SOLID SOLUTIONS AND PHASE DIAGRAMS

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ALLOY

- A substance that has metallic properties and is composed of two or more chemical elements, of which at least one is a metal.
- An alloy system contains all the alloys that can be formed by several elements combined in all possible proportions.
- A system made up of two elements is called a binary alloy system, and that made up of three elements is termed as ternary alloy system.
- Taking only 45 of most common metals, any combination of two gives 990 binary systems and combination of three gives over 14000 ternary systems.
- However, in each system, a large number of different alloys are possible. If composition is varied by 1%, each binary system will yield 100 different alloys.
- A commercial alloy often contains many elements, and apparently the number of possible alloy is almost infinite.

CLASSIFICATION OF ALLOYS

Homogeneous (uniform) or mixtures

- **A homogeneous alloy will consist of a single phase while a mixture is a combination of several phases.**
- **The uniformity of an alloy phase is not determined on an atomic scale, such as composition of each unit cell, but rather on a much larger scale.**
- **Any structure which is visible as physically distinct microscopically may be considered a phase, which for most pure elements is synonymous of state.**
- **Therefore, there is a gaseous liquid and solid phase for pure elements.**
- **Some metals are allotropic in solid state and will have different solid phases. When the metal undergoes a change in crystal structure, it undergoes a phase change since each type of crystal structure is physically distinct.**

In the solid state there are three possible phases

Pure metal

Under equilibrium conditions, all metals exhibit a definite melting or freezing point.

Intermediate alloy phase or compound solid solution

The atoms that are combined to form the molecules, are held together in definite bond.

The bond is generally strong and the atoms are not easily separated.

When a compound is formed, the elements lose their individual identity and characteristics properties to a large extent.

Solid solution

SOLID SOLUTIONS

Any solution is composed of two parts:

- ✓ **Solute The minor part of the solution or material, which is dissolved.**
- ✓ **Solvent constitutes the major portion of the solution.**
- ✓ **Solutions can have gases, liquids or solids as either the solute or solvent.**
- ✓ **Most commonly solution involves water as solvent, such as sugar or salt dissolved in water.**

The amount of solute that may be dissolved by a solvent is generally a function of temperature (with constant pressure) and usually increases with increasing temperature.

CONDITIONS FOR A SOLUTION

- **Unsaturated solution**

  If the solvent is dissolving less of the solute than it could dissolve at a given temperature and pressure.

- **Saturated Solution**

  If the solvent is dissolving the limiting amount of solute.

- **Super-saturated Solution**

  If the solvent is dissolving more of the solute then it should, under equilibrium conditions; achieved by working on the solution, such as stirring, or preventing equilibrium conditions by rapidly cooling the solution.

The super-saturated condition is unstable and given enough time or a little energy, the solution tends to become stable by rejecting or precipitating the excess solute.

Thus,

- **A solid solution is simply a solution in the solid state and consists of two kinds of atoms combined in one type of space lattice.**
- **There is usually a considerable difference in the solubility of the solute in the liquid and solid states of the solution.**
- **The solute is generally more soluble in the liquid state than in the solid state.**
- **When solidification of the solution starts, the temperature may be higher or lower than the freezing point of the pure solvent.**

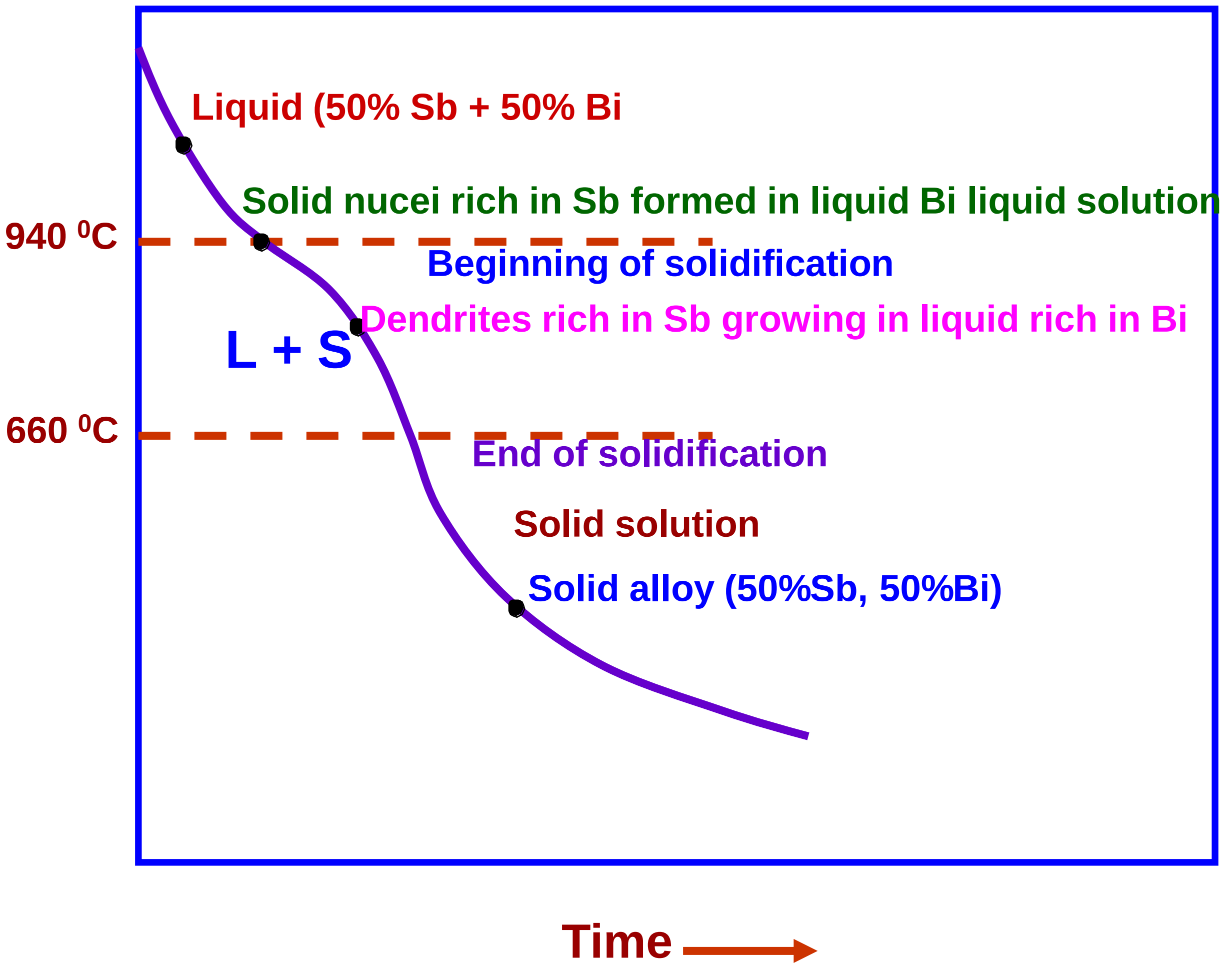


Figure shows the cooling curve for a solid solution alloy containing 50% Sb and 50% Bi, this alloy begin to solidify at a temperature lower than the freezing point of pure Sb (630 ˚C) and higher than the freezing point of pure Bi (300 ˚C).

TYPES OF SOLID SOLUTION

- **Substitutional solid solutions**
- **Interstitial Solid Solutions**

SUBSTITUTIONAL SOLID SOLUTIONS

- ✓ **The atoms of the solute substitute for atoms of the solvent in the lattice structure of the solvent.**

  Example,

  Ag atoms may substitute for Au atoms without loosing the fcc structure of Au and Au atoms may substitute for silver atoms in fcc lattice structure of Ag.

- ✓ **All alloys in the Ag-Au system consist of an fcc lattice with Ag and Au atoms distributed randomly through the lattice structure. The entire system consists of a continuous series of solid solutions.**

FACTOR AFFECTING THE RANGE OF SOLUBILITY IN ALLOY SYSTEMS

CRYSTAL STRUCTURE FACTOR

Complete solid solubility of two elements is never attained unless the elements have same type of crystal lattice structure

RELATIVE SIZE FACTOR

The favorable size factor for solid solution, when the difference in atomic radii is less than about 15 pct. If relative size factor is greater than 8 pct but less than 15 pct, the alloy system usually shows a minimum. If relative size factor is greater than 15 pct, solid solution formation is very limited

CHEMICAL AFFINITY FACTOR

Greater the chemical affinity of two metals, the more restricted is their solid solubility and greater is the tendency toward compound formation. Generally, the farther apart the elements in the periodic table, the greater is their chemical affinity.

RELATIVE VALENCE FACTOR

If the solute metal has a different valence from that of the solvent metal, the number of valence electrons per atom, called the electron ratio, will change. crystal structure are more sensitive to a decrease in the electron ratio than to an increase.

INTERSTITIAL SOLID SOLUTIONS

- **Formed when atoms of small atomic radii fit into the spaces or interstitials of the lattice structure of the larger solvent atoms.**

- **Since the spaces of the lattice structure are restricted in size, only atoms with atomic radii less than 1Å are likely to form interstitial solid solutions. e.g. H (0·46), B (0·97), C (0·77), N (0·71) and O (0·60).**

- **Normally have very limited solubility and generally are of little importance. Carbon in iron is a notable exception and forms the basic for hardening steel. Carbon dissolves in Fe interstitially.**

- **The maximum solubility of C in γ-Fe (fcc) is 2 pct at 1130 ˚C, while the maximum solubility of Carbon in α-iron (bcc) is only 0·025 pct at 723 ˚C.**

SYSTEM

A substance (or group of substances) so isolated from its surroundings that it is unaffected by these and is subjected to changes in overall composition, temperature, pressure or total volume.

It may be composed of gases, liquids, solids or many combinations of them and may involve metals and non-metals, either separately or in combination.

A system is classified according to the number of components that constitute the system.

Components

- ✓ A unit of the composition variable of the system.
- ✓ A system having one component is called a unary system
- ✓ Systems having two, three or four components are known as binary, ternary or quaternary systems respectively.

Structural constituents

- ➢ The phases in alloys are not necessarily uniformly distributed throughout the structure.
- ➢ The association of phases in recognizably distinct fashion may be referred to as structural constituents of the alloy.
- ➢ It is customary to call those parts of the microstructure that have a clearly identifiable appearance under the microscope, the constituents of the structure.

PHASE

- Macroscopically a homogeneous body of matter.
- Used more loosely in speaking of a solid or other solution, which can have a composition varying with position and is designated as a phase.
- For example, there are three separate phases for iron, denoted by α, γ and δ. Actually there are only two different iron phases since the α and δ phases are identical, both are body centered cubic (bcc).

PHASES OF PURE IRON

Stable temperature range	**Form of matter**	**Phase**	**Symbol**
Below 910 ^{0}C	Solid	BCC	α
910 ^{0}C to 1400 ^{0}C	Solid	FCC	γ
1400 ^{0}C to 1539 ^{0}C	Solid	BCC	δ
1539 ^{0}C to 2740 ^{0}C	Liquid	Liquid	Liquid
Above 2740 ^{0}C	Gas	Gas	Gas

PHASE DIAGRAMS

IMPORTANCE AND OBJECTIVES:

- **In order to specify completely the state of a system in equilibrium, it is necessary to specify three independent variables.**
- **These variables, which are externally controllable, are temperature, pressure and composition.**
- **With pressure assumed to be constant at atmospheric value, the equilibrium diagram indicates the structural changes due to variation of temperature and composition.**
- **The diagram is essentially a graphical representation of an alloy system.**
- **Ideally, the phase diagram will show the phase relationships under equilibrium conditions, i.e. under conditions in which there will be no change with time.**
- **Equilibrium conditions may be approached by extremely slow heating and cooling, so that if a phase change to occur, sufficient time is allowed.**

- In actual practice, phase changes tend to occur at slightly higher or lower temperatures, depending upon the rate at which the alloy is heated or cooled.

- Rapid variation in temperature, which may prevent phase changes that would normally occur under equilibrium conditions, will distort and sometimes limit the application of these diagrams.

- Phase diagrams are usually plotted with temperature as the ordinate (Y-axis) and the alloy composition (wt pct) as the abscissa (X-axis).
- Some times the alloy composition is expressed in atomic percent (at. pct).
- The conversion from wt. pct to at. pct may be made by the following method:

$$Atomic\ percent\ of\ A = \frac{100\,X}{X + Y(M/N)}$$

$$Atomic\ \ percent\ \ of\ \ B = \frac{100\,Y(M/N)}{X + Y(M/N)}$$

where, M is the atomic weight of A, N is the atomic weight of B

X is the weight percentage of A, Y is the weight percentage of B

THE PHASE DIAGRAMS ARE USED

- ✓ To predict which phases are in equilibrium for selected alloy compositions at desired temperatures.
- ✓ To determine the chemical composition of each phase.
- ✓ To calculate the quantity of each phase, that is present.
- ✓ To study and control the process as: phase separation, solidification of metals and alloys, purification of materials, the growth and doping of single crystals and structural changes produced by heat treatment, casting etc.

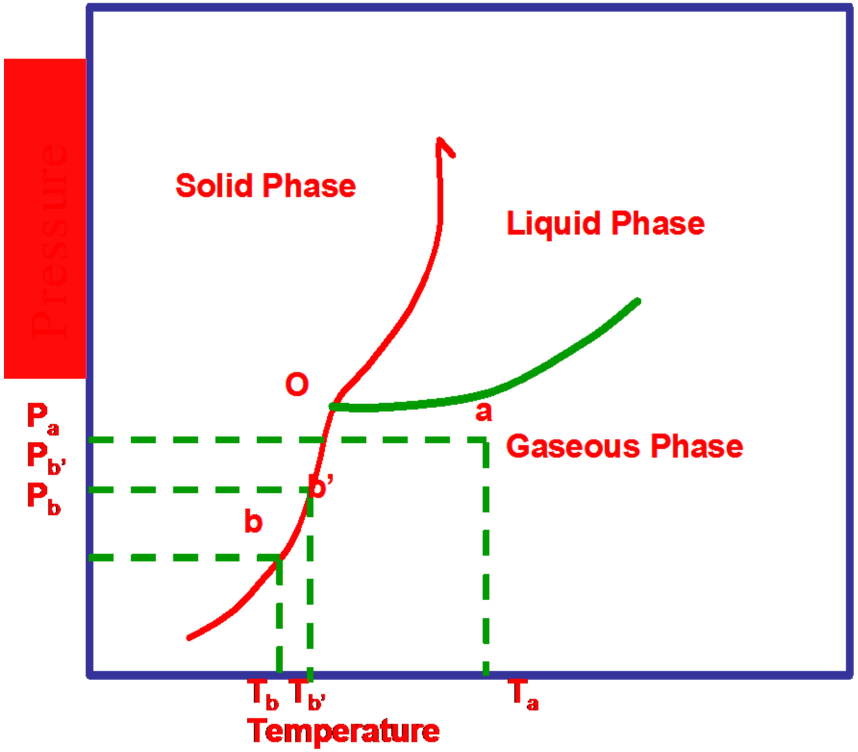
PHASE DIAGRAMS ARE CLASSIFIED AS:

- **Unary (or one component) - plotted as pressure (Y-axis) vs temperature (X-axis)**
- **Bianary (or two component) – plotted as temperature vs composition**
- **Ternary (or three component) – plotted with concentrations as abscissa (X-axis) vs temperature as the ordinate (Y-axis).**

THE PHASE RULE
(Gibb’s phase rule)

Consider a phase diagram of one component system in which the variables are temperature and pressure.

Point a- lying within the limits of gaseous phase, represents a gas whose state is determined by the temperature T_a and pressure P_a.



Changing either or both variables so as to bring the gas to some other arbitrary state (a’) is entirely possible. When a single component system exists as a single phase there are two degrees of freedom.

Consider the case of two phases in a single component system. This can occur only if the state of the system falls along one of the three lines separating the single phase field. e.g., *point b* represents a solid-vapour (gas) mixture in equilibrium at temperature T_b and pressure P_b. If now the temperature is changed to $T_{b'}$ the pressure has to be changed to exactly the $P_{b'}$. If this is not done, the two phase system would become a single phase system, either all solid or all gas, thus implying that there is only one degree of freedom.

The last possibility for the single component system corresponds to the case where three phases are in equilibrium. This can occur only at the triple point O. The 3-phase equilibrium occurs only at one specific combination of temperature and pressure and accordingly there are no degree of freedom.

Two Component (Binary) Systems

- ✓ For a SINGLE PHASE in two component system there are three degrees of freedom. These are normally considered to be temperature, pressure and composition of the phase.
- ✓ In case of TWO PHASES in equilibrium in a binary system there are two degrees of freedom. This confirms that at a chosen temperature and pressure, where two phases could be maintained in equilibrium, the compositions of phases were automatically determined. Of course, it is possible to vary the temperature and pressure, but such variations bring about determinable changes in the composition of phases.
- ✓ Now consider a binary system with THREE PHASES in equilibrium. If the pressure is fixed, three phase equilibrium at one temperature, varying the pressure naturally changes the temperature. However, this indicates that there is only one degree of freedom.
- ✓ The case of FOUR PHASES in a binary system is equivalent to a triple point in a single component system. Four phase equilibrium can occur only at a single combination of temperature and pressure and the compositions of all the phases are fixed. Accordingly, there is no degree of freedom.

The analysis could be extended to systems with larger number of components, but it is simpler to invoke the use of ***Gibb's phase rule***. The rule states that

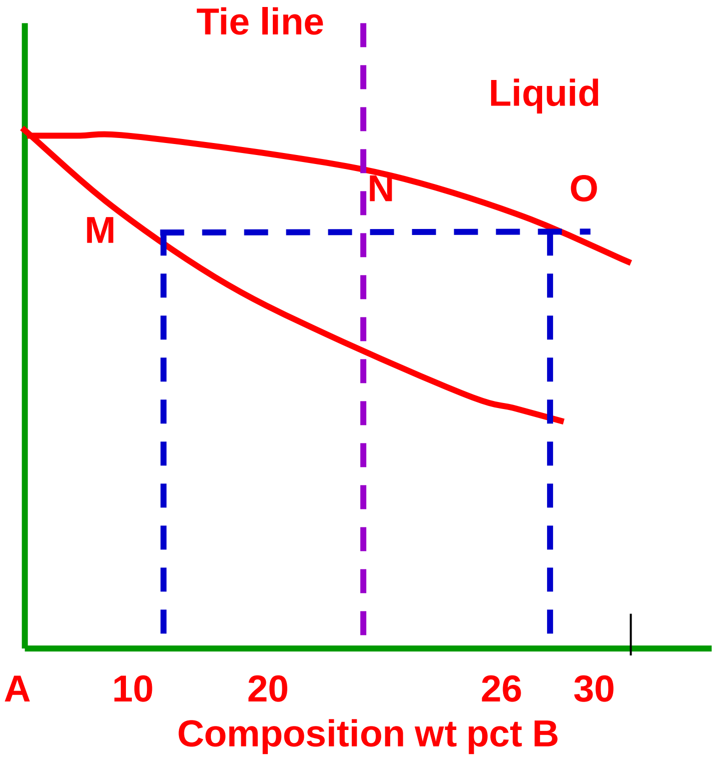
"THE NUMBER OF PHASES P PLUS THE NUMBER OF DEGREES OF FREEDOM F IS ALWAYS EQUAL TO THE NUMBER OF COMPONENTS C PLUS A FACTOR OF 2" i.e.

$$P + F = C + 2$$

Simply, **Police Force = Cops +2**

CHEMICAL COMPOSITION OF PHASES

In order to determine the actual composition of the phases of an alloy, in equilibrium at any specified temperature in a two-phase region, draw a horizontal temperature line, called a tie line, to the boundaries of the field. These points of intersections are dropped to the base line, and the composition is read directly.



- ✓ **Consider the alloy composed of 80A -20B at temperature T. The alloy is in a two phase region.**

- ✓ **MO is the tie line to boundaries of the field. The tie line intersects the solidus line at M, when dropped to the base line it gives the composition of the phase that exists at that boundary.**

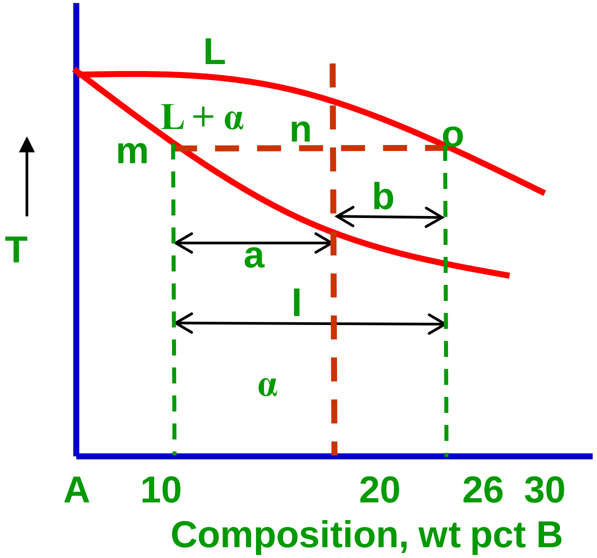
- ✓ **The phase is a solid solution α of composition 90A-10B. Similarly point O, when dropped to the base line, will give the composition of the other phase constituting the mixture, in this case the liquid solution of composition 74A-26B.**

THE LEVER RULE

(Relative amount of each phase)

To determine the relative amounts of the two phases in equilibrium at any specified temperature in a two phase region, draw a vertical line representing the alloy and a horizontal temperature line on the boundaries of the field.

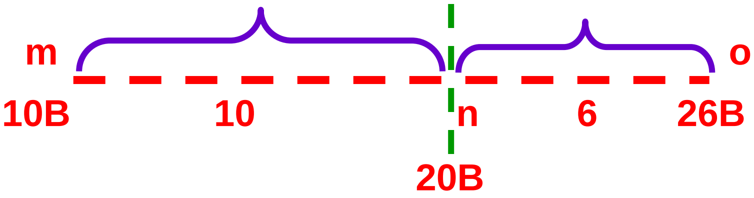
The vertical line will divide the horizontal line into two parts whose lengths are inversely proportional to the amount of phases present. Te point where the vertical line intersects the horizontal line may be considered as the fulcrum of a lever system. The relative length of the lever arms multiplied by the amounts of phases present must balance.



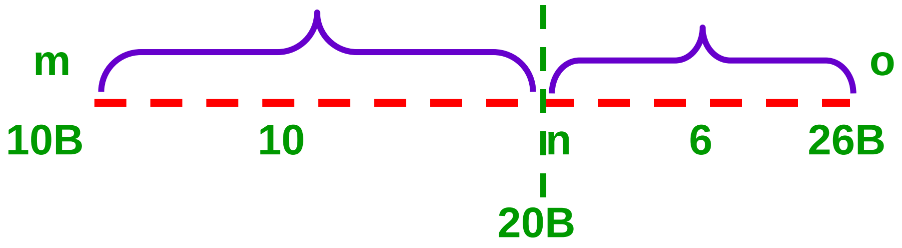
The vertical line representing the alloy 20 B, divides the horizontal tie line into two parts, mn and no. If the entire length of the tie line mo is taken to represent 100 percent, or the total weight of the two phases present at temperature T, the Lever rule may be expressed mathematically as

$$Liquid \quad (percent) = \frac{mn}{mo} \times 100$$

$$\alpha \quad (percent) = \frac{no}{mo} \times 100$$



If the tie line is removed from the phase diagram and the numerical values are inserted



$$wt\ pct\ of\ solid = \frac{composition\ liquid\ phase - average\ composition}{composition\ of\ liquid\ phase - composition\ of\ solid\ phase}$$

$$wt\ pct\ of\ liquid = 100 - wt\ pct\ of\ solid$$

or

$$wt\ pct\ of\ liquid = \frac{Average\ composition - composition\ of\ solid\ phase}{Composition\ of\ liquid\ phase - composition\ of\ solid\ phase}$$

or from Figure

$$wt\ pct\ of\ solid = \frac{mo - mn}{mo} \times 100$$

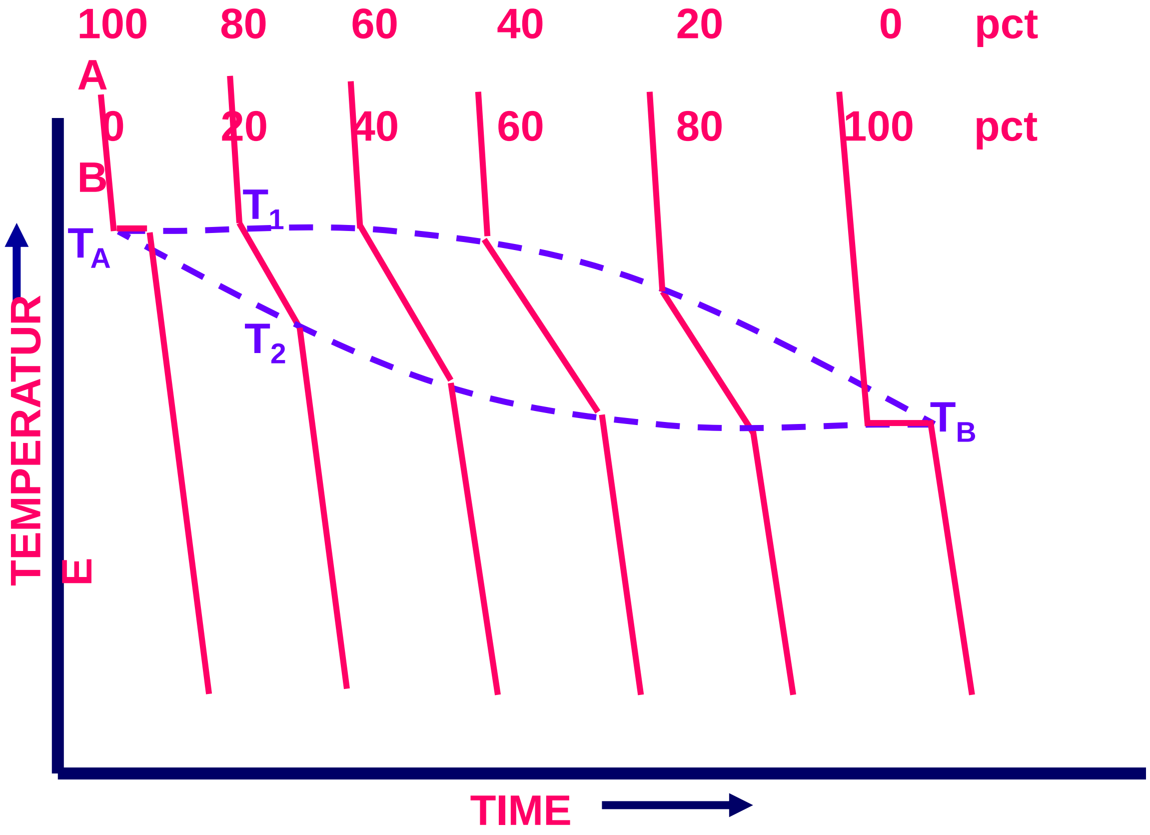
$$wt\ pct\ of\ liquid = \frac{mo - no}{mo} \times 100$$

COOLING CURVES

- **Since two metals are completely soluble in the solid and liquid state, the only type of solid phase formed will be substitutional solid solution.**

- **The two metals will generally have the same type of crystal structures and differ in atomic radii by less than 8 percent.**

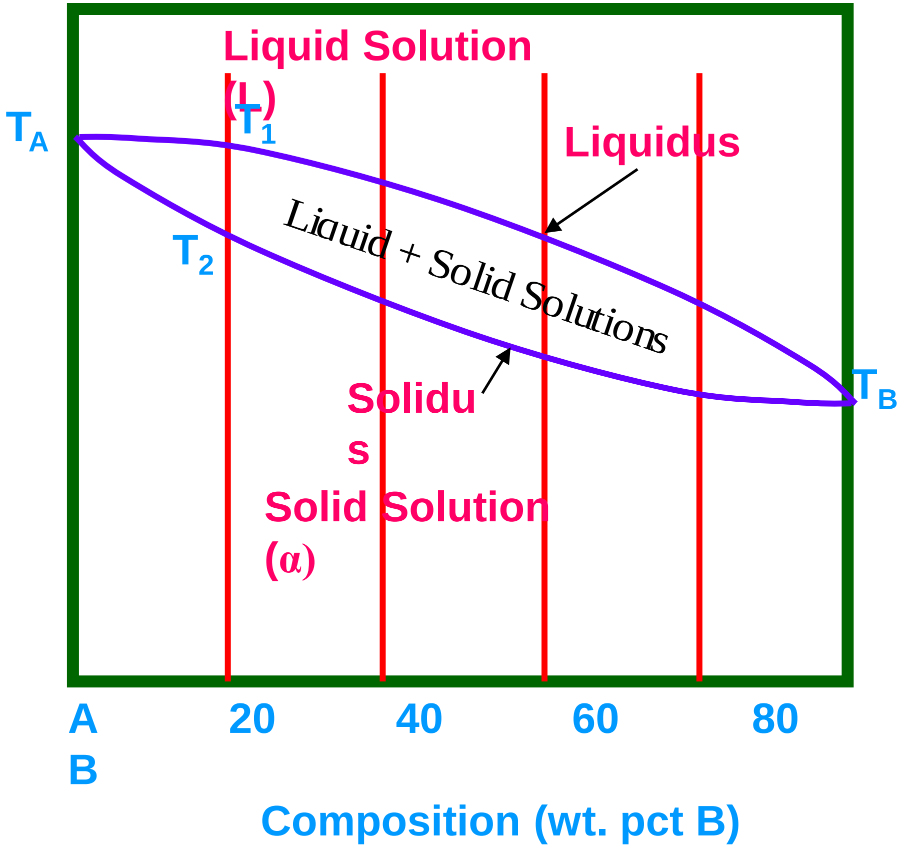
- **Consider a series of cooling curves for various combinations or alloys between A and B, varying from 100 pct - 0 pct A to 0 pct – 100 pct B.**



The cooling curves for the pure metals A and B show only a horizontal line because the beginning and end of solidification takes place at a constant temperature.

However, since intermediate compositions form solid solutions, these cooling curves show two breaks or changes in slope.

- For an alloy containing 80A and 20B, the first break is at T_1, which indicates beginning of solidification and the lower break at T_2 indicates the end of solidification.
- All intermediate alloy compositions will show a similar type of cooling curve.
- The sense of the phase diagram or some idea of its form, may be obtained by drawing a line connecting all points that show the beginning of solidification, the upper dotted line and another line connecting all the points that show the end of solidification.

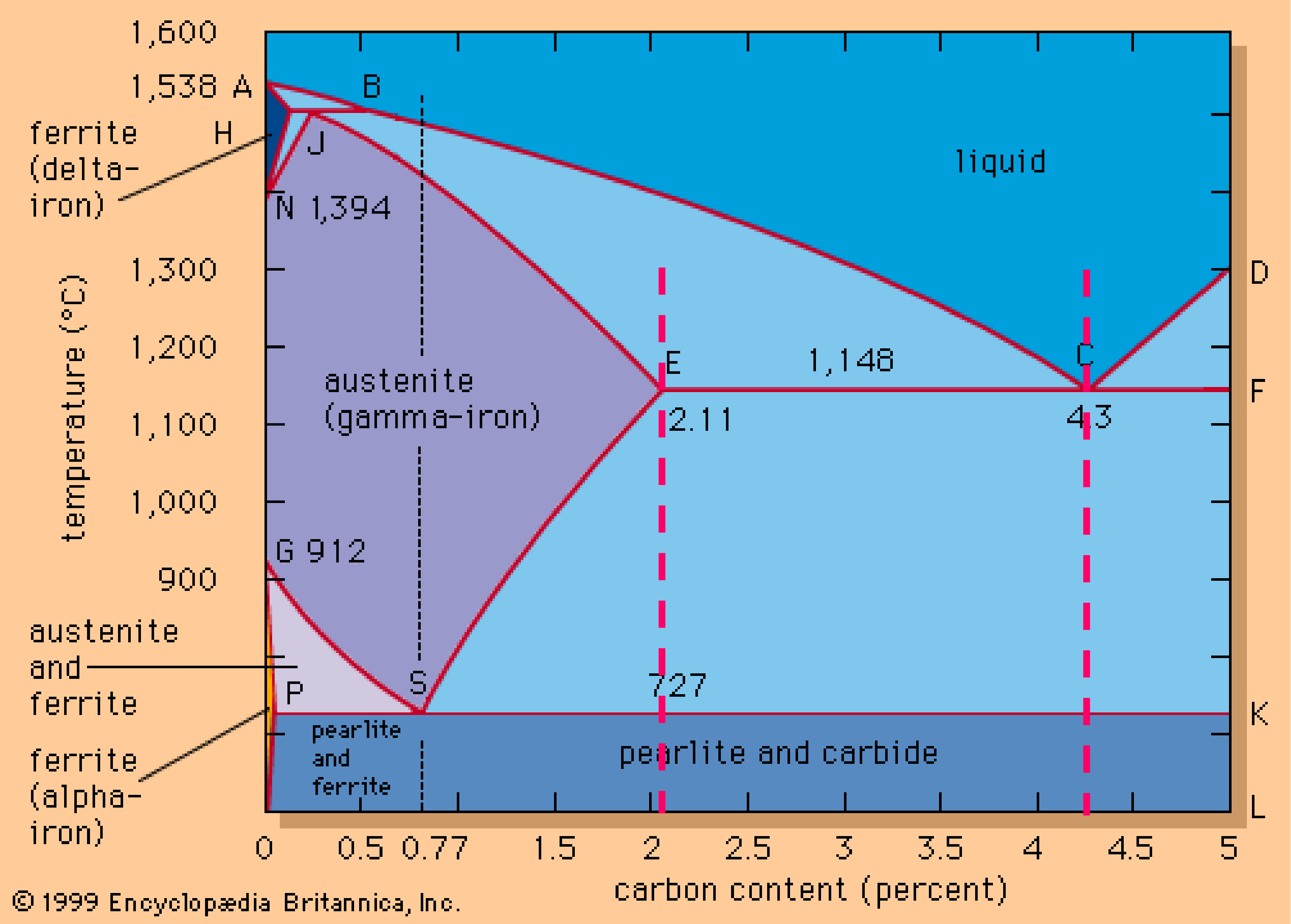


Cooling curves for a binary alloy system

- It is now possible to determine the actual phase diagram by plotting temperature vs composition.
- The appropriate points are taken from the series of cooling curves and plotted on the new diagram.
- Since the left axis represents the pure metal A, T_A is plotted along this line. Similarly T_B is plotted.
- A vertical line representing the alloy 80A – 20B is drawn and T_1 and T_2 from above Figure are plotted along this line. The same procedure is used for other compositions.

- The phase diagram consists of two points, two lines and three areas.
- The two points T_A and T_B represent the freezing points of the two pure metals.
- The upper line obtained by connecting the points showing the beginning of solidification, is called Liquidus line.
- The lower line, determined by connecting the points of end of solidification, is called solidus line.
- The area above the liquidus line is a single phase region, and any alloy in this region will consists of a homogeneous liquid solution.
- Similarly the area below the solidus line is a single phase region, and any alloy in this region will consists of a homogeneous solid solution.
- Between the liquidus and solidus lines there exists a two phase region. Any alloy in this region will consist of a mixture of a liquid solution and a solid solution.
- Specification of temperature and composition of an alloy in a two phase region indicates that the alloy consists of mixtures of two phases but does not give any information regarding this mixture.

IRON–CARBON DIAGRAM



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- **The solubility of carbon varies in different forms of Fe. In δ-iron, maximum solid solubility of C is 0.1%, in γ-iron it is 2.11%.**
- **Austenite(γ) is a solid solution of Carbon in fcc-Fe and solute atoms occupy interstitial positions in this lattice.**
- **In α-Fe (α-ferrite), Carbon has a limited solid solubility of about 0.008% at room temperature. The maximum solubility of carbon in ferrite is 0.025%.**

- There are several temperatures or critical points in the diagram, which are important, both from the basic and from the practical point of view.

- Firstly, there is the A_1, temperature at which the eutectoid reaction occurs (P-S-K), which is 723°C in the binary diagram.

- Secondly, there is the A_3, temperature when α-iron transforms to γ-iron. For pure iron this occurs at 910°C, but the transformation temperature is progressively lowered along the line GS by the addition of carbon.

- The third point is A_4 at which γ-iron transforms to δ-iron, 1390°C in pure iron, but this is raised as carbon is added.

- The A_2, point is the Curie point when iron changes from the ferro- to the paramagnetic condition. This temperature is 769°C for pure iron, but no change in crystal structure is involved.

There are three reactions, which occur in Fe-C diagram.

i. **Peritectic reaction**

In the alloy containing 0.15% C, the initial crystals of δ-solid solution and the whole of liquid phase is completely transformed to form austenite on cooling at 1492 ^{0}C:

$$L+\delta \Leftrightarrow \gamma(austenite)$$

ii. **Eutectic reaction**

Alloy with C content 4.3% (point C), the liquid is transformed into austenite and cementite on cooling at 1148 ^{0}C, i.e.

$$L \Leftrightarrow \gamma + Fe_3C$$

Where Fe_3C is compound known as cementite. It contains 6.67 wt% C. the eutectoid of austenite and cementiote is known as ladeburite.

iii. **Eutectoid reaction**

In Fe-C alloy with 0.8% C (point S), the austenite is transfomed into α-iron and cementite by eutectoid reaction on cooling at 723 0C. Thus

$$\gamma \Leftrightarrow \alpha + Fe_3C$$

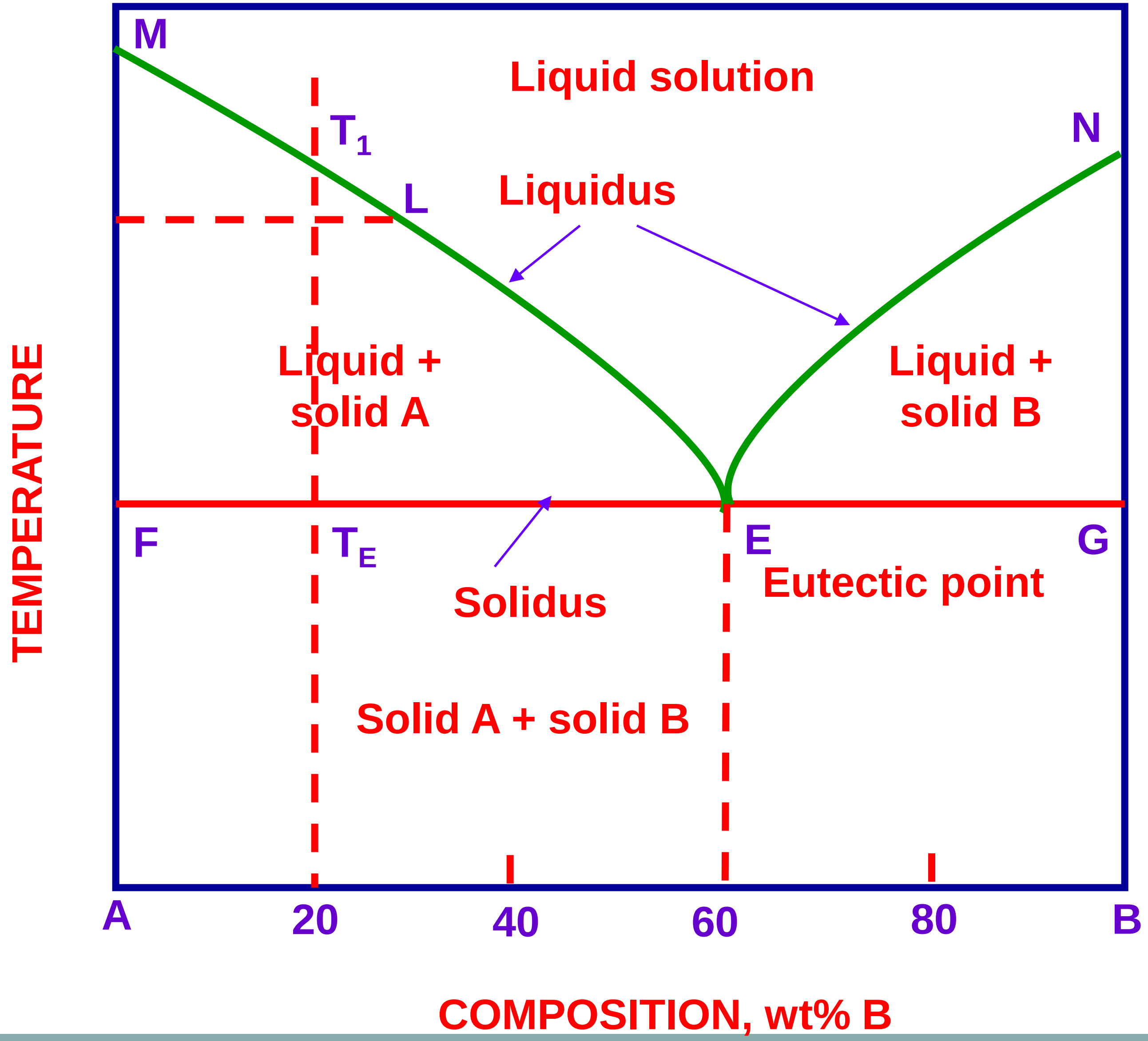
The eutectoid of ferrite and cementite (Fe_3C) is known as pearlite. The ferrite and cementite occur as alternate layers.

Depending upon the C content and reactions occuring in Fe-Fe_3C diagram, the alloys of iron are broadly divided into two groups:

(i) Steel and (ii) Cast iron

EUTECTIC SYSTEMS

- **A reaction when a single liquid phase is transformed into two solid phases is called a eutectic reaction and the transformation is called the eutectic transformation.**
- **The temperature at which reaction takes place is the eutectic temperature, and the composition undergoing the reaction is called the eutectic composition.**
- **The melting points of two pure metals, M and N are plotted on the vertical lines that represent the pure metals.**
- **For an alloy containing 80A-20B the beginning of solidification T_1 and the end of solidification T_E are plotted.**


M
Liquid solution
T_1
N
L
Liquidus
Liquid +
solid A
Liquid +
solid B
F
T_E
E
G
Eutectic point
Solidus
Solid A + solid B
TEMPERATURE
A
20
40
60
80
B
COMPOSITION, wt% B

- **The upper line connecting the two melting points, MEN, is the liquidus line and shows the beginning of solidification.**
- **The point at which the liquidus line intersects the minimum point E, is known as eutectic point. T_E is called the eutectic temperature and 40A-60B, the eutectic composition.**
- **The solidus line is always a continuous line connecting the melting points of the pure metals, so that the complete solidus line is MFGN.**
- **The phase diagram consists of four areas:**
  - ✓ **The area above the liquidus line is a single-phase homogeneous liquid solution, since the two metals are soluble in liquid state.**
  - ✓ **The remaining three areas are two-phase areas. Every two phase area on a phase diagram must be bounded along a horizontal line by single phases.**

TIME-TEMPERATURE-TRANSFORMATIONS

- ✓ **When a phase has been brought into an unstable region e.g. austenite (0.8 %C) cooled below 723 ^{0}C, the equilibrium diagram no longer applies nor does it tell anything about the structure of transformation products or the mechanism of their formation.**

- ✓ **A very slow cooling produces pearlite and very rapid cooling produces martensite. This leaves a middle ground for isothermal transformation or continuous cooling transformation, or some combination of both.**

- ✓ **Isothermal transformation of austenite at subcritical temperatures (< 723 ^{0}C for 0.8 %C) is known as “Time Temperature Transformation (TTT) diagram’, whereas continuous cooling is shown on “Continuous Cooling Transformation (CCT) diagrams”.**

- ✓ **One diagram is required for each alloy composition in contrast to an equilibrium diagram which covers an entire alloy system.**

TTT DIAGRAMS

Depending on the temperature of transformation, austenite may transform to pearlite, bainite, or martensite.

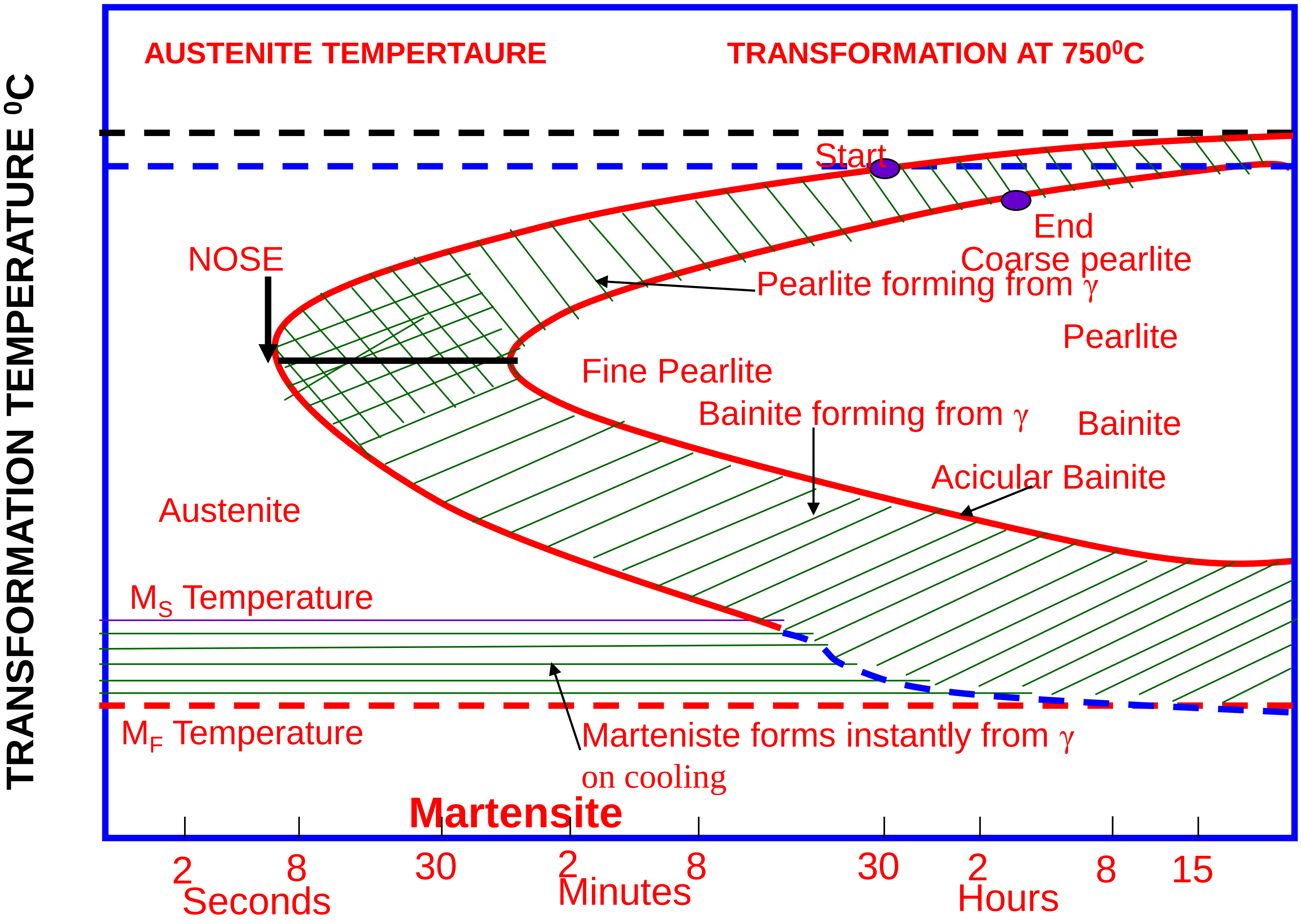
The kinetics of above transformation is indicated on TTT diagram.

IMPORTANCE

- **These diagrams indicate the phase existing in steel at various temperatures and times.**
- **Very much useful in heat-treatment of steel.**
- **One can choose a proper cooling cycle to obtain the desired transformation product (Microstructure) so as to obtain the required properties in the component.**
- **Whereas Fe-C equilibrium diagram is of limited use in the study of steels cooled under no equilibrium conditions, TTT diagram is the principle source of information on the actual process of austenite decomposition under non equibrium condition.**

DETERMINATION OF TTT DIAGRAMS

- **TTT diagrams are graphical summaries of isothermal transformation data.**
- **A large number of relatively small specimens, at equilibrium above critical temperature, are quenched in a liquid bath maintained at constant subcritical temperature.**
- **Specimens are withdrawn at regular intervals and quenched in iced brine to prevent further transfomations.**
- **Microstructures are examined to determine the beginning (usually 0.5% or 1%) and the end (99.5% or 99% respectively) of transformation at given temperatures.**
- **A series of these tests at several temperatures allow construction of such diagrams (e.g for eutectoid carbon steel (Figure)). Because of their shapes, these curves are sometimes called ‘S’ curves or ‘C’ curves.**


AUSTENITE TEMPERTAURE
TRANSFORMATION AT 750⁰C
TRANSFORMATION TEMPERATURE ⁰C
Start
End
Coarse pearlite
NOSE
Pearlite forming from γ
Pearlite
Fine Pearlite
Bainite forming from γ
Bainite
Acicular Bainite
Austenite
MS Temperature
MF Temperature
Marteniste forms instantly from γ
on cooling
Martensite
2
8
30
2
8
30
2
8
15
Seconds
Minutes
Hours

Transformation of eutectoid steel just below critical temperature is to pearlite at a very slow rate.

As the transformation temperature is decreased, the rate increase rapidly to a maximum at 540 0C.

- Transformation of austenite to pearlite is a nucleation and growth process, dependent on diffusion and therefore, on temperature. Nucleation rate increases, and growth rate decreases with decreasing temperature.
- Transformation temperatures influences both reaction rate and resulting microstructure.
- Pearlite which forms just below 723 ^{0}C has relatively thick lamellae, which are essentially parallel.
- The pearlite structure become progressively fine until final transformation temperature is about 500-600 ^{0}C, i.e., at the nose. Below this temperature, austenite transforms to bainite.
- The change in spacing between alternate lamellae in pearlite has pronounced effect on mechanical properties