Module-07

Phase Diagrams

Contents

Mixtures – Solutions – Phases

- Almost all materials have more than one phase in them. Thus engineering materials attain their special properties.
- Macroscopic basic unit of a material is called component. It refers to a independent chemical species. The components of a system may be elements, ions or compounds.
- 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.
- A component can exist in many phases.

E.g.: Water exists as ice, liquid water, and water vapor.
Carbon exists as graphite and diamond.

Mixtures – Solutions – Phases (contd…)

- 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.
- A *solution* (liquid or solid) is phase with more than one component; a *mixture* is a material with more than one phase.
- Solute (minor component of two in a solution) 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!

Gibbs phase rule

- In a system under a set of conditions, number of phases (P) exist can be related to the number of components (C) and degrees of freedom (F) by Gibbs phase rule.
- Degrees of freedom refers to the number of independent variables (e.g.: pressure, temperature) that can be varied individually to effect changes in a system.
- Thermodynamically derived *Gibbs phase rule*:

$$P + F = C + 2$$

- In practical conditions for metallurgical and materials systems, pressure can be treated as a constant (1 atm.). Thus *Condensed Gibbs phase rule* is written as:

$$P + F = C + 1$$

Equilibrium phase diagram

- A diagram that depicts existence of different phases of a system under equilibrium is termed as *phase diagram*.
- It is actually a collection of solubility limit curves. It is also known as *equilibrium* or *constitutional diagram*.
- Equilibrium phase diagrams represent the relationships between temperature, compositions and the quantities of phases at equilibrium.
- These diagrams *do not* indicate the dynamics when one phase transforms into another.
- Useful terminology related to phase diagrams: *liquidus*, *solidus*, *solvus*, *terminal solid solution*, *invariant reaction*, *intermediate solid solution*, *inter-metallic compound*, etc.
- Phase diagrams are *classified* according to the number of component present in a particular system.

Phase diagram – Useful information

- Important information, useful in materials development and selection, obtainable from a phase diagram:

  - It shows phases present at different compositions and temperatures under slow cooling (equilibrium) conditions.

  - It indicates equilibrium solid solubility of one element/compound in another.

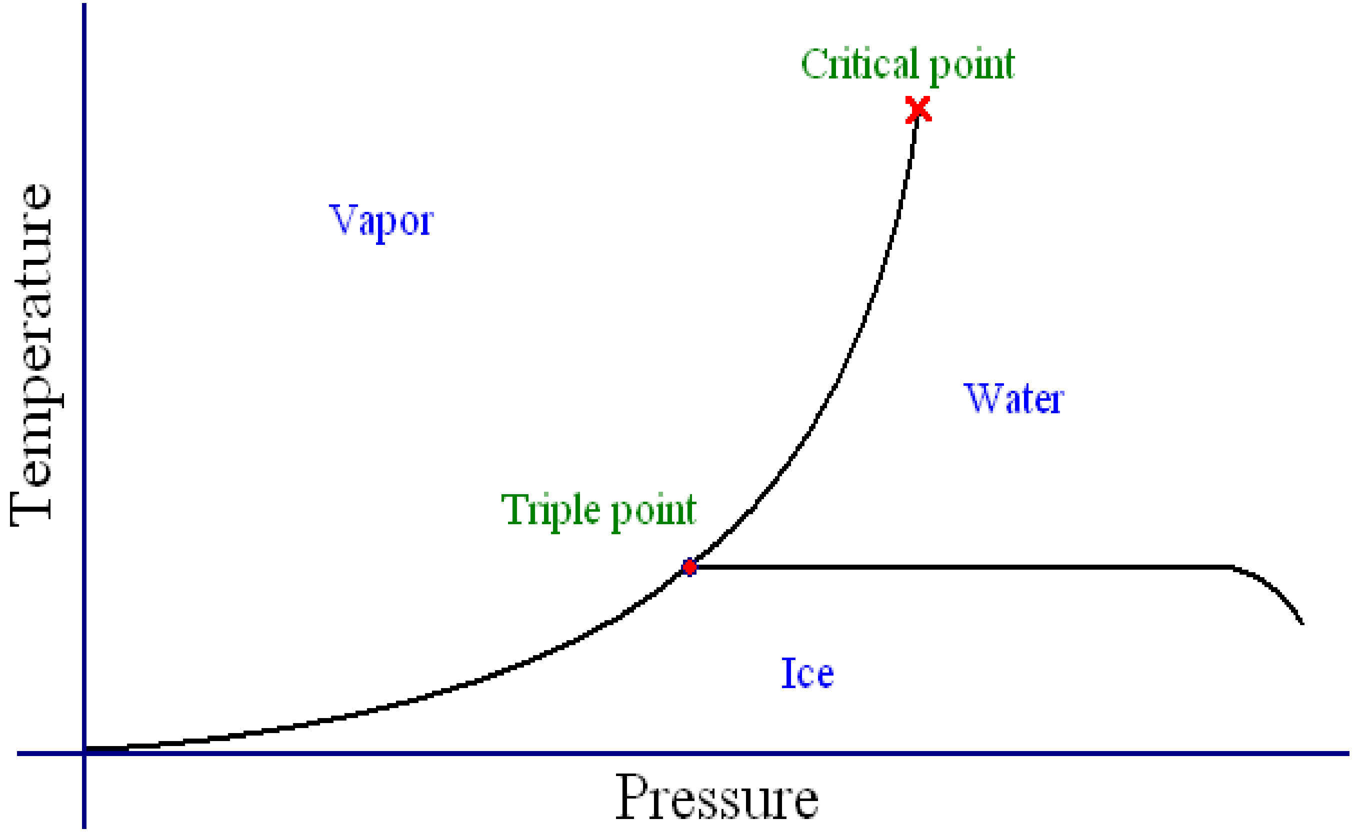
  - It suggests temperature at which an alloy starts to solidify and the range of solidification.

  - It signals the temperature at which different phases start to melt.

  - Amount of each phase in a two-phase mixture can be obtained.

Unary phase diagram

- If a system consists of just one component (e.g.: water), equilibrium of phases exist is depicted by *unary phase diagram*. The component may exist in different forms, thus variables here are – temperature and pressure.



Binary phase diagram

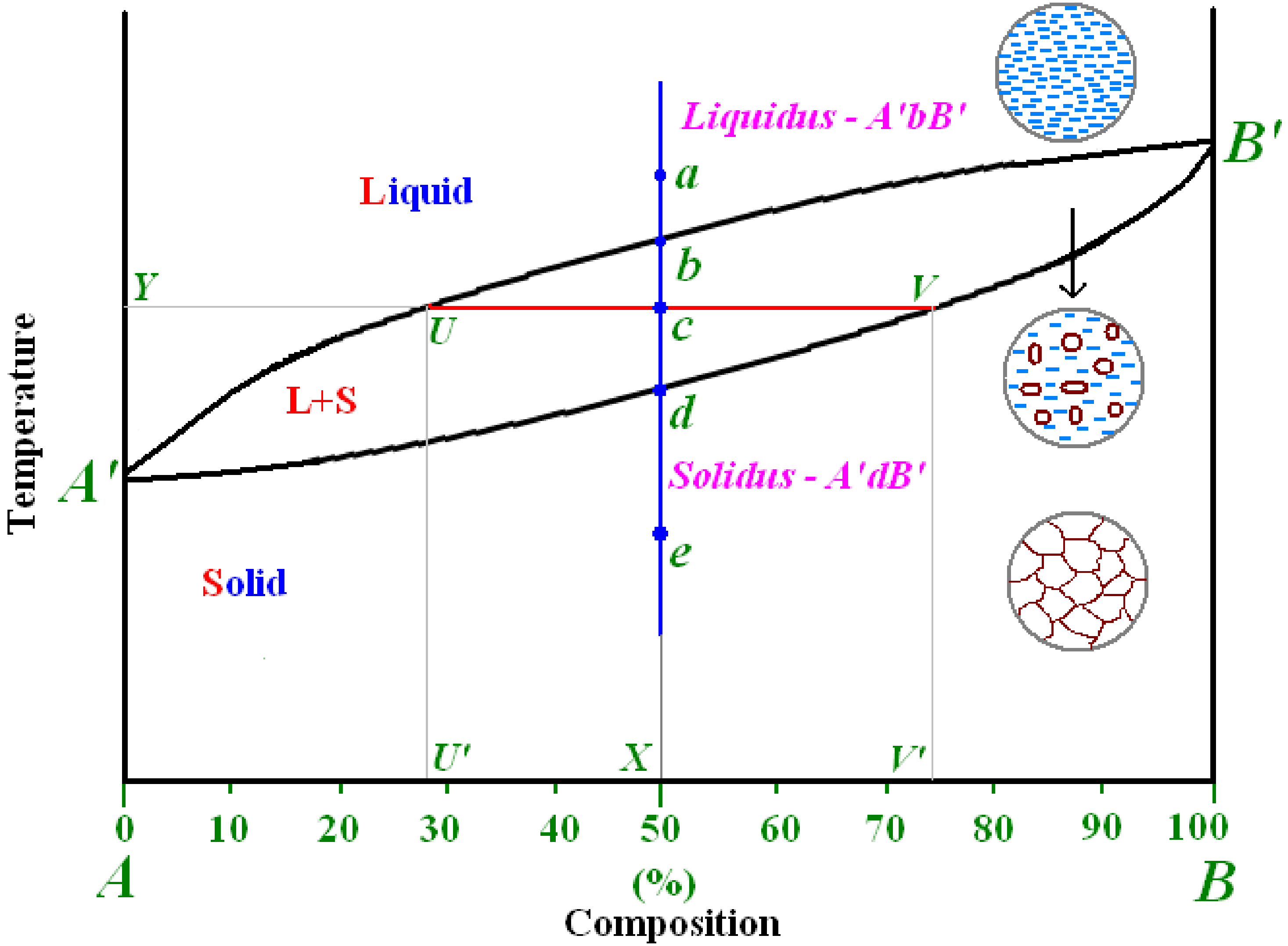
- If a system consists of two components, equilibrium of phases exist is depicted by *binary phase diagram*. For most systems, pressure is constant, thus independently variable parameters are – temperature and composition.
- Two components can be either two metals (Cu and Ni), or a metal and a compound (Fe and Fe3C), or two compounds (Al2O3 and Si2O3), etc.
- Two component systems are classified based on extent of mutual solid solubility – (a) completely soluble in both liquid and solid phases (isomorphous system) and (b) completely soluble in liquid phase whereas solubility is limited in solid state.
- For isomorphous system - E.g.: Cu-Ni, Ag-Au, Ge-Si, Al_2O_3-Cr_2O_3.

Hume-Ruthery conditions

- Extent of solid solubility in a two element system can be predicted based on Hume-Ruthery conditions.
- If the system obeys these conditions, then complete solid solubility can be expected.
- Hume-Ruthery conditions:
  - 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.

Isomorphous binary system

- An isomorphous system – phase diagram and corresponding microstructural changes.



Tie line – Lever rule

- At a point in a phase diagram, phases present and their composition (tie-line method) along with relative fraction of phases (lever rule) can be computed.

- Procedure to find equilibrium concentrations of phases (refer to the figure in previous slide):

  - 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'***, 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.

Tie line – Lever rule (contd….)

- 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.

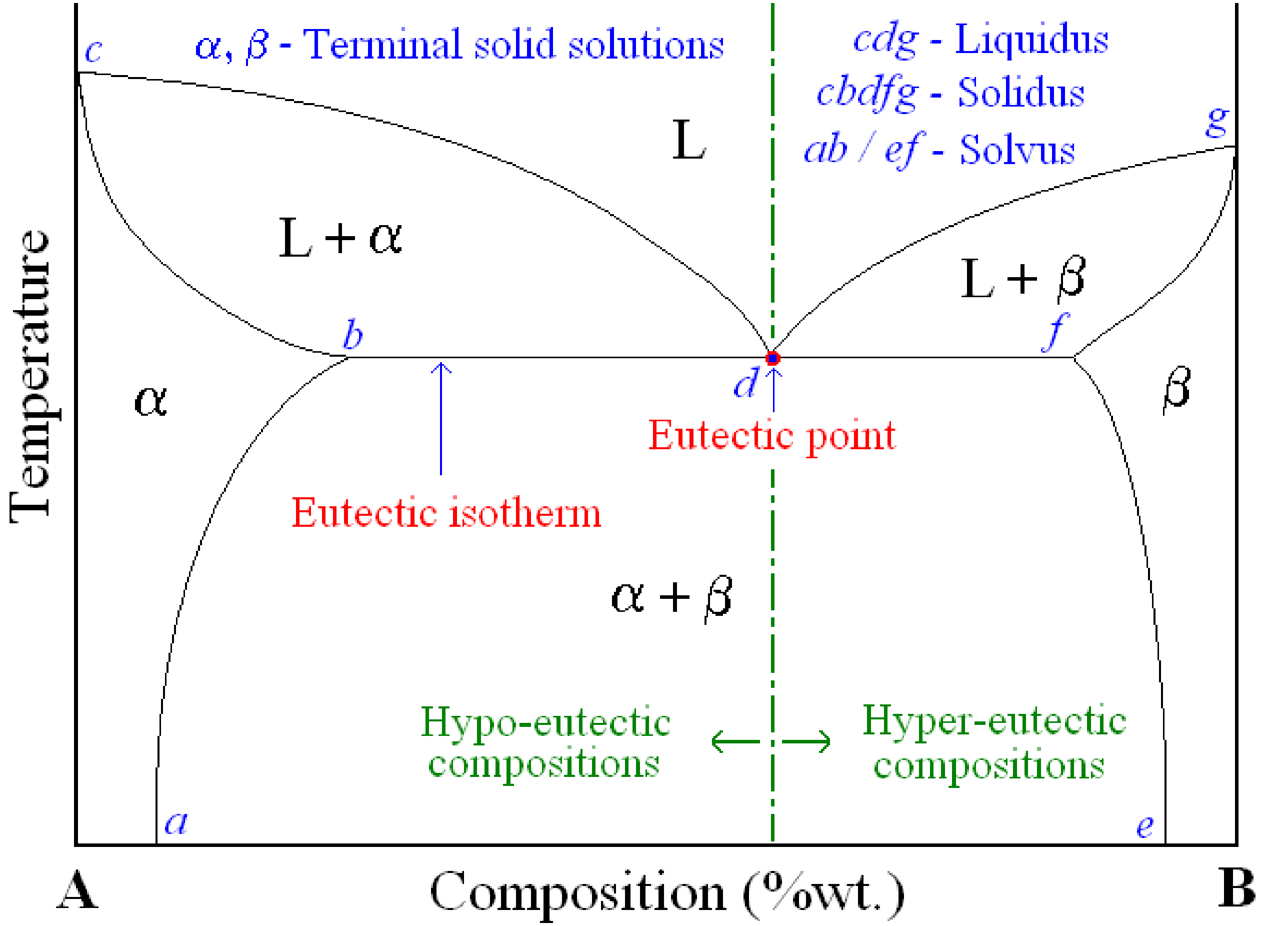
  \- The relative amount of a phase is computed by taking the length of tie line from overall composition to the phase boundary for the other phase, and dividing by the total tie-line length. In previous figure, relative amount of liquid and solid phases is given respectively by:

$$C_L = \frac{cV}{UV} \qquad C_S = \frac{Uc}{UV} \qquad C_L + C_S = 1$$

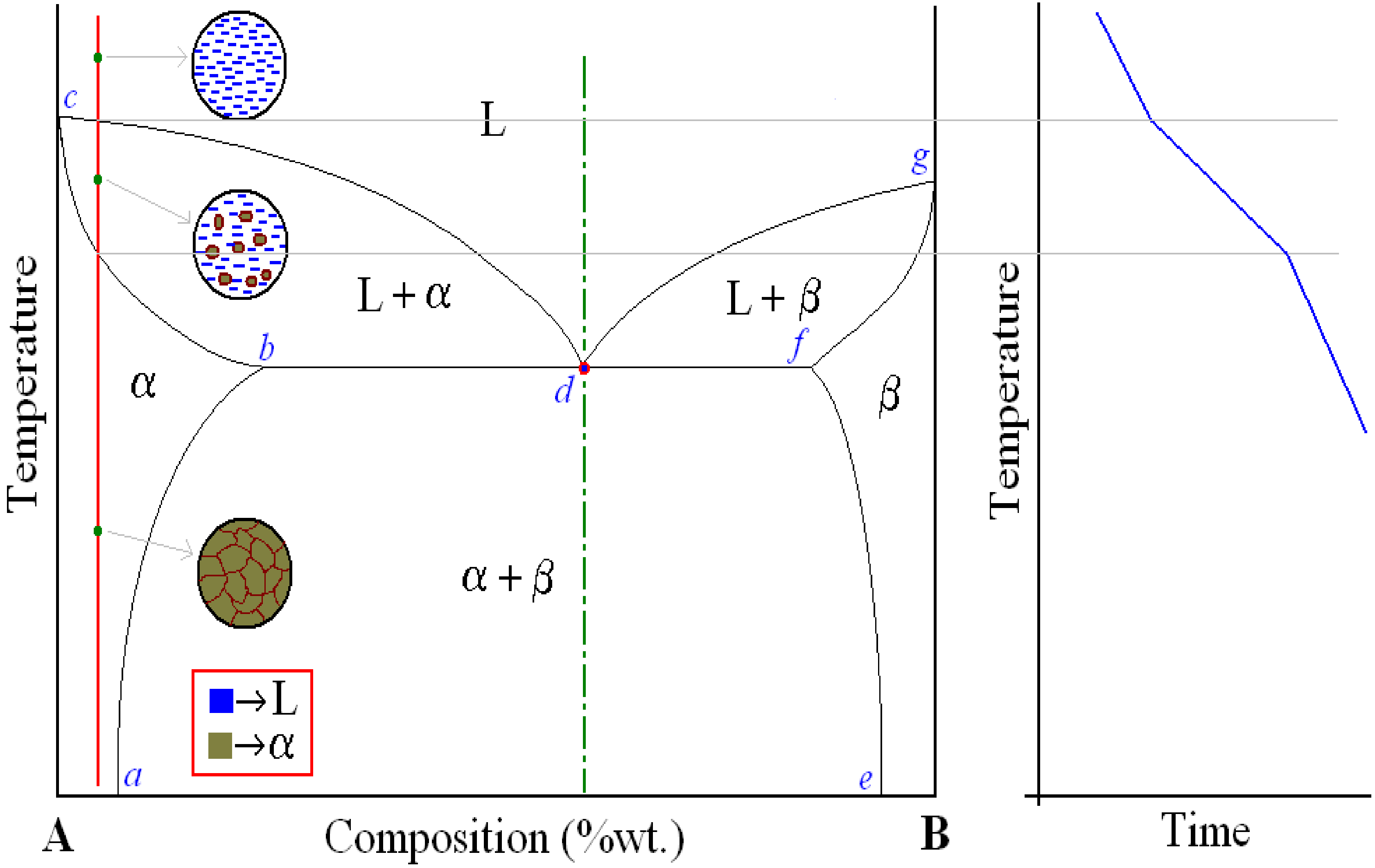
Eutectic binary system

- Many of the binary systems with limited solubility are of eutectic type – eutectic alloy of eutectic composition solidifies at the end of solidification at eutectic temperature.

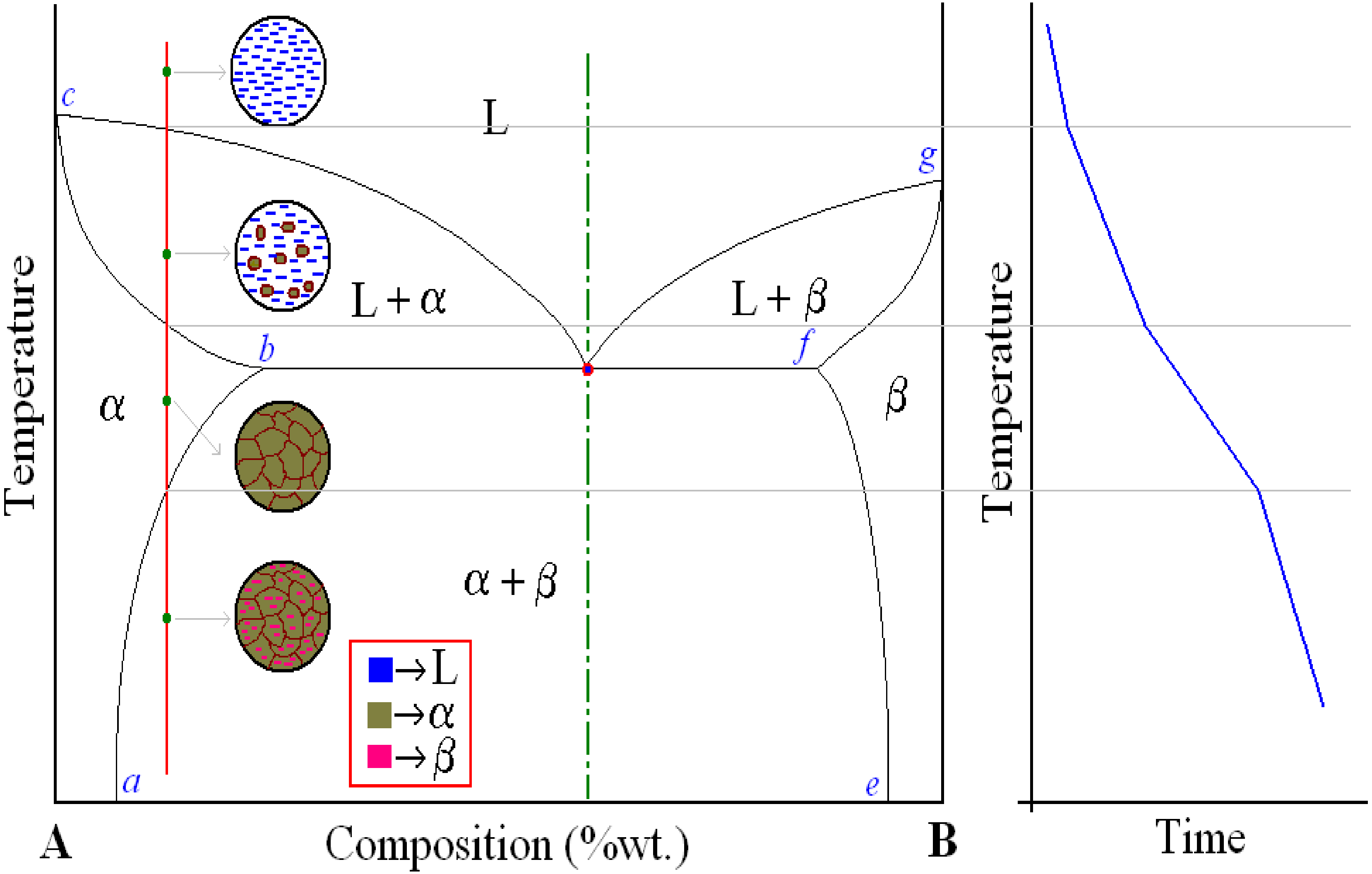
  E.g.: Cu-Ag, Pb-Sn



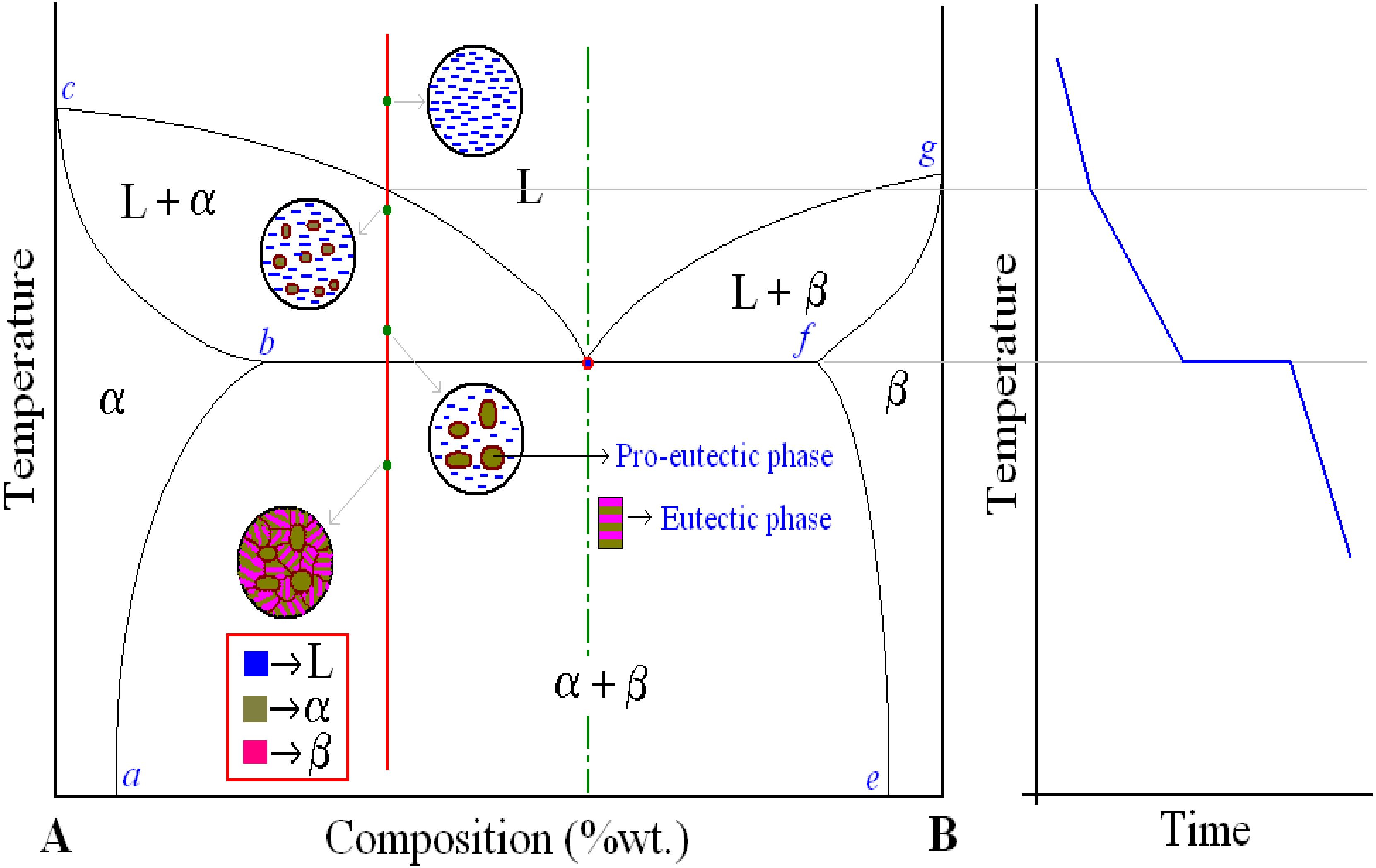
Eutectic system – Cooling curve – Microstructure



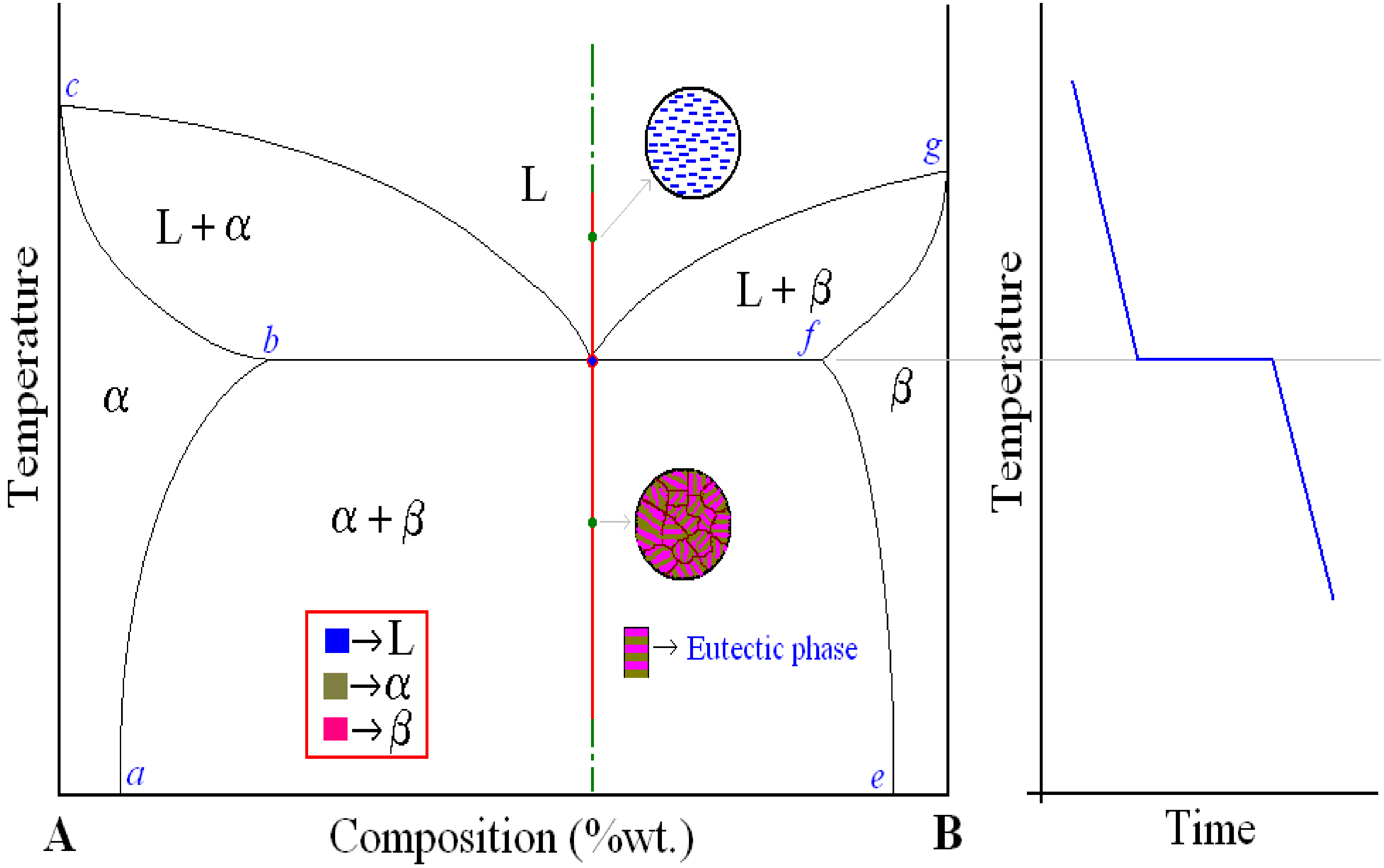
Eutectic system – Cooling curve – Microstructure (contd….)



Eutectic system – Cooling curve – Microstructure (contd….)



Eutectic system – Cooling curve – Microstructure (contd….)

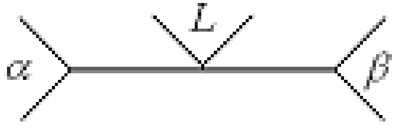
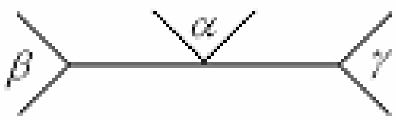
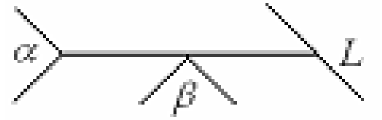
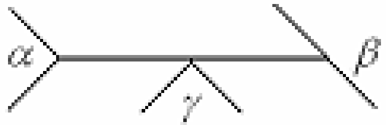
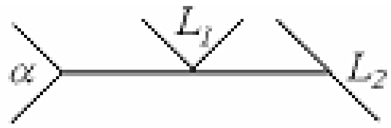
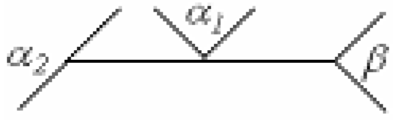
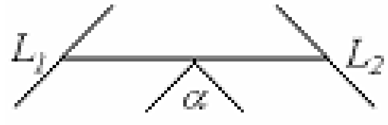


Invariant reactions

- Observed triple point in unary phase diagram for water?
- How about eutectic point in binary phase diagram?

- These points are specific in the sense that they occur only at that particular conditions of concentration, temperature, pressure etc.
- Try changing any of the variable, it does not exist i.e. phases are not equilibrium any more!
- Hence they are known as invariant points, and represents *invariant reactions*.
- In binary systems, we will come across many number of invariant reactions!

Invariant reactions (contd….)

Reaction	**Symbolic equation**	**Schematic presentation**	**Example**
Eutectic	$L \rightarrow \alpha + \beta$		Fe-C, 4.27% C, 1147°C
Eutectoid	$\alpha \rightarrow \beta + \gamma$		Fe-C, 0.80% C, 723°C
Peritectic	$L + \alpha \rightarrow \beta$		Fe-C, 0.16%C, 1495°C
Peritectoid	$\alpha + \beta \rightarrow \gamma$		
Monotectic	$L_1 \rightarrow L_2 + \alpha$		Fe-C, 0.51%C, 1495°C
Monotectoid	$\alpha_1 \rightarrow \alpha_2 + \beta$		
Syntectic	$L_1 + L_2 \rightarrow \alpha$		

Intermediate phases

- Invariant reactions result in different product phases – terminal phases and intermediate phases.
- Intermediate phases are either of varying composition (intermediate solid solution) *or* fixed composition (inter-metallic compound).
- Occurrence of intermediate phases cannot be readily predicted from the nature of the pure components!
- *Inter-metallic compounds* differ from other chemical compounds in that the bonding is primarily metallic rather than ionic *or* covalent.

  E.g.: Fe_3C is metallic, whereas MgO is covalent.
- When using the lever rules, inter-metallic compounds are treated like any other phase.

Congruent, Incongruent transformations

- Phase transformations are two kinds – congruent and incongruent.
- *Congruent transformation* involves no compositional changes. It usually occurs at a temperature.

  E.g.: Allotropic transformations, melting of pure a substance.
- During *incongruent transformations*, at least one phase will undergo compositional change.

  E.g.: All invariant reactions, melting of isomorphous alloy.
- Intermediate phases are sometimes classified on the basis of whether they melt congruently or incongruently.

  E.g.: MgNi2, for example, melts congruently whereas Mg2Ni melts incongruently since it undergoes peritectic decomposition.

Precipitation – Strengthening – Reactions

- A material can be strengthened by obstructing movement of dislocations. Second phase particles are effective.
- Second phase particles are introduced mainly by two means – direct mixing and consolidation, or by precipitation.
- Most important *pre-requisite* for precipitation strengthening: there must be a terminal solid solution which has a decreasing solid solubility as the temperature decreases.

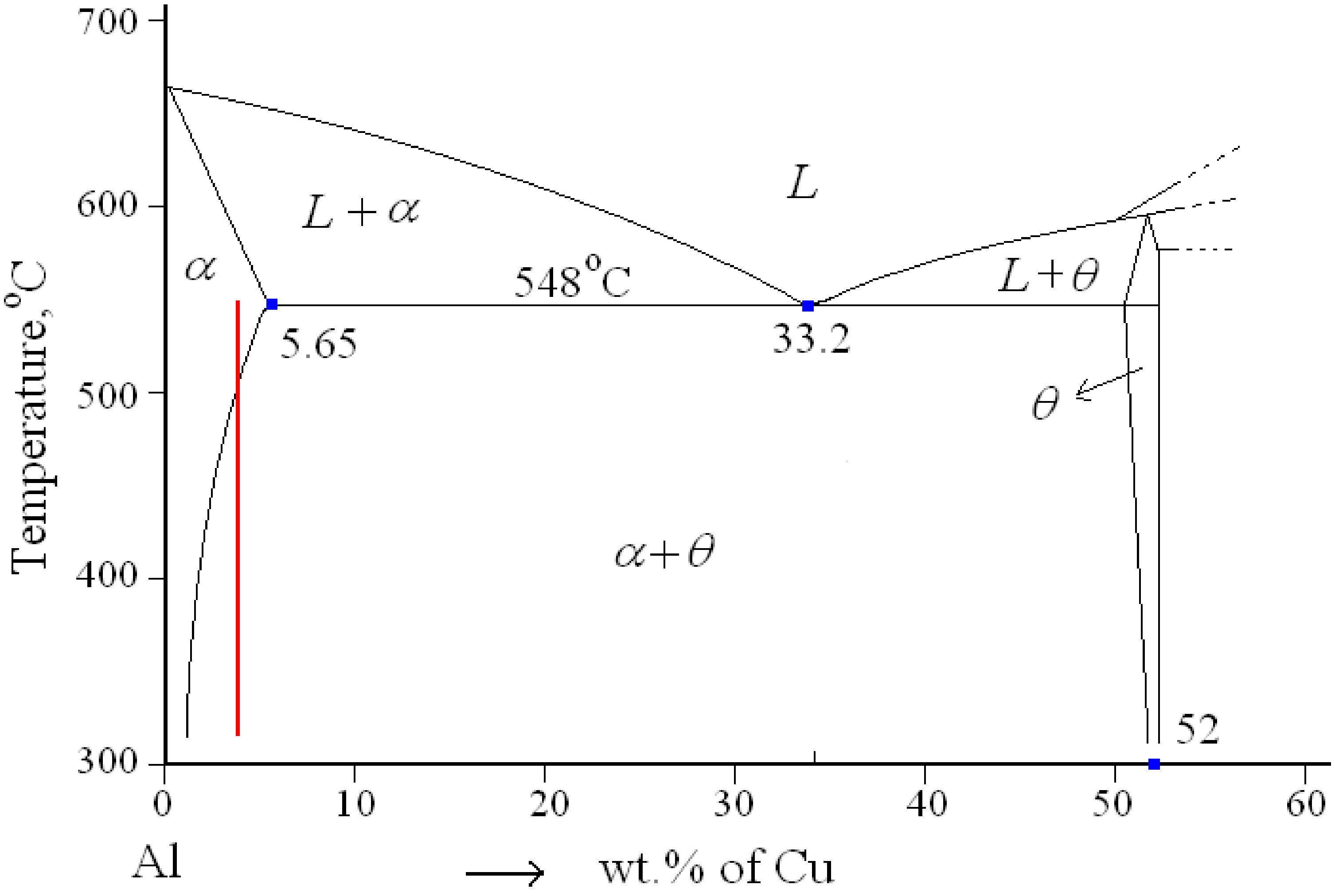
  E.g.: Au-Cu in which maximum solid solubility of Cu in Al is 5.65% at 548 C that decreases with decreasing temperature.
- Three basic steps in precipitation strengthening: *solutionizing*, *quenching* and *aging*.

Precipitation – Strengthening – Reactions (contd….)

- 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). Resultant product – 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 – Reactions (contd….)

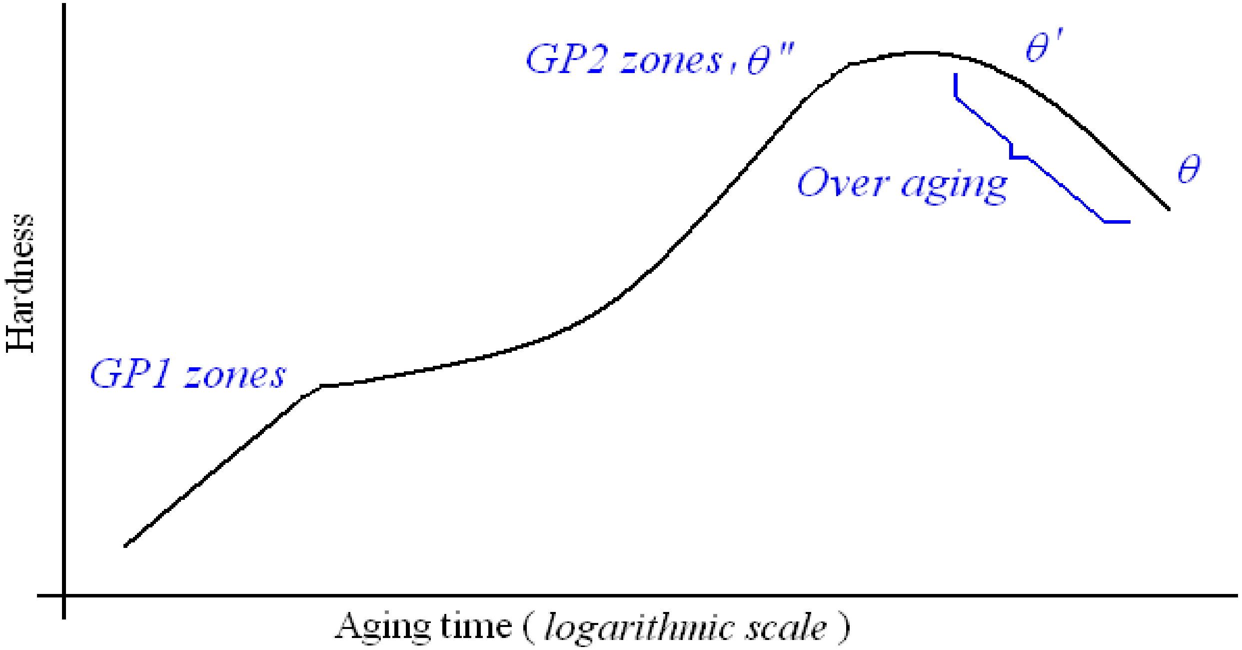
- Al-4%Cu alloy is used to explain the mechanism of precipitation strengthening.



Precipitation – Strengthening – Reactions (contd….)

- Al-4%Cu alloy when cooled slowly from solutionizing temperature, produces coarse grains – moderate strengthening.
- For precipitation strengthening, it is quenched, and aged!
- Following sequential reactions takes place during aging:

  Supersaturated ***α*** → GP1 zones → GP2 zones (***θ”*** phase) → ***θ’*** phase → ***θ*** phase (CuAl$_2$)



Nucleation and Growth

- Structural changes / Phase transformations takes place by nucleation followed by growth.
- Temperature changes are important among variables (like pressure, composition) causing phase transformations as diffusion plays an important role.
- Two other factors that affect transformation rate along with temperature – (1) diffusion controlled rearrangement of atoms because of compositional and/or crystal structural differences; (2) difficulty encountered in nucleating small particles via change in surface energy associated with the interface.
- Just nucleated particle has to overcome the +ve energy associated with new interface formed to survive and grow further. It does by reaching a critical size.

Homogeneous nucleation – Kinetics

- *Homogeneous nucleation* – nucleation occurs within parent phase. All sites are of equal probability for nucleation.
- It requires considerable under-cooling (cooling a material below the equilibrium temperature for a given transformation without the transformation occurring).
- Free energy change associated with formation of new particle

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

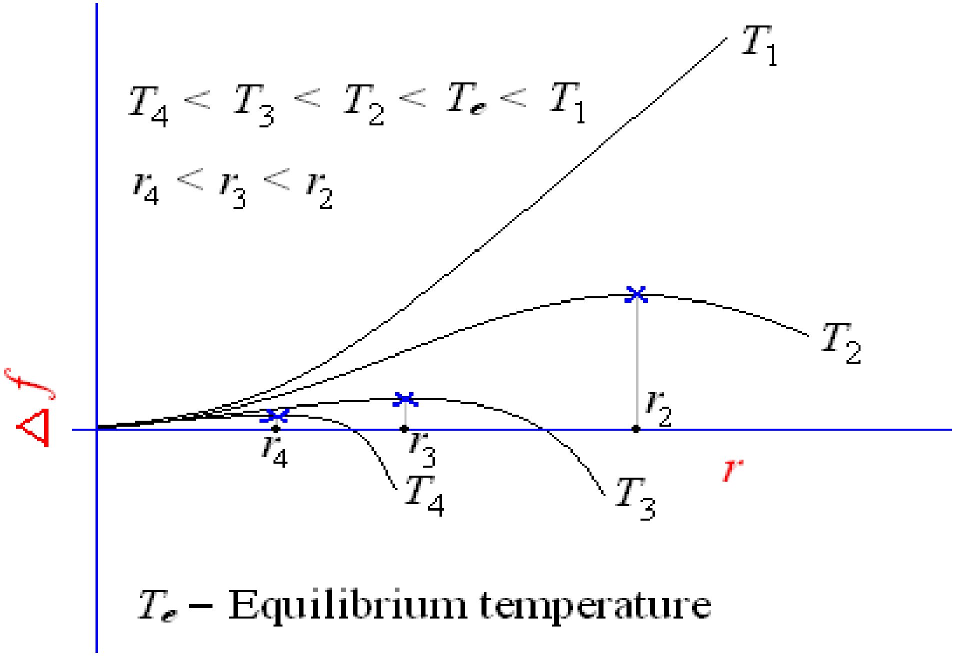
where ***r*** is the radius of the particle, Δ***g*** is the Gibbs free energy change per unit volume and ***γ*** is the surface energy of the interface.

Homogeneous nucleation – Kinetics (contd….)

- Critical value of particle size (which reduces with under-cooling) is given by

$$r^* = -\frac{2\gamma}{\Delta g} \quad or \quad r^* = \frac{2\gamma T_m}{\Delta H_f \Delta T}$$

where ***Tm*** – freezing temperature (in K), Δ***Hf*** – latent heat of fusion, Δ***T*** – amount of under-cooling at which nucleus is formed.



Heterogeneous nucleation – Kinetics

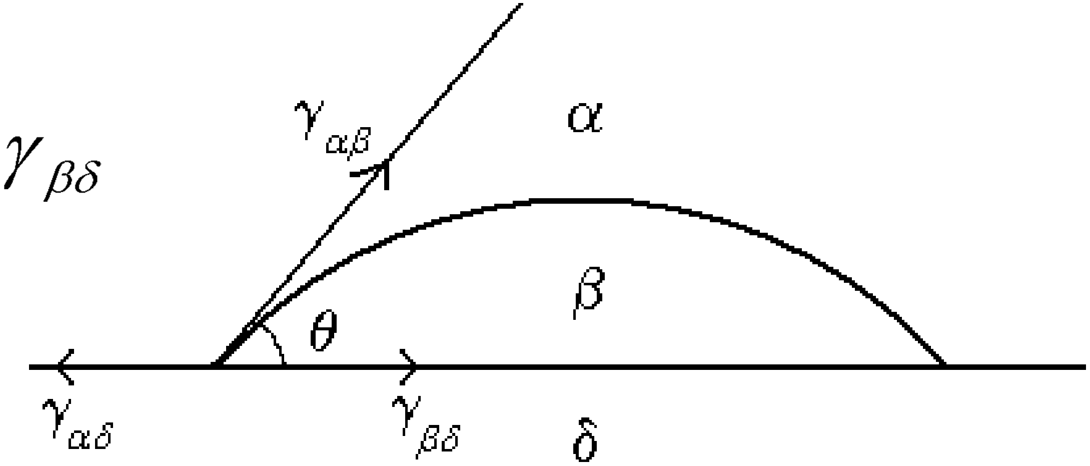
- In *heterogeneous nucleation*, the probability of nucleation occurring at certain preferred sites is much greater than that at other sites.

  E.g.: During solidification - inclusions of foreign particles (*inoculants*), walls of container holding the liquid

  In solid-solid transformation - foreign inclusions, grain boundaries, interfaces, stacking faults and dislocations.

- Considering, force equilibrium during second phase formation:

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



Heterogeneous nucleation – Kinetics (contd….)

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

- 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 → $\Delta f_{het}^{*} = \Delta f_{\mathrm{hom}}^{*}$

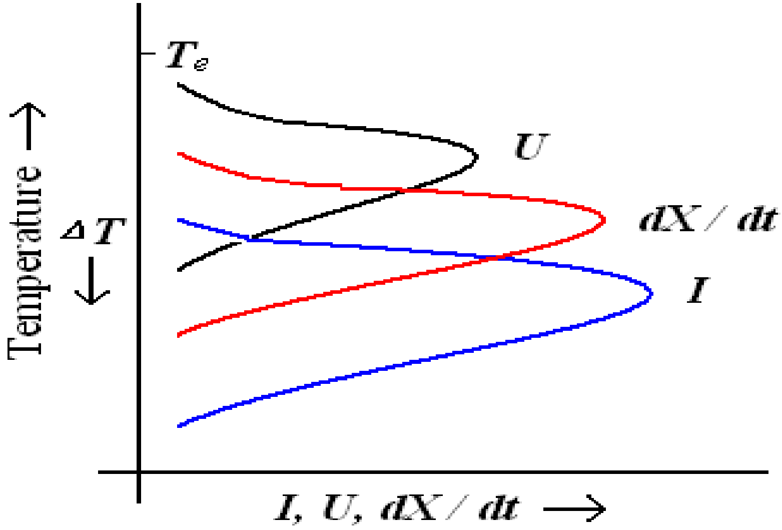
- If the product particle completely wets the foreign surface, i.e. $\theta = 0$, there is no barrier for heterogeneous nucleation →

$$\Delta f_{het}^{*} = 0$$

- In intermediate conditions such as where the product particle attains hemispherical shape, $\theta = 0$ → $\Delta f_{het}^{*} = \frac{1}{2}\Delta f_{\mathrm{hom}}^{*}$

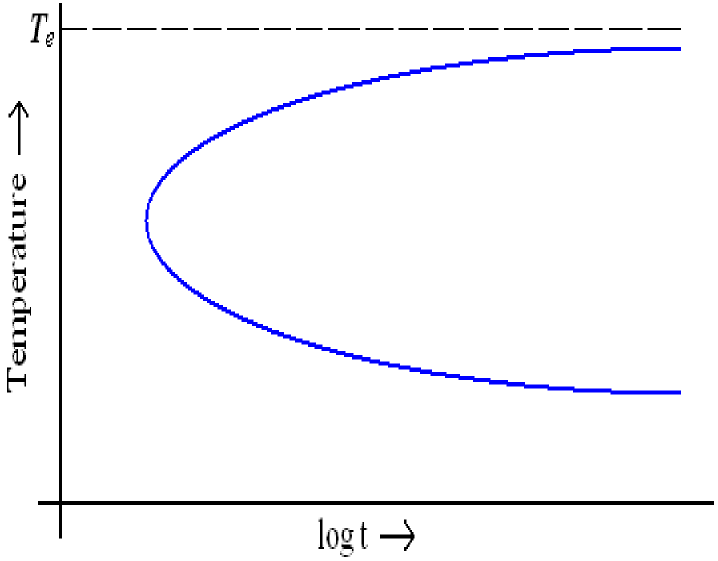
Growth kinetics

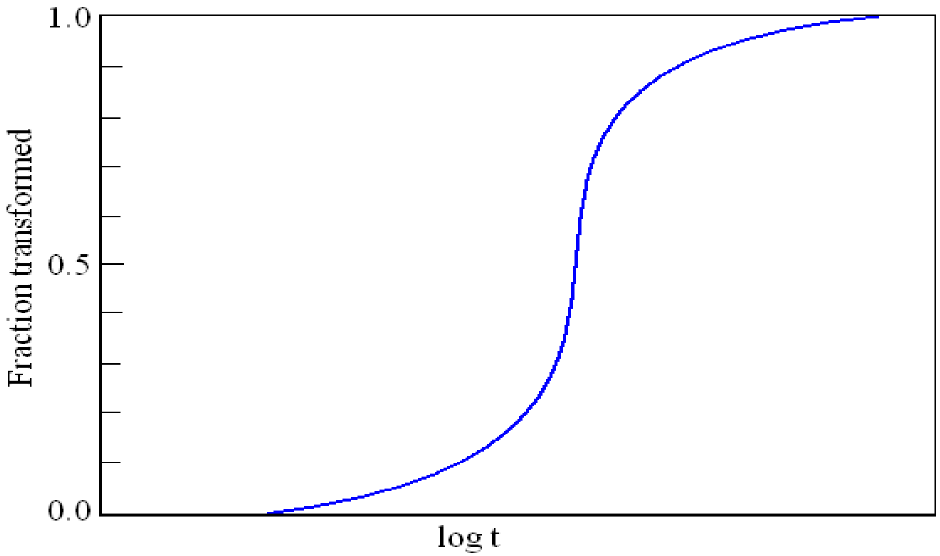
- After formation of stable nuclei, growth of it occurs until equilibrium phase is being formed.
- Growth occurs in two methods – thermal activated diffusion controlled individual atom movement, or athermal collective movement of atoms. First one is more common than the other.
- Temperature dependence 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)*:



Growth kinetics (contd….)

- Time required for a transformation to completion has a reciprocal relationship to the overall transformation rate, C-curve (time-temperature-transformation *or* TTT diagram).
- Transformation data are plotted as characteristic *S-curve*.
- 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.



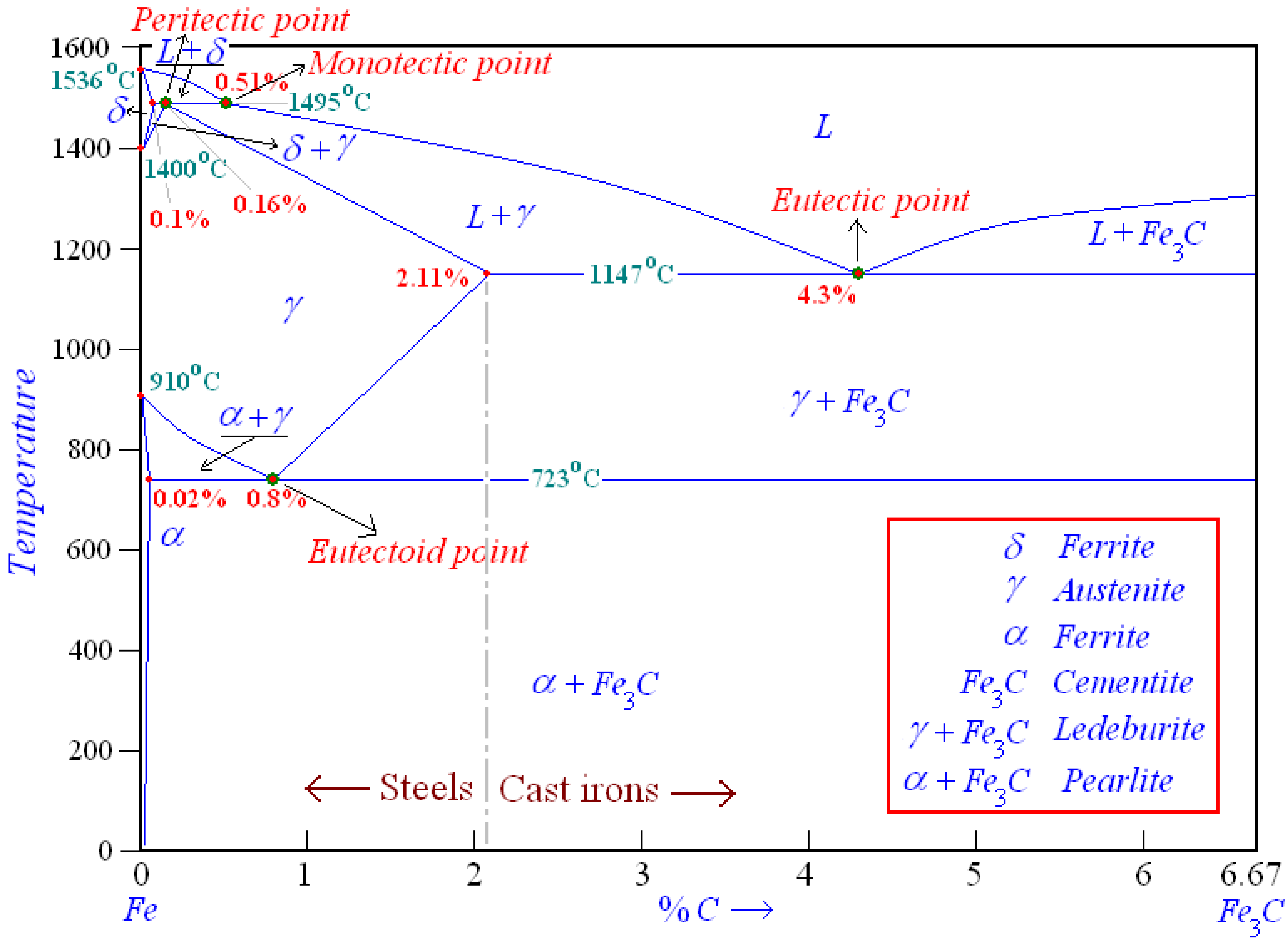


Martensitic growth kinetics

- Diffusion-less, athermal collective movement of atoms can also result in growth – Martensitic transformation.
- Takes place at a rate approaching the speed of sound. It involves congruent transformation.

  E.g.: FCC structure of Co transforms into HCP-Co *or* FCC-austenite into BCT-Martensite.
- Because of its crystallographic nature, a martensitic transformation only occurs in the solid state.
- Consequently, *Ms* and *Mf* are presented as horizontal lines on a TTT diagram. *Ms* is temperature where transformation starts, and *Mf* is temperature where transformation completes.
- Martensitic transformations in Fe-C alloys and Ti are of great technological importance.

Fe-C binary system – Phase transformations



Fe-C binary system – Phase transformations (contd….)

- Fe-Fe_3C phase diagram is characterized by *five individual phases*,: ***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 and *four invariant reactions*:

  - peritectic reaction at 1495 C and 0.16%C, ***δ***-ferrite + ***L*** ↔ ***γ***-iron (austenite)

  - monotectic reaction 1495 C and 0.51%C, ***L*** ↔ ***L*** + ***γ***-iron (austenite)

  - eutectic reaction at 1147 C and 4.3 %C, ***L*** ↔ ***γ***-iron + Fe3C (cementite) [ledeburite]

  - eutectoid reaction at 723 C and 0.8%C, ***γ***-iron ↔ ***α***–ferrite + Fe3C (cementite) [pearlite]

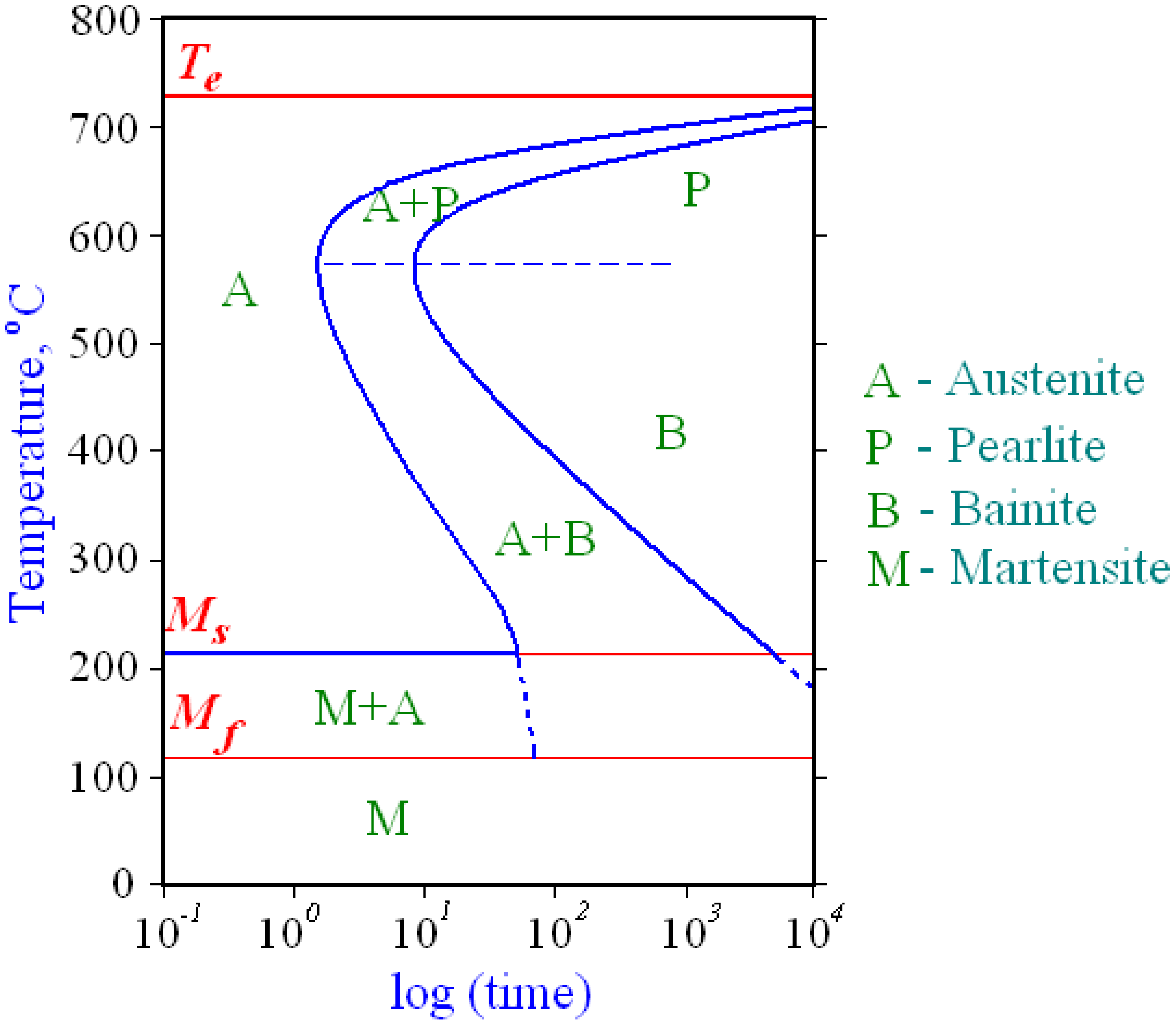
Fe-C alloy classification

- Fe-C alloys are classified according to wt.% C present in the alloy for technological convenience as follows:

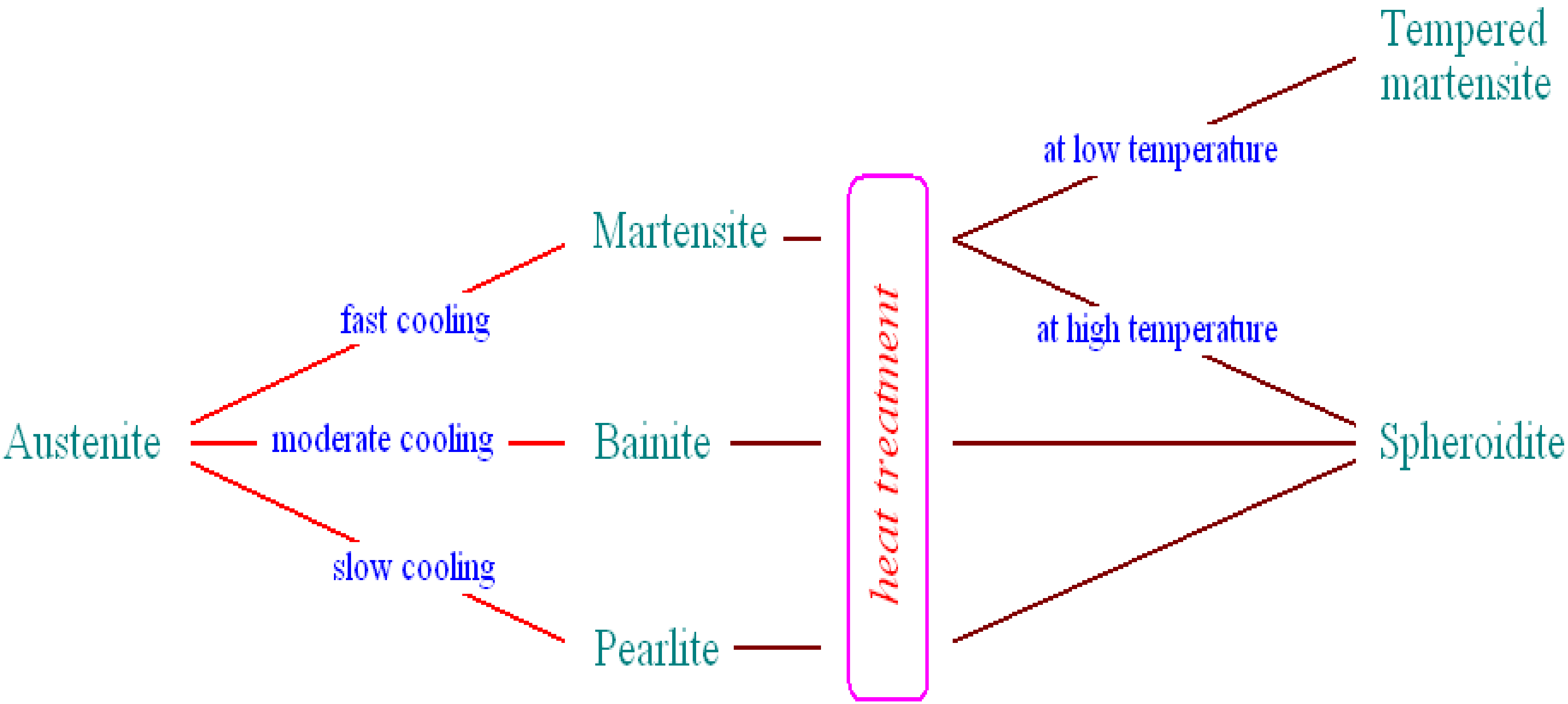
Commercial pure irons	% C < 0.008
Low-carbon/mild steels	0.008 - %C - 0.3
Medium carbon steels	0.3 - %C - 0.8
High-carbon steels	0.8- %C - 2.11
Cast irons	2.11 < %C

- Cast irons that were slowly cooled to room temperature consists of cementite, look whitish – *white cast iron*. If it contains graphite, look grayish – *gray cast iron*. It is heat treated to have graphite in form of nodules – *malleable cast iron*. If inoculants are used in liquid state to have graphite nodules – *spheroidal graphite (SG) cast iron*.

TTT diagram for eutectoid transformation in Fe-C system



Transformations involving austenite for Fe-C system



Austenite

fast cooling

moderate cooling

slow cooling

Martensite

Bainite

Pearlite

heat treatment

at low temperature

at high temperature

Tempered martensite

Spheroidite

CCT diagram for Fe-C system

- TTT diagram though gives very useful information, they are of less practical importance since an alloy has to be cooled rapidly and then kept at a temperature to allow for respective transformation to take place.
- Usually materials are cooled continuously, thus Continuous Cooling Transformation diagrams are appropriate.
- 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.
- Main difference between TTT and CCT diagrams: no space for bainite in CCT diagram as continuous cooling always results in formation of pearlite.

CCT diagram for Fe-C system (contd….)