Eutectic system

- The term EUTECTIC means Easy Melting →The alloy of eutectic composition freezes at a lower temperature than the melting points of the constituent components.
- A eutectic reaction is defined as the one which generates two solids from the liquid at a given temperature and composition.

Liquid (*L*) ↔ solid solution-1 (*α*) + solid solution-2(*β*)

- Examples: Cu-Ag, Pb-Sn and Al-Cu system.

Eutectic phase diagram

- A phase diagram in which constituents exhibit complete solubility in liquid state and partial solubility in solid state is known as partial eutectic phase diagram.
- First of all, there are three single phase regions, namely liquid phase (***L***), **α** and **β** solid solution phases. There also exist three two phase regions: ***L*+*α***, ***L+β*** and ***α*+*β*** are found on the eutectic phase diagram.
- The **α** phase is s solid solution in which elements of metal A (solvent) is more than that of metal B (solute). The **β** phase is s solid solution in which elements of metal B (solvent) is more than that of metal A (solute). The regions of limited solid solubility at each end of a phase diagram are called **terminal solid solutions (α** and **β)** as they appear at ends of the diagram.
- **Liquidus** line is the line or boundary that separates liquid and liquid + solid phase regions. The line '**cdg'** is known as liquidus line.
- **Solidus line** is the line or boundary that separates solid and solid + liquid phase regions. The line '**cbdfg'** is known as **solidus line.**

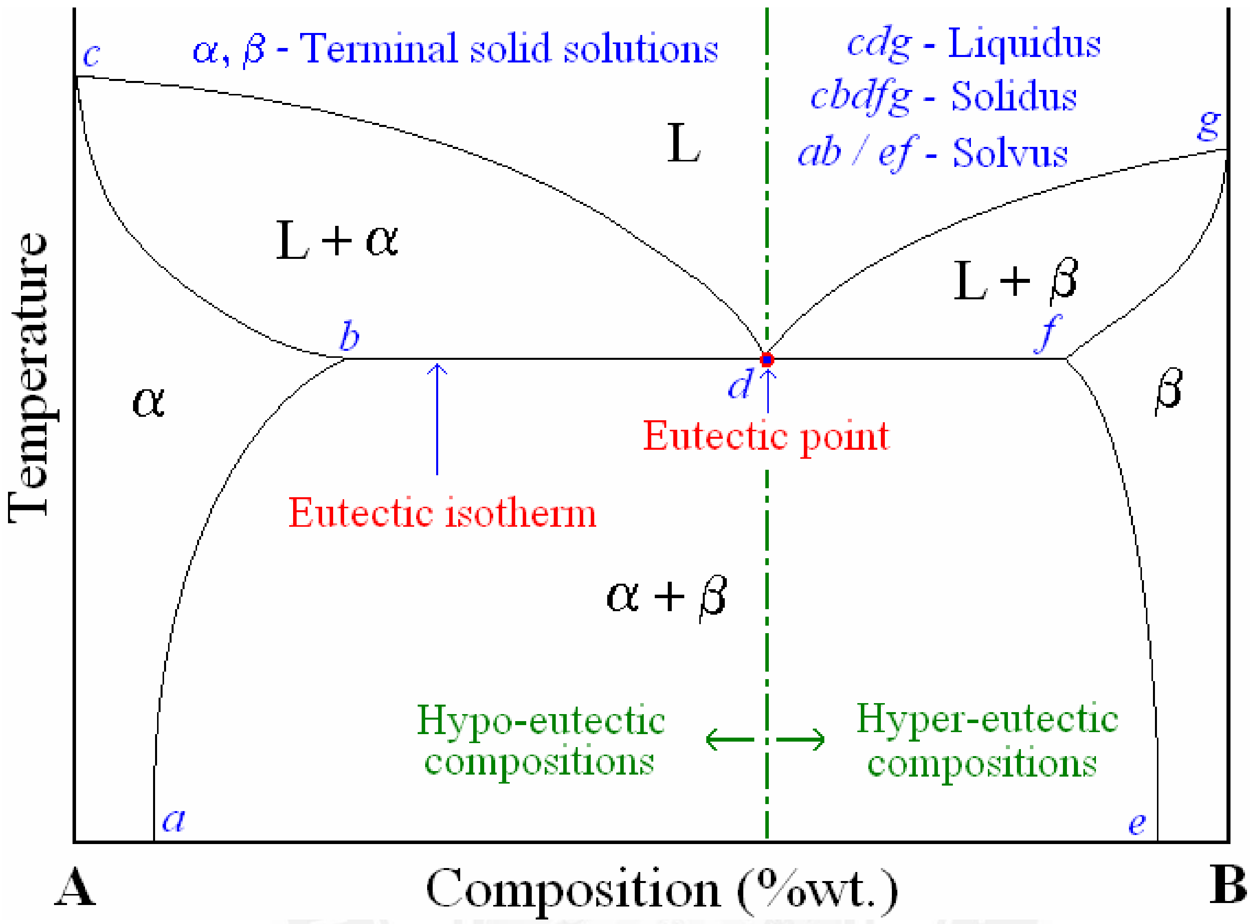


Figure.1.4. Typical phase diagram for a binary eutectic system.

- **Solvus lines** separate single phase solid regions from two phase solid regions. It also denotes the maximum solubility limits of metal A in B and of metal B in A respectively. The lines 'ab' and 'ef' are **solvus lines**.
- The introduction of metal B decreases the melting temperature of metal A along the liquidus line 'cd'. Similarly the addition of metal A decreases the melting temperature of metal B along the liquidus line 'gd'.

- These two liquidus lines met at the point'd' on the phase diagram. The point is known as **eutectic point**. Eutectic point is the lowest freezing point of the alloy. At this point three phases (L, **α** and **β**) are in equilibrium with each other.

The phase rule for a binary alloy

$$F = C - P + 1$$

Here C=2 and P=3

Hence degrees of free diagram $F = 2 - 3 + 1 = 0$

- The corresponding temperature and composition on the phase diagram is called **eutectic temperature** and **eutectic composition** respectively.
- Eutectic temperature is the minimum temperature at which a binary system is melted completely.
- 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 $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$). This transformation is known as *eutectic reaction* and is written symbolically as:

Liquid (L) ↔ solid solution-1 (α) + solid solution-2 (β)

- 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.
- 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**. The phase that forms during cooling but before reaching eutectic temperature is called **pro-eutectic phase.**

Microstructural Changes on cooling

- Development of micro-structure and respective cooling curves for eutectic alloys are shown in *figure* for different compositions.
- The 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.
- While cooling a hypoeutectic alloy from the liquid state, the temperature drops continuously till liquidus point, a, at which crystals of proeutectic α begins to form.
- On further cooling the fraction of α increases. At any point, b, in the two-phase region the α fraction is given by the lever rule. Solidification of proeutectic α continues till the eutectic temperature is reached.
- The inflection in the cooling curve between points a and e is due to evolution of the latent heat. At the eutectic point (e) the solidification of eutectic mixture ($\alpha + \beta$) begins through the eutectic reaction and proceeds at a constant temperature as F = 0 (2 –3 + 1).
- The cooling behavior in hypereutectic alloy is similar except that proeutectic β forms below the liquidus.
- For a eutectic composition, the proeutectic portion is absent and the cooling curve appears like that of a pure metal.
- Any composition left of point c or right of point d (α and β single phase region respectively) will cool and solidify like an isomorphous system.

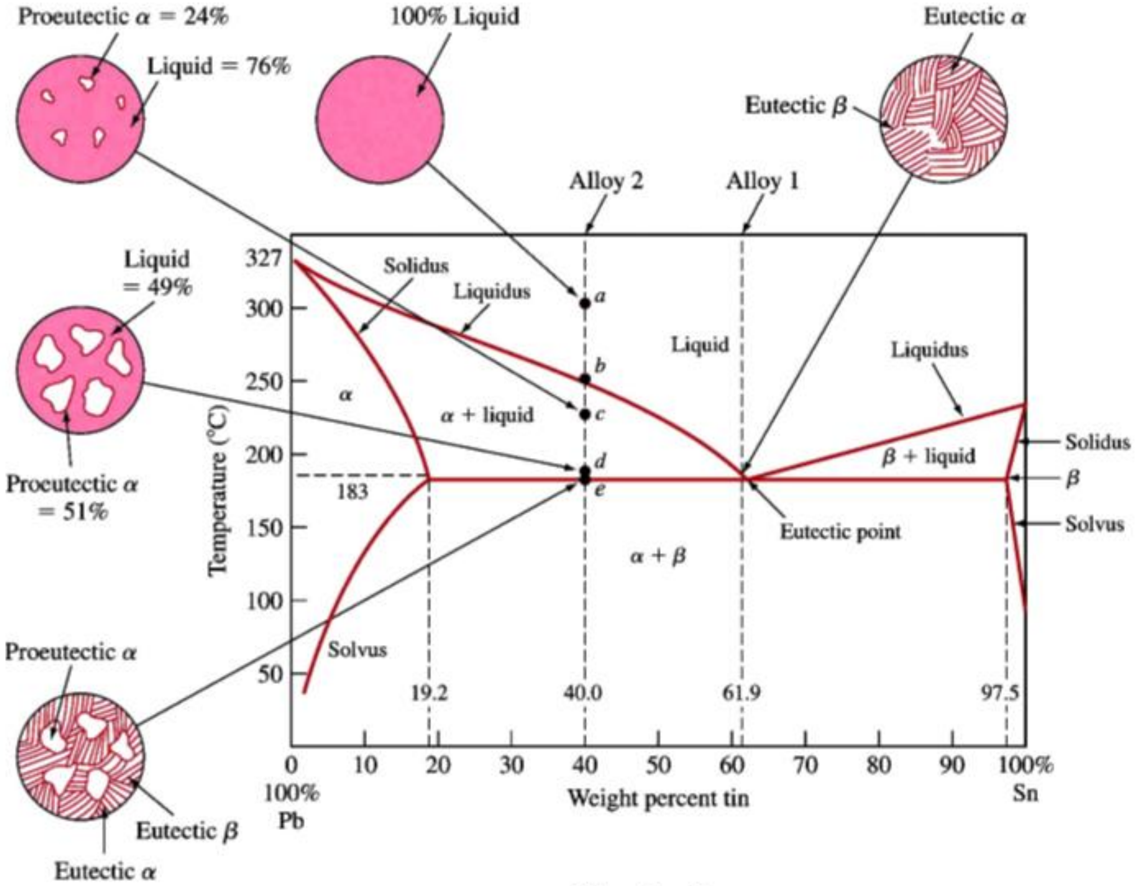


Figure.1.5.Cooling curve and micro-structure development for eutectic alloy

Invariant reactions:

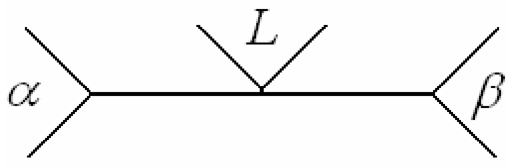
❖ Invariant means that there are zero degrees of freedom. That is, the reaction occurs with a fixed composition at a fixed temperature. There are many types of reaction that occur in binary equilibrium diagrams. Some of the important reactions that are found generally in different phase diagrams are:

1. Eutectic reaction 2. Peritectic reaction 3. Eutectoid reaction 4. Peritectoid reaction

Eutectic reaction

❖ Eutectic reaction is the reversible, isothermal reaction of a liquid phase ***L***, transforms into two different solids phases (**α** and **β**) upon cooling. Eutectics are found in many metallic and ceramic systems- Fe-C, Al-Si, Ag-Au, Sn-Pb.

$$Liquid \Leftrightarrow Solid\ 1(\alpha) + Solid\ 2(\beta)$$

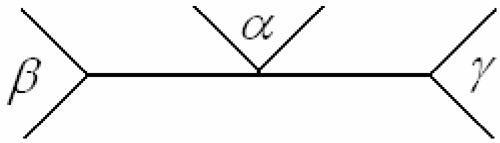


Schematic of eutectic invariant reaction

Eutectoid reaction

- Eutectoid reaction is the reversible, isothermal reaction of a solid phase (α) transforms into two different solids phases (***β and γ***) upon cooling.

$$Solid\ 1(\alpha) \Leftrightarrow Solid\ 1(\beta) + Solid\ 2(\gamma)$$

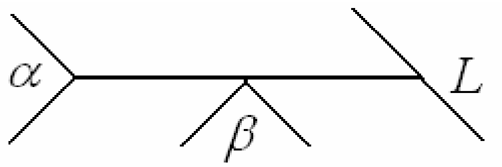


Eutectoid reaction is found in many systems such as Cu-Al, Cu-Sn, Al-Mn

Peritectic reaction

- Peritectic reaction is the reversible, isothermal reaction of a solid phase (α) reacts with a liquid phase to produce a new solid phase upon cooling.

$$Liquid(L) + Solid\ 1(\alpha) \Leftrightarrow Solid\ 2(\beta)$$

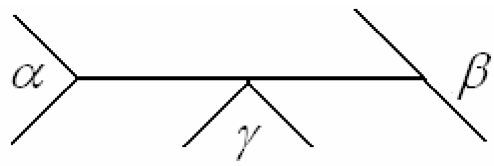


Peritectic reaction is found in Sb-Sn and Pt-Ag systems.

Peritectoid reaction

❖ Peritectoid reaction is the reversible, isothermal reaction in which two solid phases (α and β) transform into a single new solid phase (γ) upon cooling.

$$Solid\ 1(\alpha) + Solid\ 2(\beta) \Leftrightarrow Solid\ 3(\gamma)$$



Peritectoid reaction is found in many systems such as Ni-Zn, Ni-Mo, Fe-Nb

Monotectic reaction

➢ Monotectic reaction is an invariant reaction in which a liquid phase transforms into a solid phase and a liquid phase of different composition.

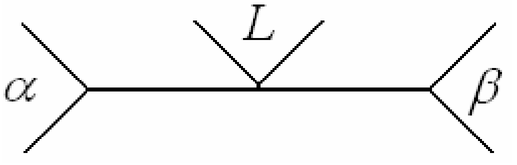
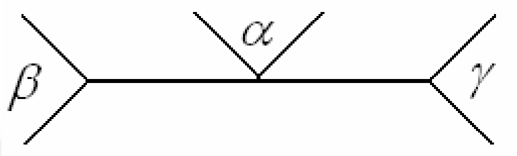
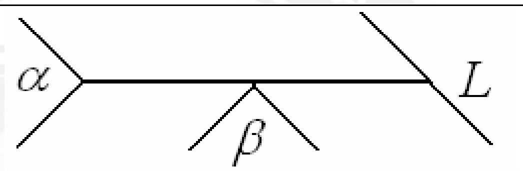
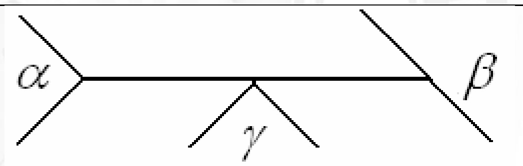
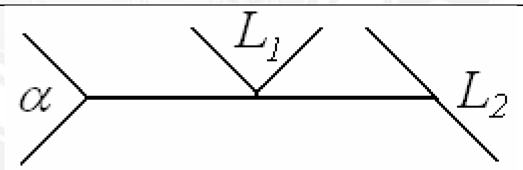
Monotectoid reaction

➢ Monotectoid reaction is an invariant reaction in which a solid phase transforms to produce two solid phases of different compositions.

Syntectic reaction

- 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.

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	$\alpha + \beta \leftrightarrow \gamma$		Ni-Zn, Ni-Mo, Fe-Nb
Monotectic	$L1 \leftrightarrow L2 + \alpha$		Fe-C, 0.51% C, 1495°C

Summary of invariant reactions in binary systems

Peritectic Phase Diagram

Like the eutectic system, the peritectic reaction is found in systems with complete liquid solubility but limited solid solubility.

- ❖ Peritectic reaction is the reversible, isothermal reaction of a solid phase (α) reacts with a liquid phase to produce a new and different solid phase upon cooling.

$$Liquid\,(L) + Solid\ \ 1(\alpha) \Leftrightarrow\ \ Solid\,2(\beta)$$

- ❖ Peritectic reaction is found in Sb-Sn and Pt-Ag systems.
- ❖ The melting points of the two components are quite different.

Pt-Ag system

- Let us consider silver-platinum as an example for peritectic phase diagram. Silver melts at 961˚C and platinum melts at 1769˚C. The melting points of the components differ more than 800˚C. In this system, the peritectic reaction $\boldsymbol{L} + \boldsymbol{\alpha} \leftrightarrow \boldsymbol{\beta}$ occurs at 42.4% Ag and $1186^\circ C$. Since the solid β forms at the interface between the L and the solid(α), further reaction is dependent on solid state diffusion.

- ✓ The region marked 'liquid' above the liquidus line shows the binary alloy present in complete liquid phase.
- ✓ The region marked "α" below the solidus line shows the presence of alloy in pure α which is a solid solution phases rich in Ag.
- ✓ The region marked "β" below the solidus line shows the presence of alloy in pure β which is a solid solution phases rich in Pt.
- ✓ The region marked "L+β" between the solidus line and liquidus line shows the presence of alloy as a mixture liquid and solid phase β.
- ✓ The region marked "L+α" between the solidus line and liquidus line below peritectic isotherm shows the presence of alloy as a mixture liquid and solid phase α.
- ✓ T_P is the peritectic temperature. The isotherm passing through peritectic temperature is called peritectic isotherm.
- ✓ The region marked "α+β" is formed below the peritectic isotherm and a heterogeneous solid consisting of a mixture of α and β is present.
- ✓ A liquid phase reacts with the solid phase to form a new and different solid phase is called peritectic reaction.

$$Liquid(L) + Solid\ 1(\alpha) \Leftrightarrow\ Solid\ 2(\beta)$$

- ✓ The peritectic horizontal is the tie-line which defines the composition of the liquid phase and the β phase at the peritectic temperature.

- ✓ At peritectic temperature, three phases namely liquid, α and β are equilibrium each other.

Hence phase rule $F = C - P + 1 = 2 - 3 + 1 = 0$

- ✓ In some peritectic reactions (e.g. the Pt-Ag system), the (pure) β phase is not stable below the peritectic temperature (T_P = 1186 ̊ C for Pt-Ag system) and splits into a mixture of (α+ β) just below T_P.

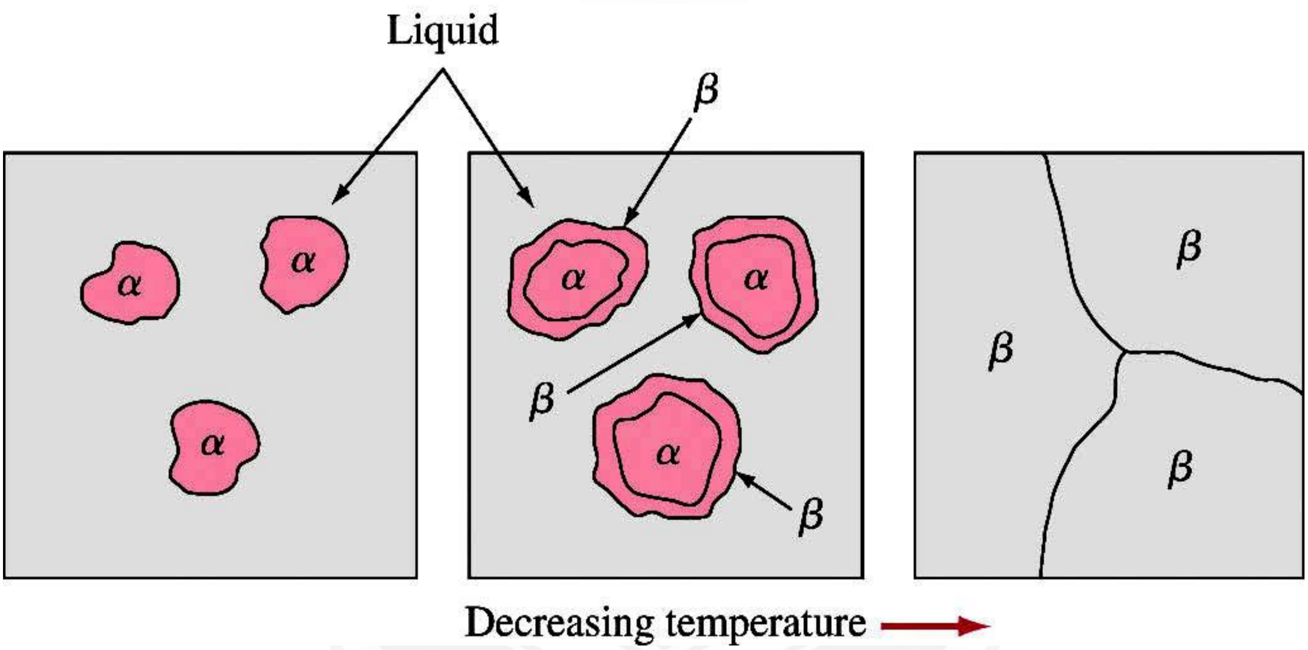


Figure.1.6. Schematic representation of the progressive development of $\boldsymbol{L + \alpha \leftrightarrow \beta}$

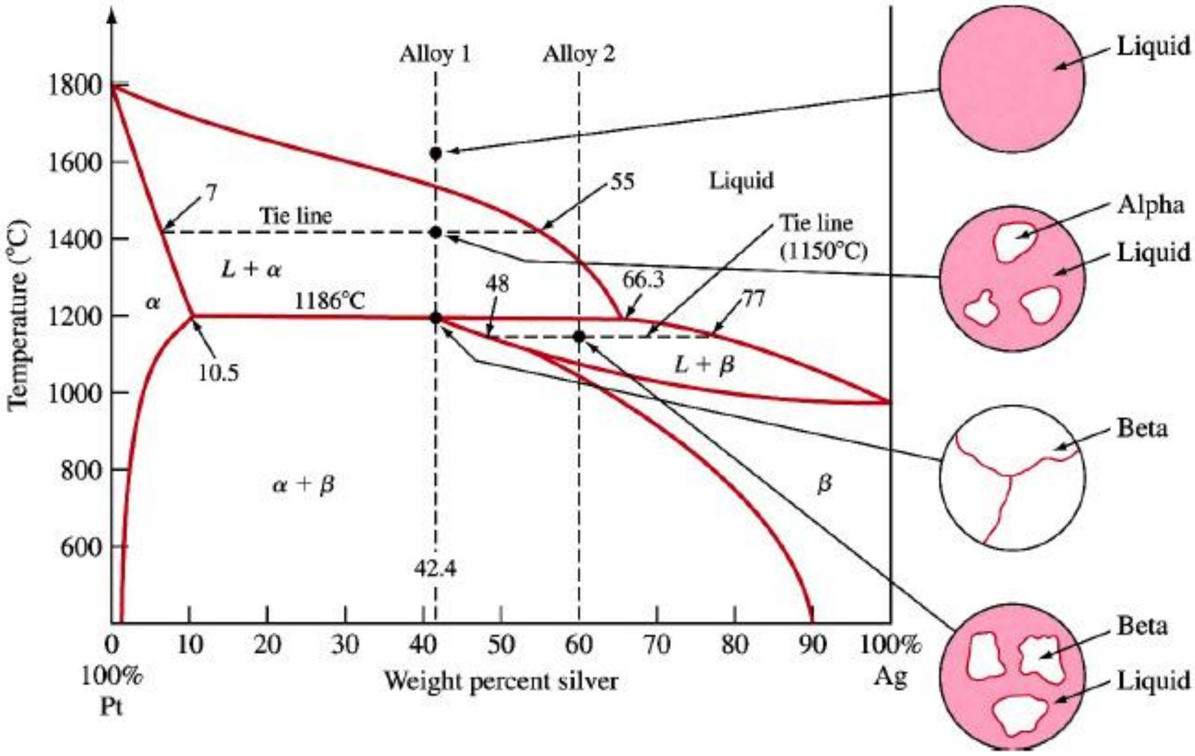


Figure.1.7. Pt-Ag peritectic phase diagram

Free energy composition curves for binary systems

- A binary phase diagram is a map which indicates the equilibrium phases present at a given temperature and composition. Free energy is a measure of a system's internal energy which gives the entropy of the system. For any phase, the Gibb's free energy is a function of pressure, temperature, and composition.

Step (I)

- Let's construct a binary phase diagram for the simplest case: A and B components are mutually soluble in any amounts in both solid (**isomorphous system**) and liquid phases, and form ideal solutions.
- We have 2 phases – liquid and solid.
- Let's consider Gibbs free energy curves for the two phases at different Temperature.

❖ **T_1** is above the equilibrium melting temperatures of both pure components: $T_1 > T_m (A) > T_m (B)$. At temperature T_1, the liquid phase will be the stable phase for any composition, because of its low Gibb's free energy.

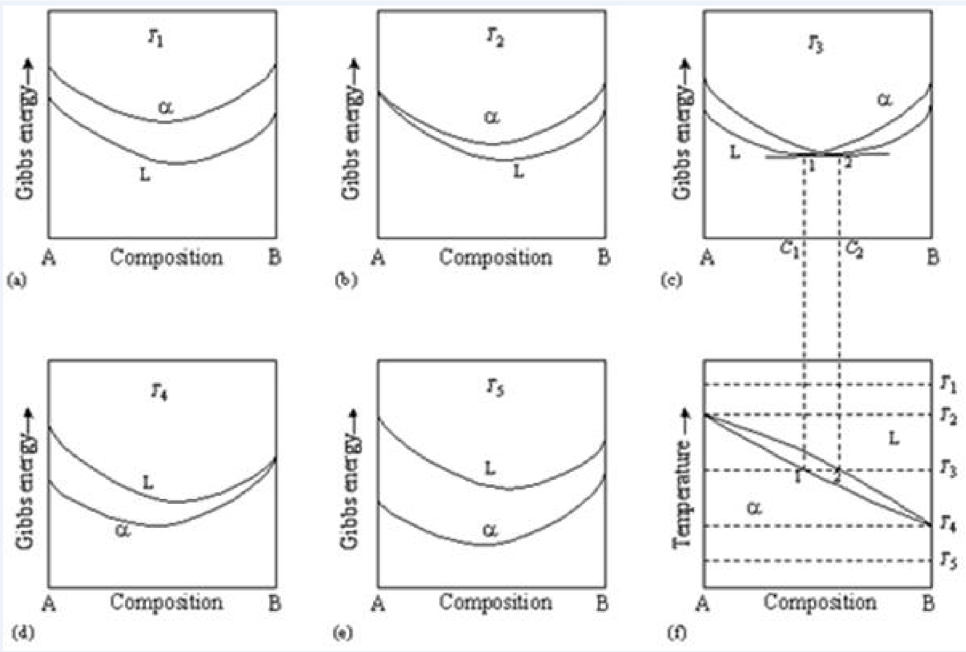


Figure.1.8 Free energy composition curves for binary systems

Step (II)

At temperature T_2, component A begins to melt. The liquid and solid phases are equally stable only at a composition of pure A i.e., $G^A_{liquid} = G^A_{solid}$

Step (III)

❖ At temperature **T_3**, the Gibbs free energy curves for the liquid and solid phases will cross each other.

Step (IV)

❖ At temperature T_4, the component begins to melt as it is the melting temperature of component B.

Step (V)

- At lower temperature Gibbs free energy of the solid phase is lower than the G of the liquid phase ($G_S < G_L$), so that solid phase is more stable at T_5.

Construction of Phase diagram of components with complete solubility

- The isomorphous phase diagrams having completely soluble components can be constructed from Gibb's free energy curves.
- At temperature T_3, the Gibbs free energy curves for the liquid and solid phases will cross each other.
- The common tangent construction can be used to show the compositions two phases in equilibrium.
- The two-phase field consists of a mixture of a mixture of liquid and solid phases.
- The compositions of the two phases in equilibrium at temperature T_3 are given as C_1 and C_2.
- The point of tangency, 1 and 2, are called solidus and liquidus respectively.
- The horizontal isothermal line meeting points 1 and 2 at temperature T_3, is called tie-line.
- Similar tie-lines meet the coexisting phases throughout all two phase field in binary system.