INTRODUCTION

Steel is an alloy of iron and carbon and with or without one or more than one of the alloying elements such as silicon, molybdenum, tungsten, chromium, nickel, vanadium, manganese etc. In addition to the above it contains trace amount of sulfur and phosphorus. Around 90% of the total amount of metals used by men for various applications are ferrous alloys which includes mainly steel and cast iron. The reasons of its wide spread applications are mainly as follows:

1. It is cheaper
2. Availability of iron bearing minerals in nature
3. Iron has the ability to be alloyed with many metals
4. A wide range of properties are possible to obtain by controlling its microstructure through a very easy heat treatment method

The extensive range of mechanical properties could be obtained from 200 MPa to as high as 2000 MPa by introducing alloying elements and heat treatment.

In addition to the above steel can also be used in various environments, at elevated temperatures and at sub zero temperatures without impairing its toughness, corrosion resistance and strength.

Therefore, the study of steel is still required because it is most widely used metallic materials even today in a large variety of applications, both simple and sophisticated. In the present lecture notes a various possibilities of microstructures in steels are discussed briefly in the following sections.

MICRO-CONSTITUENTS IN STEELS

The three allotroic forms of iron are (a) delta, ferrite (δ), (b) austenite (γ) and (c) alpha ferrite (α). These three forms have been named in decreasing order of transformation temperature. Ferrite in steel observed at higher temperature has been designated as delta ferrite (δ) and at lower temperature designated as alpha (α). The crystal structure of both δ and α is body centered cubic. On the other hand austenite is face centered cubic form of iron and has been named as austenite (γ). Austenite in pure iron exists between 910 to 1400°C.
Cementite (Fe₃C) or iron carbide: Iron and carbon form an intermetallic compound, which is very hard and brittle, and represented by the formula Fe₃C. The crystal structure of cementite is orthorhombic.

Many different kinds of ferrite are found to form in steels. Some of the commonly observed ferrite microstructures are described below:

Grain boundary allotriomorphs: Allotriomorphic ferrite crystals nucleate at prior austenite grain boundary [Fig.1(a)] and tends to grow along the austenite boundaries at a rate faster than in the direction normal to the boundary plane.

Widmanstatten Ferrite (WF): WF are plates or wedgeshaped crystals which develop into the interior of a matrix grain from the vicinity of the matrix grain boundaries [Fig.1(b)].

Acicular Ferrite (AF): The latest known micro-constituent in steels and very frequently observed in weld deposit. The term acicular means shaped and pointed like a needle. Acicular Ferrite is defined as a highly substructured, non-equiaxed phase that forms on continuous cooling by a mixed diffusion and shear mode of transformation at a temperature slightly higher than the upper bainite transformation. AF is different form bainitic ferrite with respect to prior austenite grain boundary network which is completely eliminated in AF. This structure is very fine grained.

Pearlite: It is a mixture of two phases i.e. ferrite and carbide; in which each micro-constituent takes shape like lamella. Pearlite is eutectoid reaction product of ferrite and carbide which is formed by diffusional mechanism (Fig.1c).

Bainite: The microstructural definition of bainite is non-lamellar eutectoid reaction product of ferrite and carbide. In steel bainite is formed below the nose of the time - temperature - transformation (TTT) diagram and upto the martensite start temperature. Two classical variants of bainite are upper bainite which is formed at higher transformation temperature and lower bainite which is formed above the martensite start temperature.

Martensite: The martensitic transformation is a solid state phase transformation that occurs by the co-operative movement of atoms by a shear mechanism without involving any diffusion of atoms i.e. transformation occurs without any change in the concentration. The crystal structure of martensite in steels is body centered tetragonal and degree of tetragonality depends on the percentage of carbon in steels.

THE IRON-CARBON DIAGRAM:

The micro-constituents in steels are discussed in the previous section. Alloys of iron and carbon will be discussed in details with the help of a phase diagram known as iron-carbon diagram. It is not a complete
diagram in that it is constructed only for carbon concentration of up to 6.67%, the composition of Fe₃C, or cementite. The iron-carbon diagram containing carbon concentration higher than 6.67% has very little commercial application. This diagram is not a true equilibrium diagram because cementite is not an equilibrium phase and under proper conditions cementite decomposes to graphite. The iron-carbon equilibrium diagram is shown in Fig. 2.

Above 1540°C iron remains in the liquid state and below this temperature it starts to solidify to a body centered cubic lattice, known as delta ferrite (δ). The iron-carbon diagram shows three horizontal lines each representing a reaction point involving three phases and occurring at constant temperature. These reaction points are:

(a) Peritectic point at 0.17% C and 1493°C temperature
   (0.09%C) + liquid (0.53%C) → γ (0.17%C)

(b) Eutectic point at 4.3% carbon at 1130°C
   Liquid (4.3%C) → γ (2.11%C) + Fe₃C (6.67%C)

(c) Eutectoid point at 0.8%C at 723°C temperature
   γ (0.8%C) → α (0.02%C) + Fe₃C (6.67%)C

Steels containing less than 0.8% C are called hypoeutectoid steels, and those containing more than 0.8% C are called hypereutectoid steels. The iron-carbon alloys above 2% C are generally termed as cast iron. In general cast irons are alloys of iron, carbon and silicon. Details of the cast irons will be discussed later in a separate lecture.

Better understanding of the iron-carbon diagram is possible considering a steel containing 0.25% C. This can be obtained by drawing a line between 0 and 0.5%C. Above around 1520°C steel is in liquid form. As the temperature decreases solidification starts with the formation of δ ferrite. It continues to form until the temperature reaches to 1493°C. At this temperature peritectic reaction occurs. As the cooling continues more austenite will form until a temperature (1480°C) is reached at which the solidification is completed. Below this temperature the entire mass will be composed of austenite (γ), fcc form of iron. On further cooling austenite phase does not change until temperature reaches to 815°C. At this temperature ferrite starts to form and continues to form until a temperature of 723°C is reached. At this temperature the remaining austenite disappears, and transforms to a eutectoid mixture of ferrite (α) and Fe₃C, cementite, called pearlite. Ferrite that forms prior to the eutectoid point is called proeutectoid ferrite. Similarly, cementite that forms prior to the eutectoid point is called proeutectoid cementite. Ferrite and cementite present in the pearlite is called eutectoid ferrite and cementite respectively. On further cooling of this alloy, a small amount of cementite will precipitate from the ferrite because of the
decreasing solubility of carbon in iron with the decreasing temperature. The microstructure of the steel at 0.25% C composition consists of ferrite and pearlite.

The microstructure of the other alloys in the range of 0 to 2% C can be interpreted in a similar manner, the microstructure of eutectoid steel is entirely pearlite. However, alloys with more than eutectoid composition exhibit proeutectoid cementite in place of proeutectoid ferrite. It is clear from the iron-carbon diagram that iron containing up to 2.11% carbon can be heated to a one phase structure, while the alloys containing more than 2.11% C always exhibit a two phase $\gamma + Fe_3C$ eutectic structure.

If an alloy with 3% carbon is allowed to cool from its liquid state austenite starts to form at 1300°C. Austenite that forms from liquid prior to the formation of eutectic is called proeutectic austenite. On further cooling formation of austenite continues until the temperature reaches to 1130°C. At this temperature liquid eutectic reaches to 1.3%C. This liquid eutectic transforms to austenite and cementite, called leduburite. Proeutectic austenite contains 2.11% carbon, on further cooling from 1130°C to 723°C, will precipitate cementite, because of decreasing solubility of carbon in austenite. Cementite precipitates from austenite prior to eutectoid reaction is called proeutectoid cementite. The proeutectoid cementite has been formed from proeutectic austenite, therefore, this cementite can be designated as proeutectic cementite. The austenite, of eutectoid composition will transform to pearlite.

The phase transformation so far discussed on iron-carbon diagram, the foundation on which all heat treatment of steels is based. This diagram describes the temperature-composition regions where various phases in steels are stable. However, this diagram does not convey how various arrangements of phases or microstructures are produced by austenite transformation due to different rates of cooling. Similarly this diagram does not convey the austenite formation rate due to different rate of heating. Therefore, some ideas are necessary to know the time required for the transformation of austenite at different cooling rates. Initially a basic concept of the transformation of austenite can be obtained at constant temperature, called isothermal transformation (IT) or time-temperature-transformation (TTT). Fig.3 shows the TTT diagram of 0.89% carbon and 0.29% manganese steel. The microstructure that is formed by the transformation of austenite at subcritical temperature is dependent upon the temperature of transformation. If the transformation is occurred just below the critical temperature, 723°C (AC1), coarse pearlite is formed. On further decreasing the isothermal transformation temperature down to about 550°C, will produce fine lamellar structure. However, below about 550°C, the ferrite and carbide mixture does not show lamellar form but instead, the eutectoid mixture exhibits a non-lamellar mixture, termed as bainite. Lamellar form of eutectoid mixture, pearlite is formed by diffusional mechanism while the formation mechanism of bainite is partly controlled by diffusional mechanism and partly controlled by diffusionless shear mechanism. When
austenite transforms below 200°C, face centered cubic structure is completely transformed to body centered tetragonal structure of ferrite. Transformation at lower temperature is occurred by diffusionless shear mechanism and the transformation product is called martensite.

Commercial application of TTT diagram is limited to special cases only. In almost all cases, steel is heated into the austenitic range and continuously cooled to room temperature. Therefore, the concept of continuous cooling transformation diagrams to predict microstructural development is very important. The difference between isothermal and continuous cooling transformation diagrams can be clearly understood form Fig.4 for an eutectoid steel. It is clear from the Fig.4 that although curves indicating beginning and end of transformation resemble similar curves of the IT diagrams, they have shifted to lower temperatures and longer times. Fig.5 shows different transformation products due to different cooling rates. On increasing the cooling rates, the transformation products varies from coarse pearlite-fine pearlite to finally fully martensite. The minimum cooling rates at which γ transforms to completely martensite is called critical cooling rate.

The iron-carbon, IT or CCT diagram so far discussed only applicable to plain carbon steels. However, the γ-transformation behaviour changes significantly with the addition of alloying elements.

THE EFFECT OF ALLOYING ELEMENTS

Alloying elements can influence in two ways:

(a) By expanding γ-field; these elements are called γ-stabiliser i.e. C, N, Ni Mn etc.

(b) By contracting γ-field; these elements are ferrite stabiliser. i.e. Cr, Mo, W, V etc.

Fig.6 shows how the iron-carbon equilibrium diagram changes its shape with the influence of alloying elements. The effect of different alloying elements on Fe-C diagram is discussed below:

Type 1 (Open γ-field)

The important alloying elements are nickel, manganese and cobalt. Ni and Mn, if added in sufficiently high amount, completely eliminate bcc, α-iron as shown in Fig.6.

Type 2 (Expanded γ-field)

Carbon and nitrogen are the most important element.
Type 3 (Close $\gamma$-field)

Alloying elements in this group are silicon, aluminium, phosphorus, titanium, vanadium, molybdenum, chromium. These elements encourages the formation of bcc iron, $\gamma$-area contracts to a small closed loop.

Type 4 (Contracted $\gamma$-field)

Here $\gamma$-loop is strongly contracted but is accompanied by compound formation. The alloying elements in this group are, boron, tantalum, molybdenum and zirconium.

Alloying elements also change the transformation temperature and eutectoid composition of iron-carbon diagram. Fig.7 shows the effect of alloying elements on eutectoid temperature and eutectoid composition.

Similarly alloying elements influence strongly IT and CCT diagram i.e. most of the common alloying elements shift IT diagram towards right side, thus increase the hardenability. The effect of alloying elements on isothermal transformation and continuous cooling transformation diagrams are shown in Figs. 8 and 9 respectively. Hardenability is defined as susceptibility to hardening by rapid cooling or the property in ferrous alloys that determines the depth and distribution of hardness produced by quenching. In another way hardenability can be "as the capacity of a steel to transform partially or completely from austenite to some percentage of martensite at a given depth when cooled under some given condition".

HEAT TREATMENT

Heat treatment can be defined as the heating or cooling of steels in solid state to obtain a desirable mechanical properties by producing different microstructures during heating or cooling cycles. A large variety of microstructures could be obtained in steels by heat treatment. The iron-carbon, IT and CCT diagrams which have been discussed earlier are the foundation on which entire heat treatment processes are based.

Hardening: Hardening consists of heating the steels to a sufficiently high temperature and time to produce austenitic structure and then quenching it to room temperature to obtain a fully martensite structure. Therefore, hardening process can be divided into two steps: Formation of Austenite and Quenching of Austenite.

Formation of Austenite: The transformation from ferrite-carbide to austenite is accomplished by the dissolution of carbide particles. This process is a diffusion controlled which is dependent on time and temperature. Another factor which influences the time required for austenitising is the composition of steels. In a steel, if appreciable
amount of alloying elements are present which are carbide former i.e. strong affinity to carbon than iron, then a carbide phase will not be simply Fe₃C, but a complex alloy carbide, the dissolution rate of alloy carbide is slow therefore, diffusivity of the carbide former at that temperature will be considered rate controlling. The time required to austenite formation and carbide dissolution depends on the original ferrite-carbide matrix as shown in Fig.10. For conventional hardening treatment, hypo-eutectoid steel is generally heated about 30°C above AC₃ temperature, to transform all ferrite and carbide into austenite. In hypereutectoid steel, the austenitising temperature is chosen between AC₁ and AC₃.

**Quenching** : Quenching is the process of cooling the steels in controlled manner to obtain a fully martensite structure. The common quenchants are, brine, water, oil, salt, air etc. Generally, water is used for plain carbon steels while in the case of alloy steels oil, salt and air are used as quenchant.

**Tempering of steel** : Tempering is defined as the heating of hardened steels in the temperature range of 150 to 700°C to improve the mechanical properties. As hardened microstructures are usually a mixture of austenite and martensite. Both the microconstituents are unstable and changes very slowly at room temperature. Martensite is, although a very hard phase also very brittle phase. The major objective of tempering is reduction of brittleness or increasing the toughness of a hardened steels. The as-hardened martensite is a complex structure i.e. supersaturated solid solution of carbon in body centred tetragonal crystal lattice. The tempering of plain carbon steels can be divided into the following stages:

**First stage of Tempering** : The temperature range for this stage is between 100 to 250°C. Epsilon (ε ) carbide is formed in this stage and carbon content of martensite is also decreases.

**Second stage of Tempering** : The temperature range for this stage is between 200 to 300°C. Retained austenite transforms to bainite or ferrite and carbide in this stage.

**Third stage of Tempering** : The temperature range for this stage is from 100°C to 350°C. ε-carbides dissolve and picks up additional carbon from martensite and transforms into very fine plate or rod of cementite (Fe₃C).

**Fourth stage of Tempering** : The temperature range for this stage is from 300°C to 700°C. Cementite particles starts coarsening between 300 to 400°C, while spheroidisation of cementite particles starts on further increasing temperature up to 700°C. The changes of hardness with tempering temperature of plain carbon steel is shown in Fig.11 and hardness as a function of time at three tempering temperatures is shown in Fig.12.

**Tempering of alloy steels** : The alloying elements commonly used in steels are Cr, Mo, W, V, Ni, Si etc. The tempering behaviour of alloy
Highly alloyed austenite (FeCr)23C6 lower alloy austenite (MoW)6C

The changes upon tempering of alloy steels can be described in tabular form

<table>
<thead>
<tr>
<th>Tempering Temp. °C</th>
<th>Structural Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>Highly alloyed martensite</td>
</tr>
<tr>
<td></td>
<td>Highly alloyed martensite</td>
</tr>
<tr>
<td></td>
<td>Undissolved carbides</td>
</tr>
<tr>
<td></td>
<td>ε-carbide</td>
</tr>
<tr>
<td></td>
<td>Fe3C</td>
</tr>
<tr>
<td>425</td>
<td>(FeCr)23C6</td>
</tr>
<tr>
<td></td>
<td>(Fe,Cr)23C6</td>
</tr>
<tr>
<td>540</td>
<td>(MoW)6C</td>
</tr>
<tr>
<td></td>
<td>(MoW)6C</td>
</tr>
<tr>
<td></td>
<td>(Secondary Hardening)</td>
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<tr>
<td></td>
<td>To martensite</td>
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<tr>
<td></td>
<td>on cooling or</td>
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<tr>
<td></td>
<td>Ferrite and</td>
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<tr>
<td></td>
<td>carbide on</td>
</tr>
<tr>
<td></td>
<td>Isothermal</td>
</tr>
<tr>
<td></td>
<td>holding</td>
</tr>
<tr>
<td></td>
<td>(Secondary Hardening)</td>
</tr>
<tr>
<td></td>
<td>Growth of carbides</td>
</tr>
<tr>
<td></td>
<td>No change</td>
</tr>
</tbody>
</table>

The changes of hardness with tempering temperatures of alloy steel martensite is shown in Fig.13.

**Tempered Martensite Embrittlement**

When martensite is tempered in the temperature range of 250 to 400°C, the loss in impact toughness is observed as shown in Fig.14. In high purity steels, this phenomena is occurred due to the transformation of retained austenite to thin plates or cementite on tempering in the range of 250 to 400°C. This loss in toughness observed after tempering is more pronounced if phosphorus segregates at the prior austenite grain boundaries in the as quenched martensite. The interaction between phosphorus and cementite is responsible for this loss in toughness. The appearance of fracture surface is intergranular type.

**Temper Embrittlement (TE)**: When many steels tempered in the range of 500 - 650°C or very slowly heated or cooled in this temperature range loss in toughness occurs. The presence of temper embrittlement is detected by measuring impact transition...
temperature. Impact transition temperature increases significantly as shown in Fig.6.

The important impurities such as antimony, phosphorus, tin, arsenic, bismuth play a greater role in temper embrittlement. Very small amount of these elements even in the order of 100 ppm (0.01%) or less is also detrimental. Plain carbon steels are not susceptible to TE if manganese content is kept below 0.5%. Alloying elements such as Ni, Cr, Mn are very harmful in this regard. Therefore, interaction of impurities and alloying elements is responsible for segregation of impurities at the prior austenite grain boundaries. Molybdenum reduces the segregation of impurity elements and suppresses embrittlement by scavenging phosphorus through the formation of a Mo-P compound.

Martempering: Martempering or interrupted quenching process consists of holding the austenitised steel above the Ms temperature usually by quenching in a salt bath and then air cooling to room temperature. The schematic diagram of martempering process is shown in Fig.16. Because of interrupted cooling of austenite distortion, residual stresses, and cracking are almost eliminated by this treatment. The final microstructure obtained after martempering is martensite.

Austempering: Austempering is a process in which austenitised steel is isothermally hold in molten salt bath at a temperature above Ms. The final microstructure obtained after austempering is bainite. The heat treatment cycle of austempering is shown in Fig.17.

Annealing: Annealing is a heat treatment process and can be defined as the heating a steel to the single phase austenite field and then slowly cooling to room temperature. The cooling rate may be of the order of 10-2°C/second and this can be accomplished by furnace cooling.

Spheroidizing Annealing: Spheroidizing annealing treatment is given to a steel to obtain a structure which consist of uniform dispersion of carbides in the form of spheroids in ferrite matrix. The heat treatment cycle for spheroidizing annealing treatment is shown in Fig.18.

(a) Long time isothermal holding below AC$_1$ temperature i.e. subcritical annealing
(b) Repeated heating and cooling of steels above or below the AC$_1$ temperature
(c) Heating just above AC$_1$ temperature and then slow cooling.

The rate of spheroidisation depends on the initial microstructure and alloying elements in steels.

Normalising: Normalising process is defined as cooling the steel in air from austenitising temperature. Very fine grained ferrite-carbide structure is obtained after normalising treatment. The heat treatment
cycle for normalising is shown in Fig.19. The austenitising temperature for normalising is same as that for annealing.

**Function of alloying elements**: Alloying elements are added in plain carbon steels to modify mechanical properties of plain carbon steels. Effects of alloying elements on iron-carbon, TTT and CCT diagrams have already discussed. Effect of alloying elements on the softening during tempering have also been discussed. Here, effects of alloying elements on mechanical properties will be discussed. Common alloying elements in steels are: C, Si, Mn, Ni, Cr, Mo, V, W etc. Alloying elements are used in steels due to the following reason:

1. To improve hardenability
2. To improve resistance to softening
3. To improve resistance to corrosion and oxidation
4. To improve high temperature properties
5. To improve resistance to abrasion
6. To strengthen steels.

**Nickel steels**: Extensively used for engineering purposes up to about 5%. It improves strength and toughness. It is used in larger amount in stainless and maraging steels. Nickel does not form carbides. Presence of nickel in steel makes iron carbide less stable. It reduces the coefficient of thermal expansion.

**Manganese**: It increases strength and toughness when added 1.5 to 2%. Manganese is widely used for deoxidation and desulphurisation. Manganese is not a strong carbide former but it has a very powerful effect to stabilize carbide.

If manganese content is increased to between 11 to 14% and carbon 1 to 1.2%, a very tough and wear resistant steel is obtained known as Hadfield steel.

**Chromium**: Chromium improves hardenability, strength and wear resistance. Chromium is carbide stabilizer and forms hard carbides, Cr7C3 or Cr23C6. These carbides are harder than ordinary cementite, Fe3C. The main disadvantage in the use of chromium is its tendency to promote grain growth and temper embrittlement. With 1% carbon and 1.4% chromium, steel is used to manufacture ball bearings. Higher percentage of chromium is used in stainless steels.

**Molybdenum**: One of the main uses of molybdenum in low alloy steel is to reduce the tendency of temper brittleness. Molybdenum is a stable carbide former, it forms Mo3C, Fe3Mo3C and Fe21Mo2C6. Creep resistance is improved because of the stability of the carbides.

**Tungsten**: Tungsten forms a very hard and brittle carbides W2C, WC and a double carbide Fe4W2C. Tungsten is mainly used in tool and die steels. Tungsten is also used in heat resistant steels in which it improves creep strength. With suitable heat treatment tungsten bearing steels develop high temperature i.e. hot hardness up to 600°C. It is extensively used in high speed steels.
Vanadium: Vanadium is a strong and stable carbide former. It forms VC or V₄C₃ type carbide. It is also a very important grain refiner. It stabilises martensite and bainite on heat treatment. It also induces resistance to softening at high temperatures. The combine effect of Cr, Mo, and V in steels will be discussed in brief.

To obtain required properties at higher service temperature for long time proper alloying element addition and heat treatment are very important. This means secondary hardening reactions must be used to achieve required mechanical properties at higher service temperatures.

Addition of chromium only can not impart to optimum mechanical properties. Chromium containing steels retard softening during aging or long term service, but it is less effective beyond 500°C as shown in Fig.20. Secondary hardening by molybdenum and vanadium additions markedly increases the tempering resistance as shown in Fig.21.

The MoC₂ carbide can dissolve both chromium and vanadium. Chromium causes Mo₂C less stable, whereas vanadium stabilises Mo₂C. However, too much vanadium cannot be used in steels due to its low solubility and higher austenitising temperature is required for dissolving vanadium carbide. Therefore, steels containing Cr, Mo and V are widely used in power plant components.

CLASSIFICATION OF STEELS

This means a systematic arrangement or division of steels into groups on the basis of some common characteristics. Here classification of steel has been described on the basis of chemical composition. Plain carbon steels are classified on the basis of the carbon content. According to the carbon content it can be classified as low carbon, medium carbon and high carbon steels. Low carbon steels contain carbon up to 0.25% C with manganese up to 1.5% Mn. Medium carbon steels contain carbon ranges from 0.25 to 0.60% and manganese from 0.60 to 1.65%. High carbon steels contain carbon ranges from 0.6 to 1.25% with manganese ranging from 0.30 to 0.90%. In addition to the above, ultra high carbon steels contain carbon ranging from 1.25 to 2.0%.

High strength low alloy steels

These are commonly used in oil and gas line pipe, ships, offshore structures, automobiles, highway equipment and pressure vessels etc. The chemical composition of HSLA steels are; Carbon (0.05 to 0.25%), manganese content up to 2.0%. Small amount of other alloying elements like chromium, nickel, molybdenum, copper, nitrogen, vanadium, niobium, titanium and zirconium are used in various combinations. Micro alloyed steels, with very small additions of alloying elements such as niobium, vanadium and or titanium for
refinement of grain size and or precipitation hardening are widely used in recent years.

**Low alloy steels**

Total alloy content in the low alloy steels can range from 2% to about 5%, in medium alloy steels, total alloy content is in the range of 5 to 10% and high alloy steels contain total alloy content more than 10%.

Low alloy steels can be classified as nickel steels, nickel-chromium steels, molybdenum steels, chromium-molybdenum, chromium-molybdenum-vanadium steels etc.

Therefore, carbon and low alloy steels groups comprise a large number of steels that differ in chemical composition, strength, heat treatment, corrosion resistance and weldability. The classification of steels given in Fig.22.

**STAINLESS STEELS**

Stainless steels are a large family of specialised steels in which the first and the most important property is the corrosion resistance. Therefore, stainless steels are widely used in various industries where corrosion and oxidation resistance in operating environment is required. Stainless steels are also used widely for high temperature creep resisting or heat resisting applications.

**Classification of stainless steels**

Stainless steels can be classified into three major categories:

(a) Austenitic
(b) Ferritic
(c) Martensitic

Austenitic stainless steels contain 18-25% Cr with 8-20% Ni and low carbon (0.1% C maximum). The crystal structure of austenitic stainless steels is FCC. The structure of 18% Cr steel can be made fully austenitic by the addition of 8% Ni. Corrosion resistance of 18% Cr - 8% Ni is superior to that of the ferritic or martensitic steels.

Ferritic stainless steels contain 15-30% Cr and low carbon, with some molybdenum, niobium or titanium. Nickel is not added in ferritic stainless steel. The crystal structure of this type of stainless steel is BCC and they remain ferritic over the whole solid state temperature range.

Martensitic stainless steels contain 12-17% Cr and 0.1 to 1.0% C. These steels are austenitic in the temperature range of 950 to 1000°C but transform to martensite on cooling.
Phase diagrams for stainless steels

Fig. 23 shows Fe-Cr phase diagram, chromium is ferrite stabiliser and tends to stabilize α-iron and its high temperature counterpart, which merge to form closed γ-loop. Beyond 16% chromium there will be no austenite in binary Fe-Cr alloys. From Fe-Cr diagram it is observed that α-phase forms only at chromium contents higher than 17%, σ-phase can form in the temperature range between (510 to 1000°C). At lower temperature rate of precipitation is very slow, σ-phase precipitation is accelerated by cold working or in presence of ferrite forming elements such as silicon, niobium and molybdenum. Elements dissolve in σ-phase and extend the temperature range over which it is stable σ-phase is a hard iron-chromium compound. In addition molybdenum can lead to the formation of iron-chromium-molybdenum compound, Chi-phase, which is stable over a wider range than σ-phase.

In ferrite steels, molybdenum, a strong ferrite former, is added to increase corrosion resistance, whilst niobium and titanium are added to stabilize the steels against intergranular corrosion by lowering the carbon and nitrogen dissolved in the steel.

The martensitic grade of stainless steels can be understood with the help of Fe-12% Cr-C diagram as shown in Fig.24. Chromium restricts the γ-field of the Fe-C diagram. Eutectoid composition decreases to 0.7% carbon.

When FCC nickel is added to iron, as discussed earlier, only austenite can be obtained at all temperature, the effect of increasing Ni content on Fe-Cr alloys are shown in Figs. 25 & 26. These diagrams clearly indicate that higher Ni contents would tend to give a more stable austenite.

The development of σ-phase

Austenitic stainless steels containing high proportion of ferrite forming elements, when pass through the temperature range from 600-900°C σ-phase is expected to form. σ-phase is an extremely brittle constituent. Therefore, stainless steel will suffer a substantial loss of ductility when heated in the σ-phase forming temperature range.

Chromium carbide precipitation

When austenitic stainless steels of 18-8 composition (18% Cr - 8% Ni) is heated within the temperature range of 500 to 600°C, for any appreciable length of time, chromium rich carbide will precipitate along the grain boundaries. Chromium rich carbides are expected to form in unstabilised steels. The carbide precipitation process is called "Sensitization". Within the sensitisation range, carbon atoms diffuse to
the grain boundaries combine with chromium atoms to form chromium carbide. As a result of chromium carbide precipitation, the area adjacent to the grain boundaries generally deplete of chromium content. The low chromium content area become anodic to the bulk of the metal. Therefore, these areas are preferentially attacked by the corrosive media. Sensitisation can be avoided in following manner.

Very low carbon steels i.e. below 0.03% is recommended to avoid carbide precipitation.

Stabilisation of stainless steel with niobium or titanium is not always completely effective under corrosive conditions. If a stabilized steel is heated to above 1100°C for titanium bearing steels and above 1300°C for niobium bearing steels, carbides of titanium or niobium goes into solution and consequently, chromium carbide precipitation may take place along the grain boundaries if the steel is cooled slowly or held for long time within the carbide precipitation range. Therefore, the degree of chromium carbide precipitation can be minimised effectively by reducing the carbon content in steels.

**Steels for Thermal Power Plants**

0.5 Cr-0.5 Mo-0.25V, 2.25Cr-1Mo, 1Cr-1Mo-0.25V and 1Cr-0.5Mo steels are widely used in thermal power plants. Carbon content of this group of steels are from 0.1 to 0.3%. A large variety of microstructures could be obtained by heat treatment. The heat treatment cycles of the four steels are discussed here.

**1Cr-1Mo-0.25V**

1Cr-1Mo-0.25V steels are most widely used for power generating plant components, such as bolts, steam turbine casings high pressure (HP) and intermediate pressure (IP) turbine rotors etc. This steel is heat treated to obtain predominantly upper bainitic microstructures with fine dispersion of vanadium carbides. Rotor forging are austenitised either at 1010°C or 955°C followed by either air cooled or oil quenched. In UK, the rotors are oil quenched from austenitising temperature to achieve better toughness while in USA, the rotors are air cooled from austenitising temperature to achieve better creep strength. Air cooled or oil quenched rotors are then tempered in the temperature range of 650 to 700°C. Continuous cooling transformation for this steel is shown in Fig.27. Tempering behaviour of rotor steel is shown in Fig.28. The as heat treated microstructure consists predominantly Fe₃C either plate type or rounded and fine spheroidal vanadium carbide with very little amount of Mo₂C.

Tensile properties of Cr-Mo-V rotor steel austenitized at two different temperatures is given below:
Austenitizing Temperature : 1010°C

Ultimate Tensile Strength (MPa) : 940
Yield Strength (MPa) : 780
Elongation (%) : 13
Reduction of Area (%) : 24.8

Austenitizing Temperature : 955°C

Ultimate Tensile Strength (MPa) : 775
Yield Strength (MPa) : 620

1% Cr-0.5%Mo Steel and 2.25Cr-0.1Mo Steel

This steel is extensively used in power plant for superheater tubes and headers. The steel is austenitised in the temperature range of 900 to 950°C followed by either air cooled or furnace cooled. Air cooled steel is then tempered in the range of 650 to 730°C. The continuous cooling transformation diagram for the steels are shown in Fig.29. Depending upon the cooling rate a large variety of microstructures such as, ferrite-pearlite, ferrite-bainite or bainite could be obtained.

The steels so far discussed are mainly used up to 550°C. However, for increasing the operating temperature up to 650°C, new materials i.e. high chromium ferritic steels have been developed for advanced power plants. The base composition of new rotor steels is as follows:

C : 0.1-0.15%, Si : 0.03-0.05%
Mn : 0.5%; Ni : 0.5-0.8%
Cr : 10-11%; Mo : 0.15-1%; W : 2%
V : 0.2%; Nb : 0.08%; N : 0.025%

and other alloying elements like, cobalt about 3% and boron about 0.015% may also present in the steel. The austenitising temperature for this steel is in the temperatures ranges of 1000 to 1050°C followed by air cooling from austenitising. Carbon content of this steel is maintained very low level i.e. 0.12 - 0.13% to minimise the carbide formation. The steel is then tempered in the temperature range of 700 to 720°C.

For boiler tubes 9Cr-0.1Mo or 12Cr-0.1Mo steels exhibit excellent high temperature properties. The chemical composition for boiler tubes are 9-12% Cr, 0.05% - 0.2%C, 0.1-0.3%V, 0.03%-0.08%Nb, Mo + 0.5W > 1.0%.

The steel is austenitized in the range of 1050 to 1150°C followed by either air cooled or oil quenched. Then tempered in the temperature range of 750 to 800°C and then air cooled.

For casing, valves, turbine blades and bolts etc., 9-12% Cr, 0.15%C, 0.1% Ni, 0.2% Mo, 2% W, 0.2% V, 0.08% Nb, 0.025% N and 0.015% B steel could be used. This steel have higher carbon content.
than the steels for boiler tubes. It is not possible to cover all grades of steels in a single lecture. Some selected references were given in Bibliography for further study.

**BIBLIOGRAPHY**

Fig. 1: (a) Grain boundary allotriomorphs of ferrite, 0.29% C, reacted 13 sec, at 750°C, 1000 X; (b) Primary side plates of ferrite; 0.29% C, reacted 90 sec at 725°C, 2000 X; (c) Pearlite in a 0.8% C steel, slowly cooled from austenite (annealed).
Fig. 3: Isothermal transformation diagram of eutectoid carbon steel: C - 0.89%, Mn - 0.29%.
END-QUENCH HARDENABILITY

Fig. 4. Relationship of CT (heavy lines) and IT (light lines) diagrams of eutectoid steel. Also shown are Jominy end-quench specimen and four cooling rates from different positions on the specimen superimposed on the CT diagram.
Fig. 5 CT diagram (heavy lines) for 4140 steel. Also shown are Jominy end-quench data and IT diagram (light lines).
Fig. 6: Effects of alloying on iron-carbon phase diagram
Fig. 7 — The effect of alloying elements on the eutectoid composition.

Fig. 7 — The effect of alloying elements on the eutectoid temperature.
Comparison chart showing influence of chromium on the isothermal transformation curve. Left, beginning curves; right, ending curves. (After Davenport)

Comparison chart showing influence of carbon on the isothermal transformation curve. Left, beginning curves; right, ending curves. (After Davenport)

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Fig. 9 CT diagram for plain carbon steel containing 0.38% C and 0.70% Mn. Transformation and microstructures are plotted as a function of bar diameter.

Fig. 9 CT diagram for an alloy steel with 0.40% C, 1.50% Ni, 1.20% Cr and 0.30% Mo, plotted as a function of bar diameter. Steel was austenitized at 850 °C (1562 °F), previous treatments: rolling, then softening at 650 °C (1202 °F).
Fig. 10. Graph showing time for austenitization of a plain carbon eutectoid steel, starting with a pearlitic structure obtained by normalizing from 875°C. The first curve (0.5% γ) represents the first visible evidence of austenite; the second curve (99.5% γ) represents the disappearance of pearlite, although some residual carbides remain undissolved. The third line, dashed, represents the approximate time-temperature limits for solution of all residual carbide; and the last dashed curve represents the probable attainment of homogeneity in the austenite. (Meck.)

Fig. 11. Decrease in hardness with increasing tempering temperature for steels of various carbon contents. Reference numbers after investigators are from list in Grossmann and Bain.

Fig. 12. Hardness as a function of time at three tempering temperatures for martensite in an Fe-1.22C alloy.
Fig. 13 a  Softening, with increasing tempering temperature, of quenched 0.40 to 0.45% C steels as influenced by chromium content.

Fig. 13 b  Softening, with increasing tempering temperature, of quenched 0.35% C steels as influenced by molybdenum content.
Fig. 14  Impact toughness as a function of tempering temperature of hardened, low-alloy, medium-carbon steels.

Fig. 15  Shift in impact transition curve to higher temperature as a result of TE produced in SAE 3140 steel by isothermal holding and furnace cooling through the critical range.
Fig. 16 Schematic diagram of martempering heat treatment cycle superimposed on an IT diagram for a medium-carbon steel.

Fig. 17 Schematic diagram of austempering heat treatment cycle superimposed on an IT diagram for a medium-carbon steel.
Fig. 16 Schematic heat treatment cycle for spheroidizing an air-hardening steel. Martensite forms first and then is tempered close to the $A_c_1$ to produce a spheroidized structure. (Ref 5.5)

Fig. 19 Schematic time-temperature cycles for normalizing and full annealing. The slower cooling of annealing results in higher temperature transformation to ferrite and pearlite and coarser microstructures than does normalizing. (Courtesy of M. D. Geib, Colorado School of Mines, Golden, Colo.)
Fig. 2 (a) Effect of chromium on the tempering characteristics of 0.3% C, 1% Mn steels.

Fig. 2 (b) Effect of molybdenum on the tempering characteristics of 0.4% C, 1% Mn, 1% Cr steels.

Fig. 21 (a) Effect of vanadium on the tempering characteristics of 0.4% C, 1% Mn, 1% Cr steels.

Fig. 21 (b) Effect of vanadium on the tempering characteristics of 0.4% C, 1% Mn, 1% Cr steels.
Ferrous alloys

Classification by commercial name or application

Steel

Plain carbon steel

Low-carbon steel
(<0.2% C)

Medium-carbon steel
(0.2-0.5% C)

High-carbon steel
(>0.5% C)

Low-alloy steel
≤8% alloying elements

High-alloy steel
>8% alloying elements

Corrosion resistant

Heat resistant

Wear resistant

Ferritic

Ferritic-pearlitic

Pearlitic

Martensitic

Bainitic

Austenitic

Precipitation hardened

Austenitic-ferritic

Duplex structure

Alloys without eutectic (<2% C on Fe-C diagram)

Classification by structure

Fig. 22 Classification of steels. Source: D.M. Stefanescu, University of Alabama, Tuscaloosa
Pro. 23. Binary Fe-Cr phase diagram showing the closed \( \gamma \) loop as body-centered chromium and body-centered iron form ferrite solid solutions.

Fig. 24. Pseudo-binary phase diagram of iron plus 12% Cr, with varying percentages of carbon. Tie lines in two-phase fields do not show compositions of the two phases or relative proportions. The crosshatched areas are three-phase fields. A second carbide may exist at the higher carbon contents.
Pseudo-binary phase diagrams of Fe + 18% Cr + 4% Ni versus varying carbon content (12.4) and Fe + 18% Cr + 8% Ni versus varying carbon content ( ). The carbide in both cases is (CrFe),C, at least up to 0.5% C. Note how increasing nickel content stabilizes austenite, restricting the high-temperature δ and room-temperature α. The three-phase fields are crosshatched. Phase compositions and relative proportions cannot be obtained from tie lines in two- or three-phase fields in these diagrams.
Fig. 27  Idealized continuous-cooling transformation diagram for 1%Cr–Mo–V rotor forgings

Fig. 28  Tempering behavior of Cr–Mo–V rotor steel.
Fig. Continuous cooling transformation diagrams for (a) 2%Cr-Mo steel austenitized at 955 °C (1750 °F) and (b) 1%Cr-1%Mo steel austenitized at 910 °C (1675 °F) (Ref 17).