Material Science

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Chapter 6. Phase Diagrams

Many of the engineering materials possess mixtures of phases, e.g. steel, paints, and composites. The mixture of two or more phases may permit interaction between different phases, and results in properties usually are different from the properties of individual phases. Different components can be combined into a single material by means of solutions or mixtures. *A solution (liquid or solid) is phase with more than one component; a mixture is a material with more than one phase*. Solute does not change the structural pattern of the solvent, and the composition of any solution can be varied. In mixtures, there are different phases, each with its own atomic arrangement. It is possible to have a mixture of two different solutions!

A pure substance, under equilibrium conditions, may exist as either of a phase namely vapor, liquid or solid, depending upon the conditions of temperature and pressure. A *phase* can be defined as a homogeneous portion of a system that has uniform physical and chemical characteristics i.e. it is a physically distinct from other phases, chemically homogeneous and mechanically separable portion of a system. In other words, a phase is a structurally homogeneous portion of matter. When two phases are present in a system, it is not necessary that there be a difference in both physical and chemical properties; a disparity in one or the other set of properties is sufficient.

There is only one vapor phase no matter how many constituents make it up. For pure substance there is only one liquid phase, however there may be more than one solid phase because of differences in crystal structure. A liquid solution is also a single phase, even as a liquid mixture (e.g. oil and water) forms two phases as there is no mixing at the molecular level. In the solid state, different chemical compositions and/or crystal structures are possible so a solid may consist of several phases. For the same composition, different crystal structures represent different phases. A solid solution has atoms mixed at atomic level thus it represents a single phase. A single-phase system is termed as homogeneous, and systems composed of two or more phases are termed as mixtures or heterogeneous. Most of the alloy systems and composites are heterogeneous.

It is important to understand the existence of phases under various practical conditions which may dictate the microstructure of an alloy, thus the mechanical properties and

usefulness of it. Phase diagrams provide a convenient way of representing which state of aggregation (phase or phases) is stable for a particular set of conditions. In addition, phase diagrams provide valuable information about melting, casting, crystallization, and other phenomena.

Useful terminology:-

Component – is either pure metal and/or compounds of which an alloy is composed. The components of a system may be elements, ions or compounds. They refer to the independent chemical species that comprise the system.

System – it can either refer to a specific body of material under consideration or it may relate to the series of possible alloys consisting of the same components but without regard to alloy composition.

Solid solution – it consists of atoms of at least two different types where solute atoms occupy either substitutional or interstitial positions in the solvent lattice and the crystal structure of the solvent is maintained.

Solubility limit – for almost all alloy systems, at a specific temperature, a maximum of solute atoms can dissolve in solvent phase to form a solid solution. The limit is known as solubility limit. In general, solubility limit changes with temperature. If solute available is more than the solubility limit that may lead to formation of different phase, either a solid solution or compound.

Phase equilibrium – it refers to the set of conditions where more than one phase may exist. It can be reflected by constancy with time in the phase characteristics of a system. In most metallurgical and materials systems, phase equilibrium involves just solid phases. However the state of equilibrium is never completely achieved because of very slow rate of approach of equilibrium in solid systems. This leads to non-equilibrium or meta-stable state, which may persist indefinitely and of course, has more practical significance than equilibrium phases. An equilibrium state of solid system can be reflected in terms of characteristics of the microstructure, phases present and their compositions, relative phase amounts and their spatial arrangement or distribution.

Variables of a system – these include two external variables namely temperature and pressure along with internal variable such as composition (C) and number of phases (P). Number of independent variables among these gives the degrees of freedom (F) or variance. All these are related for a chosen system as follows:

$$P + F = C + 2$$

which is known as *Gibbs Phase rule*. The degrees of freedom cannot be less than zero so that we have an upper limit to the number of phases that can exist in equilibrium for a given system. For practical purpose, in metallurgical and materials field, pressure can be considered as a constant, and thus the *condensed phase rule* is given as follows:

$$P + F = C + 1$$

7.1 Equilibrium Phase Diagrams, Particle strengthening by precipitation and precipitation reactions

7.1.1 Equilibrium Phase Diagrams

A diagram that depicts existence of different phases of a system under equilibrium is termed as *phase diagram*. It is also known as *equilibrium* or *constitutional diagram*. Equilibrium phase diagrams represent the relationships between temperature and the compositions and the quantities of phases at equilibrium. In general practice it is sufficient to consider only solid and liquid phases, thus pressure is assumed to be constant (1 *atm.*) in most applications. These diagrams do not indicate the dynamics when one phase transforms into another. However, it depicts information related to microstructure and phase structure of a particular system in a convenient and concise manner. Important information, useful for the scientists and engineers who are involved with materials development, selection, and application in product design, obtainable from a phase diagram can be summarized as follows:

- To show phases are present at different compositions and temperatures under slow cooling (equilibrium) conditions.
- To indicate equilibrium solid solubility of one element/compound in another.
- To indicate temperature at which an alloy starts to solidify and the range of solidification.
- To indicate the temperature at which different phases start to melt.
- Amount of each phase in a two-phase mixture can be obtained.

A phase diagram is actually a collection of solubility limit curves. The phase fields in equilibrium diagrams depend on the particular systems being depicted. Set of solubility curves that represents locus of temperatures above which all compositions are liquid are called *liquidus*, while *solidus* represents set of solubility curves that denotes the locus of temperatures below which all compositions are solid. Every phase diagram for two or more components must show a liquidus and a solidus, and an intervening freezing range, except for pure system, as melting of a phase occurs over a range of temperature. Whether the components are metals or nonmetals, there are certain locations on the phase diagram where the liquidus and solidus meet. For a pure component, a contact point lies at the edge of the diagram. The liquidus and solidus also meet at the other invariant positions on the diagram. Each invariant point represents an invariant reaction that can occur only under a particular set of conditions between particular phases, so is the name for it!

Phase diagrams are classified based on the number of components in the system. Single component systems have unary diagrams, two-component systems have binary diagrams, three-component systems are represented by ternary diagrams, and so on. When more than two components are present, phase diagrams become extremely complicated and difficult to represent. This chapter deals mostly with binary phase diagrams.

Unary diagrams: In these systems there is no composition change ($C=1$), thus only variables are temperature and pressure. Thus in region of single phase two variables (temperature and pressure) can be varied independently. If two phases coexist then, according to Phase rule, either temperature or pressure can be varied independently, but not both. At triple points, three phases can coexist at a particular set of temperature and pressure. At these points, neither temperature nor the pressure can be changed without disrupting the equilibrium i.e. one of the phases may disappear. *Figure-1* depicts phase diagram for water.
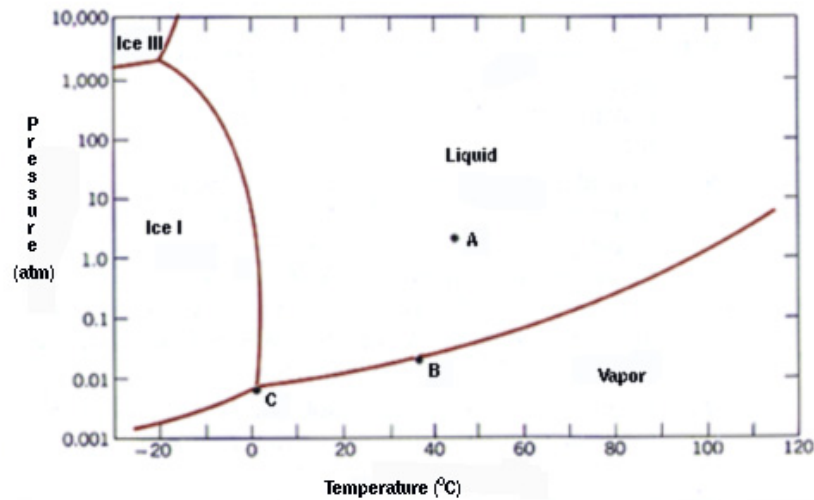

Figure-1: Unary phase diagram for water.

Binary diagrams: These diagrams constitutes two components, e.g.: two metals (Cu and Ni), or a metal and a compound (Fe and Fe_3C), or two compounds (Al_2O_3 and Si_2O_3), etc. In most engineering applications, as mentioned before, condensed phase rule is applicable. It is assumed that the same is applicable for all binary diagrams, thus the presentation of binary diagrams becomes less complicated. Thus binary diagrams are usually drawn showing variations in temperature and composition only. It is also to be noted that all binary systems consist only one liquid phase i.e. a component is completely soluble in the other component when both are in liquid state.

Hence, binary systems are classified according to their solid solubility. If both the components are completely soluble in each other, the system is called *isomorphous* system. E.g.: Cu-Ni, Ag-Au, Ge-Si, Al_2O_3-Cr_2O_3. Extent solid solubility for a system of two metallic components can be predicted based on Hume-Ruthery conditions, summarized in the following:

- Crystal structure of each element of solid solution must be the same.
- Size of atoms of each two elements must not differ by more than 15%.

- Elements should not form compounds with each other i.e. there should be no appreciable difference in the electro-negativities of the two elements.
- Elements should have the same valence.

All the Hume-Rothery rules are not always applicable for all pairs of elements which show complete solid solubility.

In systems other than isomorphous systems i.e. in case of limited solid solubility, there exist solid state miscibility gaps; number of invariant reactions can take place; intermediate phases may exist over a range of composition (*intermediate solid solutions*) or only at relatively fixed composition (*compound*). These intermediate phases may undergo polymorphic transformations, and some may melt at a fixed temperature (*congruent transformations*, in which one phase changes to another of the same composition at definite temperature). A solid solution based on a pure component and extending to certain finite compositions into a binary phase diagram is called a *terminal solid solution*, and the line representing the solubility limit of a terminal solid solution *w.r.t* a two-phase solid region is called a *solvus* line (*figure-4*).

Isomorphous system: *Figure-2* depicts a typical phase diagram for an isomorphous system made of two metallic elements *A* and *B*. As cited earlier, any phase diagram can be considered as a map. A set of coordinates – a temperature and a composition – is associated with each point in the diagram. If the alloy composition and temperature specified, then the phase diagram allows determination of the phase or phases that will present under equilibrium conditions. There are only two phases in the phase diagram, the liquid and the solid phases. These single-phases regions are separated by a two-phase region where both liquid and solid co-exist. The area in the *figure-2* above the line marked liquidus (*A'bB'*) corresponds to the region of stability of the liquid phase, and the area below the solidus line (*A'dB'*) represents the stable region for the solid phase.
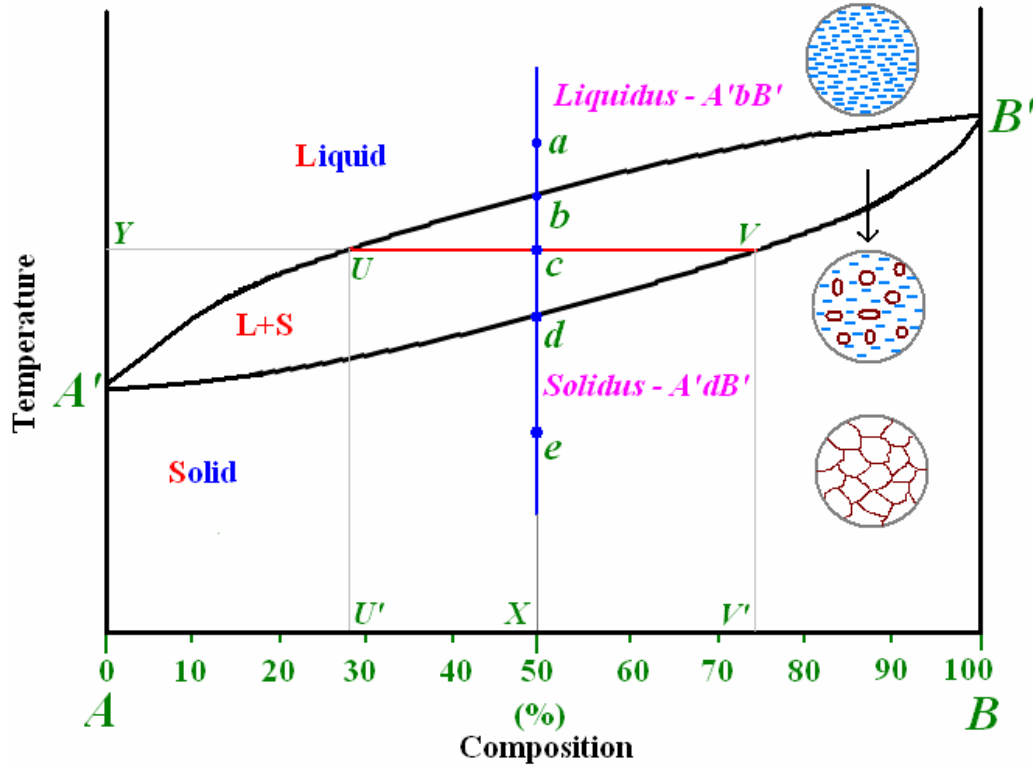
Figure-2: *Phase diagram for typical isomorphous binary system.*

For the interpretation of the phase diagram, let's consider the vertical line *ae* drawn corresponding to composition of 50%*A* +50%*B* and assume that the system is undergoing equilibrium cooling. The point *a* on the line *ae* signifies that for that particular temperature and composition, only liquid phase is stable. This is true up to the point *b* which lies on the liquidus line, representing the starting of solidification. Completion of solidification of the alloy is represented by the point, *d*. Point *e* corresponds to single-phase solid region up to the room temperature. Point *c* lies in the two-phase region made of both liquid and solid phases. Corresponding micro-structural changes are also shown in *figure-2*. As shown in figure-2, above liquidus only a liquid phase exists, and below the solidus single solid phase exists as completely solidified grains. Between these two lines, system consist both solid crystals spread in liquid phase. It is customary to use *L* to represent liquid phase(s) and Greek alphabets (*α, β, γ*) for representing solid phases.

Between two extremes of the horizontal axis of the diagram, cooling curves for different alloys are shown in *figure-3* as a function of time and temperature. Cooling curves shown in *figure-3* represent *A, U', X, V'* and *B* correspondingly in *figure-2*. Change in slope of the cooling curve is caused by heat of fusion. In fact these changes in slope are nothing but points on either solidus or liquidus of a phase diagram. An experimental procedure where repeated cooling/heating of an alloy at different compositions, and corresponding changes in slope of cooling curves will be used to construct the phase diagram.
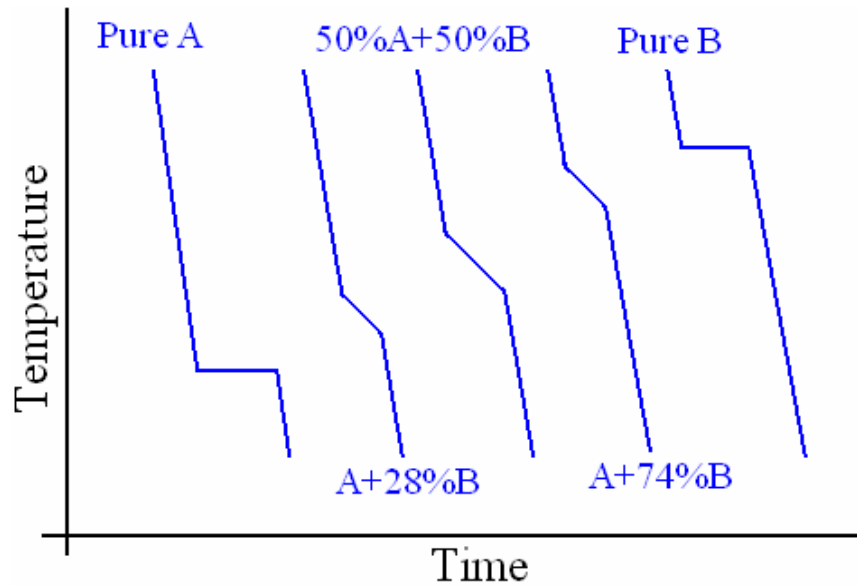
Figure-3: *Cooling curves for isomorphous binary system.*

Another important aspect of interpreting phase diagrams along with phases present is finding the relative amount of phases present and their individual composition.

Procedure to find equilibrium concentrations of phases:

- A *tie-line* or *isotherm* (**UV**) is drawn across two-phase region to intersect the boundaries of the region.
- Perpendiculars are dropped from these intersections to the composition axis, represented by **U'** and **V'** in *figure-2*, from which each of each phase is read. **U'** represents composition of liquid phase and **V'** represents composition of solid phase as intersection **U** meets liquidus line and **V** meets solidus line.

Procedure to find equilibrium relative amounts of phases (*lever rule*):

- A tie-line is constructed across the two phase region at the temperature of the alloy to intersect the region boundaries.
- The relative amount of a phase is computed by taking the length of tie line from overall composition to the phase boundary for the other phase, and dividing by the total tie-line length. From *figure-2*, relative amounts of liquid and solid phases is given respectively by

$$C_L = \frac{cV}{UV}, \ C_S = \frac{Uc}{UV}, \text{ and it is to be noted that } C_L + C_S = 1.$$

Eutectic system: Many binary systems have components which have limited solid solubility, e.g.: Cu-Ag, Pb-Sn. The regions of limited solid solubility at each end of a phase diagram are called *terminal solid solutions* as they appear at ends of the diagram.

Many of the binary systems with limited solubility are of eutectic type, which consists of specific alloy composition known as *eutectic composition* that solidifies at a lower temperature than all other compositions. This low temperature which corresponds to the lowest temperature at which the liquid can exist when cooled under equilibrium conditions is known as *eutectic temperature*. The corresponding point on the phase diagram is called *eutectic point*. When the liquid of eutectic composition is cooled, at or below eutectic temperature this liquid transforms simultaneously into two solid phases (two terminal solid solutions, represented by *α* and *β*). This transformation is known as *eutectic reaction* and is written symbolically as:

$$\text{Liquid } (L) \leftrightarrow \text{ solid solution-1 } (\alpha) + \text{ solid solution-2 } (\beta)$$
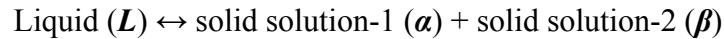
This eutectic reaction is called invariant reaction as it occurs under equilibrium conditions at a specific temperature and specific composition which can not be varied. Thus, this reaction is represented by a thermal horizontal arrest in the cooling curve of an alloy of eutectic composition. A typical eutectic type phase diagram is shown in *figure-4* along with a cooling curve.

As shown in *figure-4*, there exist three single phase regions, namely liquid (*L*), *α* and *β* phases. There also exist three two phase regions: *L+α*, *L+β* and *α+β*. These three two phase regions are separated by horizontal line corresponding to the eutectic temperature. Below the eutectic temperature, the material is fully solid for all compositions. Compositions and relative amount of the phases can be determined using tie-lines and lever rule. Compositions that are on left-hand-side of the eutectic composition are known as *hypo-eutectic compositions* while compositions on right-hand-side of the eutectic composition are called *hyper-eutectic compositions*. Development of micro-structure and respective cooling curves for eutectic alloys are shown in *figure-5, 6, 7 and 8* for different compositions. The phase that forms during cooling but before reaching eutectic temperature is called *pro-eutectic phase*.
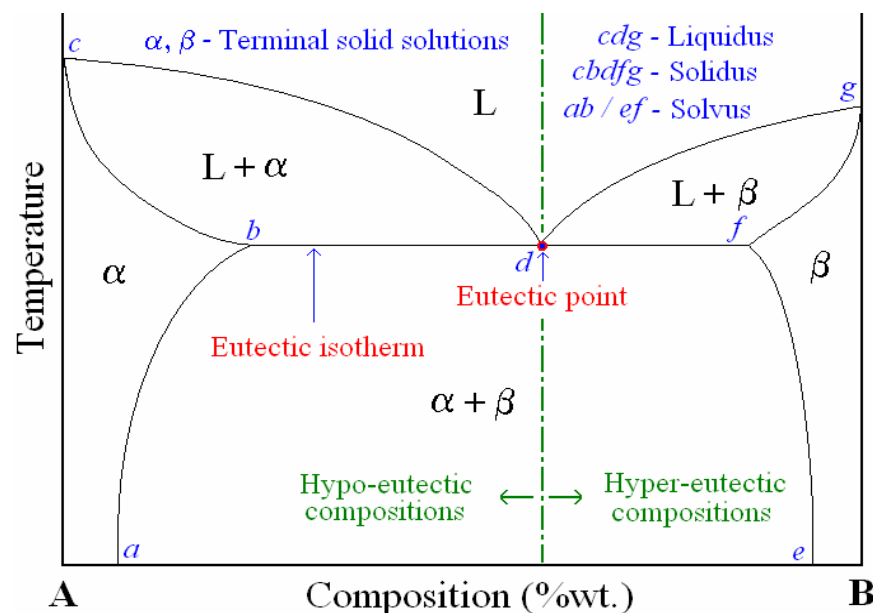
Figure-4: *Typical phase diagram for a binary eutectic system.*

In many systems, solidification in the solid + liquid region may lead to formation of layered (cored) grains, even at very slow cooling rates. This is as a result of very slow or no-diffusion in solid state compared with very high diffusion rates in liquids. The composition of the liquid phase evolves by diffusion, following the equilibrium values that can be derived from the tie-line method. However, new layers that solidify on top of the grains have the equilibrium composition at that temperature but once they are solid their composition does not change.
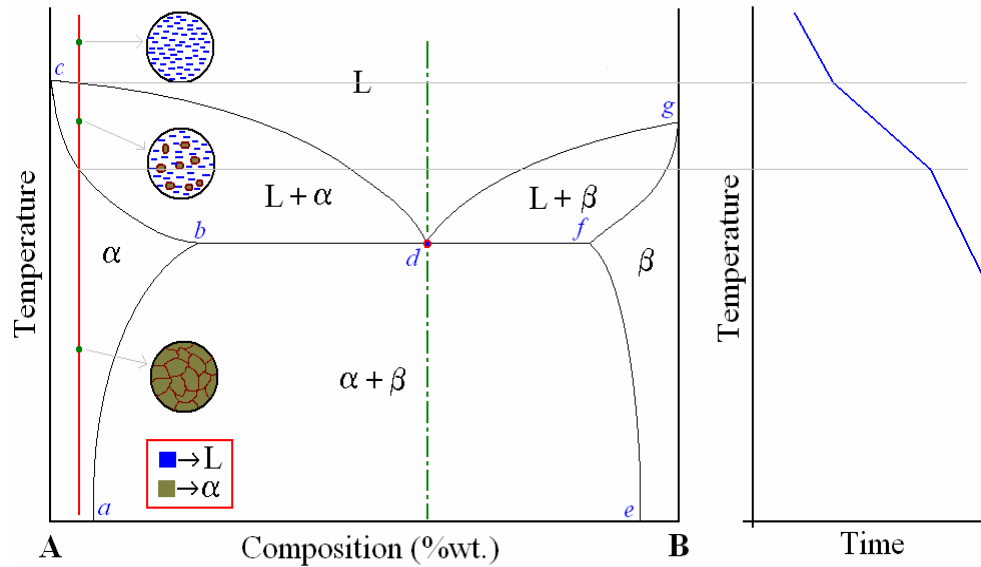

Figure-5: *Cooling curve and micro-structure development for eutectic alloy that passes mainly through terminal solid solution.*
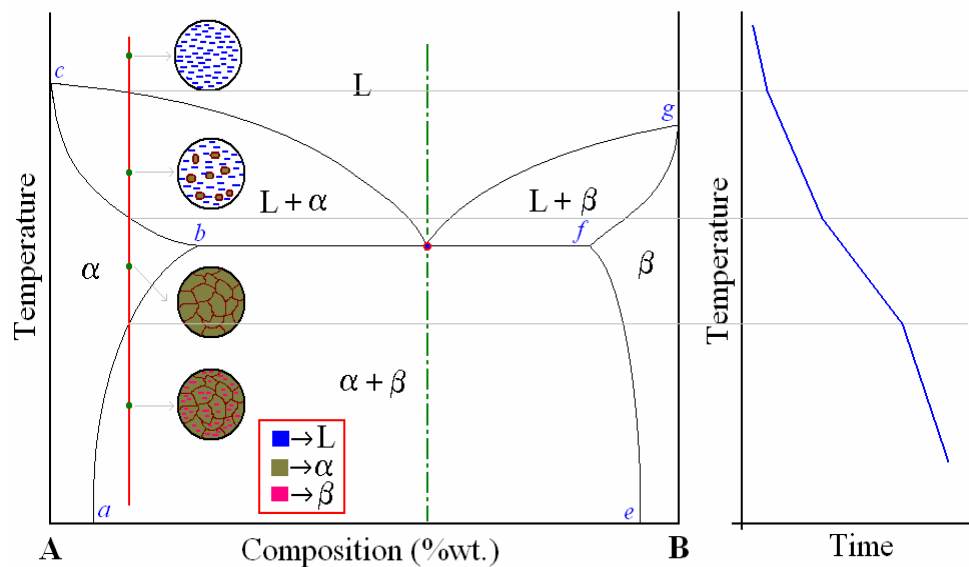
Figure-6: *Cooling curve and micro-structure development for eutectic alloy that passes through terminal solid solution without formation of eutectic solid.*
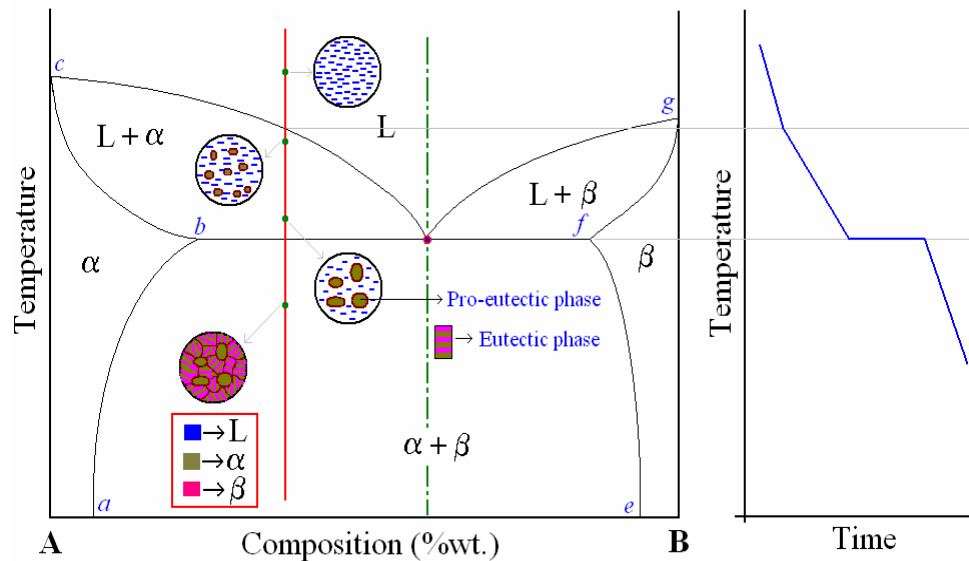

Figure-7: *Cooling curve and micro-structure development for eutectic alloy that passes through hypo-eutectic region.*
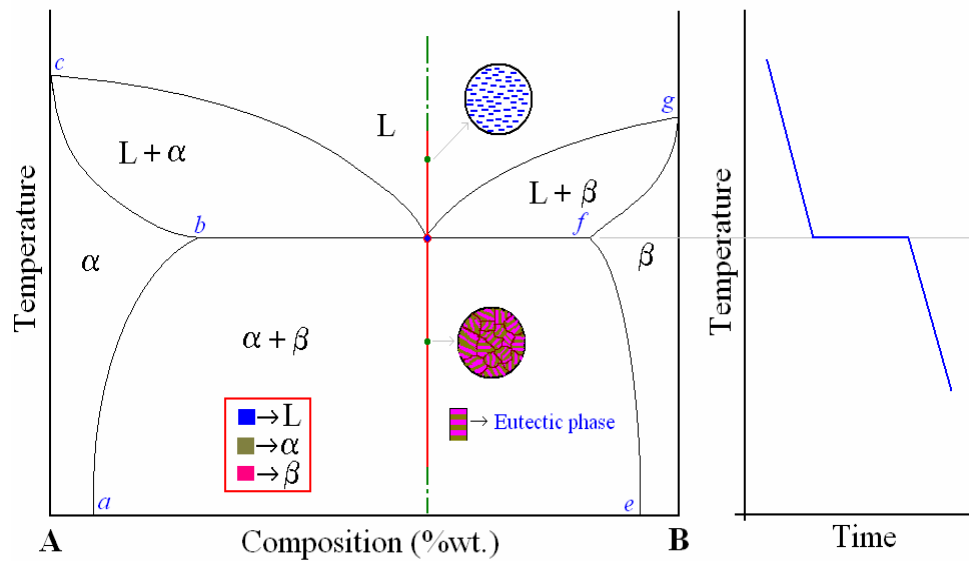

Figure-8: *Cooling curve and micro-structure development for eutectic alloy that passes through eutectic-point.*

Invariant reactions: The *eutectic reaction*, in which a liquid transforms into two solid phases, is just one of the possible three-phase invariant reactions that can occur in binary systems those are not isomorphous. Schematically it can be shown as in *figure-9*. It represents that a liquid phase, *L*, transforms into two different solids phases (*α* and *β*) upon cooling during the eutectic reaction.
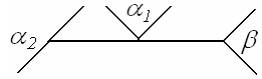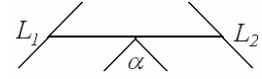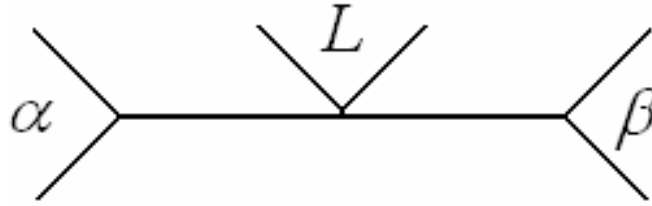
Figure-9: *Schematic of eutectic invariant reaction.*

In the solid state analog of a eutectic reaction, called a *eutectoid reaction*, one solid phase having eutectoid composition transforms into two different solid phases. Another set of invariant reactions that occur often in binary systems are - *peritectic reaction* where a solid phase reacts with a liquid phase to produce a new solid phase, and in *peritectoid reaction*, two solid phases react to form a new solid phase. Peritectic reaction is commonly present as part of more-complicated binary diagrams, particularly if the melting points of the two components are quite different. Peritectic and peritectoid reactions do not give rise to micro-constituents as the eutectic and eutectoid reactions do. Another invariant reaction that involves liquid phase is *monotectic reaction* in which a liquid phase transforms into a solid phase and a liquid phase of different composition. Over a certain range of compositions the two liquids are immiscible like oil and water and so constitute individual phases, thus monotectic reaction can said to be associated with miscibility gaps in the liquid state. Example system for monotectic reaction: Cu-Pb at 954 ˚C and 36%Pb. Analog to monotectic reaction in solid state is *monotectoid reaction* in which a solid phase transforms to produce two solid phases of different compositions. Another notable invariant reaction that is associated with liquid immiscibility is *syntectic reaction* in which two liquid phases react to form a solid phase. All the invariant reactions are summarized in the *table-1* showing both symbolic reaction and schematic part of phase diagram.

Table-1: *Summary of invariant reactions in binary systems.*

Reaction	Symbolic equation	Schematic presentation	Example
Eutectic	$L \leftrightarrow \alpha + \beta$		Fe-C, 4.27% C, 1147 ˚C
Eutectoid	$\alpha \leftrightarrow \beta + \gamma$		Fe-C, 0.80% C, 723 ˚C
Peritectic	$L + \alpha \leftrightarrow \beta$		Fe-C, 0.16%C, 1495 ˚C
Peritectoid	$\alpha + \beta \leftrightarrow \gamma$		
Monotectic	$L_1 \leftrightarrow L_2 + \alpha$		Fe-C, 0.51%C, 1495 ˚C

| Monotectoid | $\alpha_1 \leftrightarrow \alpha_2 + \beta$ | | |
| Syntectic | $L_1 + L_2 \leftrightarrow \alpha$ | | |

Intermediate phases: An intermediate phase may occur over a composition range (intermediate solid solution) or at a relatively fixed composition (compound) inside the phase diagram and are separated from other two phases in a binary diagram by two phase regions. Many phase diagrams contain intermediate phases whose occurrence cannot be readily predicted from the nature of the pure components. Intermediate solid solutions often have higher electrical resistivities and hardnesses than either of the two components. Intermediate compounds form relatively at a fixed composition when there exists a stoichiometric relationship between the components, for example: Mg_2Ni and $MgNi_2$ in Mg-Ni system. These are called _inter-metallic compounds_, and differ from other chemical compounds in that the bonding is primarily metallic rather than ionic or covalent, as would be found with compounds in certain metal-nonmetal or ceramic systems. Some metal-nonmetal compounds, Fe_3C, are metallic in nature, whereas in others, MgO and Mg_2Si, bonding is mainly covalent. When using the lever rules, inter-metallic compounds are treated like any other phase, except they appear not as a wide region but as a vertical line.

Number of phase transformations may takes place for each system. Phase transformations in which there are no compositional alternations are said to be _congruent transformations_, and during _incongruent transformations_ at least one of the phases will experience a change in composition. Examples for (1) congruent transformations: allotropic transformations, and melting of pure materials (2) incongruent transformations: all invariant reactions, and also melting of alloy that belongs to an isomorphous system. Intermediate phases are sometimes classified on the basis of whether they melt congruently or incongruently. $MgNi_2$, for example, melts congruently whereas Mg_2Ni melts incongruently since it undergoes peritectic decomposition.

7.1.2 Particle strengthening by precipitation and precipitation reactions

As explained in an earlier chapter (_chapter-6: Dislocations and Strengthening Mechanisms_), by obstructing dislocation motion in different means, material's strength can be increased. One of the methods that are applicable to multi-phase material is particle strengthening in which second phase particles are introduced into the matrix by either mixing-and-consolidation (dispersion strengthening) or precipitated in solid state (precipitation hardening).

The object of the precipitation strengthening is to create in a heat-treated alloy a dense and fine dispersion of precipitated particles in a matrix of deformable metal. The particles act as obstacles to dislocation motion. In order for an alloy system to be able to precipitation-strengthened for certain alloy compositions; there must be a terminal solid solution which has a decreasing solid solubility as the temperature decreases. For

example: Au-Cu in which maximum solid solubility of Cu in Al is 5.65% at 548 ˚C that decreases with decreasing temperature.

The precipitation strengthening process involves the following three basic steps:

- Solutionizing (solution heat treatment), where the alloy is heated to a temperature between solvus and solidus temperatures and kept there till a uniform solid-solution structure is produced.
- Quenching, where the sample is rapidly cooled to a lower temperature (room temperature) and the cooling medium is usually water. Alloy structure in this stage consists of supersaturated solid solution.
- Aging is the last but critical step. During this heat treatment step finely dispersed precipitate particle will form. Aging the alloy at room temperature is called natural aging, whereas at elevated temperatures is called artificial aging. Most alloys require artificial aging, and aging temperature is usually between 15-25% of temperature difference between room temperature and solution heat treatment temperature.

Precipitation strengthening and reactions that occur during precipitation can be best illustrated using the Al-4%Cu (duralumin) system. *Figure-10* depicts the Al-rich end of the Al-Cu phase diagram. It can be observed that the alloy with 4%Cu exists as a single phase α-solid solution at around 550 ˚C, and at room temperature as a mixture of α (with less than 0.5%Cu) and an inter-metallic compound, $CuAl_2$ (θ) with 52%Cu. On slow cooling α rejects excess Cu as precipitate particles of θ. These particles relatively coarse in size and can cause only moderate strengthening effect.
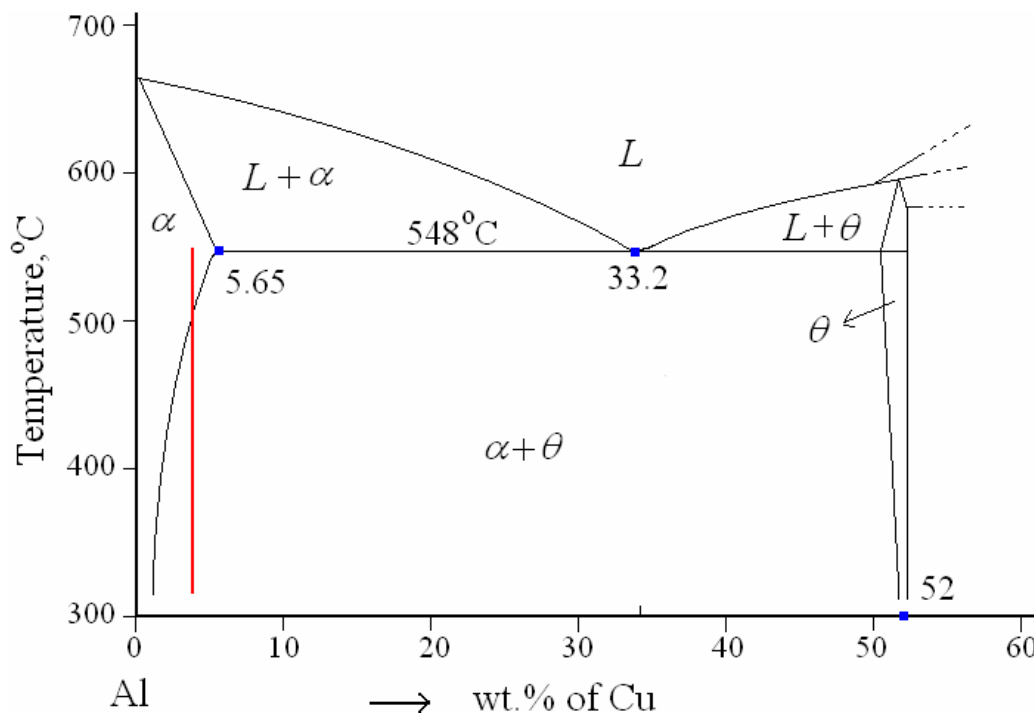
Figure-10: *Aluminium rich end of Al-Cu phase diagram.*

By rapidly cooling the alloy, a supersaturated solution can be obtained at room temperature. As a function of time at room temperature, and at higher temperatures up to 200 ° C, the diffusion of Cu atoms may take place and the precipitate particles can form. For this particular alloy, Al-4%Cu, five sequential structures can be identified: (a) supersaturated solid solution α, (b) GP1 zones, (c) GP2 zones (θ" phase), (d) θ' phase and (e) θ phase, $CuAl_2$. Not all these phases can be produced at all aging temperatures. GP1 and GP2 zones are produced at lower temperatures, and θ' and θ phases occur at higher temperatures. The initial stages of precipitation are the most difficult to analyze because of the extremely small size of the particles and their relatively uniform distribution. GP zones meant for *Guinier-Preston* zones which have a definite composition and structure that is not the same as that of the final stable precipitate. Evidently these particles are easier to nucleate than the final precipitate, as a result, form first. Eventually they disappear as later more stable phases appear. θ" and θ' are meta-stable transition precipitates with distinct crystal structure of their own, while θ is the equilibrium stable precipitate of $CuAl_2$.

GP1 zones:- These zones are created by Cu atoms segregating in α, and the segregated regions are of disk shape with thickness of 0.4-0.6 nm, and 8-10 nm in diameter and form on the {100} cubic planes of the matrix. As Cu atoms which replace Al atoms are smaller in diameter, matrix lattice strains tetragonally. These zones are said to be coherent with the matrix lattice.

GP2 zones / θ" phase:- With additional aging, ordering of larger clumps of Cu atoms on {100} occurs. These zones have tetragonal structure which therefore introduces coherency in the lattice with {100} planes of the matrix, accompanied by further hardening. However, their size ranges from 1-4 nm thick and 10-100 nm in diameter as aging proceeds.

θ' phase:- This phase nucleates heterogeneously especially on dislocations. It has tetragonal structure but is partially coherent with the matrix. This phase forms platelets with thickness 10-150 nm.

θ phase:- With still further aging the equilibrium phase $CuAl_2$ or θ is formed from the transition lattice θ' or directly from the matrix accompanied by a reduction in hardness. It has a BCT (body-centered-tetragonal) structure, and is incoherent with the matrix. As these particles are no longer coherent with the matrix, hardness is lower than at the stage when coherent was present. Over-aging continues with the growth of these particles controlled by diffusion. Variation of hardness with aging time is shown in *figure-11*.

The general sequence of precipitation in binary Al-Cu alloys can represented as:

Supersaturated α → GP1 zones → GP2 zones (θ" phase) → θ' phase → θ phase ($CuAl_2$)

Most precipitation-hardening systems operate in a similar way, peak hardness usually being attained in the later stages of coherency or at the onset of incoherency. It is quite common for a coherent precipitate to form and then lose coherency when the particle grows to a critical size. However, in some systems there is no evidence of coherency strains, and the fine particles appear to act alone as impediments to dislocation movements, for example – systems with dispersion strengthening.
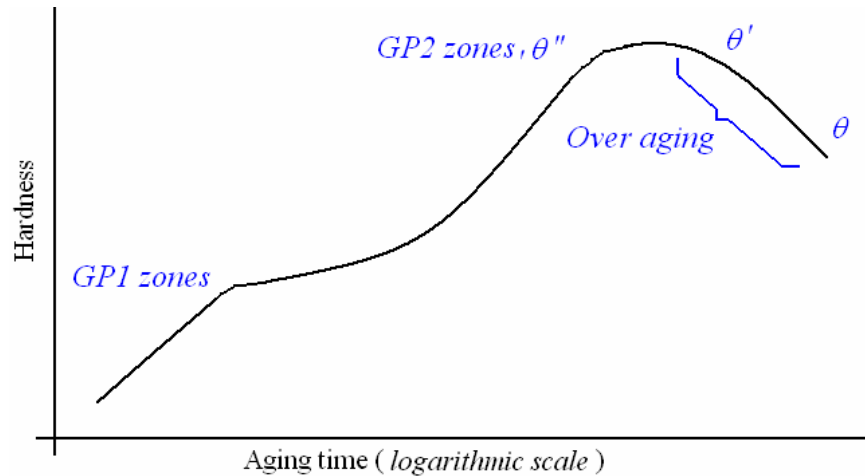

Figure-11: *Correlation of structures and hardness for Al-4%Cu alloy.*

7.2 Kinetics of nucleation and growth

Structural changes in metallic systems usually take place by nucleation and growth whether it is just a phase change within one of the three states, or a simple structural rearrangement within a single phase, or a phase transformation. An equilibrium phase diagram presents the phases and phase changes expected under equilibrium conditions, but it provides no information about the rates of transformation. Although changes in pressure, composition, or temperature can cause phase transformations, it is temperature changes that are more important. From a micro structural standpoint, the first process to accompany a phase transformation is nucleation (i.e. the formation of very small particles or nuclei of the product phase from the parent phase) of the new phase particles which are capable of growing. The second stage is growth, in which the nucleated particles increase their size. The transformation reaches completion if growth of these new phase particles is allowed to proceed until the equilibrium fraction is attained.

Both nucleation and growth require that the accompanying free energy change be negative. Consequently, the super-heating or super-cooling that is necessary for a phase change is to be expected. That is a transformation cannot tale place precisely at the equilibrium transformation temperature because at that temperature free energies of phases are equal. In addition to temperature, two other factors that affect transformation rate – first, diffusion controlled rearrangement of atoms because of compositional and/or crystal structural differences; second, difficulty encountered in nucleating small particles via change in surface energy associated with the interface. Diffusion limits both the nucleation and growth rates in many cases.

With the nucleation of new particle, new interface is created between the particle and liquid. This interface will have positive energy that must be supplied during the transformation process. A tiny particle has a large surface area to volume ratio and therefore be unstable. Thus energy of the surface can effectively prevent the initial formation of a tiny particle. A particle said to have nucleated when it becomes stable and will not disappear due to thermal fluctuations. After a particle attained a critical size, it can grow further with a continuous decrease in energy. The surface energy is no longer a dominant factor in the growth process.

7.2.1 Nucleation kinetics

In *homogeneous nucleation*, the probability of nucleation occurring at any given site is identical to that at any other site within the volume of the parent phase. When a pure liquid metal is cooled below its equilibrium freezing temperature to a sufficient degree, numerous homogeneous nuclei are created by slow-moving atoms bonding together. Homogeneous nucleation usually requires a considerable amount of *undercooling* (cooling a material below the equilibrium temperature for a given transformation without the transformation occurring). Undercooling enhances the formation of nuclei that eventually grow. If Δf is the free energy change accompanying the formation of a spherical new phase particle,

$$\Delta f = \frac{4}{3}\pi r^3 \Delta g + 4\pi r^2 \gamma$$

where r is the radius of the particle, Δg is the Gibbs free energy change per unit volume and γ is the surface energy of the interface. As surface energy, γ, is always positive, and Δg is negative, passes through a maximum. From calculus, critical values can be found from the following:

$$r^* = -\frac{2\gamma}{\Delta g} \; ; \; \Delta f^*_{\text{hom}} = \frac{16}{3}\pi\gamma^3 /(\Delta g)^2$$

Particles which are smaller than the critical size are called embryos; those larger than the critical size are called nuclei. As Δg becomes more negative with a lowering of the temperature, the critical values of Δf and r becomes smaller as shown in *figure-12*. At sufficiently low temperatures, nucleation can be triggered by a few atoms statistically clustering as a nucleus, so a small critical radius is exceeded. With added growth, the new phase attains stability. Of course atom movements are sluggish at low temperatures, so growth is generally slow.
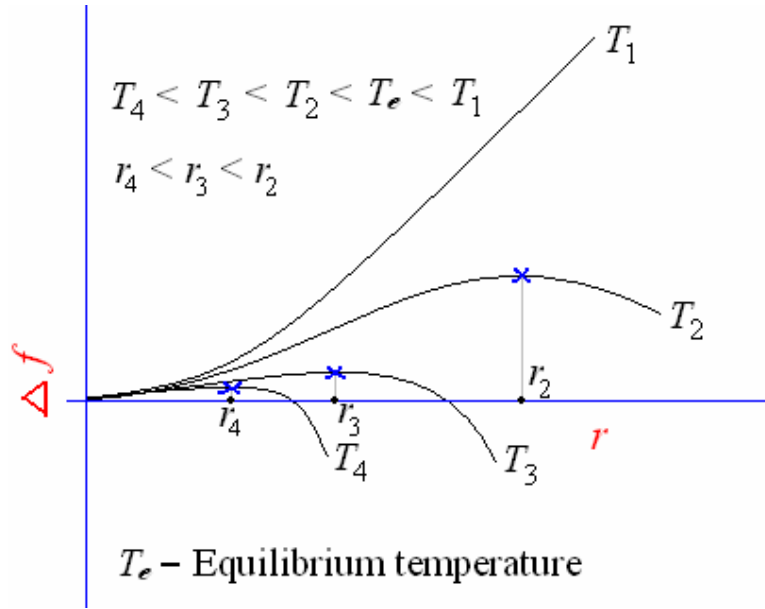
Figure-12: *Effect of temperature on free energy change and particle radius.*

The greater the degree of undercooling below the equilibrium melting temperature of the metal, the greater the change in volume free energy, however, the change in free energy due to surface energy does not change much with temperature. Thus, the critical size of nuclei is mainly determined by volume free energy. Near the freezing temperature, critical nucleus size must be infinite since ΔT approaches zero. As the amount of undercooling increases, critical size decreases, and are related as follows:

$$r^* = \frac{2\gamma T_m}{\Delta H_f \Delta T}$$

where T_m – freezing temperature (in K), ΔH_f – latent heat of fusion, ΔT – amount of undercooling at which nucleus is formed.

In *heterogeneous nucleation*, the probability of nucleation occurring at certain preferred sites is much greater than that at other sites. During solidification, inclusions of foreign particles (*inoculants*), walls of container holding the liquid provide preferred sites. Irregularities in crystal structure such as point defects and dislocations possess strain energy. In solid-solid transformation, foreign inclusions, grain boundaries, interfaces, stacking faults and dislocations can act as preferred sites for nucleation as the strain energy associated with them will be reduced. The released strain energy can reduce the energy requirements for free energy change, Δf. Therefore, nucleation proceeds with a smaller critical radius. A majority of reactions are initiated by some type of heterogeneous nucleation which is common among the two types.

For example, consider the nucleation of β from α occurring on a foreign inclusion, δ, as shown in *figure-13*. Considering the force equilibrium in surface tension terms,

$$\gamma_{\alpha\delta} = \gamma_{\alpha\beta} \cos\theta + \gamma_{\beta\delta}$$

where θ is the contact angle. An expression for Δf can be written in terms of volume energy and surface energies as follows:

$$\Delta f^*_{het} = \frac{4\pi\gamma^3_{\alpha\beta}}{3(\Delta g)^2}(2 - 3\cos\theta + \cos^3\theta) = \Delta f^*_{hom}\frac{2 - 3\cos\theta + \cos^3\theta}{4}$$
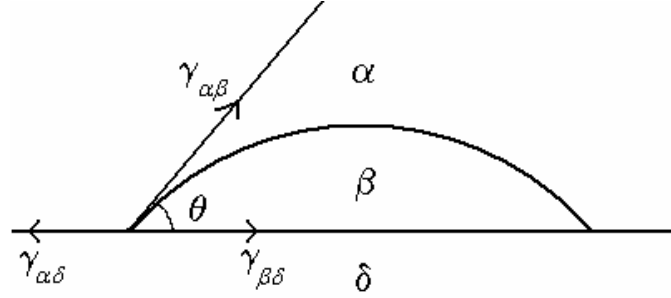

Figure-13: *Schematic of heterogeneous nucleation.*

By comparing the free energy terms for homogeneous and heterogeneous nucleation processes for various contact conditions:

- When product particle makes only a point contact with the foreign surface, i.e. $\theta = 180°$, the foreign particle does not play any role in the nucleation process → $\Delta f^*_{het} = \Delta f^*_{hom}$
- If the product particle completely wets the foreign surface, i.e. $\theta = 0°$, there is no barrier for heterogeneous nucleation → $\Delta f^*_{het} = 0$
- In intermediate conditions such as where the product particle attains hemispherical shape, $\theta = 0° → \Delta f^*_{het} = \frac{1}{2}\Delta f^*_{hom}$

The above derivations are helpful in selecting a heterogeneous nucleation agent. It shows that a small contact angle is very helpful in heterogeneous nucleation. For a system of $\alpha - \beta$ interface, θ can be minimized by choosing δ such that energy of β- δ interface is kept to minimum. If the crystal structure two phases are similar and their lattice parameters are nearly equal, energy of the interface between those two phases will be minimum. This criterion is useful in selecting a agent for heterogeneous nucleation.

7.2.2 Growth kinetics

Many transformations occur as a result of continuous formation of critical nuclei in the parent phase and the subsequent growth of the particles. Growth is the increase in size of the particle after it has nucleated i.e. growth kinetics become important once an embryo has exceeded the critical size and become a stable nucleus. Growth may proceed in two

radically different manners. In one type of growth, individual atoms move independently from the parent to the product phase, thus it is diffusion controlled and is thermally activated. In the other type of growth that occurs in solid-solid transformations many atoms move cooperatively without thermal assistance. Growth that is diffusion controlled is more common the other.

Growth usually occurs by the thermally activated jump of atoms from the parent phase to the product phase. The unit step in the growth process thus consists of an atom leaving the parent phase and jumping across the interface to join the product phase. At the equilibrium temperature, both phases have the same free energy, hence the frequency of jumps from parent phase to product phase will be equal to that from product phase to parent phase i.e. the net growth rate is zero. At lower temperatures, product phase is expected to have lower free energy, and thus a net flow of atoms from parent phase to product phase. This net flux of atoms results in interface motion i.e. growth rate is taken as the rate of increase of a linear dimension of a growing particle. As a function of temperature, the growth rate first increases with increasing degree of supercooling, but eventually slows-down as thermal energy decreases. This is same as for nucleation; however the maximum in the growth rate usually occurs at a higher temperature than the maximum in the nucleation rate. *Figure-14(a)* depicts the temperature dependence of nucleation rate (*U*), growth rate (*I*) and overall transformation rate (*dX/dt*) that is a function of both nucleation rate and growth rate i.e. *dX/dt= fn (U, I)*. On the other-hand, the time required for a transformation to completion has a reciprocal relationship to the overall transformation rate. Temperature dependence of this time is shown in *figure-14 (b)*. The *C-curve* shown in *figure-14(b)* is characteristic of all thermally activated nucleation and growth transformations involving the transformation of a high-temperature phase to low-temperature phase. This curve is also known as *time-temperature-transformation (TTT) curve*. The nose of the C-curve corresponds to the minimum time for a specified fraction of transformation. It is also the place where overall transformation rate is a maximum.
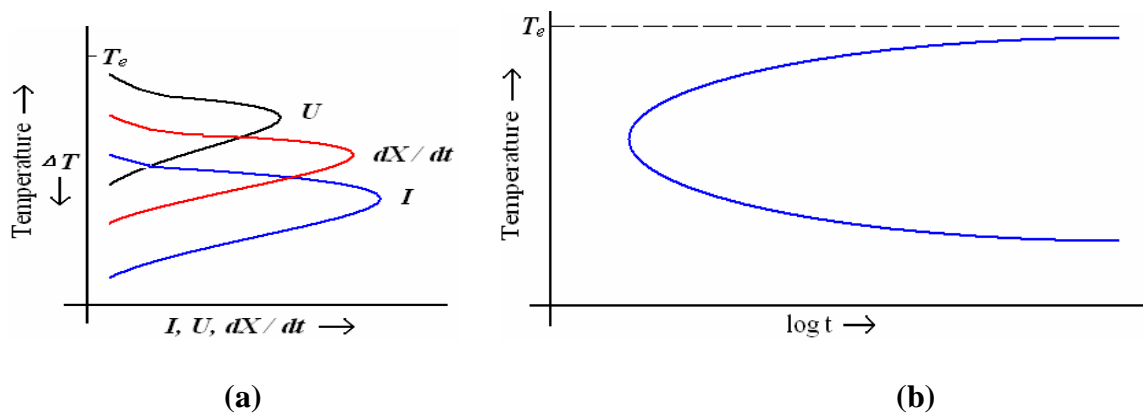

(a)   **(b)**

Figure-14: *(a) Temperature dependence of rates, (b) Time dependence of transformation as a function of temperature.*

In many investigations, the fraction of transformation that has occurred is measured as a function of time, while the temperature is maintained constant. Transformation progress

is usually ascertained by either microscopic examination *or* measurement of some physical property. Transformation data are plotted as the fraction of transformed material versus the logarithm of time, which results in characteristic *S-curve* (*figure-15*), largely because diffusion plays such an important role in both nucleation and growth. Conditions under which transformation may take place greatly affect the nature of the resulting microstructure. At small degrees of supercooling, where slow nucleation and rapid growth prevail, relatively coarse particles appear; at larger degrees of supercooling, relatively fine particles result. The time dependence of the transformation rate is an important consideration in the heat treatment of materials.
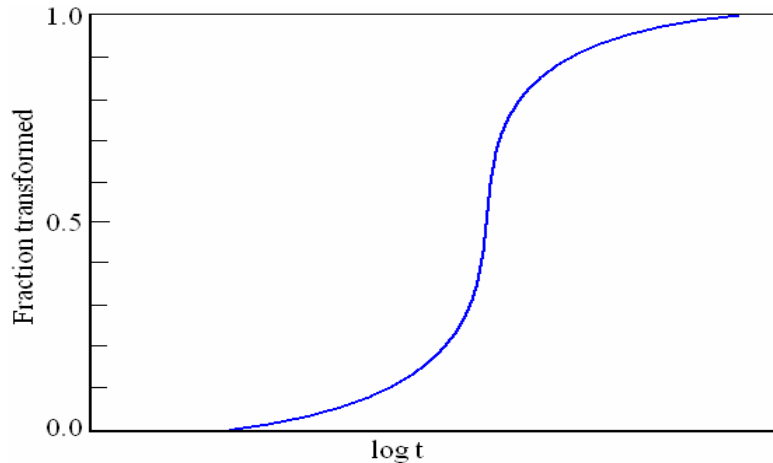

Figure-15: *Fraction of transformation Vs the logarithm of time at constant temperature.*

The other kind of growth involves congruent transformation which is considered as diffusion-less because it takes place at a rate approaching the speed of sound. It can be visualized as a cooperative type of process in which, without aid of thermal activation, atoms move into new locations because of the strain energy resulting from like movements of adjacent atoms. However the strains set-up in the parent phase may impede the further transformation, thus a lower temperature or mechanical deformation may be required to complete this *martensitic* transformation. The cooperative displacement of atoms here resembles a shear process during which, for example, FCC structure of Co transforms into HCP-Co *or* FCC-austenite into BCT-martensite. This merely requires that atoms in the FCC-phase move a fraction of an inter-atomic distance.

Because of its crystallographic nature, a martensitic transformation only occurs in the solid state. In addition, the crystal structure of the product phase must be easily generated from that of the parent phase without diffusive motion of atoms. This is true for most allotropic transformations in metals that occur at low temperatures or for high-temperature transformations of metals brought about by a quench. Reasons for martensitic transformation: (a) the free energy difference between the high-temperature phase and low-temperature phases becomes increasingly negative with decreasing temperature (b) the crystal structures of allotropes of a metal are relatively simple and share similar features with each other. It is also said that diffusion-controlled nucleation and growth and a martensitic change are competitive processes in many cases.

The martensitic transformation starts at a temperature designated M_s, which is generally below the equilibrium temperature, T_e. The transformation is completed at a lower temperature, M_f. The amount of parent phase transformed into product phase depends on temperature only, and is independent of time. Furthermore, in most cases, M_s temperature and the fractional amount of product phase as a function of temperature are independent of quenching rate. Consequently, M_s and M_f are presented as horizontal lines on a TTT diagram. Catalytic effect of cold working can be used to make M_s approach T_e. Martensitic transformations in Fe-C alloys and Ti are of great technological importance. Fe-C alloy transformations are dealt in detail in the following sections.

7.3 The iron – carbon system, phase transformations

A study of iron-carbon system is useful and important in many respects. This is because (1) steels constitute greatest amount of metallic materials used by man (2) solid state transformations that occur in steels are varied and interesting. These are similar to those occur in many other systems and helps explain the properties.

Iron-carbon phase diagram shown in *figure-16* is not a complete diagram. Part of the diagram after 6.67 wt% C is ignored as it has little commercial significance. The 6.67%C represents the composition where an inter-metallic compound, cementite (Fe_3C), with solubility limits forms. In addition, phase diagram is not true equilibrium diagram because cementite is not an equilibrium phase. However, in ordinary steels decomposition of cementite into graphite never observed because nucleation of cementite is much easier than that of graphite. Thus cementite can be treated as an equilibrium phase for practical purposes.
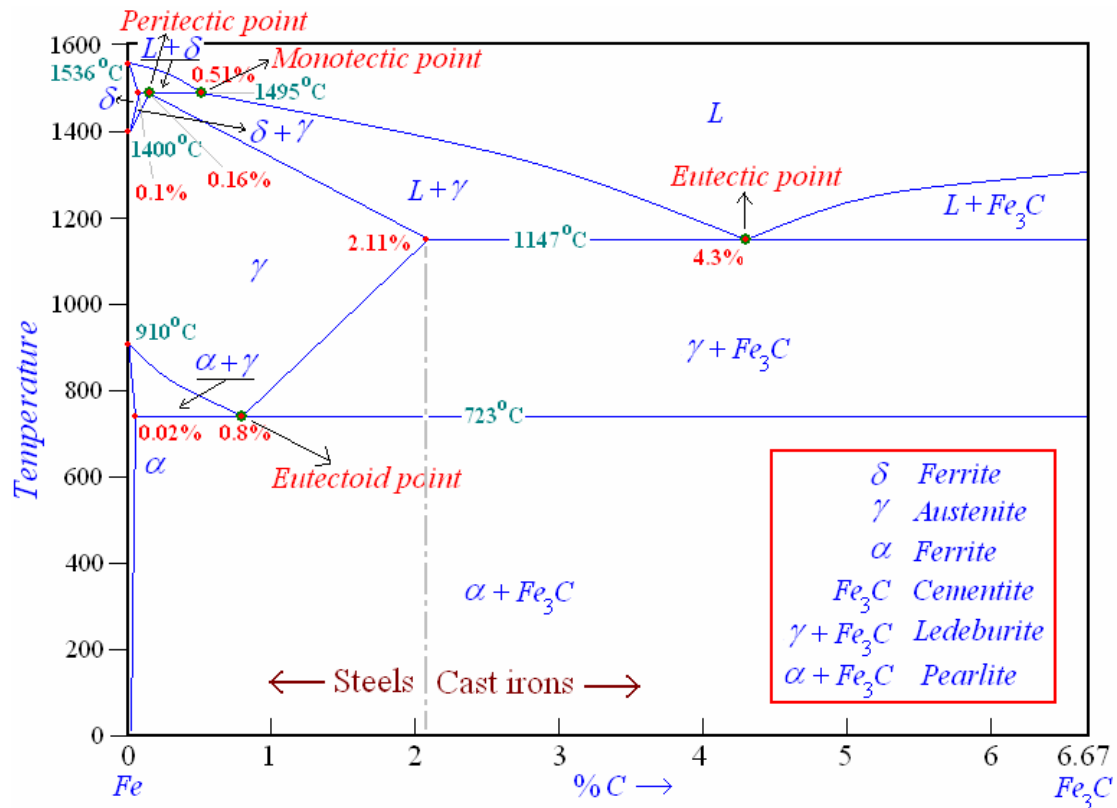
Figure-16: *Iron – Iron carbide phase diagram.*

The Fe-Fe₃C is characterized by five individual phases and four invariant reactions. Five phases that exist in the diagram are: α–ferrite (BCC) Fe-C solid solution, γ-austenite (FCC) Fe-C solid solution, δ-ferrite (BCC) Fe-C solid solution, Fe₃C (iron carbide) *or* cementite - an inter-metallic compound and liquid Fe-C solution. Four invariant reactions that cause transformations in the system are namely eutectoid, eutectic, monotectic and peritectic.

As depicted by left axes, pure iron upon heating exhibits two allotropic changes. One involves α–ferrite of BCC crystal structure transforming to FCC austenite, γ-iron, at 910 ℃. At 1400 ℃, austenite changes to BCC phase known as δ-ferrite, which finally melts at 1536 ℃.

Carbon present in solid iron as interstitial impurity, and forms solid solution with ferrites / austenite as depicted by three single fields represented by α, γ and δ. Carbon dissolves least in α–ferrite in which maximum amount of carbon soluble is 0.02% at 723 ℃. This limited solubility is attributed to shape and size of interstitial position in BCC α–ferrite. However, carbon present greatly influences the mechanical properties of α–ferrite. α–ferrite can be used as magnetic material below 768 ℃. Solubility of carbon in γ-iron reaches its maximum, 2.11%, at a temperature of 1147 ℃. Higher solubility of carbon in austenite is attributed to FCC structure and corresponding interstitial sites. Phase transformations involving austenite plays very significant role in heat treatment of different steels. Austenite itself is non-magnetic. Carbon solubility in δ-ferrite is maximum (0.1%) at 1495 ℃. As this ferrite exists only at elevated temperatures, it is of

no commercial importance. Cementite, Fe_3C an inter-metallic compound forms when amount of carbon present exceeds its solubility limit at respective temperatures. Out of these four solid phases, cementite is hardest and brittle that is used in different forms to increase the strength of steels. α–ferrite, on the other hand, is softest and act as matrix of a composite material. By combining these two phases in a solution, a material's properties can be varied over a large range.

For technological convenience, based on %C dissolved in it, a Fe-C solution is classified as: *commercial pure irons* with less than 0.008%C; *steels* having %C between 0.008-2.11; while *cast irons* have carbon in the range of 2.11%-6.67%. Thus commercial pure iron is composed of exclusively α–ferrite at room temperature. Most of the steels and cast irons contain both α–ferrite and cementite. However, commercial cast irons are not simple alloys of iron and carbon as they contain large quantities of other elements such as silicon, thus better consider them as ternary alloys. The presence of Si promotes the formation of graphite instead of cementite. Thus cast irons may contain carbon in form of both graphite and cementite, while steels will have carbon only in combined from as cementite.

As shown in *figure-16*, and mentioned earlier, Fe-C system constitutes four invariant reactions:

- peritectic reaction at 1495 ℃ and 0.16%C, δ-ferrite + L ↔ γ-iron (austenite)
- monotectic reaction 1495 ℃ and 0.51%C, L ↔ L + γ-iron (austenite)
- eutectic reaction at 1147 ℃ and 4.3 %C, L ↔ γ-iron + Fe_3C (cementite) [ledeburite]
- eutectoid reaction at 723 ℃ and 0.8%C, γ-iron ↔ α–ferrite + Fe_3C (cementite) [pearlite]

Product phase of eutectic reaction is called ledeburite, while product from eutectoid reaction is called pearlite. During cooling to room temperature, ledeburite transforms into pearlite and cementite. At room temperature, thus after equilibrium cooling, Fe-C diagram consists of either α–ferrite, pearlite and/or cementite. Pearlite is actually not a single phase, but a micro-constituent having alternate thin layers of α–ferrite (~88%) and Fe_3C, cementite (~12%). Steels with less than 0.8%C (mild steels up to 0.3%C, medium carbon steels with C between 0.3%-0.8% i.e. hypo-eutectoid Fe-C alloys) i.e. consists pro-eutectoid α–ferrite in addition to pearlite, while steels with carbon higher than 0.8% (high-carbon steels i.e. hyper-eutectoid Fe-C alloys) consists of pearlite and pro-eutectoid cementite. Phase transformations involving austenite i.e. processes those involve eutectoid reaction are of great importance in heat treatment of steels.

In practice, steels are almost always cooled from the austenitic region to room temperature. During the cooling upon crossing the boundary of the single phase γ-iron, first pro-eutectoid phase (either α–ferrite or cementite) forms up to eutectoid temperature. With further cooling below the eutectoid temperature, remaining austenite decomposes to eutectoid product called pearlite, mixture of thin layers of α–ferrite and cementite. Though pearlite is not a phase, nevertheless, a constituent because it has a definite

appearance under the microscope and can be clearly identified in a structure composed of several constituents. The decomposition of austenite to form pearlite occurs by nucleation and growth. Nucleation, usually, occurs heterogeneously and rarely homogeneously at grain boundaries. When it is not homogeneous, nucleation of pearlite occurs both at grain boundaries and in the grains of austenite. When austenite forms pearlite at a constant temperature, the spacing between adjacent lamellae of cementite is very nearly constant. For a given colony of pearlite, all cementite plates have a common orientation in space, and it is also true for the ferrite plates. Growth of pearlite colonies occurs not only by the nucleation of additional lamellae but also through an advance at the ends of the lamellae. Pearlite growth also involves the nucleation of new colonies at the interfaces between established colonies and the parent austenite. The thickness ratio of the ferrite and cementite layers in pearlite is approximately 8 to 1. However, the absolute layer thickness depends on the temperature at which the isothermal transformation is allowed to occur.

The temperature at which austenite is transformed has a strong effect on the inter-lamellar spacing of pearlite. The lower the reaction temperature, the smaller will be inter-lamellar spacing. For example, pearlite spacing is in order of 10^{-3} mm when it formed at 700 ̊C, while spacing is in order of 10^{-4} mm when formed at 600 ̊C. The spacing of the pearlite lamellae has a practical significance because the hardness of the resulting structure depends upon it; the smaller the spacing, the harder the metal. The growth rate of pearlite is also a strong function of temperature. At temperatures just below the eutectoid, the growth rate increases rapidly with decreasing temperature, reaching a maximum at 600 ̊C, and then decreases again at lower temperatures.

Additions of alloying elements to Fe-C system bring changes (alternations to positions of phase boundaries and shapes of fields) depends on that particular element and its concentration. Almost all alloying elements causes the eutectoid concentration to decrease, and most of the alloying elements (e.g.: Ti, Mo, Si, W, Cr) causes the eutectoid temperature to increase while some other (e.g.: Ni, Mn) reduces the eutectoid temperature. Thus alloying additions alters the relative amount of pearlite and pro-eutectoid phase that form.

Fe-C alloys with more than 2.11% C are called cast irons. Phase transformations in cast irons involve formation of pro-eutectic phase on crossing the liquidus. During the further cooling, liquid of eutectic composition decomposes in to mixture of austenite and cementite, known as ledeburite. On further cooling through eutectoid temperature, austenite decomposes to pearlite. The room temperature microstructure of cast irons thus consists of pearlite and cementite. Because of presence of cementite, which is hard, brittle and white in color, product is called *white cast iron*. However, depending on cooling rate and other alloying elements, carbon in cast iron may be present as graphite or cementite. *Gray cast iron* contains graphite in form of flakes. These flakes are sharp and act as stress risers. Brittleness arising because of flake shape can be avoided by producing graphite in spherical nodules, as in *malleable cast iron* and *SG (spheroidal graphite) cast iron*. Malleable cast iron is produced by heat treating white cast iron (Si < 1%) for prolonged periods at about 900 ̊C and then cooling it very slowly. The cementite decomposes and temper carbon appears approximately as spherical particles. SG iron is produced by

adding inoculants to molten iron. In these Si content must be about 2.5%, and no subsequent heat treatment is required.

7.4 Transformation rate effects and TTT diagrams, Microstructure and Property Changes in Fe-C Alloys

Solid state transformations, which are very important in steels, are known to be dependent on time at a particular temperature, as shown in *figure-14(b)*. Isothermal transformation diagram, also known as TTT diagram, measures the rate of transformation at a constant temperature i.e. it shows time relationships for the phases during isothermal transformation. Information regarding the time to start the transformation and the time required to complete the transformation can be obtained from set of TTT diagrams. One such set of diagram for reaction of austenite to pearlite in steel is shown in *figure-17*. The diagram is not complete in the sense that the transformations of austenite that occur at temperatures below about 550 ℃ are not shown.
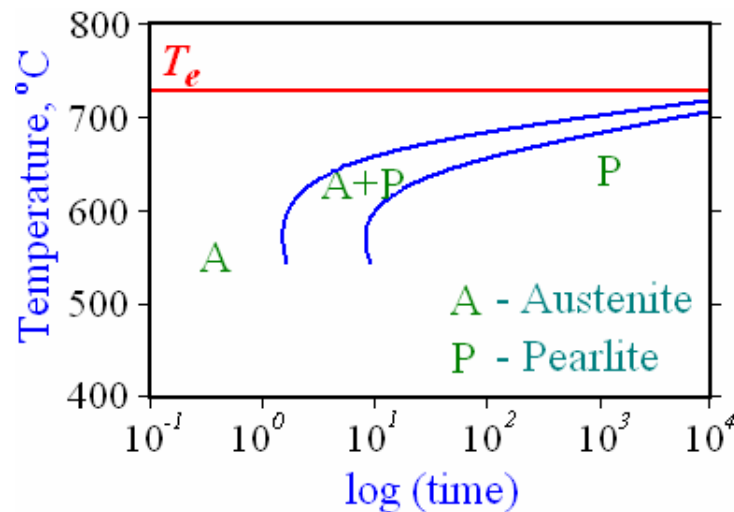

Figure-17: *Partial TTT diagram for a eutectoid Fe-C alloy.*

As mentioned in previous section, thickness of layers in pearlite depends on the temperature at which the transformation occurred. If the transformation took place at a temperature that is just below the eutectoid temperature, relatively thick layers of α–ferrite and cementite are produced in what is called *coarse pearlite*. This is because of high diffusion rates of carbon atoms. Thus with decreasing transformation temperature, sluggish movement of carbon results in thinner layers α–ferrite and cementite i.e. *fine pearlite* is produced.

At transformation temperatures below 550 ℃, austenite results in different product known as bainite. Bainite also consists of α–ferrite and cementite phases i.e. transformation is again diffusion controlled but morphologically it consists of very small particles of cementite within or between fine ferrite plates. Bainite forms needles or plates, depending on the temperature of the transformation; the microstructural details of bainite are so fine that their resolution is only possible using electron microscope. It

differs from pearlite in the sense that different mechanism is involved in formation ob bainite which does not have alternating layers of α–ferrite and cementite. In addition, because of equal growth rates in all directions pearlite tends to form spherical colonies, whereas bainite grows as plates and has a characteristic acicular (needlelike) appearance. *Upper bainite*, formed at the upper end of the temperature range (550 ˚C-350 ˚C), is characterized by relatively coarse, irregular shaped cementite particles in α–ferrite plates. If the transformation is taking place at lower temperatures (350 ˚C-250 ˚C), the α–ferrite plates assume a more regular needlelike shape, and the transformation product is called *lower bainite*. At the same time carbide particles become smaller in size and appear as cross-striations making an angle of about 55 ˚to the axis of the α–ferrite plate. Upper bainite has large rod-like cementite regions, whereas lower bainite has much finer cementite particles as a result of sluggish diffusion of carbon atoms at lower temperatures. Lower bainite is considerably harder than upper bainite. Another characteristic of bainite is that as it has crystallographic orientation that is similar to that found in simple ferrite nucleating from austenite, it is believed that bainite is nucleated by the formation of ferrite. This is in contrast to pearlite which is believed to be nucleated by formation of cementite.

Basically, bainite is a transformation product that is not as close to equilibrium as pearlite. The most puzzling feature of the bainite reaction is its dual nature. In a number of respects, it reveals properties that are typical of a nucleation and growth type of transformation such as occurs in the formation pearlite and also a mixture of α–ferrite and cementite though of quite different morphology (no alternate layers), but at the same time it differs from the Martensite as bainite formation is athermal and diffusion controlled though its microstructure is characterized by acicular (needlelike) appearance.

The time-temperature dependence of the bainite transformation can also be presented using TTT diagram. It occurs at temperatures below those at which pearlite forms i.e. it does not form until the transformation temperature falls below a definite temperature, designated as B_s. Above this temperature austenite does not form bainite except under external stresses. Below B_s, austenite does not transform completely to bainite. The amount of bainite formed increases as the isothermal reaction temperature is lowered. By reaching a lower limiting temperature, B_f, it is possible to transform austenite completely to bainite. The B_s and B_f temperatures are equivalent to the M_s and M_f temperatures for Martensite.

In simple eutectoid steels, pearlite and bainite transformations overlap, thus transition from the pearlite to bainite is smooth and continuous i.e. knees of individual pearlite and bainite curves are merged together. However each of the transformations has a characteristic C-curve, which can be distinguishable in presence of alloying elements. As shown in complete TTT diagram for eutectoid steel in *figure-18*, above approximately 550 ˚C-600 ˚C, austenite transforms completely to pearlite. Below this range up to 450 ˚C, both pearlite and bainite are formed. Finally, between 450 ˚C and 210 ˚C, the reaction product is bainite only. Thus bainite transformation is favored at a high degree of supercooling, and the pearlite transformation at a low degree of supercooling. In middle region, pearlitic and bainitic transformations are competitive with each other.
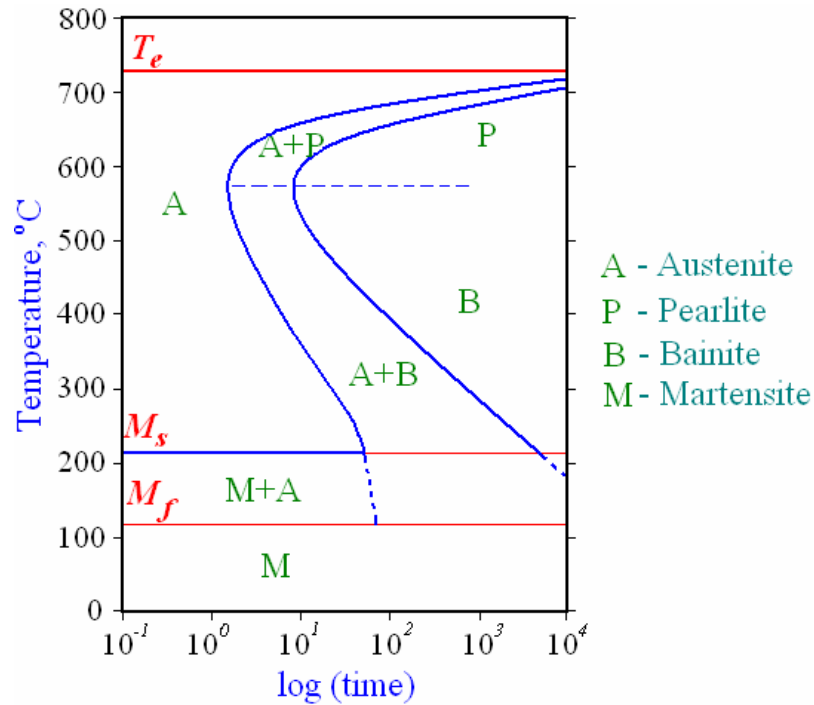
Figure-18: *Complete TTT (isothermal transformation) diagram for eutectoid steel.*

As explained in earlier section, martensitic transformation can dominate the proceedings if steel is cooled rapid enough so that diffusion of carbon can be arrested. Transformation of austenite to Martensite is diffusion-less, time independent and the extent of transformation depends on the transformation temperature. Martensite is a *meta-stable* phase and decomposes into ferrite and pearlite but this is extremely slow (and not noticeable) at room temperature. Alloying additions retard the formation rate of pearlite and bainite, thus rendering the martensitic transformation more competitive. Start of the transformation is designated by M_s, while the completion is designated by M_f in a transformation diagram. Martensite forms in steels possesses a body centered tetragonal crystal structure with carbon atoms occupying one of the three interstitial sites available. This is the reason for characteristic structure of steel Martensite instead of general BCC. Tetragonal distortion caused by carbon atoms increases with increasing carbon content and so is the hardness of Martensite. Austenite is slightly denser than Martensite, and therefore, during the phase transformation upon quenching, there is a net volume increase. If relatively large pieces are rapidly quenched, they may crack as a result of internal stresses, especially when carbon content is more than about 0.5%.

Mechanically, Martensite is extremely hard, thus its applicability is limited by brittleness associated with it. Characteristics of steel Martensite render it unusable for structural applications in the as-quenched form. However, structure and thus the properties can be altered by *tempering*, heat treatment observed below eutectoid temperature to permit diffusion of carbon atoms for a reasonable period of time. During tempering, carbide particles attain spherical shape and are distributed in ferrite phase – structure called *spheroidite*. Spheroidite is the softest yet toughest structure that steel may have. At lower

tempering temperature, a structure called *tempered Martensite* forms with similar microstructure as that of spheroidite except that cementite particles are much, much smaller. The tempering heat treatment is also applicable to pearlitic and bainitic structures. This mainly results in improved machinability. The mechanism of tempering appears to be first the precipitation of fine particles of hexagonal ε-carbide of composition about $Fe_{2.4}C$ from Martensite, decreasing its tetragonality. At higher temperatures or with increasing tempering times, precipitation of cementite begins and is accompanied by dissolution of the unstable ε-carbide. Eventually the Martensite loses its tetragonality and becomes BCC ferrite, the cementite coalesces into spheres. A schematic of possible transformations involving austenite decomposition are shown in *figure-19*.
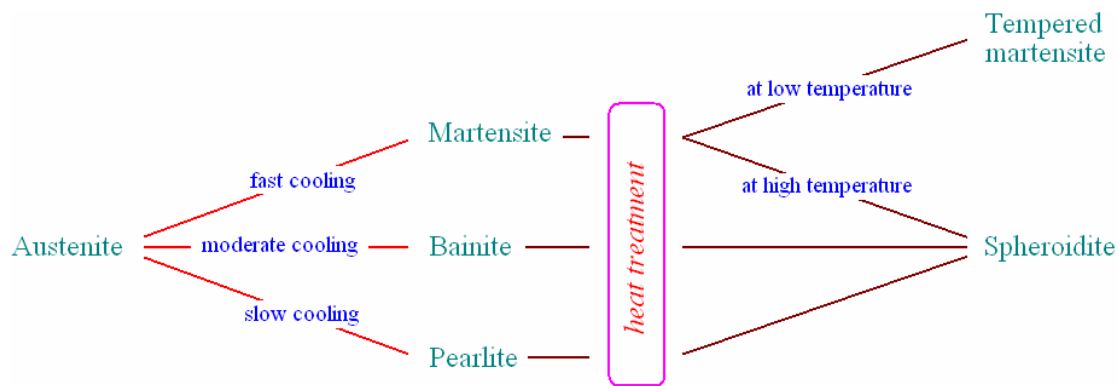

Figure-19: *Possible transformation involving austenite decomposition.*

Tempering of some steels may result in a reduction of toughness what is known as *temper embrittlement*. This may be avoided by (1) compositional control, and/or (2) tempering above 575 *or* below 375, followed by quenching to room temperature. The effect is greatest in Martensite structures, less severe in bainitic structures and least severe in pearlite structures. It appears to be associated with the segregation of solute atoms to the grain boundaries lowering the boundary strength. Impurities responsible for temper brittleness are: P, Sn, Sb and As. Si reduces the risk of embrittlement by carbide formation. Mo has a stabilizing effect on carbides and is also used to minimize the risk of temper brittleness in low alloy steels.

TTT diagrams are less of practical importance since an alloy has to be cooled rapidly and then kept at a temperature to allow for respective transformation to take place. However, most industrial heat treatments involve continuous cooling of a specimen to room temperature. Hence, Continuous Cooling Transformation (CCT) diagrams are generally more appropriate for engineering applications as components are cooled (air cooled, furnace cooled, quenched etc.) from a processing temperature as this is more economic than transferring to a separate furnace for an isothermal treatment. CCT diagrams measure the extent of transformation as a function of time for a continuously decreasing temperature. For continuous cooling, the time required for a reaction to begin and end is delayed, thus the isothermal curves are shifted to longer times and lower temperatures.

Both TTT and CCT diagrams are, in a sense, phase diagrams with added parameter in form of time. Each is experimentally determined for an alloy of specified composition. These diagrams allow prediction of the microstructure after some time period for constant temperature and continuous cooling heat treatments, respectively. Normally, bainite will not form during continuous cooling because all the austenite will have transformed to pearlite by the time the bainite transformation has become possible. Thus, as shown in *figure-20*, region representing austenite-pearlite transformation terminates just below the nose.
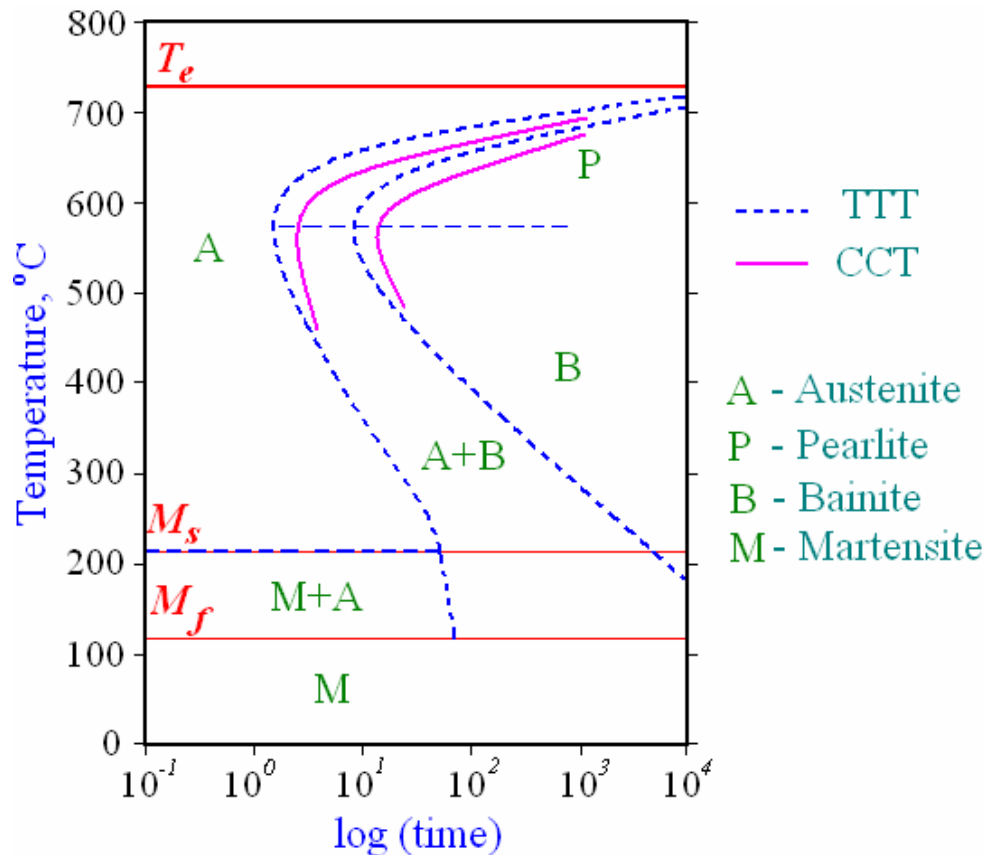

Figure-20: *Superimposition of TTT and CCT diagrams for a eutectoid steel.*

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