

HEAT TREATING OF METALS, FERROUS & NON-FERROUS ALLOYS

6. HEAT TREATING OF METALS

- Introduction
 - Transformation curves: *TTT & CCT curves*
 - Classification of heat treatment processes
 - Full heat treatment: *annealing, normalizing, hardening, tempering, martempering, austempering*
 - Surface heat treatment: *carburizing, cyaniding, nitriding, flame hardening and induction hardening*
 - Age hardening/precipitation hardening
-

6.1 INTRODUCTION

Heat treatment can be defined as a combination of heating and cooling operations carried out on a metal or alloy in the solid state so as to produce a particular microstructure and properties. It effectively alters the size and shape of the grains and also the type, extent and distribution of different phases. In this chapter the heat treatment of steels is discussed in particular.

Stages of heat treatment

- Heating the specimen to a specific temperature
- Holding the specimen at that temperature for a suitable duration, and
- Cooling the specimen at a specific rate

Need for Heat treatment:

- To refine the grains
- To improve mechanical properties
- To relieve internal stresses
- To modify electrical and magnetic properties
- To improve machinability
- To increase resistance to wear and corrosion

6.2 PHASE TRANSFORMATION AND TRANSFORMATION CURVES

The development of microstructure and the properties during a heat treatment process involves certain phase transformation i.e., alteration in the number of phases or its characteristics. The phase transformation may be diffusion dependent (e.g., pearlite or bainitic transformation) or diffusion less (e.g., martensitic transformation) based on the reaction time/ transformation rate.

The phase transformations as seen in Fe-Fe₃C diagram are due to equilibrium cooling (slow cooling) and the resulting phases are known as equilibrium phases such as pearlite. But at higher rates of cooling non equilibrium phases such as bainite and martensite can be formed; hence for such transformations Time Temperature Transformation (TTT) or Continuous Cooling Transformation (CCT) diagrams can be referred.

6.2.1 Transformation Diagram

Transformation diagrams are helpful in predicting the response of the metals to heat treatment and the resulting phases, microstructure and properties.

- Time Temperature Transformation (TTT) / Isothermal Transformation (IT) diagram
- Continuous Cooling Transformation (CCT) diagram

TTT Diagram measures the rate of transformation at a constant temperature whereas the CCT diagram measures the degree of transformation as a function of time for a constantly changing temperature.

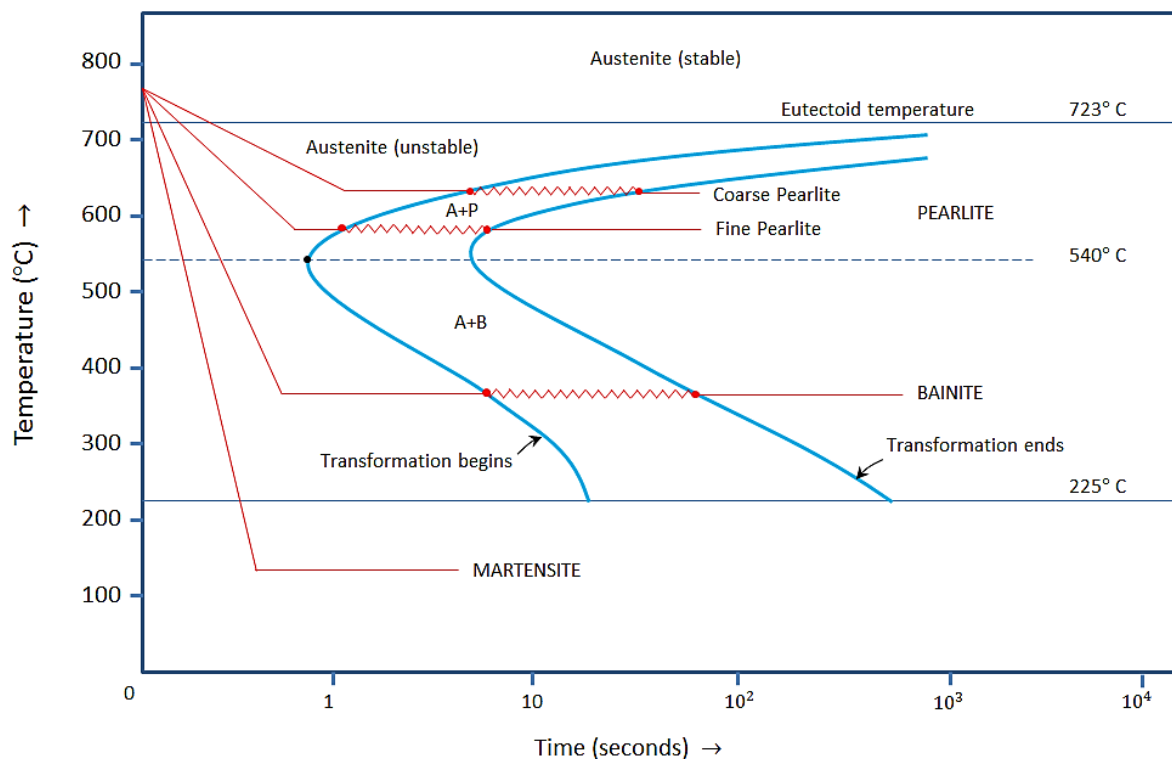


Figure 6.1: Time Temperature Transformation (TTT) diagram for 0.8% carbon steel

The TTT diagram depicts the relationship between the phases, temperature and time; it features the isothermal transformation of austenite into both equilibrium and non-equilibrium phases.

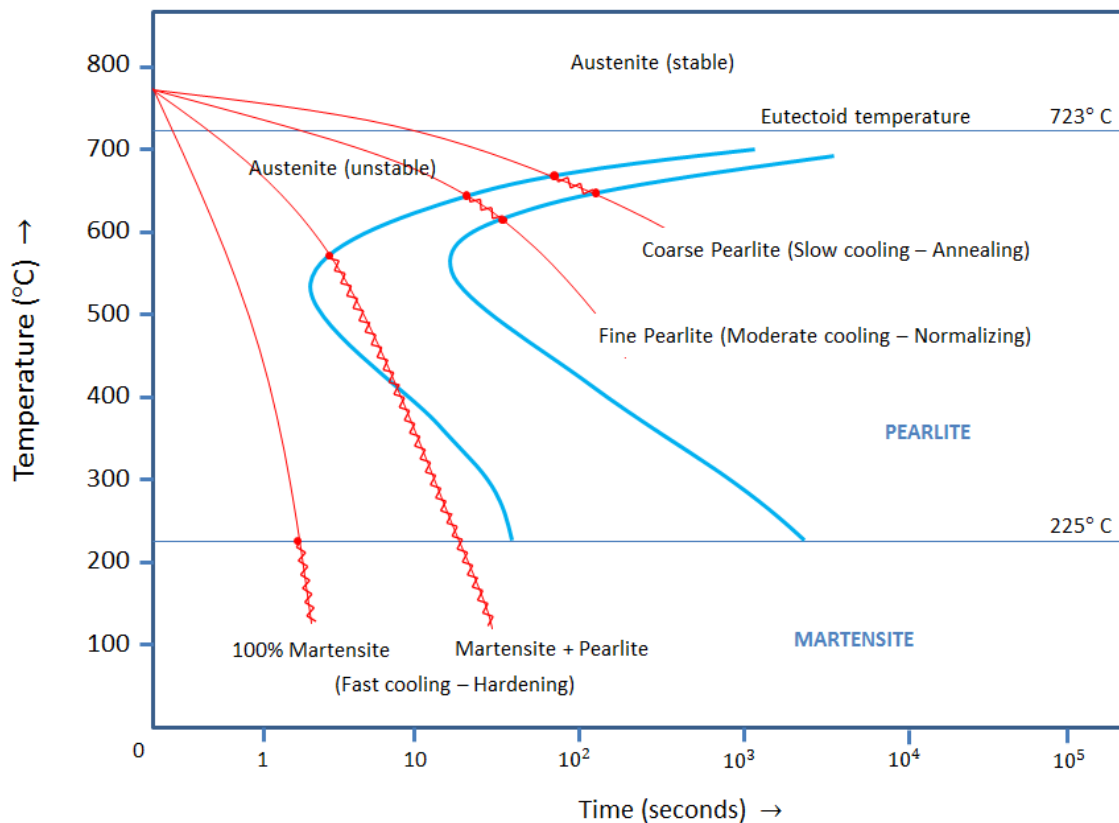


Figure 6.2: Continuous Cooling Transformation (CCT) diagram for 0.8% carbon steel

The CCT diagram depicts the phase transformations, temperature and time relationships during continuous cooling from austenitizing temperature to room temperature at different rates.

6.3 CLASSIFICATION OF HEAT TREATMENT PROCESSES

The heat treatment processes may be classified as;

1. Full heat treatments

- a) Annealing
- b) Normalizing
- c) Hardening
- d) Tempering

2. Surface heat treatments

- | | |
|---|--|
| <ol style="list-style-type: none"> a) <u>Surface quenching</u> <ol style="list-style-type: none"> 1. Flame hardening 2. Induction hardening | <ol style="list-style-type: none"> b) <u>Chemical treatment</u> <ol style="list-style-type: none"> 1. Carburizing 2. Nitriding 3. Cyaniding |
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6.3.1 Full Heat Treatments

6.3.1(a) Annealing

Annealing is a heat treatment process wherein the metal is heated above recrystallization temperature, held at that temperature for certain duration so as to homogenize the temperature and then cooled at a very slow rate to obtain an equilibrium structure.

Objectives of Annealing

- To reduce hardness
- Grain refinement
- Improve toughness and machinability
- Relieve internal stresses
- Facilitate cold working

Types of Annealing:

- Full Annealing
- Spheroidizing Annealing
- Recrystallization Annealing
- Stress-relief Annealing

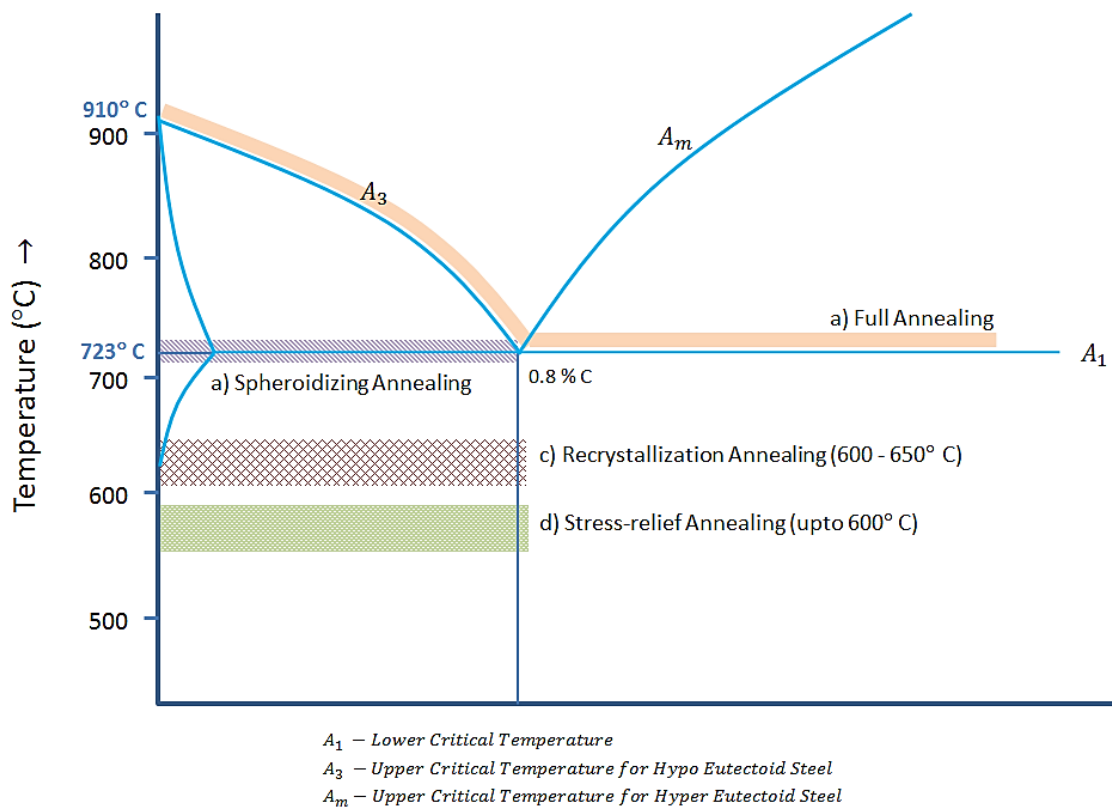


Figure 6.3: Annealing (Steel)

Full Annealing:

Heating the steel above the upper critical temperature for hypo-eutectoid steels (A_3) and above lower critical temperature for hyper-eutectoid steel (A_1) and holding them at that temperature for a certain time, based on size and shape of the specimen; thereafter cooling them at a very slow rate (furnace cooled) is termed as *full annealing*.

During this effective grain refinement can be achieved for hypo-eutectoid steels but for hyper-eutectoid steels the austenite undergoes grain growth when held at high temperature for long duration which on cooling will transform to coarse lamellar pearlite surrounded by a network of proeutectoid cementite. The cementite network being brittle results in poor machinability and impact properties of the heat treated steel, thus annealing should never be a final heat treatment for hyper-eutectoid steels.

Full annealing is expensive due to the prolonged heat treatment.

Spheroidizing Annealing:

Heating the steel slightly above or below the lower critical temperature (A_1) and holding it at the same temperature for certain duration so that the lamellar cementite in the pearlite colonies tends to spheroidize and reduce their surface area; this corresponds to the softest state of steel. It is then furnace cooled. This process is suitable for increasing the machinability (suitable for hyper-eutectoid steels).

Recrystallization Annealing:

This process is carried out at subcritical temperature, i.e., at about 600 to 650° C in order to remove the strain hardening effects due to cold working. During this process the cold worked ferrite recrystallizes; the grain size of the recrystallized microstructure decreases with the degree of cold work. This process is suitable for enhancing the ductility. (Note: Higher the degree of cold working, more will be the strain hardening effects and accordingly the recrystallization temperature will be low)

Stress-relief Annealing:

A recovery process carried out at sub critical temperature of about 600° C for hypo-eutectoid steels. There is no recrystallization taking place rather a mild atomic mobility to diminish the concentration of point defects and to remove residual stress due to cold working or machining; there is a slight decrease in the hardness. This process requires sufficiently long holding time.

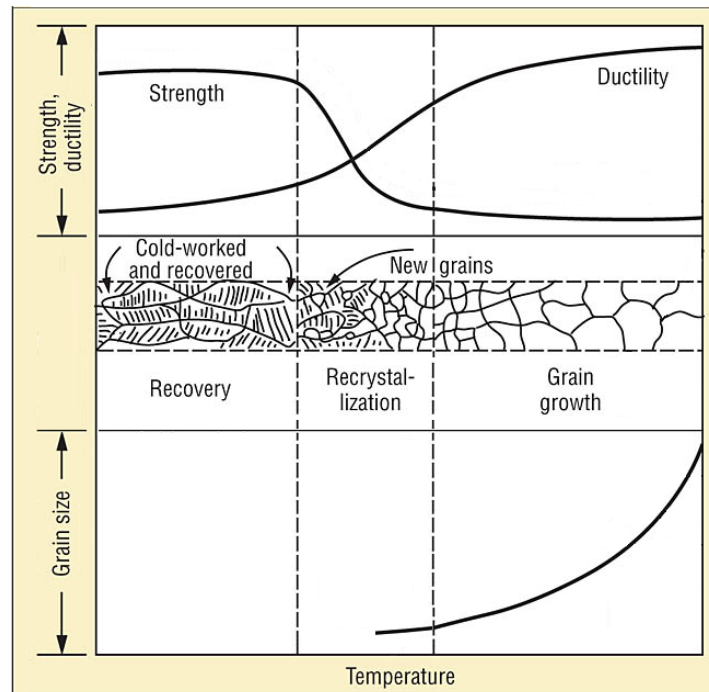


Figure 6.4: Recrystallization and grain growth during annealing

6.3.1(b) Normalizing

Heating the steel to about 40 - 50° C above the upper critical temperature (A_3 and A_m) and holding at that temperature for a short duration followed by cooling in the still air to room temperature is termed as *normalizing*. Normalizing results in a fine pearlitic structure.

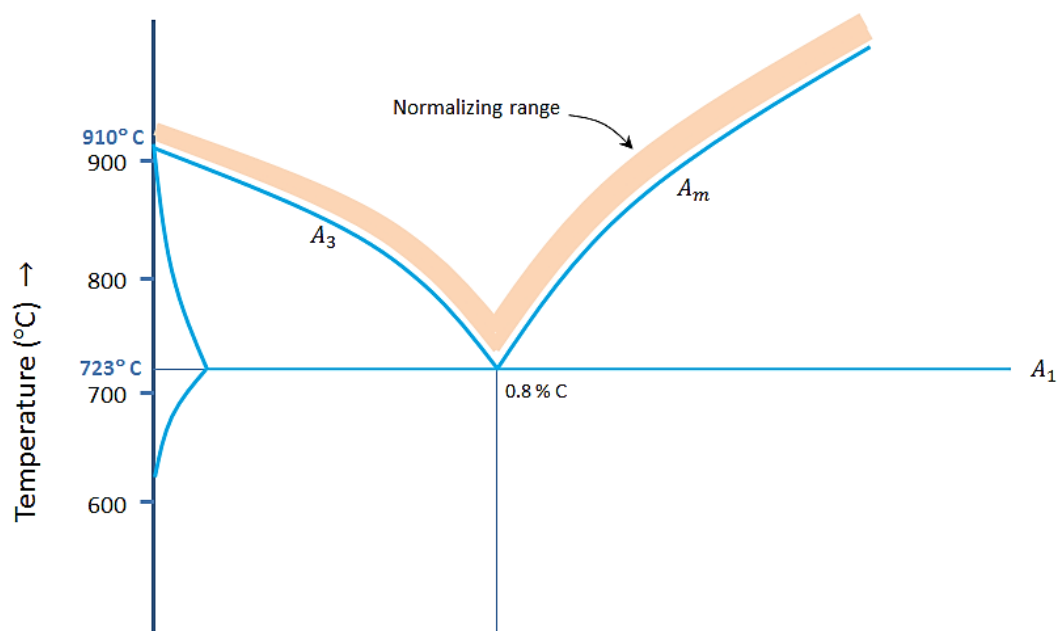


Figure 6.5: Normalizing (Steel)

Objectives:

- To refine the grain structure
- To improve mechanical properties (strength and hardness)
- To modify and refine cast dendritic structure
- To homogenize the microstructure in order to improve the response to hardening operations

Note:

Hypereutectoid steels are often heated above the upper critical temperature to breakdown any network of proeutectoid cementite around the austenite grain boundaries. The subsequent air cooling is fast enough to prevent the reformation of cementite network.

6.3.1(c) Hardening

Heating the steel to produce austenitic structure, holding at that temperature and then quenching in water or oil to obtain a martensite structure is known as hardening. The cooling rate at the center of the specimen should exceed the critical cooling rate to get full hardening.

Under slow or moderate cooling rates the carbon atoms diffuse out of austenite and transforms to BCC. With an increased rate of cooling sufficient time is not allowed for carbon to diffuse out of austenite which upon transformation yields martensite having a BCT structure with the carbon entrapped in the interstices. Thus, the resulting lattice distortion due to martensite formation enhances hardness.

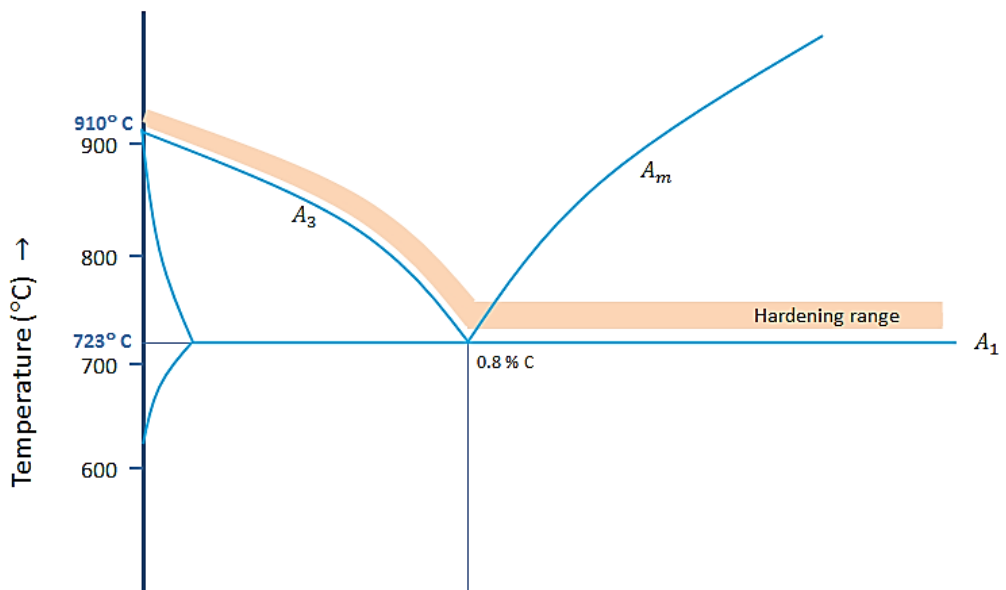


Figure 6.6: Hardening (Steel)

Note:

Hypo-eutectoid steels are heated above A_3 to avoid soft ferrite in microstructure whereas hyper-eutectoid steels heated just above A_1 ; as Fe_3C itself is a hard phase, heating above A_m makes steel susceptible to grain growth and also it might crack when cooled from such a high temperature (A_m) due to high carbon content. Hyper-eutectoid steel features hard cementite in a matrix of martensite which offers excellent wear resistance.

Hardenability:

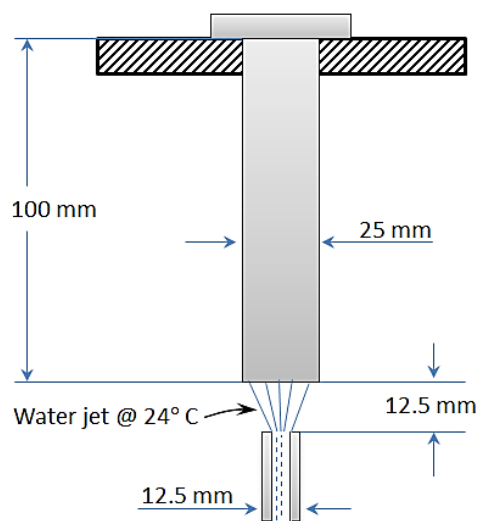
The ability of steel to harden throughout its cross section upon quenching depends on the rate of cooling; the rate of cooling increases (severe quenching) as the diameter increases. When quenched beyond certain diameter (critical diameter), different cooling rates are observed at the core and the surface. This difference in cooling rates or drastic quenching can lead to higher buildup of residual stress, warping and cracking steel.

Thus, Hardenability is referred to as the ability of steel to harden by forming martensite throughout its cross section without having to resort to drastic quenching.

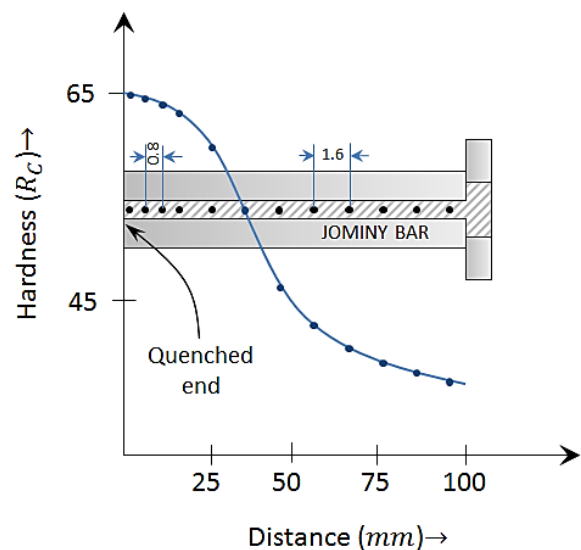
The hardenability of steel depends on

1. Composition of steel
2. Quenching medium
3. Thickness of steel

To determine hardenability *Jominy end quench* test is used.



(a) Jominy end quench test setup



(b) Hardness profile of Jominy Bar

Figure 6.7: Jominy End Quench test

Procedure: A steel rod (25 mm diameter and 100 mm long) is austenitized and transferred quickly to a fixture and a jet of water is sprayed at one end through a standardized orifice (12.5 mm dia) placed at a distance of 12.5 mm from the quenched end, the water jet is kept for 20 min to bring the sample to room temperature.

Measurement: The two flat surfaces are ground opposite to each other along the length of the Jominy bar. The hardness is measured at interval of 1.6 mm from the quenched end (Near quenched end the intervals may be 0.8 mm as the hardness variations are large). The hardness is plotted against the distance from the quenched end as shown in the figure 6.7(b) (Note: Higher the carbon content, higher will be the hardenability of steel).

6.3.1(d) Tempering

Hardening heat treatment develops extreme hardness in steels but reduces their toughness. They become very brittle and are unsuitable to be used in most of the service conditions; moreover the retained austenite obtained upon quenching is unstable and tends to change its dimensions with temperature. Hence a secondary heat treatment called tempering is carried out after hardening.

Objectives:

1. To relieve residual stresses
2. To improve ductility, toughness and impact strength.
3. To convert retained austenite into more stable phases.

6.3.1(e) Martempering and Austempering:

Metals subjected to conventional quenching and tempering are prone to develop residual stresses and cracks due to different cooling rates of the surface and center of the quenched samples. For example, Steel when quenched beyond its critical diameter forms a hard martensite case and a soft pearlitic core; the martensite being a brittle phase tends to develop cracks.

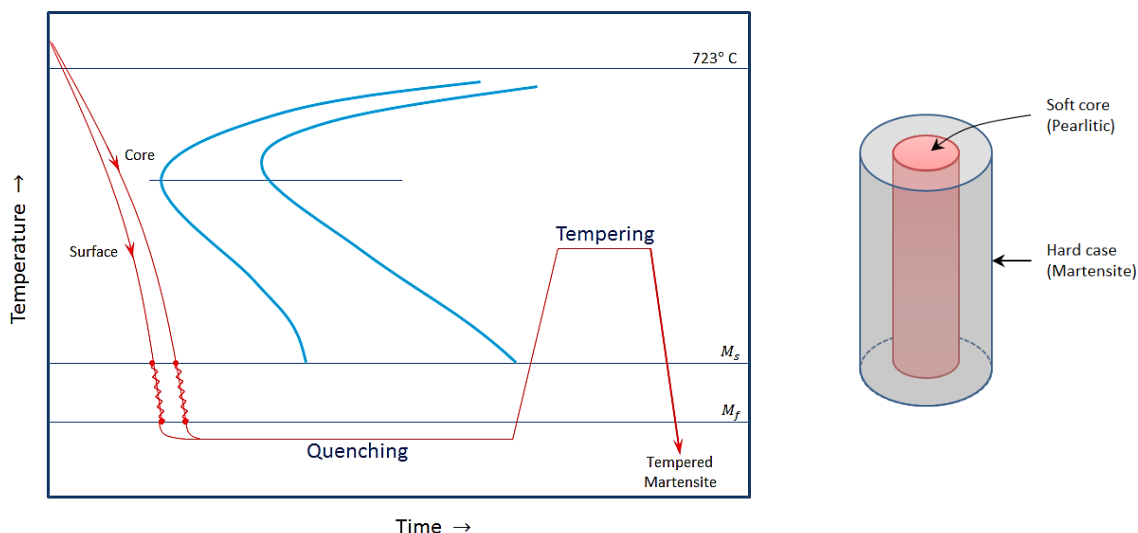


Figure 6.8: Conventional quenching and tempering

Thus, there are special heat treatment processes namely martempering and austempering, that are adopted for reducing the residual stresses and minimizing the tendency for cracking.

Martempering:

The steel is quenched into a bath kept just above M_s (martensite start temperature). After allowing sufficient time for the temperature to become uniform throughout the cross section it is then air cooled in martensitic range.

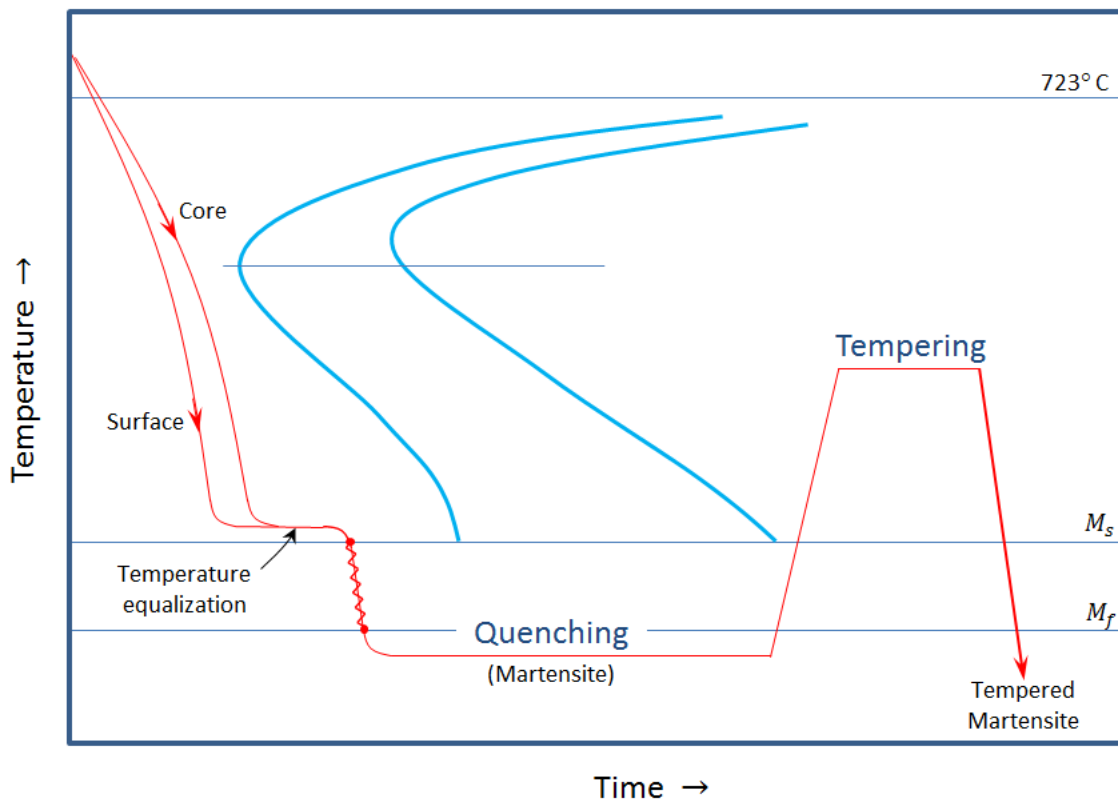


Figure 6.9: Martempering

- Transformation to martensite occurs more or less simultaneously across the section.
- Residual stresses induced are minimal.
- Subsequent tempering may be carried out.
- It is also known as Marquenching.

Austempering:

Steel is quenched into the bainitic bay above M_s (martensite start temperature) and kept isothermally till all the austenite is transformed to lower bainite.

- The hardness is due to highly fine grained bainitic structure.
- It is advantageous by avoiding costly reheat process (tempering is not essential).
- Being a slow process due to prolonged holding time, it also offers good ductility with toughness.

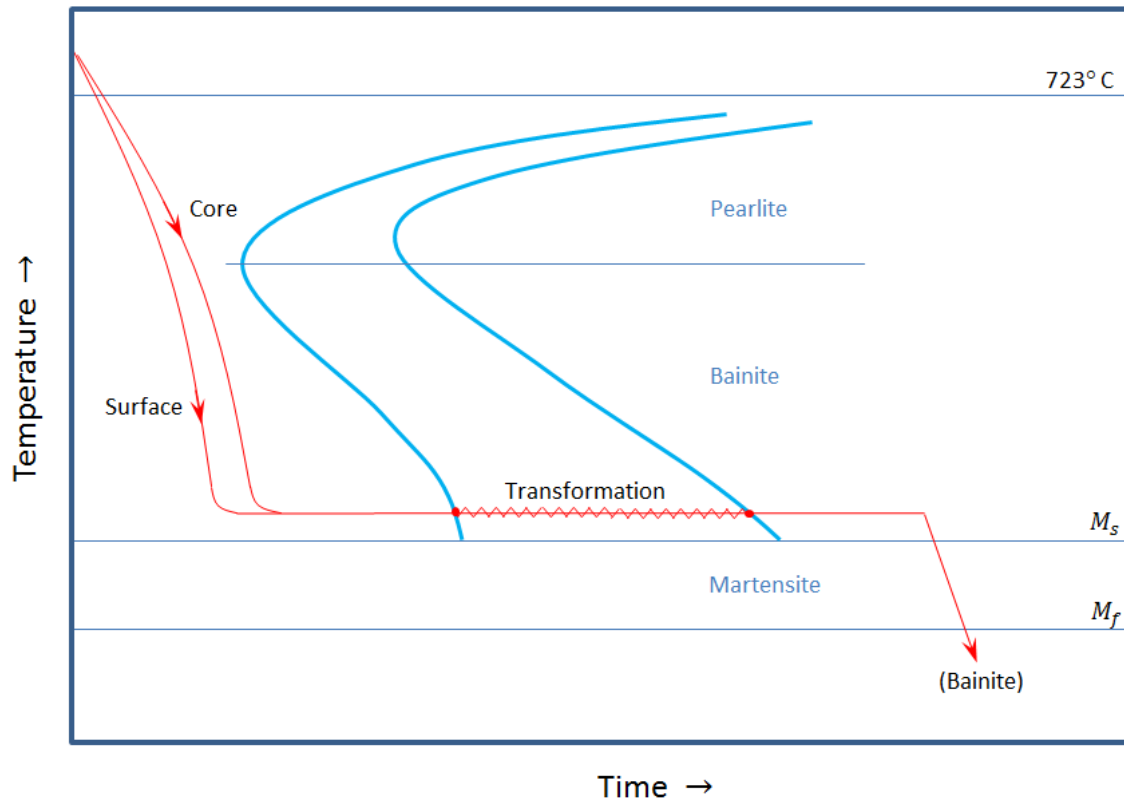


Figure 6.10: Austempering

6.3.2 Surface heat treatments

In some applications, a very hard wear resistant surface is required with the ductility and toughness of the core retained, for example: gears, cam shafts, piston, etc. There are two distinct approaches to obtain a hard surface with a tough core.

The first approach is to use steel containing sufficient carbon (more than 0.35%) and subjecting it to surface heating and quenching (flame hardening, induction hardening, etc.) so as to form a hard martensitic case with the soft pearlitic core unaltered. The second approach is to alter the surface composition of steel when its original carbon content is not sufficient enough to obtain a hard case by direct quenching; the surface composition can be changed by subjecting the steel to chemical treatments (such as carburizing, nitriding, cyaniding, etc.) followed by quenching. (Note: Some chemical treatments impart high hardness to the steel surface by forming a hard compound layer without the need for quenching)

- Surface hardening by direct quenching - if the carbon content is more than 0.35 %
(*Flame hardening, Induction hardening*)
- Surface hardening by chemical treatment - if the carbon content is between 0.15 - 0.2 %
(*Carburizing, Nitriding, Cyaniding*)

6.3.2(a) Flame Hardening

Hardening is achieved by means of heating the steel surface with an oxyacetylene flame to austenitic range followed by quenching; the surface hardens by the formation of martensite with the tough pearlitic core unaltered. The heating procedure can be stationary, progressive, spinning or the combined progressive-spinning; the selection of the appropriate mode of operation depends on size, shape and composition of the specimen, the surface area to be hardened, depth of hardening and the number of pieces to be hardened.

The figure below (Fig 6.11) shows a progressive heating and quenching technique wherein a travelling carriage containing heating and quenching unit moves along the face of the work piece to be hardened; alternatively the flame and quench heads may be held stationary with the work piece moving underneath. Thus, the specimen surface is progressively heated and hardened as either the work or the torch moves along.

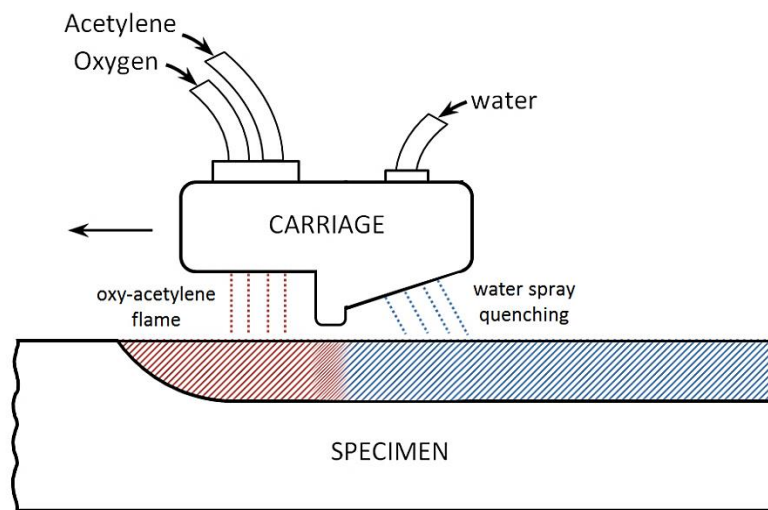


Figure 6.11: Flame Hardening

Using this method hardened layer up to 6 mm thick can be obtained; the depth of hardening depends on the time duration for which the surface is held against the flame. For short durations, only a thin skin is made austenitic and hardened; with longer holding times, the heat penetrates to a greater depth and results in deeper hardening.

Applications: specimen with long flat areas (machine tool ways) and complex shape (mill rolls, gears, etc.)

6.3.2(b) Induction Hardening

A high frequency alternating current is passed through the induction coils surrounding the specimen. The current in the coil induces eddy currents in the surface layers; the induced currents tend to travel along the surface as a result a thin layer of steel is heated, this is known as

skin effect. The surface layer is heated almost instantaneously which is quickly followed by quenching.

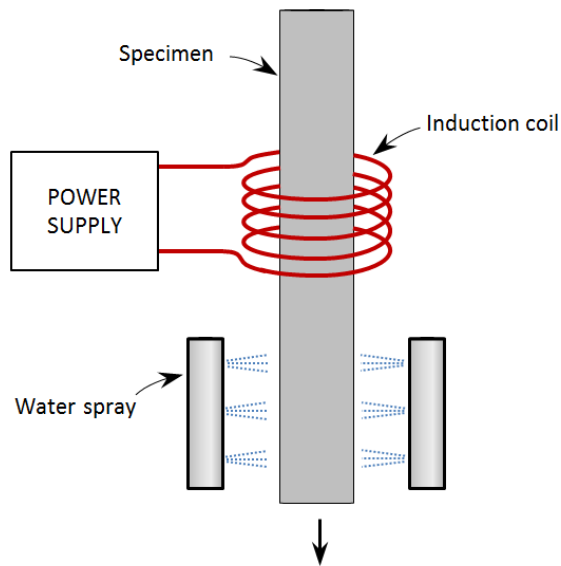


Figure 6.12: Induction hardening

The depth can be controlled by varying the frequency of alternating current; the depth of current penetration decreases as frequency increases (Note: depth is inversely proportional to square root of alternating current). Thus, high frequency current is used for shallow hardening whereas low or intermediate frequency current for deeper hardening.

Advantages: It is quick, automated with flexibility in depth control and is suitable for mass production of specimen with uniform cross section.

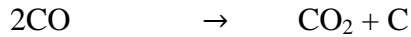
Disadvantages: High cost and is suitable for ferromagnetic materials only. Also, it is difficult to harden specimen of irregular shapes.

6.3.2(c) Carburizing

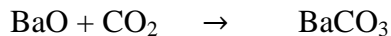
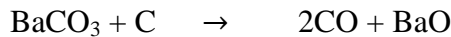
Carburizing is the widely used surface hardening method for low carbon steel ($C \leq 0.25\%$) wherein the steel specimen is subjected to carbon enrichment up to 0.8 to 1% at the surface. The carbon enters the steel through diffusion and hence is a time dependent process. To activate the diffusion of carbon, the specimen is heated to a temperature about 920 to 950 °C so that the microstructure is completely austenitic as the ferrite has limited solubility for carbon. The carburizing can be done in a gaseous environment, in a liquid salt bath, or with the sample surface covered with a solid carbonaceous compound; thus, carburizing is further classified as;

- Pack carburizing
- Liquid carburizing
- Gas carburizing

Pack carburizing: The samples are packed with carbonaceous compound (charcoal) in a steel box which is sealed and placed in a furnace. The carbon monoxide derived from the solid compound decomposes into nascent carbon and carbon dioxide. The nascent carbon is then absorbed into the metal. The carbon dioxide resulting from this decomposition reacts with the carbonaceous material to produce fresh carbon monoxide.



The reaction is enhanced by adding barium carbonate (BaCO_3) as an accelerator which reacts with carbon to form additional carbon monoxide and an oxide of the accelerator compound (BaO). The latter reacts in part with carbon dioxide to re-form carbonate. Thus, in a closed system, the accelerator is continuously being used and re-formed. Carburizing continues as long as enough carbon is present to react with the excess of carbon dioxide.



The carbon content obtained at the sample surface, increases directly with an increase in carbon monoxide to carbon dioxide ratio. Thus, more carbon is made available at the sample surface by the use of accelerators as they promote carbon monoxide formation. Typical carburizing time is about 6 to 8 hours and a case depth of about 1 to 2 mm can be obtained.

Liquid carburizing: The samples are dipped in a salt bath and heated, the salt decomposes and releases carbon; the carbon concentration is controlled principally by control of the salt bath composition.

Most liquid carburizing baths contain cyanide which introduces both carbon and nitrogen into the case. On the other hand a non-cyanide salt bath produces a case that contains only carbon as the hardening agent.

Example:

(a) Cyanide bath:

(8% Sodium cyanide, 82% barium chloride and 10% sodium chloride)



Sodium cyanide reacts with barium chloride to form barium cyanide which again forms cyanamide releasing carbon.



(b) Non-cyanide bath:

(75-80% sodium carbonate, 6-10% silicon carbide and 10-15% sodium chloride)



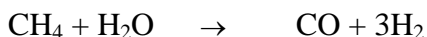
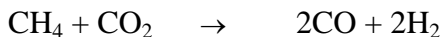
Sodium carbonate reacts with silicon carbide to produce carbon and carbon monoxide. The other products include oxides and silicates of sodium which will form the slag. Sodium chloride is added as an activator.

Gas carburizing: It is carried out in a carbon rich furnace atmosphere produced from gaseous hydrocarbons. Controlled carburizing atmospheres are produced by blending a carrier gas with an enriching gas, which serves as the source of carbon. Most commonly used carrier gas is endothermic gas which is a blend of carbon monoxide, hydrogen, and nitrogen (with smaller amounts of carbon dioxide, water vapor, and methane) produced by reacting methane with air in a separately fired retort furnace. The amount of enriching gas required by the process depends primarily on the carbon demand.

With suitably choosing the process variables such as temperature, time and furnace atmosphere composition, following reactions may be observed:



The above reversible reactions govern the addition of carbon to steel leaving CO_2 and H_2O as products. The methane added in excess to endothermic gas reacts with the products of the above equation and regenerate CO and H_2 , thereby reducing the concentration of CO_2 and H_2O keeping the course of the above reversible reactions towards right.



The above reactions can be reduced and represented by an overall reaction as shown below;



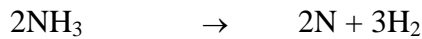
Gas carburizing is more effective than liquid or pack carburizing, and deeper and higher carbon content cases may be obtained more rapidly.

Post Carburizing heat treatment:

The sufficiently long holding times at the elevated temperature during carburizing results in a coarse grained microstructure. To have a remarkable improvement in the hardness the steel is usually not quenched directly after carburizing, rather it is given a two stage heat treatment. First the steel is heated above A_3 (upper critical temperature) and then cooled in air to refine the grain size. The second stage heat treatment involves quenching to obtain a hard martensite case with the core having less hardenability owing to low carbon content.

6.3.2(d) Nitriding

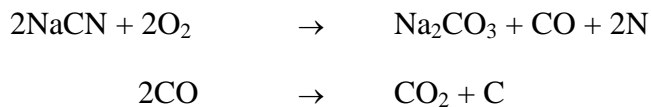
It is a process of obtaining a hard and wear resistant surface on components made from alloy steel which contain stable nitride forming elements such as Al, Cr, W, Mo, etc. In this process the specimen is heated to a temperature of about 500 °C and held for considerable duration in an atmosphere of gaseous nitrogen. Nitrogen is produced when ammonia gas is passed through the furnace at 550 °C, the reaction being;



This nascent nitrogen is readily absorbed into the surface of steel and forms hard nitrides (Fe_3N) having a hardness value, $R_C \approx 70$. Nitriding develops a high hardness on the surface of steel and hence any machining operation is carried out prior to nitriding.

6.3.2(e) Cyaniding

The steel surface is hardened by adding both carbon and nitrogen to the surface. The sample is dipped in a liquid bath of Sodium Cyanide (NaCN) and heated to 800 to 870 °C. The following reaction takes place;



The nascent nitrogen and carbon diffuse into the surface of the steel. The process time is about 0.5 to 3 hrs and a case depth of about 0.3 mm is achievable. Cyaniding is similar to liquid carburizing but differs in characteristics and composition of the case produced; in cyaniding case contains more nitrogen and lesser carbon while the reverse is seen for liquid carburizing.

6.3.3 Age Hardening

Age hardening is a hardening heat treatment that involves formation of precipitates of an impurity phase over a prolonged time, which impedes the movement of dislocations throughout the lattice; the precipitates form from a supersaturated solid solution i.e., when the solubility limit is exceeded. It is employed to enhance hardness of mostly non-ferrous metals such as aluminium, magnesium, nickel, titanium and some steels. Unlike ferrous metals, the non-ferrous metals are not amenable to conventional hardening by quenching so as to form martensite.

6.3.3(a) Age Hardening Process

The age hardening process involves;

- Solution heat treatment* where all the solute atoms are dissolved to form a single-phase solution.

b) *Rapid cooling* across the solvus line to exceed the solubility limit. This leads to a supersaturated solid solution that remains stable (metastable) due to the low temperatures, which prevent diffusion.

c) *Precipitation heat treatment* where the supersaturated solution is heated to an intermediate temperature to induce precipitation and kept there for some time (aging).

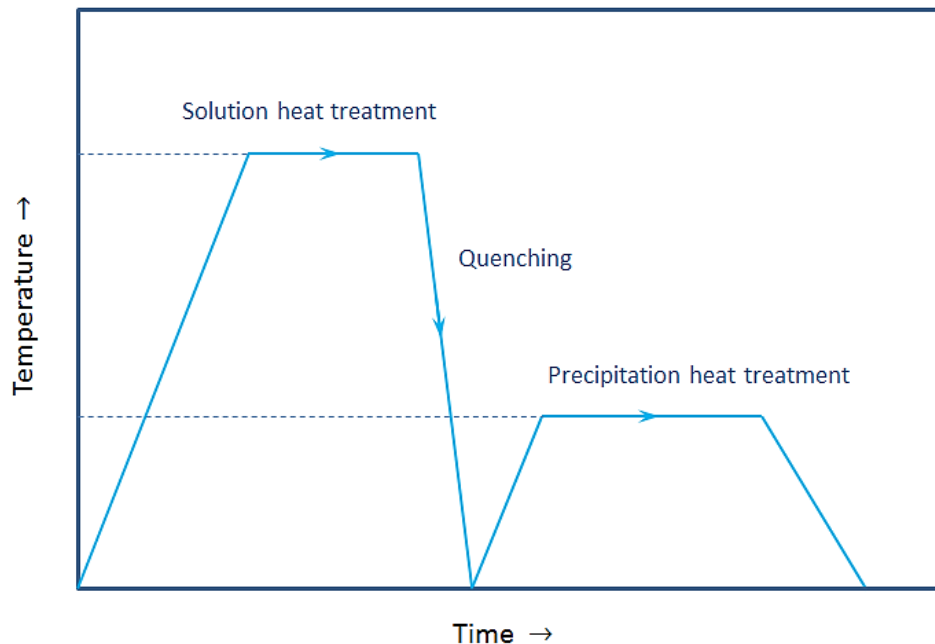


Figure 6.13: Age hardening process

During age hardening, nucleation occurs at a relatively high temperature (often just below the solubility limit) so that the kinetic barrier of surface energy can be more easily overcome and the maximum number of precipitate particles can form. These particles are then allowed to grow at lower temperature in a process called aging. This is carried out under conditions of low solubility so that thermodynamics drive a greater total volume of precipitate formation.

6.3.3(b) Stages of aging

The different stages observed during aging are;

- Stage 1 – clustering of solute atoms takes place (under-aging)
- Stage 2 – nucleation and growth of second phase particles until an equilibrium precipitate volume fraction is reached (optimum-aging)
- Stage 3 – coarsening of precipitates (over-aging)

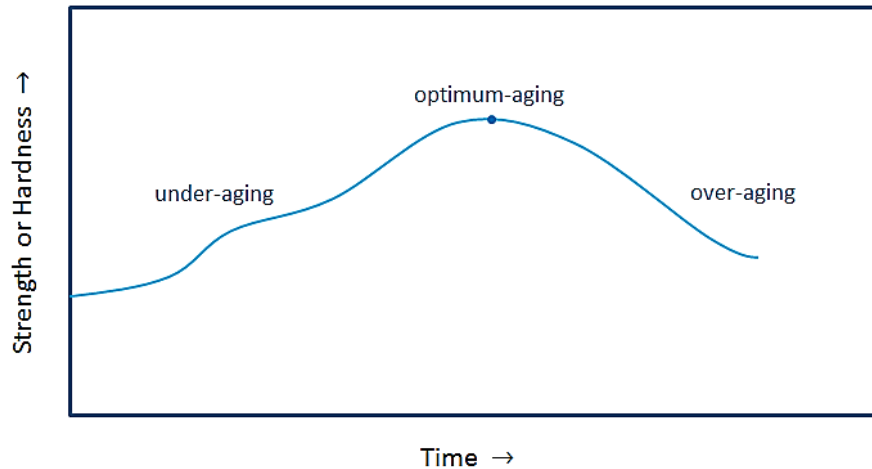


Figure 6.14: Stages of aging

Too little diffusion (under aging), and the particles will be too small to impede dislocations effectively; too much (over aging), and they will be too large and dispersed to interact with the majority of dislocations. Hence, only an optimum aging will impede dislocations efficiently to enhance hardness.

6.3.3(c) Age hardening of Al-Cu Alloy

Age hardening was first reported by Dr. Alfred Wilm; who was working on Al - 4% Cu alloy, most commonly known as Duralumin.

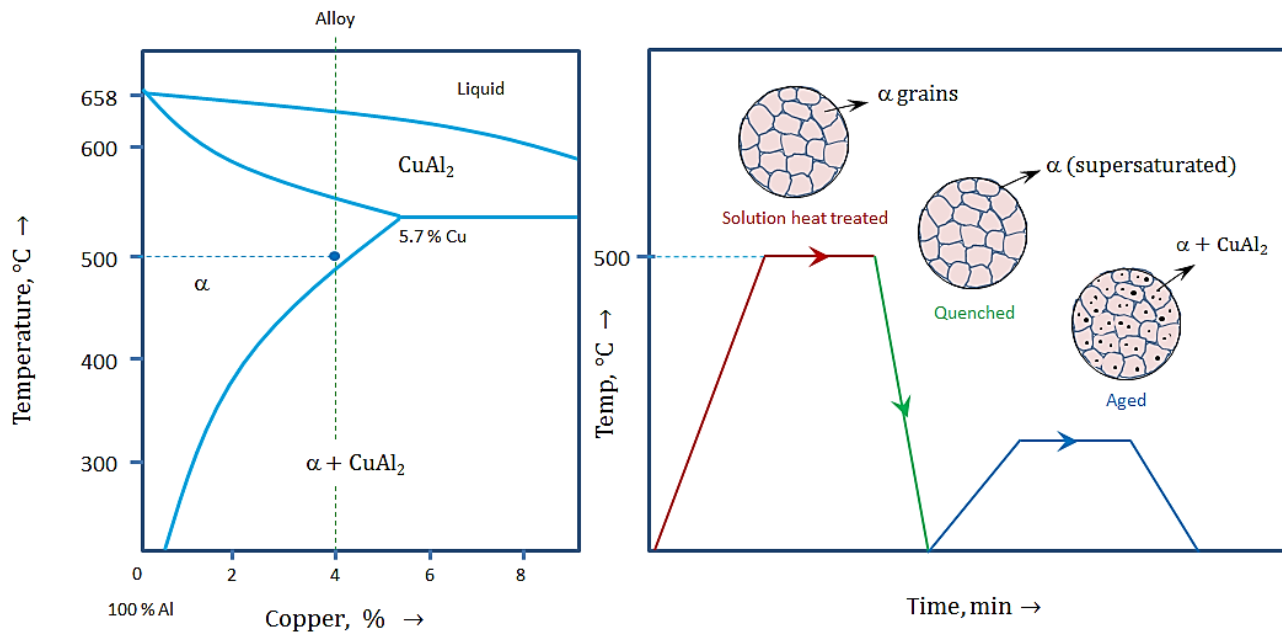


Figure 6.15: Age hardening of Al-Cu alloy

The alloy when heated to 500 °C forms α solid solution; upon slow cooling the copper starts precipitating out of it and forms an intermetallic compound cuprous aluminate (CuAl_2). On the other hand, if the alloy is rapidly cooled by quenching the microstructure would contain only α solid solution which is supersaturated; this is an unstable state and fine precipitate of CuAl_2 comes out of α over a long duration of time. These second phase particles helps in impeding the dislocation motion by distorting the lattice, thus providing a hardening effect.

Age hardening usually takesplace in metals which are partially soluble in each other having better solubility at elevated temperature than an lower temperature.

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