

Table 10.1 Relevant Factors Regarding Hume-Rothery Conditions

System		Crystal structure	Atomic radius (Å)	Valency	Electro-negativity
Si-Ge	Si	DC	1.18	4	1.8
	Ge	DC	1.22	4	1.8
Cu-Al	Cu	FCC	1.28	1	1.9
	Al	FCC	1.43	3	1.5
Ni-Cu	Ni	FCC	1.25	2	1.8
	Cu	FCC	1.28	1	1.9
Au-Ag	Au	FCC	1.44	1	2.4
	Ag	FCC	1.44	1	1.9
Cu-Zn	Cu	FCC	1.28	1	1.9
	Zn	HCP	1.39	2	1.6

10.5 PHASES

Physically-distinct, mechanically-separable, and chemically-homogeneous portion of a system is called a *phase*. A substance can have different phases such as

1. gaseous phase,
2. liquid phase,
3. solid phase,
4. solid-liquid phase, and others.

The gaseous state or a liquid solution are single phases in themselves. The atoms or molecules of chimney exhaust gases mix readily in air. Sugar dissolves in water and a liquid solution is formed. In the above cases, each system has a single phase. Contrary to these, a liquid mixture of water and petrol has two phases. These two liquids do not form a chemically homogeneous mixture as they do not mix together.

Solids may have one or many phases. Hence, they are grouped as

1. single phase solids, and
2. multi phase solids

Normally single crystal materials and pure metals have single phase. *Quartz, monocrystal titanium and pure copper* are such examples. Polycrystalline materials and alloys may have single or multiphase. Multiphase solids are rocks, ceramics, polymers, wood; iron and steel, and alloys. Multiphases for single solid and two solid systems are explained in this chapter later on.

10.5.1 Gibb's Phase Rule

Composition and phases of materials may be understood well if the phase relations are known. Gibb has enunciated a rule, better known as *Gibbs phase rule*, which is given by

$$D = C - P + \lambda \quad (\lambda = 2) \quad \dots (10.1)$$

where D is degrees of freedom; C represents number of components, P the number of phases in equilibrium, and λ the system variables. The system variables are only 2 viz. pressure and temperature, therefore $\lambda = 2$ in Eq. 10.1.

In a system, the number of degrees of freedom D which is equal to the number of independent variables, cannot exceed total number of variables (dependent and independent). Total number of variables in a system is equal to

$$P(C - 1) + 2 \quad \dots(10.2)$$

Therefore

$$D = C - P + 2 \leq P(C - 1) + 2 \quad \dots (10.3)$$

For $C = 2$ in a phase, the number of variables is $(C - 1) = (2 - 1)$. For a system having P phases, total number of variables in the composition will be $P(C - 1)$. By adding 2 external variables p and T , total number of variables become $P(C - 1) + 2$.

The degree of freedom cannot be negative. At the most it can be zero. It is evident from Eq. 10.1 that the degree of freedom decreases when number of phases increases. For example, in a two phase system like Cu and Ni, the degree of freedom is two.

Example 10.1 How many phases are possible in a two component system ? Compute total number of variables and degrees of freedom for all the possible number of phases.

Solution. Recall Eq. 10.1,

$$D = C - P + 2$$

where $C = 2$ for two components system. Let $P = 1, 2, 3, 4, 5 \dots$ etc.

From Eq. 10.2, we know that the total number of variables

$$= P(C - 1) + 2$$

The required computations are done as below.

No. of phases	No. of total variables	Degrees of freedom
P	$P(C - 1) + 2$	$D = C - P + 2$
1	$1(2 - 1) + 2 = 3$	$2 - 1 + 2 = 3$
2	$2(2 - 1) + 2 = 4$	$2 - 2 + 2 = 2$
3	$3(2 - 1) + 2 = 5$	$2 - 3 + 2 = 1$
4	$4(2 - 1) + 2 = 6$	$2 - 4 + 2 = 0$
5	$5(2 - 1) + 2 = 7$	nonexistent

The degree of freedom = 0 when $P = 4$. Hence a two component system cannot have more than 4 phases in equilibrium.

10.6 PHASE DIAGRAMS

Plots showing relations between phases in equilibrium versus composition, pressure and temperature are called *phase diagrams*. These are also known as equilibrium diagrams. Temperature is plotted on ordinate (y-axis) and composition (in binary phase diagrams) or pressure (in unary phase diagram) on abscissa (x-axis)

in a phase diagram. The composition is expressed in percent weight. We can see from these diagrams the change in phases with respect to the changes in temperature or composition. Phase diagrams are always drawn at equilibrium state because a system always tries to be stable. The alloy systems involve a number of components. Based on these, the phase diagrams are classified as below.

1. Unary phase diagram (single component system)
2. Binary phase diagram (two components system)
3. Ternary phase diagram (three components system),
4. Quaternary phase diagram (four components system), and so-on.

We shall deal here with unary and binary phase diagrams. Ternary phase diagram may be referred to in reference [1].

10.6.1 Unary Phase Diagram

Such phase diagrams are drawn for a single component system. Question of composition and compositional variable does not arise in it. Hence the phase map indicates temperature T on y-axis and pressure p on x-axis.

Consider the case of iron (Fe) whose phase diagram is shown in Fig. 10.2. The diagram indicates different phases as a function of temperature and pressure. The

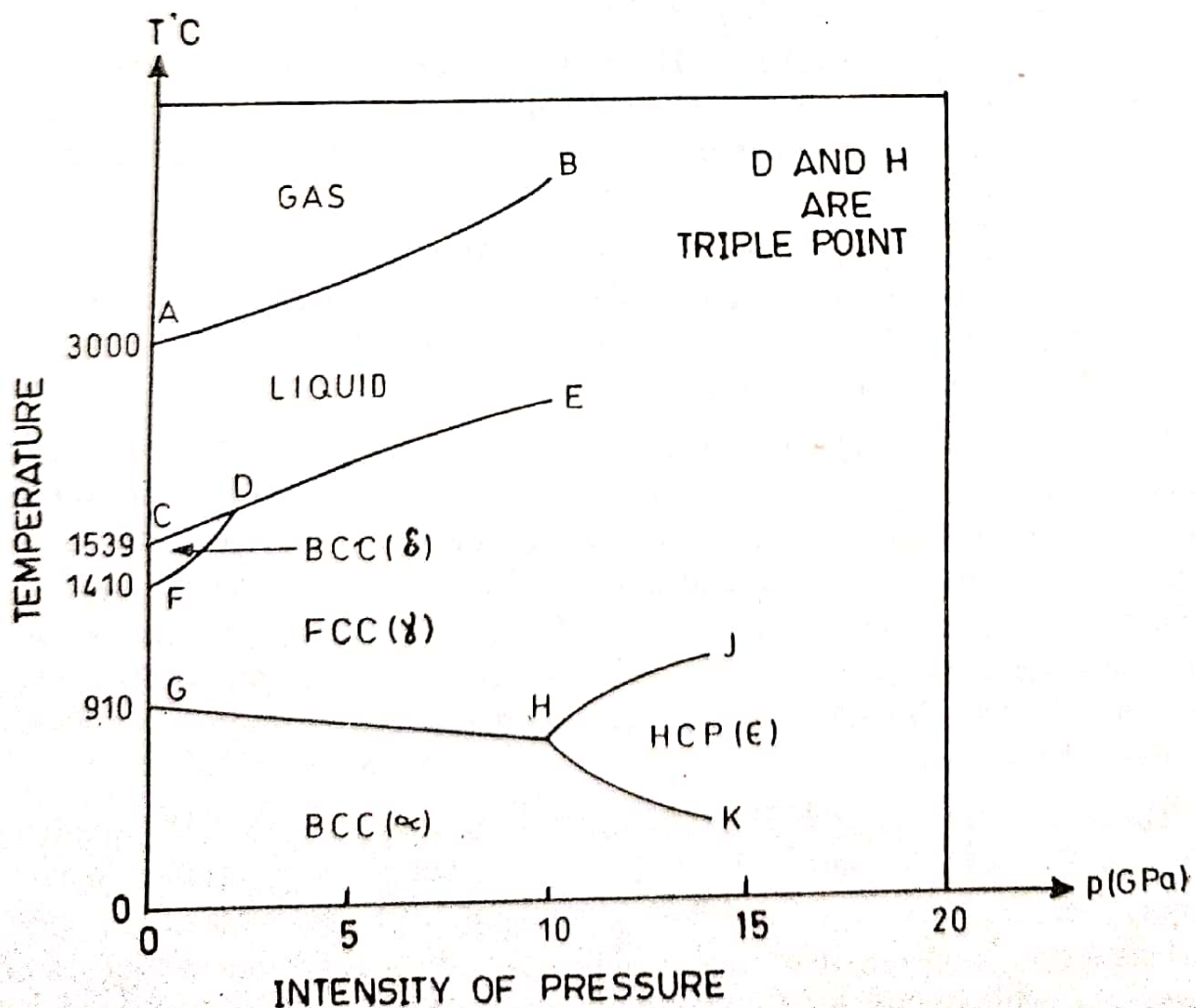


Fig. 10.2 Unary phase diagram of single component system of iron showing gas, liquid and phases as a function of temperature and pressure.

gases, liquids, and solid forms of iron are single phases. The boundaries AB , CDE , FDE , GHJ and GHK are phase boundaries for two phase equilibrium. Here $D = 1$ which implies that either temperature or pressure may be varied. If we want to maintain two phase equilibrium on these boundaries, then pressure and temperature both are required to be changed accordingly.

Three phase boundaries meet at points D and H . These points are known as *triple points*. Here, $D = 0$ and three phase equilibrium exists. As the degree of freedom is zero *i.e.* system is constraint, neither pressure nor temperature can be varied. Crystal forms of iron such as BCC (α), FCC (γ) and BCC (δ) are obtained at increasing temperatures. BCC (α) form converts to HCP (ϵ) form near a pressure of about 15 GPa.

10.7 BINARY PHASE DIAGRAM

Such diagrams are a result of two components systems. In addition to *pressure* and *temperature*, a third variable 'composition' is also involved now. It, therefore, necessitates a three dimensional diagram to depict phases. However for simplicity of plotting phase diagrams on paper; the temperature is taken on ordinate and composition on abscissa for a specified pressure. The specified pressure is generally atmospheric. As pressure variable is avoided arbitrarily, Eq. 10.1 may be written as

$$D = C - P + 1 \quad \dots(10.4)$$

Two component systems obeying Hume-Rothery's conditions, and exhibiting complete solid solubility as well as liquid solubility result into binary phase diagrams. The two involved components dissolve in all proportions into each other in solid and liquid states.

A schematic binary phase diagram is shown in Fig. 10.3. The two components are A and B . Percentage weight composition of A varies between 0 to 100 from left to right while that of B varies between 0 to 100 from right to left on horizontal axis named as composition or c -axis. Temperature is plotted on ordinate.

There are two single phase regions, viz. the solid and the liquid. Solid phase region lies below $T_S MNT_L$ boundary. The liquid phase region lies above $T_S Q T_L$ boundary. There is also present a two-phase region marked $L + S$. It lies between the above two boundaries. Solid and liquid phases co-exist in this region. The boundary $T_S MNT_L$ between solid phase and $(L + S)$ phase, is called solidus while $T_S Q T_L$ between liquid phase and $(L + S)$ phase, is known as liquidus. T_S is the temperature below which the system is in solid phase, and T_L is the temperature above which the liquid phase exists.

The horizontal line $Q N$ at temperature T_1 is called the tie-line. Another horizontal line RS is tie-line at T_2 temperature. If our interest is to obtain mix composition of components A and B at T_1 temperature, we consider tie-line QN . The intersection of this tie-line with liquidus at Q gives liquid composition C_L , and intersection with solidus at N gives solid composition C_S . From Eq. 10.4, the degrees of freedom are

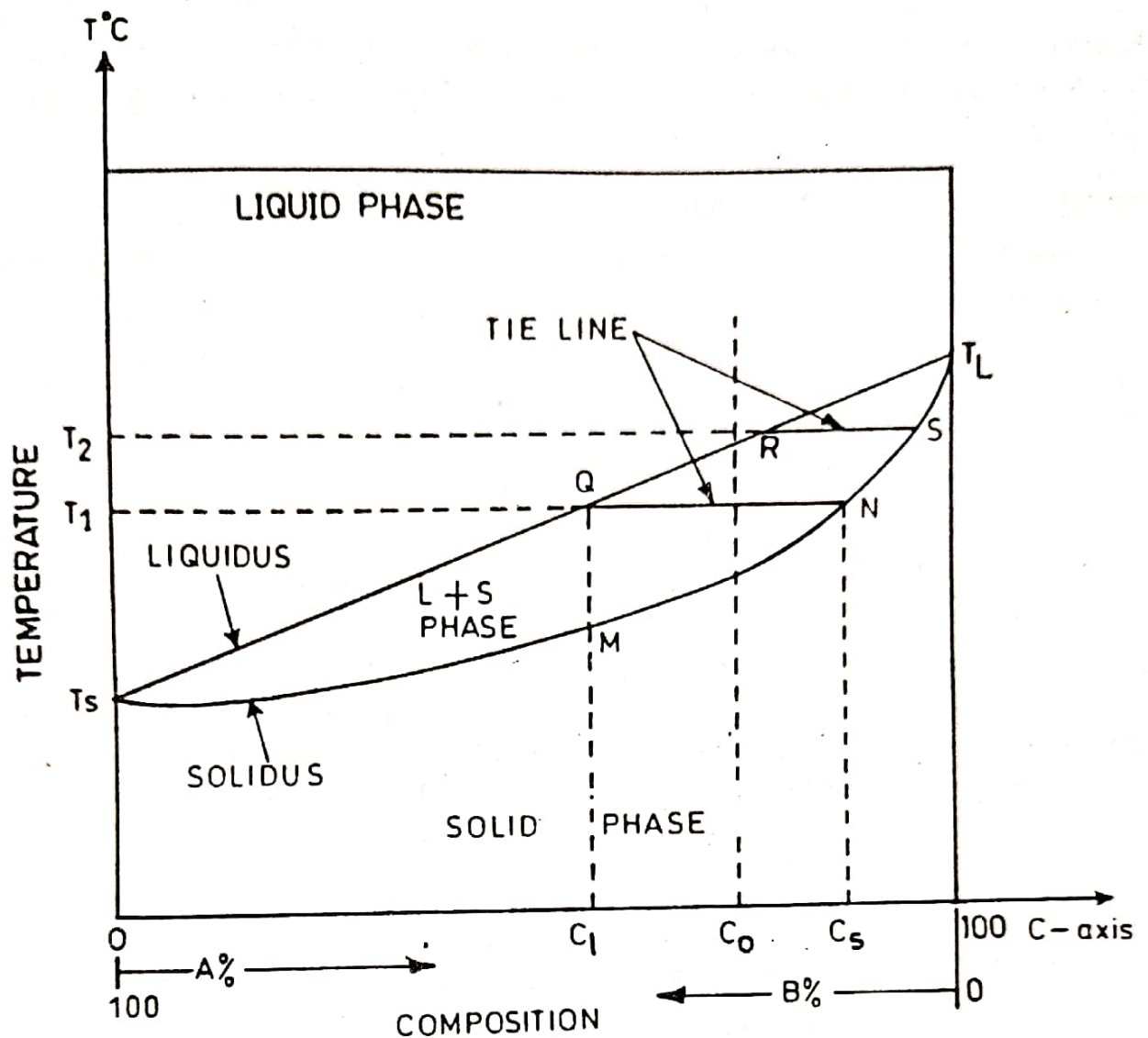


Fig. 10.3 Binary phase diagram between two components showing different phases as a function of composition and temperature.

$$D = 2 - 1 + 1 = 2 \text{ for single phases,}$$

and

$$D = 2 - 2 + 1 = 1 \text{ for two phase region.}$$

As $D = 1$ for two-phase region, only one out of three variables named below may be varied.

1. Temperature
2. Liquid composition C_L , and
3. Solid composition C_S .

We are not free to choose any percent combination of two components at any arbitrary temperature. Either temperature is to be pre-fixed or composition of one phase is to be specified initially.

Depending on small or large, complete or incomplete, and limited or unlimited solid solubility of elements and compounds; and also the melting points of the two components; the binary phase diagrams may be further classified as follows.

1. Eutectic phase diagram
2. Eutectoid phase diagram
3. Peritectic phase diagram
4. Peritectoid phase diagram

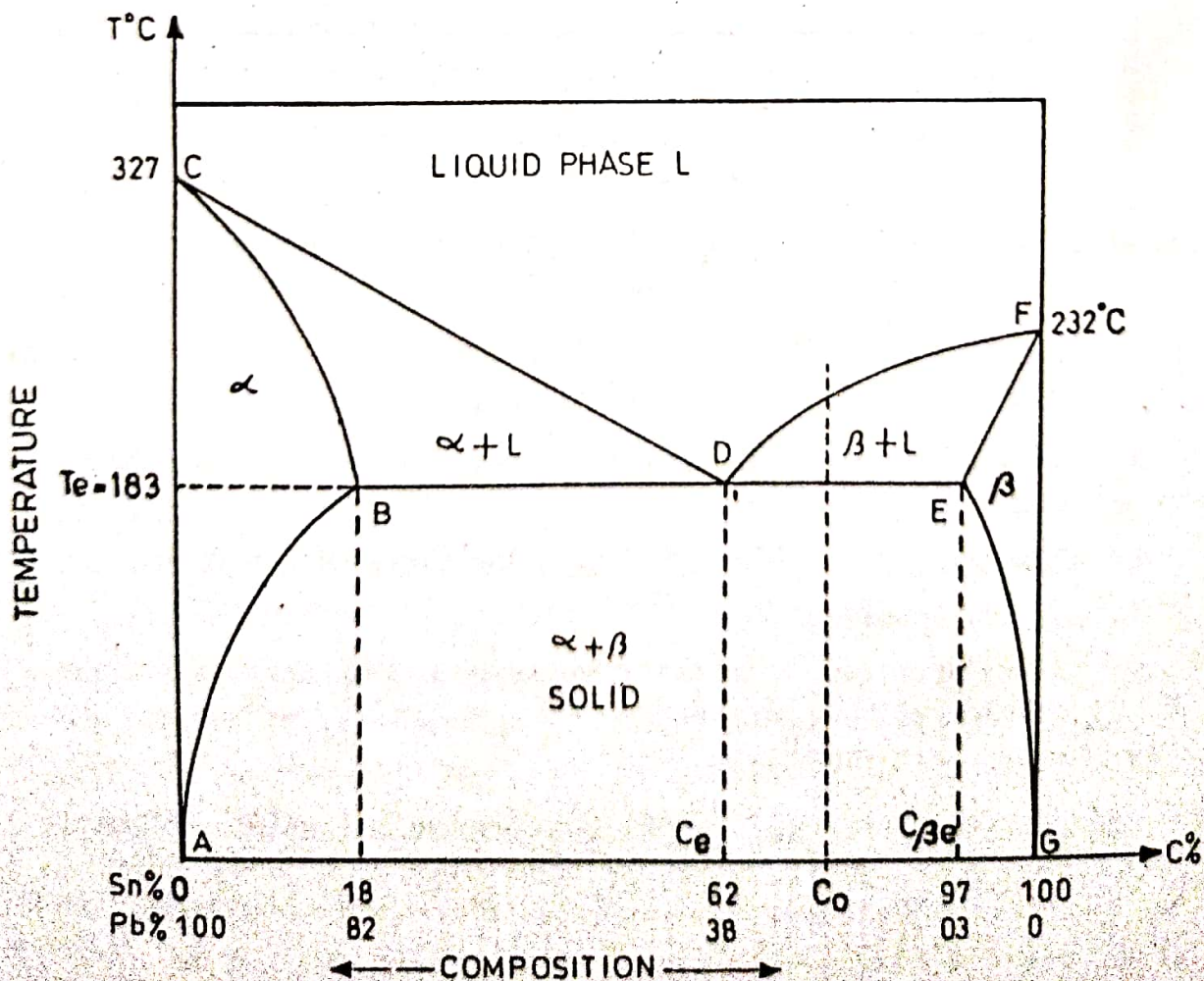
Eutectic, eutectoid, peritectic and peritectoid terms are related to phase transformations, and are discussed in following sections with their respective phase diagrams.

10.7.1 Eutectic Phase Diagram

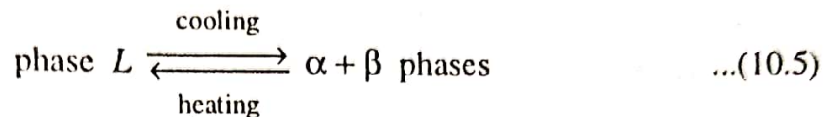
An eutectic phase diagram is obtained when the melting points of the two components of phase diagram are neither very close nor much different. Only liquid solubility exists in such cases. The solid solubility may be negligible or partial. Solid solubility is never zero even in an unfavourable condition. Thus, there are two cases of eutectic phase diagrams viz.

1. *Complete liquid solubility with negligible solid solubility.* Cadmium-bismuth system is the example, and
2. *Complete liquid solubility with partial solid solubility.* Lead-tin system is the example of this case.

The phase diagram of lead-tin alloy system is shown in Fig. 10.4. Melting points of lead (Pb) and tin (Sn) are 327°C and 232°C respectively. In the solid α phase, a very small amount of tin is dissolved in lead. The other solid phase is β in which very small quantity of lead is dissolved in tin. Both the components dissolve



in each other sufficiently in $(\alpha + \beta)$ phase. Two-phase regions $(\alpha + \beta)$ and $(\alpha + L)$, $(\alpha + \beta)$ and L ; $(\alpha + \beta)$ and $(\beta + L)$ are separated by a horizontal line BDE . This line corresponds to a temperature T_e known as *eutectic temperature*. Composition at point D is called *eutectic composition* C_e . At this point, the liquid phase L transforms to $(\alpha + \beta)$ phase during cooling and vice-versa during heating. It can be expressed by an *eutectic reaction* as given below.



Composition of Sn and Pb at points B, D and E are shown at eutectic temperature. These cannot be varied because degree of freedom for three phases in equilibrium is zero. It can be verified by Eq. 10.4 which yields

$$D = 2 - 3 + 1 = 0$$

The eutectic temperature and eutectic reaction are called *invariant temperature* and *invariant reaction* respectively to indicate $D = 0$.

In Fig. 10.4 different phases are separated by various phase boundaries, whose details are given below.

- Boundary CD between L and $\alpha + L$ phases is liquidus I.
- Boundary DF between L and $\beta + L$ phases is liquidus II.
- Boundary BC between α and $\alpha + L$ phases is Solidus I.
- Boundary EF between β and $\beta + L$ phases is Solidus II.
- Boundary AB between α and $\alpha + \beta$ phases is Solvus I.
- Boundary EG between β and $\alpha + \beta$ phases is Solvus II.

Composition of alloys left to the point D are called *hypoeutectic alloys*, and those to the right are known as *hypereutectic alloys*.

Example 10.2 In the microstructure of Pb-Sn solder alloy, it was found that 88% of the area is occupied by the eutectic constituent and the remaining area by the proeutectic β phase. Assuming that the area fractions are equal to the volume fractions, determine the approximate composition of the alloy. The densities of α and β phases are 10300 kg/m^3 and 7300 kg/m^3 respectively.

Solution. Let the densities of Pb and Sn be ρ_{Pb} and ρ_{Sn} . From Fig. 10.4, it is obvious that at point B, the composition of lead in α -phase = 82%, and composition of tin in α -phase = 18%.

Therefore,

$$\frac{82}{\rho_{\text{Pb}}} + \frac{18}{\rho_{\text{Sn}}} = \frac{100}{10300} \quad \dots(i)$$

Similarly at point E, for β -phase, these compositions are 97% and 3% for tin and lead respectively. Hence

$$\frac{3}{\rho_{\text{Pb}}} + \frac{97}{\rho_{\text{Sn}}} = \frac{100}{7300} \quad \dots(ii)$$

On solving Eqs. (i) and (ii) we obtain

$$\rho_{\text{Pb}} = 11364.1 \text{ kg/m}^3 \text{ and } \rho_{\text{Sn}} = 7220.14 \text{ kg/m}^3$$

Let density of eutectic composition is ρ_e . Knowing the compositions at point D, we can write

$$\frac{38}{\rho_{\text{Pb}}} + \frac{62}{\rho_{\text{Sn}}} = \frac{100}{\rho_e} \quad \dots(iii)$$

Substitution of densities of lead and tin in Eq. (iii), gives

$$\frac{38}{11364.1} + \frac{62}{7220.14} = \frac{100}{\rho_e}$$

$$\therefore \rho_e = 8381.6 \text{ kg/m}^3$$

It is given that there is 88% eutectic composition by volume. Its conversion in weight proportions yields

$$W = 88\% \times \rho_e = 0.88 \times 8381.6 = 7375.77 \text{ kgf}$$

$$\therefore W_{\text{Pb}} = 38\% W = 0.38 \times 7375.77 = 2802.8 \text{ kgf}$$

$$\text{and } W_{\text{Sn}} = 62\% W = 0.62 \times 7375.77 = 4572.98 \text{ kgf}$$

There is 12% β -phase by volume which on conversion to weight proportions gives

$$W' = 12\% \rho_{\beta} = 0.12 \times 7300 = 876 \text{ kgf}$$

$$W'_{\text{Pb}} = 3\% W' = 0.03 \times 876 = 26.28 \text{ kgf}$$

$$\text{and } W'_{\text{Sn}} = 97\% W' = 0.97 \times 876 = 849.72 \text{ kgf}$$

Total weight of lead and tin can be estimated now as

$$W''_{\text{Pb}} = W_{\text{Pb}} + W'_{\text{Pb}} = 2802.8 + 26.28 = 2829.08 \text{ kgf}$$

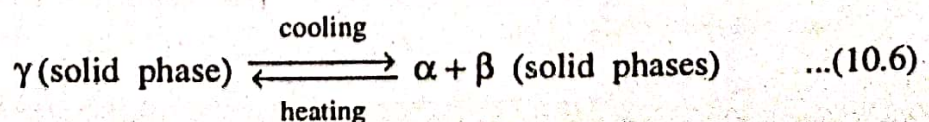
$$\text{and } W''_{\text{Sn}} = W_{\text{Sn}} + W'_{\text{Sn}} = 4572.98 + 849.72 = 5422.7 \text{ kgf}$$

Hence

$$\begin{aligned} \% \text{ of Sn} &= \frac{W''_{\text{Sn}}}{W''_{\text{Pb}} + W''_{\text{Sn}}} \times 100 = \frac{5422.7}{2829.08 + 5422.7} \times 100 \\ &= 65.71 \end{aligned}$$

10.7.2 Eutectoid Phase Diagram

The transformation of liquid phase into solid phases on cooling and vice-versa has been described in the previous section. In eutectoid system, a solid phase replaces the liquid phase of eutectic system. The eutectoid reaction involves transformation of a solid phase into two other solid phases on cooling and vice- versa, and is expressed as



Recall Eq. 10.5 whose phase L has been replaced here by γ phase. If this replacement is done in Fig. 10.4, it will constitute $\alpha + L$ phase as $\alpha + \gamma$, and $\beta + L$ phase as $\beta + \gamma$ phase respectively. T_e will now be known as eutectoid temperature, and the composition at point D will be called *eutectoid composition*. The alloy compositions left to point D is known as hypo-eutectoid, and towards right of D is called *hyper-eutectoid*.

An eutectoid reaction takes place at 723°C in iron-carbon system (art. 10.8) where eutectoid composition contains 0.83% carbon. Here, the austenite, a solid solution of carbon in γ -iron decomposes into two solid phases named ferrite (α -iron) and the cementite (Fe_3C). These are shown later in Fig. 10.9. Eutectoid reaction occurs in other systems also such as Cu-Be, Al-Mn, Cu-Sn, Cu-Al etc.

10.7.3 Peritectic Phase Diagram

Such a phase diagram is obtained when the melting points of two components differ too much from each other. The gold-lead system is an example. Here the melting points of gold and lead are 1063°C and 327°C respectively. Thus a vast difference of 736°C exists. Another example is that of silver (Ag) and platinum (Pt) system whose phase diagram is shown in Fig. 10.5. The difference in melting point of platinum (1769°C) and silver (961°C) is more than 800°C . Various solid phases,

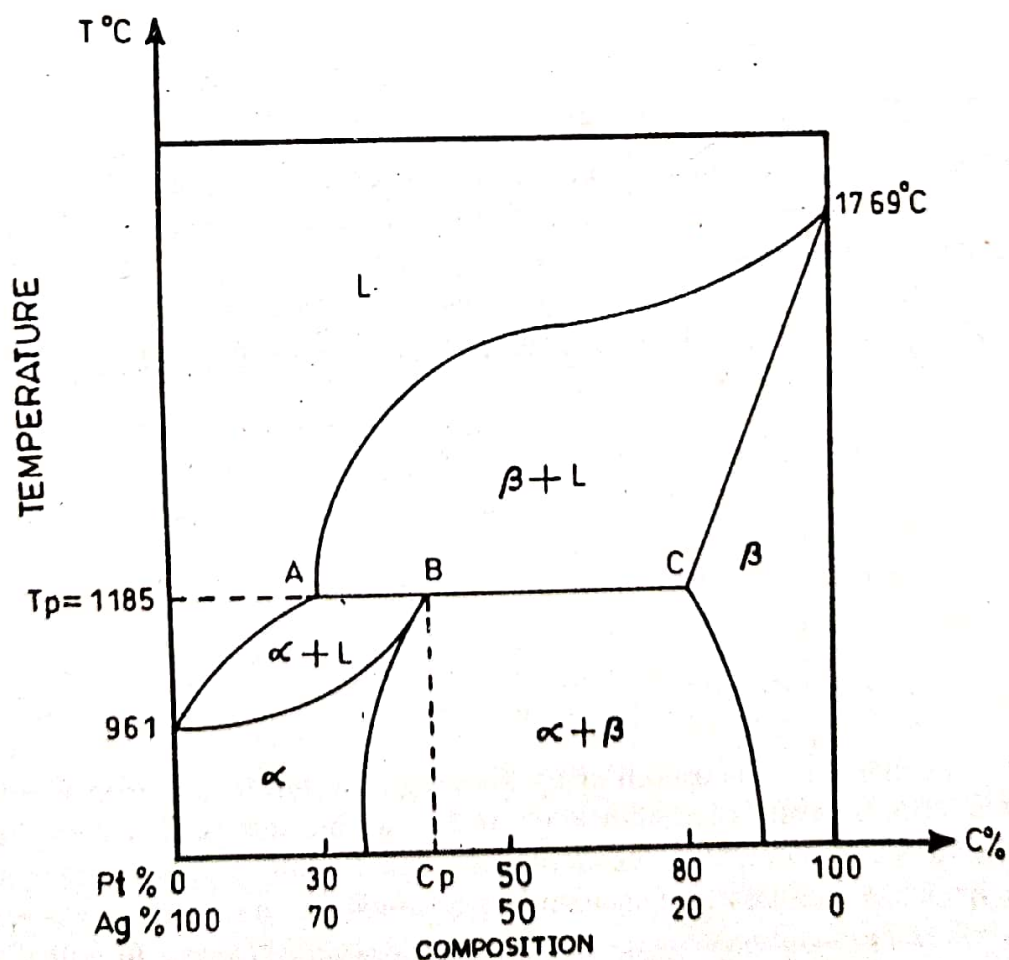
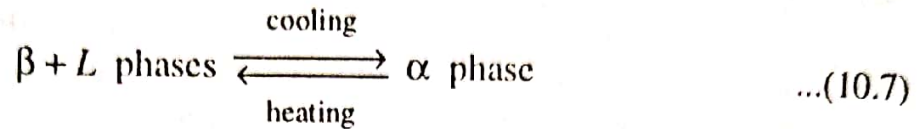


Fig. 10.5 Binary Ag-Pt phase diagram showing phases, peritectic temperature and peritectic composition.

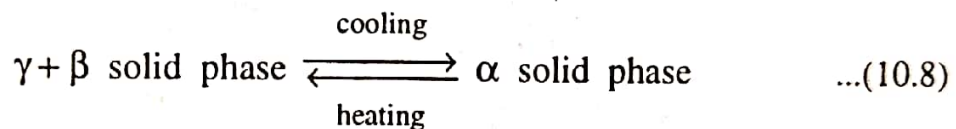
two-phase regions and liquid phase are shown. Horizontal tie-line ABC denotes *peritectic temperature* T_p which is 1185°C . The composition C_p at point B is called *peritectic composition*. At this point, the solid-liquid phase $\beta + L$ transforms to a single solid phase α on cooling, and vice-versa. The degree of freedom is zero here. So the peritectic reaction is an invariant reaction, and follows



Different phase boundaries are named in a similar manner as described for eutectic phase diagram.

10.7.4 Peritectoid Phase Diagram

Such phase diagrams involve transformation of two solid phases into a different solid phase on cooling, and vice-versa. Contrary to peritectic reaction where solid-liquid phase $\beta + L$ changes to another solid phase α ; here solid-solid phase changes to another solid phase. It is given by



10.7.5 Microstructural Changes

Refer to phase diagrams of preceding articles. Liquid phase first changes to solid-liquid phase, and finally to solid phase during cooling. If variation in the rate of cooling is slow to fast, say 200°C per hour to 200°C per second, different microstructures will develop. If we consider the slow rate of cooling which is a general procedure, the likely microstructural changes in overall composition of binary system will be shown by Figs. 10.6a-f.

Microstructure of single liquid phase above the liquidus is shown in Fig. 10.6a. On cooling we obtain two phase co-existing solid- liquid phase, Fig. 10.6b. The solid crystals float on the liquid phase. On further cooling, the system crosses the solidus and crystallizes into a polycrystalline solid, Fig. 10.6d. The above changes are true for the case when two components have almost similar melting points. However for eutectic solid solutions, Fig. 10.6c, the β crystals float in the liquid of eutectic composition below eutectic temperature,

The eutectic composition of Pb-Sn alloy on solidification is shown by Fig. 10.6e. The α -crystals are embedded in the eutectic matrix. The compositional adjustments are brought by the atoms moving across the liquid-crystal boundary. Such adjustments are a rare phenomenon in solids due to slow atomic movement. This induces inhomogeneity in composition that is called *Coring*. In cubic crystals, the preferential grow occurs along $\langle 100 \rangle$ directions. During initial solidification, a tree like structure develops, Fig. 10.6f. This is called *dendritic structure*.

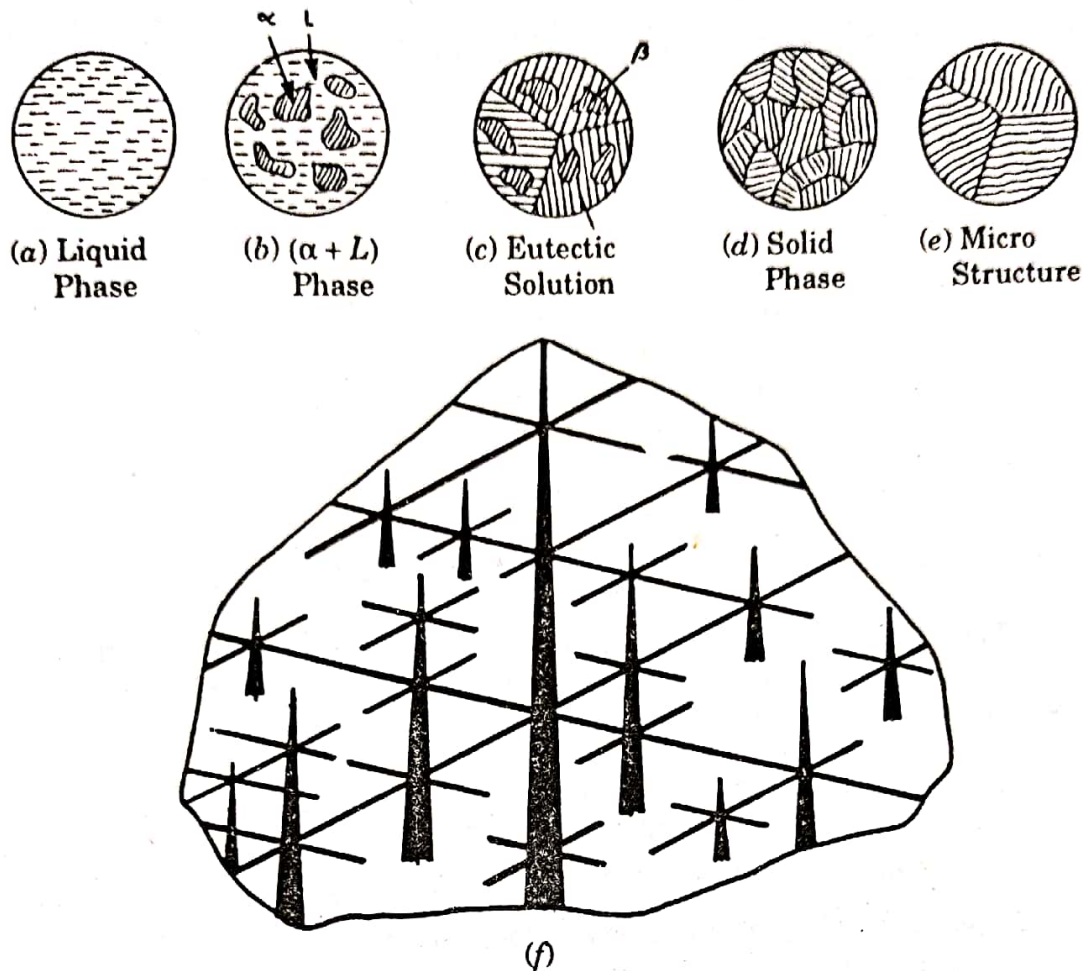


Fig. 10.6 (a–e) Microstructural changes in alloy systems showing different phases, and (f) dendritic structure.

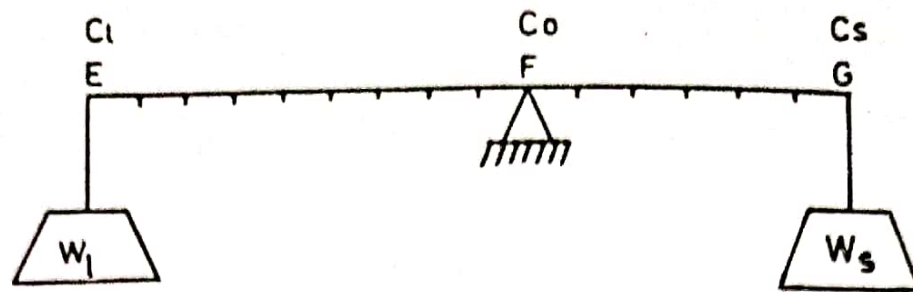
10.7.6 Lever Rule

Lever rule is employed to obtain relative amounts of co-existing phases of a binary system. For overall compositions C_o lying on the tie-line in Fig. 10.3, the compositions of the liquid and solid phases C_l and C_s remain the same. The tie-line is analogous to a lever arm of mass balance having its fulcrum at C_o .

For arm to be horizontal *i.e.* the two components to be in phase equilibrium, the weight W to be hung at the ends of lever arm must be proportional to the length of the arm on two opposite sides of the fulcrum. The weight, here, corresponds to the amount of phase at that end. The relative amounts of solid and liquid phases at specified temperature and overall composition are determined by depiction of lever rule as shown in Fig. 10.7. Weight fractions of liquid and solid are W_l and W_s respectively on lever arm EFG whose fulcrum is at F . These are obtained as

$$W_l = \frac{FG}{EG} = \frac{C_s - C_o}{C_s - C_l} \quad \dots(10.9)$$

$$\text{and } W_s = \frac{EF}{EG} = \frac{C_o - C_l}{C_s - C_l} \quad \dots(10.10)$$



EFG = ARM OF THE LEVER
 C_o = OVERALL COMPOSITION
 C_l = LIQUID COMPOSITION
 W_l = WEIGHT FRACTION OF LIQUID
 F = FULCRUM
 C_s = SOLID COMPOSITION
 W_s = WEIGHT FRACTION OF SOLID

Fig. 10.7 Lever rule showing weight percentage of component A in binary components system A and B.

The lever rule is not applicable at eutectic or peritectic points as three phases exist in equilibrium at these temperatures. It can be applied just below or just above the invariant line. The lever rule may be used to calculate

1. The fraction of a proeutectic phase.
2. The fraction of an eutectic mixture, and
3. The fraction of phase of an eutectic mixture.

In all the above cases, overall composition C_o is always kept at the fulcrum.

Refer Fig. 10.4 in which C_o is the overall composition. The two ends of the lever arm correspond to phase boundary compositions of $C_{\beta e}$ and C_e where C_e is the average composition of eutectic mixture. We then obtain

$$W_{\text{pro}\beta} = \frac{C_o - C_e}{C_{\beta e} - C_e} \quad \dots(10.11)$$

and
$$W_{\text{eut}} = \frac{C_{\beta e} - C_o}{C_{\beta e} - C_e} \quad \dots(10.12)$$

To obtain total β , which is the sum of proeutectic β and the β in eutectic mixture, we use

$$W_{\text{total}\beta} = \frac{C_o - C_{\alpha e}}{C_{\beta e} - C_{\alpha e}} \quad \dots(10.13)$$

Example 10.3 In Al-Si system, eutectic reaction occurs at 577°C and phases α (containing 1.65 wt % Si), liquid (containing 12.6 wt % Si) and pure Si are in equilibrium. The solubility of α -phase decreases with decreasing temperature. Melting points of Al and Si are 660°C and 1410°C respectively. Sketch an approximate phase diagram and calculate the weight fractions of α in an alloy containing 10% Si at 576.9°C .

Solution. The phase diagram is drawn in a similar manner as given in the text for different systems. The composition axis is taken on the horizontal and

10.8 IRON-CARBON EQUILIBRIUM DIAGRAM

It has already been discussed that carbon has different forms. Iron (Fe) with carbon (C) in graphite form is more stable than iron with iron carbide (Fe_3C) component in Fe- Fe_3C phase diagram. Fe_3C is contained by steels having widely varying carbon content, hence we shall study the metastable phase diagram of Fe- Fe_3C . Weight percent of carbon is plotted on x-axis against the temperature on y-axis as shown in Fig. 10.9. Various solid phases are marked by α and γ symbols. Single liquid phase L , solid-liquid phases $\gamma + L$ etc. and the solid-solid phases $\alpha + \text{Fe}_3\text{C}$ and $\gamma + \text{Fe}_3\text{C}$ etc. are shown in it.

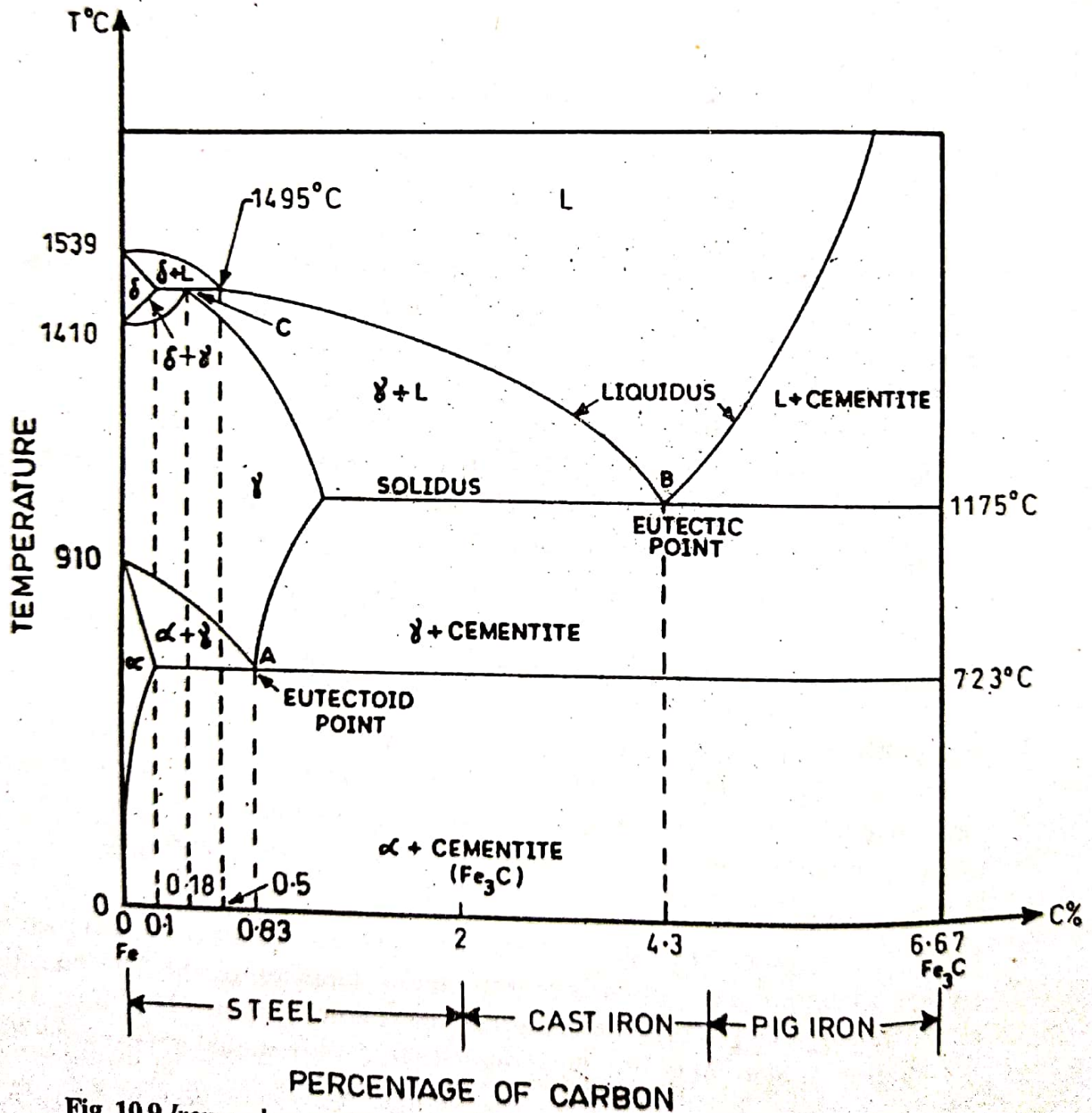
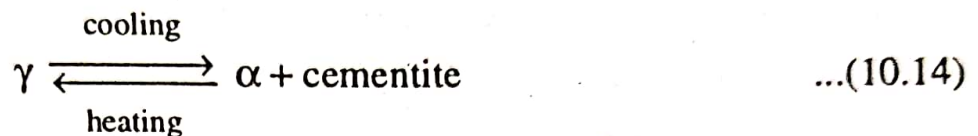
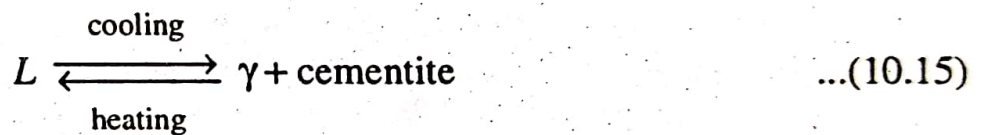


Fig. 10.9 Iron-carbon equilibrium diagram showing different phases and salient features.

In Fig. 10.9, point A is eutectoid point. The eutectoid temperature is 723°C and eutectoid composition is 0.83% carbon. Eutectoid reaction is expressed by



The eutectoidal mixture of ferrite and cementite is called *pearlite*. This is a microconstituent. Fraction of ferrite in eutectoid steel is 88%. Point B is eutectic point whose coordinates are $C_e = 4.3\%$ carbon and $T_e = 1175^\circ\text{C}$. The eutectic reaction is expressed as



Peritectic reaction occurs at point C where peritectic composition is 0.18% carbon and peritectic temperature is 1495°C. Here, the invariant reaction is



Melting point of iron in its purest form is 1539°C. It lowers down with an increase in the percentage of carbon and is lowest (about 1175°C) at 4.3% carbon. The α -phase is called *ferrite*, Fe_3C is *cementite* and γ -phase is known as *austenite*. We have already described in chapter 1, the classification of iron and steel based on percentage of carbon. Iron and steel are also termed as *ferritic steel* in α -region, *austenitic steel* in γ -region and *cast iron* when carbon percentage exceeds 2%.

12.1 TERMINOLOGIES AND PHASE TRANSFORMATIONS INVOLVED WITH HEAT TREATMENT

Before understanding the mechanism of heat treatment processes, it is desired to learn some terms and the involved phase transformations. These terms are given below and the phase transformations are given in subsequent articles.

Nucleation is the process of formation of tiny stable particles from a liquid. Nucleation may be *homogeneous* or *heterogeneous*. In homogeneous nucleation the formation of particles is identical, but in heterogeneous nucleation it is non-identical.

Growth is the process in which the size of stable particles increases when more atoms join the nucleated particles.

Supercooling is an occurrence in which a melt at high temperature T_1 cools down when brought into direct contact with a container which has a much lower temperature T_2 ($T_2 \ll T_1$). Supercooling causes nucleation at a very fast rate and results in the formation of fine crystals.

Decalescence points. During heating of steel, the temperature becomes almost constant at certain points though the heat input remains unaltered. These points are called decalescence points. Structural changes occur at these critical points. These points A_{c1} , A_{c2} , A_{c3} are shown in Fig. 12.5.

Recalescence points are similar to decalescence points, but are noticed during cooling of steel. These critical points A_{r1} , A_{r2} , A_{r3} are shown in Fig. 12.5. Each critical point is separated from the other by about 30°C . The recalescence points are lower than the decalescence points.

Solidification is a phase transformation process in which *liquid* phase transforms to a crystalline solid phase on cooling.

12.2 EFFECT OF RATE OF COOLING ON CRYSTALLIZATION AND HEAT TREATMENT

Transformation of a material from liquid or glassy state to crystalline solid state on cooling is referred to as *crystallization*. A liquid or glassy state may not always

transform to a solid that is crystalline. The transformed solid may be non-crystalline too. Infact, the rate of cooling plays a vital role in determining the nature of the solid.

Slow rate of cooling promotes crystallization whereas a faster cooling rate may prevent crystallization. The slow or fast rate of cooling differs for different materials. A cooling rate of 10^6 K/s may prevent crystallization in metals while a rate of less than 1 K/hour may do so in silicates. In some alloys, crystallization may not occur even due to *splat cooling* (i.e. at cooling rate of 10^7 or more K/s). Low viscosity of liquid metals (1 to 10 poise) helps in rapid crystallization.

Recall art. 9.4.1 in which it was explained that the materials having fine grains possess better mechanical properties. An increase in the cooling rate yields finer crystals. *Ultrafine grain sizes* may be obtained by rapid solidification at a cooling rate of the order of 10^4 to 10^5 K/s. Higher the cooling rate, lower is the dimension of a component produced. Rate of cooling and related information are given in Table 12.1.

Table 12.1 Nature of Cooling and Transformation Time

<i>Nature of cooling</i>	<i>Transformation time (second)</i>	<i>Dimension of a component (μm)</i>	<i>Application</i>
Splat	10^{-7}	0.1-10	Some alloys
Extremely fast	10^{-6} to 10^{-5}	100	Ultrafine grain sizes are obtained
Very fast	10^{-5} to 10^{-3}	1000	Metallic glasses
Fast	10^{-3} to 10^0	10 000	Quenching
Average (Normal)	10^1 to 10^2	—	—
Slow	10^2 to 10^3	—	—
Very slow	10^4 to 10^5	—	Small sand castings
Extremely slow	10^6 to more	—	Large sand castings

Besides rapid cooling, finer grain sizes can also be obtained by adding grain refining agents (nucleating agents). Ni, NaCl, AgI and TiO_2 are used as nucleating agents. They increase the rate of heterogeneous nucleation. *Synthetic diamond* is produced from graphite by adding nickel. *Ice crystals* can be easily nucleated in the presence of NaCl and AgI. These agents are also employed to form *artificial clouds*. TiO_2 is used to produce crystallized glass (*pyroceram*). Some oxides are added in silica to impart crystallinity.

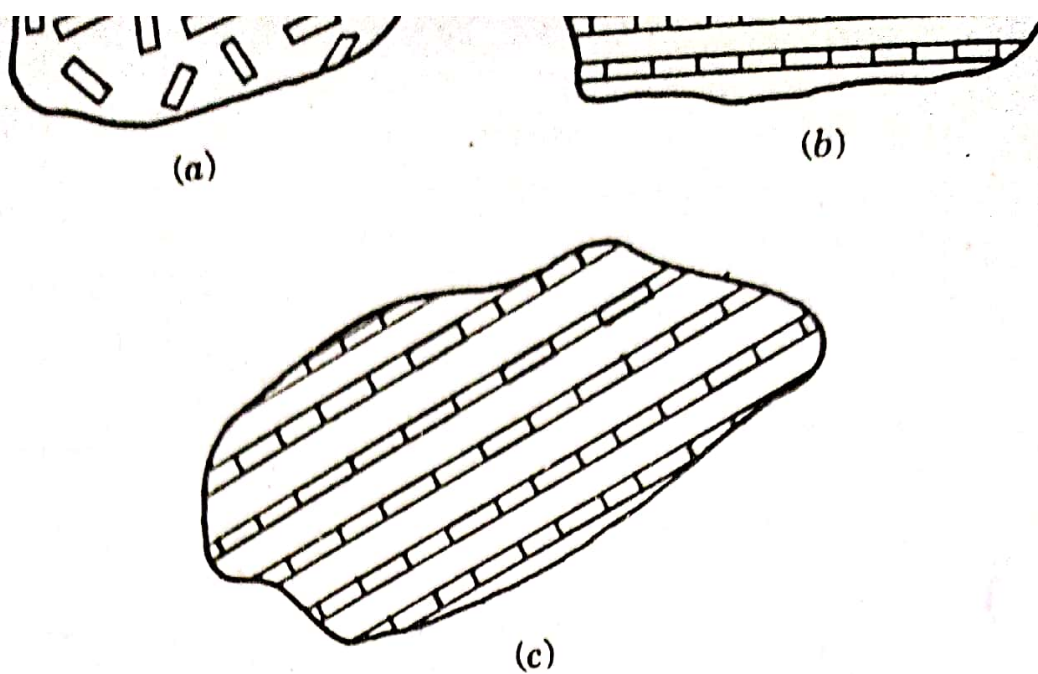


Fig. 12.3 Grains orientation (a) random, and (b) (c) preferred.

12.6 HEAT TREATMENT: AN INTRODUCTION

The properties of metals and alloys can be changed by heating followed by cooling under definite conditions to make them suitable for specific applications. Accordingly steel can be hardened to resist cutting action and prevent abrasion. The rate of cooling and the manner of cooling are the controlling factors in heat treatment processes. Heat treatment not only increases the hardness but also increases the tensile strength and toughness. Different heat treatment processes are carried-out in temperature controlled furnaces and ovens.

12.6.1 Various Types of Heat Treatment

Various heat treatment processes may be classified as follows.

1. Tempering

- (a) Austempering, (b) Martempering, and
- (c) Temperature based
 - (i) low temperature tempering,
 - (ii) medium temperature tempering, and
 - (iii) high temperature tempering.

2. Annealing

- (a) Process annealing (b) Full annealing
- (c) Spheroidise annealing (d) Diffusion annealing.

3. Normalising

4. Hardening

- (a) Case hardening (or carburising)
 - (i) solid or pack (ii) liquid, and (iii) gaseous
- (b) Flame hardening (c) Induction hardening
- (d) Age hardening or Precipitation hardening
- (e) Cyaniding (f) Nitriding

Besides these conventional methods, some advanced techniques are also adopted on steel. These are

- 1. Ion nitriding 2. Plasma carburizing
- 3. Electron beam hardening 4. Laser hardening

Details on these advanced techniques may be referred in related texts.

12.7 PURPOSE OF HEAT TREATMENT

The heat treatment processes serve the following purposes. They

- 1. produce hard surfaces and tough interior portions.
- 2. increase resistance to wear, abrasion and corrosion.
- 3. modify magnetic and electrical properties.
- 4. improve mechanical properties such as tensile strength, ductility, shock resistance etc.
- 5. improve machinability.
- 6. refine the grains.
- 7. relieve the internal stresses produced during cold working and other operations.
- 8. change the chemical composition.

12.8 MICROSTRUCTURES OF STEEL AND IRON

Carbon is found in different forms in iron and steel, therefore various microstructures are found in them. These are as given below.

- 1. Ferrite 2. Cementite
- 3. Pearlite 4. Ludeburite
- 5. Martensite 6. Troostite
- 7. Sorbite 8. Austenite
- 9. Bainite 10. Allotropic forms

Ferrite. It is soft and ductile. It cannot be hardened by rapid cooling. Low carbon steel and wrought iron consist of ferrite. It is in the form of flakes, Fig. 12.4a.

Cementite. It is carbide of iron (Fe_3C), and is extremely hard. The hardness increases with the increase in carbon content. Presence of carbon in iron and steel increases the hardness but decreases the ductility. The carbon is in the form of knots in cementite, Fig. 12.4b.

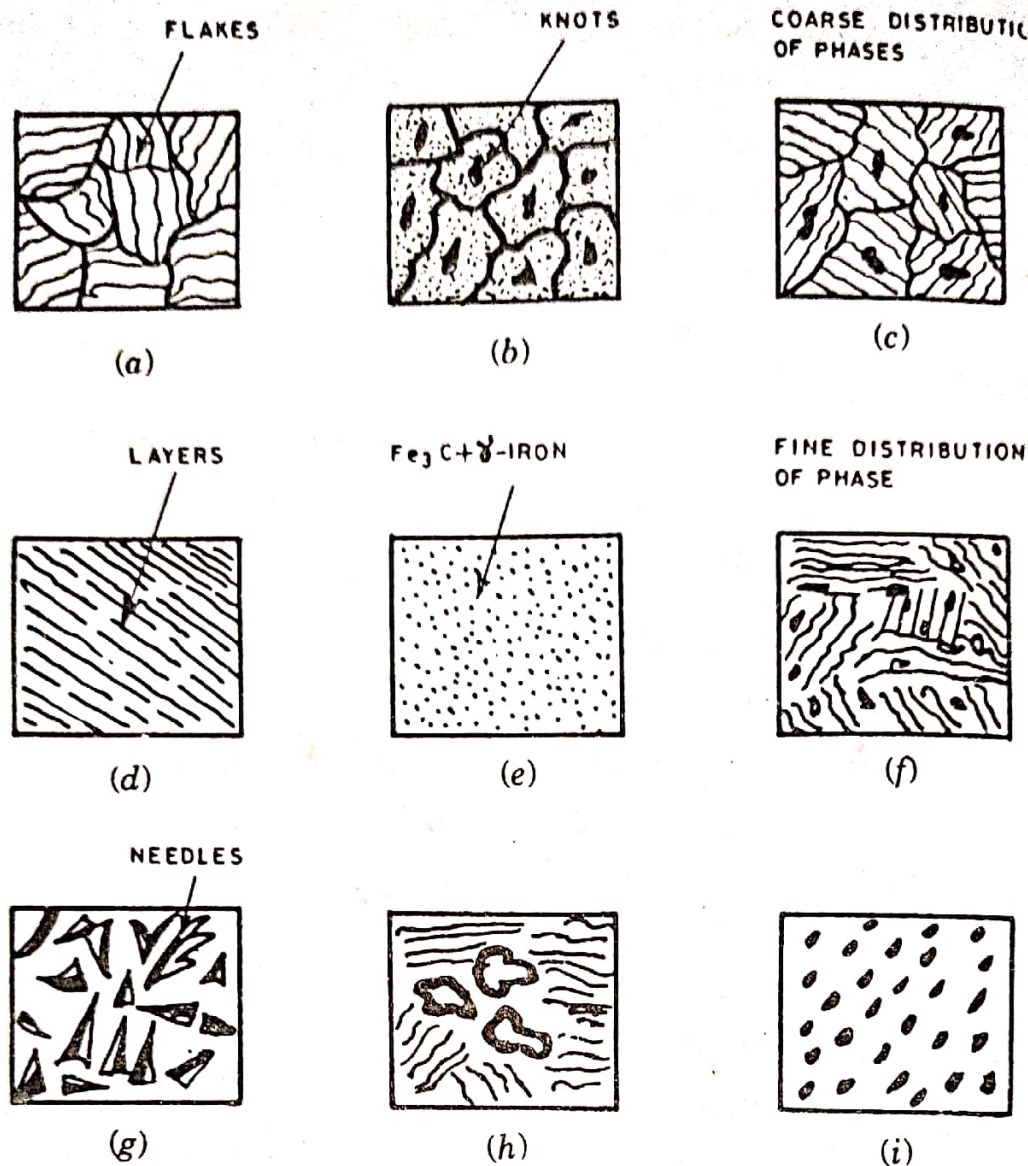


Fig. 12.4 Microstructures of iron and steel (a) ferrite, (b) cementite, (c) pearlite, (d) ludeburite, (e) austenite, (f) bainite, (g) martensite, (h) troosite, and (i) sorbite.

Pearlite. It is a mixture of ferrite and cementite, and is found in low and medium carbon steels. Hardness of steel increases with the increasing proportion of pearlite. The coarse crystals of pearlite (Fig. 12.4c) are formed during slow rate of cooling between 723°C and 625°C .

Ludeburite. Its microstructure is of layered formation, Fig. 12.4d, and is found in cast iron. It possesses lubricating property that imparts good machinability to cast iron. It is brittle, cannot be forged or rolled, but can be easily casted.

Austenite. The solid solution of iron carbide (Fe_3C) in γ -iron is known as austenite, Fig. 12.4e. Complete structural changes occur in steel when it is heated above higher critical temperature shown in Fig 12.9. The non-magnetic austenite absorbs excess ferrite and cementite.

Bainite. It is a mixture of ferrite and cementite having finer crystals (Fig. 12.4f) than pearlite. Its formation starts below 625°C when formation of pearlite finishes.

Martensite. It is the hardest constituent of steel, and has a needle like structure, Fig. 12.4g. It is a solid solution of iron carbide in α -iron. It is produced when steel

heated above 723°C is rapidly cooled by sudden quenching. Martensite is least ductile and negligibly tough.

Troostite. It is obtained by sudden quenching of heated steel, or by cooling the steel rapidly. Its structure is slightly granular, Fig. 12.4h. Troostite may be of primary or secondary types. Primary troostite is formed directly from austenite. Secondary troostite results from tempering of martensite. Troostite is intermediate in hardness between martensite and sorbite.

Sorbite. When the reheating temperature is increased, decomposition of steel begins that causes change of troostite into sorbite. The formation of sorbite does not take place spontaneously, rather it occurs gradually. Although sorbite is less ductile than pearlite but its tensile strength and yield point is higher. Depending upon the chemical composition, size of the job, and degree of hardening, the sorbite begins to form at about 400°C and ends at about 680°C . Its structure is shown in Fig. 12.4i.

In liquid condition, 0.83% carbon is homogeneously mixed with the molten iron. 0.83% carbon steel does not solidify at some specific temperature, rather it has a solidification range. The structure of 0.4% carbon steel consists of 50% pearlite and 50% ferrite. Similarly the structure of 0.2% carbon steel consists of 25% pearlite and 75% ferrite. The 1.2% carbon steel solidifies at temperatures much lower than that of 0.4% or 0.8% carbon steel. After solidification, the 1.2% carbon steel in austenitic solid solution is in the form of γ -iron. On further cooling, more cementite separates as the temperature further decreases. In hypoeutectoid steels, ferrite separates and austenite gets richer in carbon; but in hypereutectoid steels, the cementite separates and austenite gets poorer in carbon.

12.11 TIME-TEMPERATURE-TRANSFORMATION (TTT) DIAGRAMS

The transformations in steel can be conveniently understood by time-temperature-transformation ($T-T-T$) curve as shown in Fig. 12.7. Due to its shape from the start to the end of transformation, it is also called C -curve. The nose indicates the least time taken for certain transformation. Line AB passing through the nose indicates fall in temperature in OB time. This line is known as critical cooling curve, and its rate is termed as **critical cooling rate**. Its value is about 300°C/s .

The rate of cooling whether slow or fast, decides the transformation processes. These processes may be summarized as follows, and are shown in respective figures.

1. Annealing, when rate of cooling is very slow, as slow as 10°C/s or less.
2. Normalizing, when rate of air cooling is slow, as slow as 50°C/s or less.
3. Hardening, (by sudden quenching), when rate of cooling is faster than the critical cooling rate. This rate may be 350°C/s or more.

In Fig. 12.7 various phases and microstructures are shown for different temperatures as a function \log (time). The time is given in seconds. The formation of martensite starts at M_s , and finishes at M_f . In ferrous alloys, martensitic structure distorts to *Body Centred Tetragon* (BCT) due to interstitial carbon atoms. The height and base ratio (c/a) of a unit cell determines the tetragonality of martensitic lattice. It is expressed by

$$\frac{c}{a} = (1 \pm 0.005) + 0.045 (W_c) \quad \dots(12.2)$$

where W_c is the weight percent of carbon. When $W_c \rightarrow 0$, $(c/a) \rightarrow 1$. In this case, the structure will be BCC ferrite.

The hardness of different phases and microconstituents as a function of carbon content of steel is shown in Fig. 12.8.

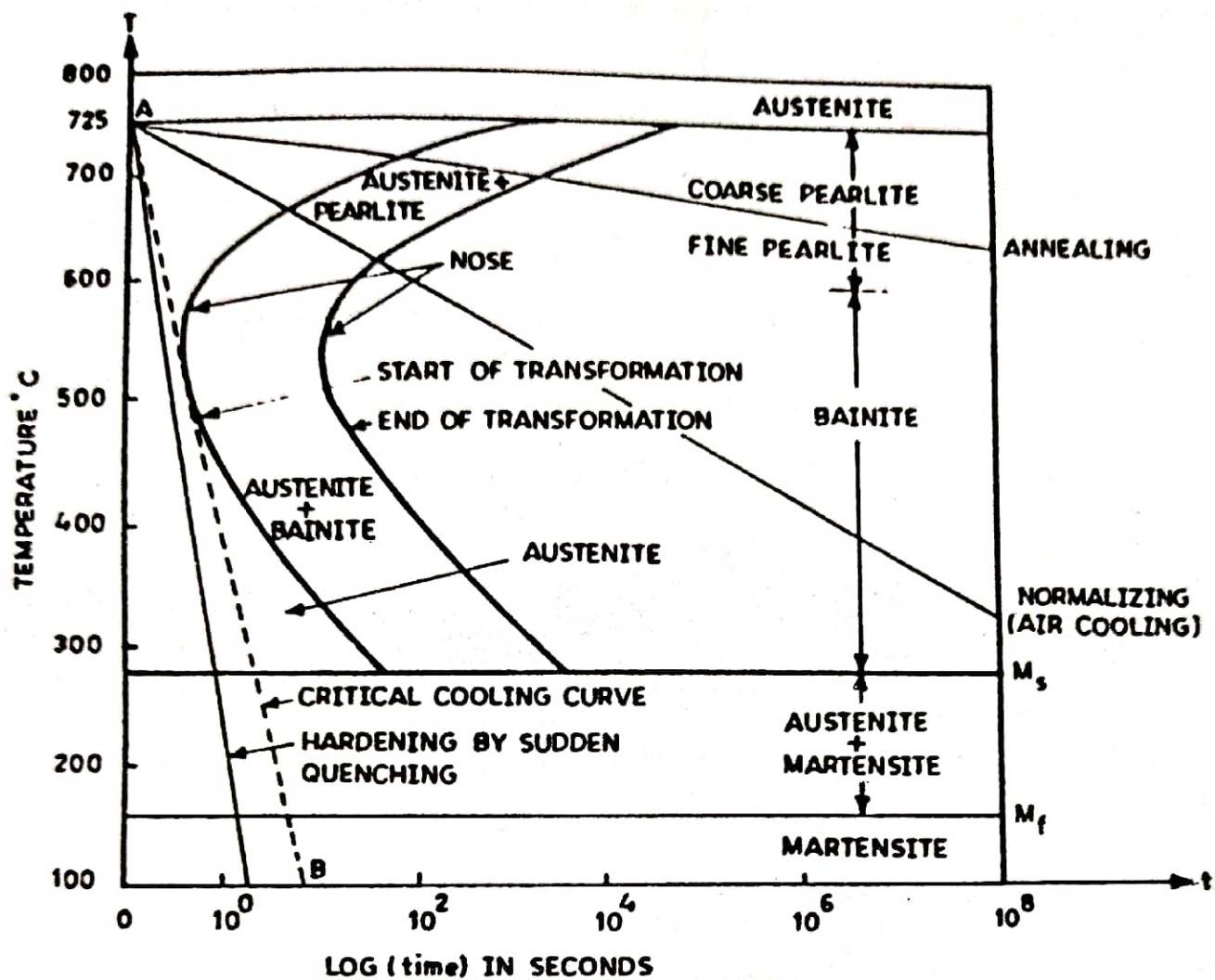


Fig. 12.7 The T-T-T curve showing temperature and log (time) variation for an eutectoid steel, and its different phases.

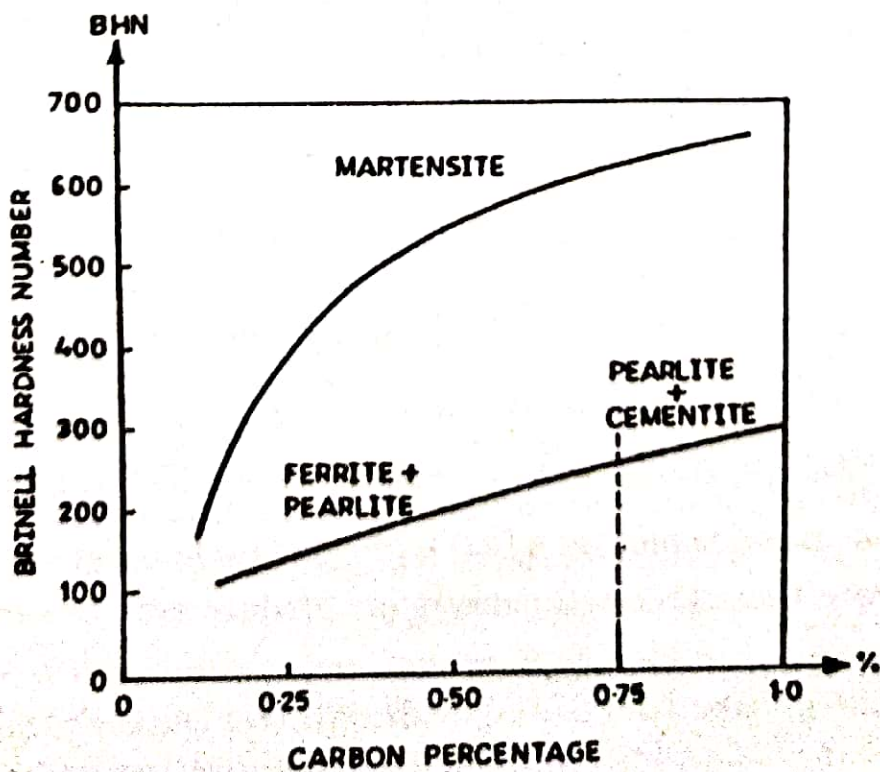


Fig. 12.8 Hardness of phases and microconstituents as a function of carbon percentage in steel

12.12 HEATING TEMPERATURE RANGE IN VARIOUS HEAT TREATMENT PROCESSES

To understand the heat treatment processes, it is essential to know their heating temperature range. Figure 12.9 illustrates heating range for various processes and the corresponding phases. The two important temperature ranges are

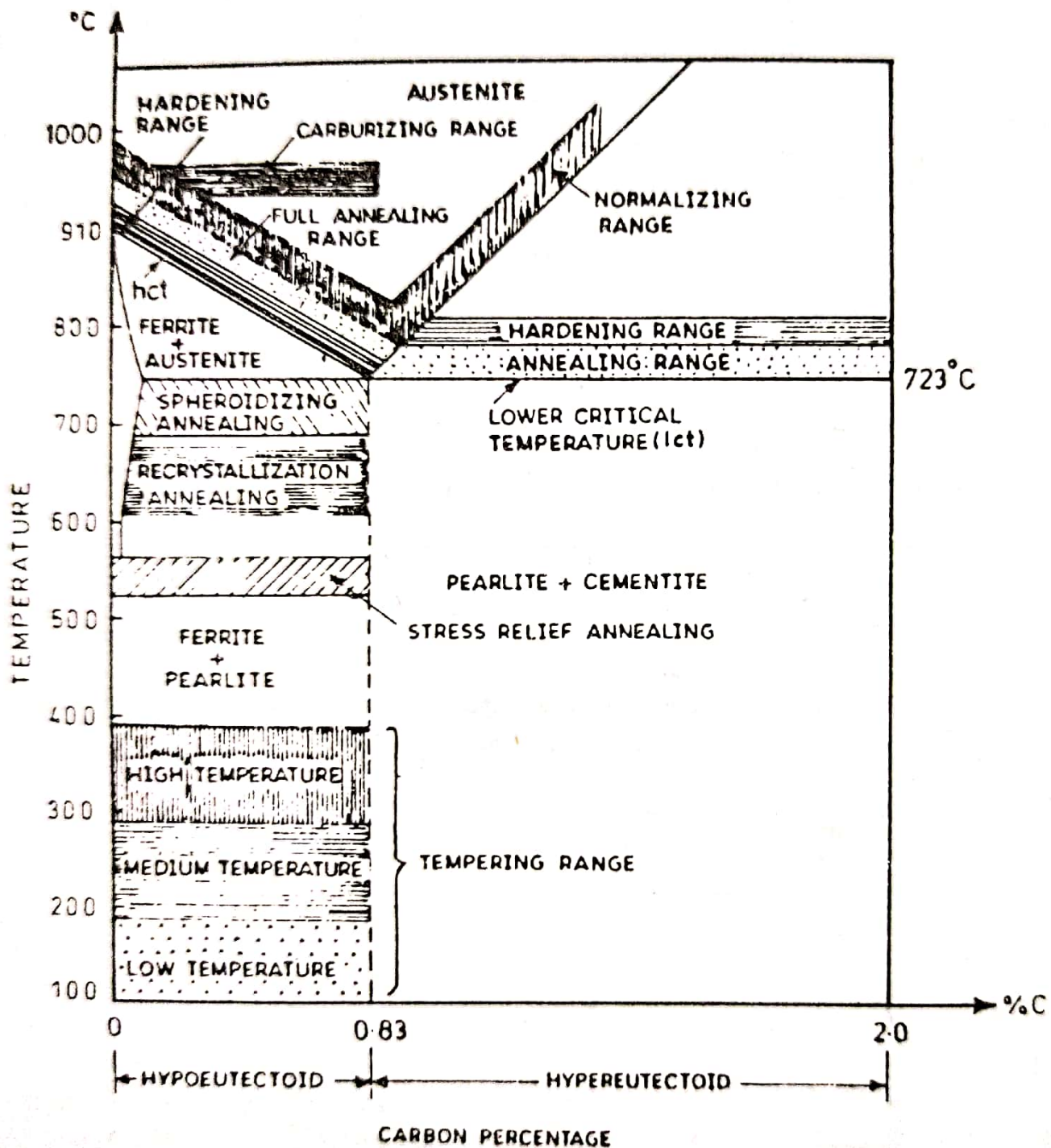


Fig. 12.9 Heating temperature range for different heat treatment processes.

1. Lower critical temperature (l_{ct}) for hypereutectoid steel, and
2. Higher (or upper) critical temperature (h_{ct}) for hypoeutectoid steel.

The tempering process requires heating much below the l_{ct} ; while full annealing, hardening, carburizing and normalizing processes require heating above h_{ct} . Spheroidizing annealing, recrystallization annealing and stress relief annealing are performed below l_{ct} . The temperature range of tempering may be further sub-classified into