating and cooling rates associated with laser heating. There is hardly any effect due to differences in hardenability between plain carbon steels and alloy steels since the cooling rates normally achieved during laser heat treatment are much higher than the critical cooling rate required for martensitic transformation.

(ii) It has generally been observed that the level of hardness achieved by laser hardening is higher than that obtained by conventional hardening.

(iii) Laser heat treatment is not well suited for alloys requiring rather long soaking time such as steels containing spheroidal carbides or cast irons rich in graphite instead of pearlite. The large soaking time required for the diffusion of carbon would restrict the operating parameters associated with the laser. Consequently, the process would lose its inherent advantage of rapid heating and cooling rate.

Cast irons with a combination of pearlite and graphite, on the other hand, can be heat treated successfully with lasers. When the pearlite is being dissolved to be converted into austenite and subsequently to martensite, some carbon diffusion takes place out of graphite flakes which will produce martensite around the original graphite flakes. However, the predominant hardening mechanism will be based on austenite formed by dissolution of pearlite. Some of the major independent process variables connected with laser heat treatment are incident laser beam power, diameter of incident laser beam, absorptivity of laser beam by the coating, and the substrate and transverse speed across the substrate surface. Another important factor in this context is the thermophysical properties of the substrate.

The depth of hardness, geometry of the heat-affected zone, and microstructure and metallurgical properties of the laser heat treated material are the dependent variables. For efficient laser heat treatment, it is necessary that proper absorption of light energy by the work-piece takes place. All heat transfer calculations for laser processing are based on this absorbed energy.

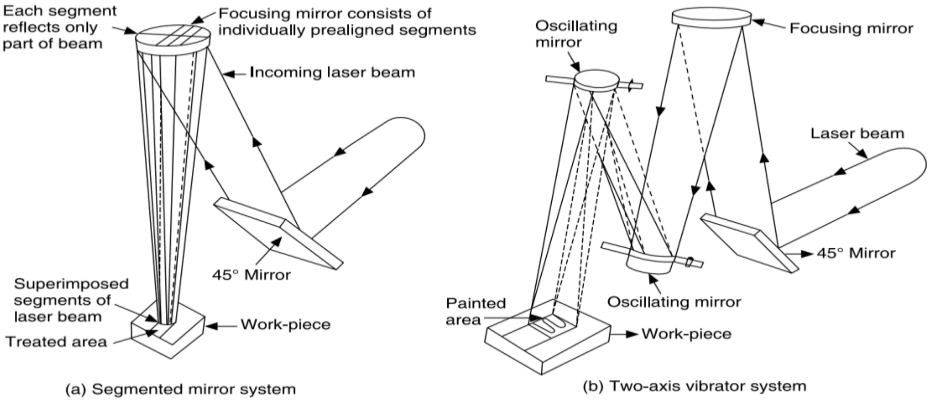
Melting and key hole formation should be strictly avoided during laser heat treatment. Hence, some absorbent coatings are invariably used during laser heat treatment. Colloidal graphite, manganese phosphate, zinc phosphate and black paint are some of the commonly used absorbent coatings. High absorptivity can also be achieved with the help of a mixer of sodium and potassium silicate. Absorptivity depends on coating thickness, coarseness and adherence to the substrate. Heat transfer between the coating and the substrate also plays an important role in this context.

With a given beam diameter and traverse speed, the depth of hardening by laser heat treatment is proportional to the laser power. The surface heat source is defined by the diameter of the laser beam and distribution intensity.

The power density as also the coverage rate depends on the diameter of the laser beam. For laser heat treatment, a wide beam with uniform intensity distribution is preferable. This in turn ensures uniform case depth.

Different methods of beam manipulation can be adopted to obtain a broad beam with uniform intensity distribution. Different techniques used for this purpose are shown in Figure 5.43.

The interaction time depends on traverse speed. The depth of hardening is inversely proportional to traverse speed. For proper hardening, it is necessary to ensure a minimum interaction time of the order of 10^{-2} s with a power density exceeding 10^3 W/cm^2.



(a) Segmented mirror system

(b) Two-axis vibrator system

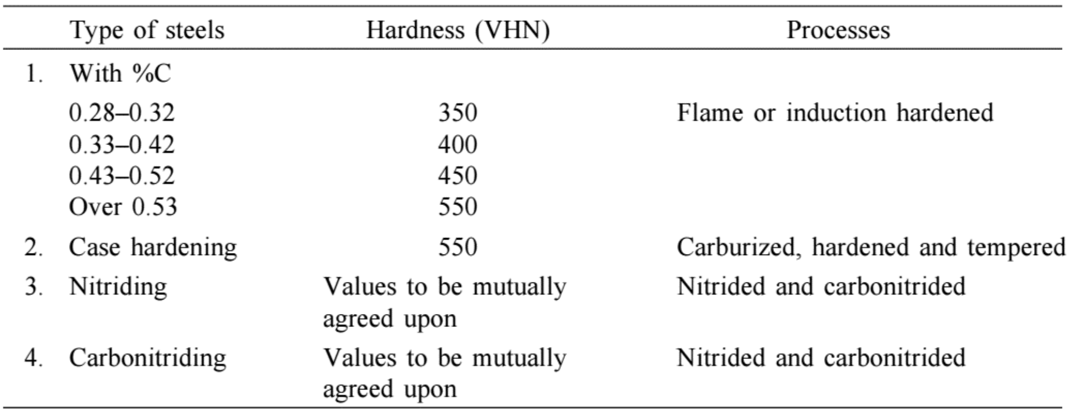
Figure 5.43 Beam manipulation technique used for laser.

5.7.5 Case Depth Measurement

Case depth (CD) 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 core cannot be distinguished". This is the total case depth of steel.

The effective case depth of steel is the perpendicular distance from the surface to that point of core at which hardness values are given in Table 5.3.

Table 5.3 Critical Hardness Values for Defining Case Depth



	Type of steels	Hardness (VHN)	Processes
1.	With %C		
	0.28–0.32	350	Flame or induction hardened
	0.33–0.42	400	
	0.43–0.52	450	
	Over 0.53	550	
2.	Case hardening	550	Carburized, hardened and tempered
3.	Nitriding	Values to be mutually agreed upon	Nitrided and carbonitrided
4.	Carbonitriding	Values to be mutually agreed upon	Nitrided and carbonitrided

Case depth is one of the deciding factors for a steel to be used in practice. Hence, it is necessary to measure the case depth of the steel so that the component can be used in service safely. There are four methods of measuring case depth:

(i) Hardness method

(ii) Chemical method

(iii) Macrostructure method

(iv) Microscopic method.

These methods measure the case depth of the steel which is surface hardened by carburizing, nitriding, carbonitriding, cyaniding or induction and flame hardening processes.

5.7.5.1 Hardness method

In this method, hardness values are taken along the case and core. It is a very accurate method since sharp change in hardness across case and core region can be measured. Specimens for this method are prepared by (i) cross-section procedure, (ii) taper-grind procedure, and (iii) step-grind procedure (IS: 6396).

5.7.5.2 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 (e.g. nitriding), nitrogen content is estimated. This is the most accurate method of determining case depth.

5.7.5.3 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 ×20.

5.7.5.4 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.

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