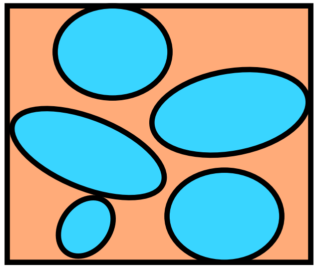


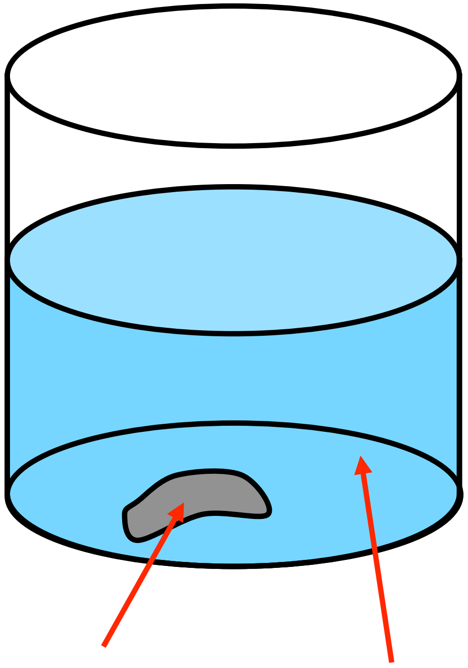
Phase Diagrams a Review

Topic 2

Review of
Phase Transformation
Diagrams

Solution and Solubility

Example: Solubility of salt in water
There exists a maximum amount of salt that can be completely dissolved in water; excess of salt stays as solid. This maximum amount is the **solubility** of salt in water. The solution containing the maximum concentration of salt is a **saturated solution**.



Cooling of saturated solution results in the formation of solid salt from the solution, indicating that solubility decreases with decreasing T. This process is called **precipitation** and the solid formed is a **precipitate**. Heating the solution will lead to the dissolving of the precipitate back into solution.

In this example there exist two phases in the system and the two phases stay in equilibrium:

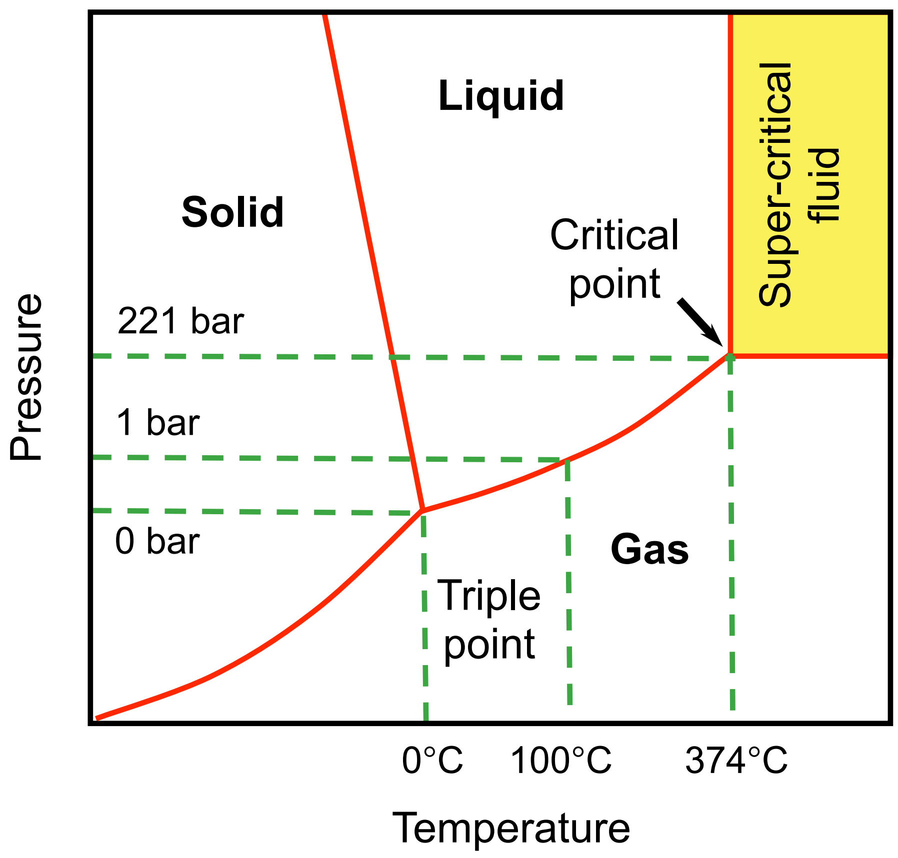
$$\text{Solution} \underset{\textit{precipitation}}{\overset{\textit{dissolving}}{\leftrightarrows}} \text{Solid}$$

The same concepts apply to solids: solid solution, saturation, solubility, precipitation

Phase Diagrams

Phase diagrams are used to map out the existence and conditions of various phases of a give system. The phase diagram of water is a common example. Water may stay in liquid, solid or gaseous states in different pressure-temperature regions. Boundaries of the regions express the equilibrium conditions in terms of P and T. Water is a monolithic system. For binary systems, which contains two constituents, such as binary alloys, phase diagrams are often expressed in the temperature-composition plane.

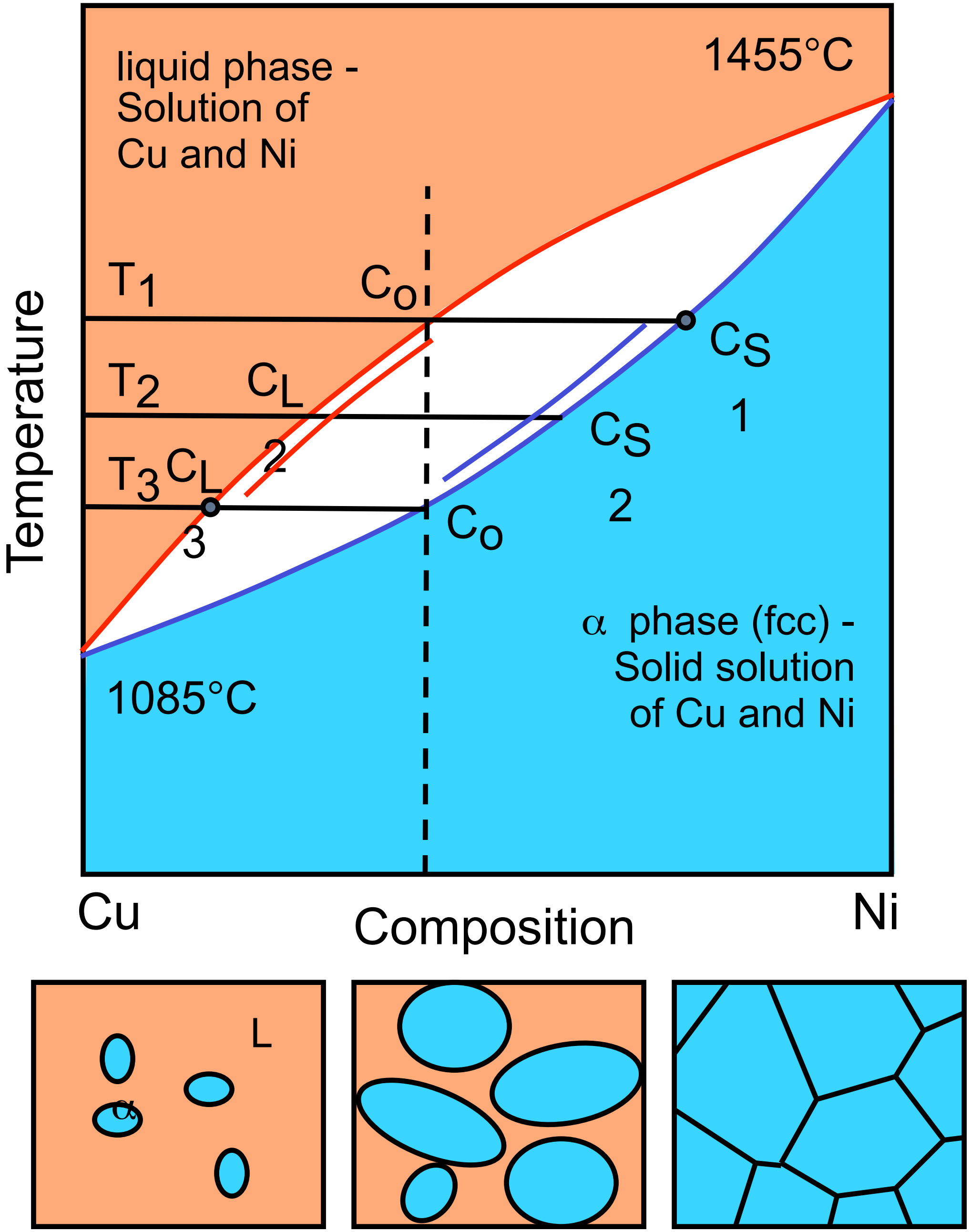
phase diagram of water



Binary Phase Diagrams

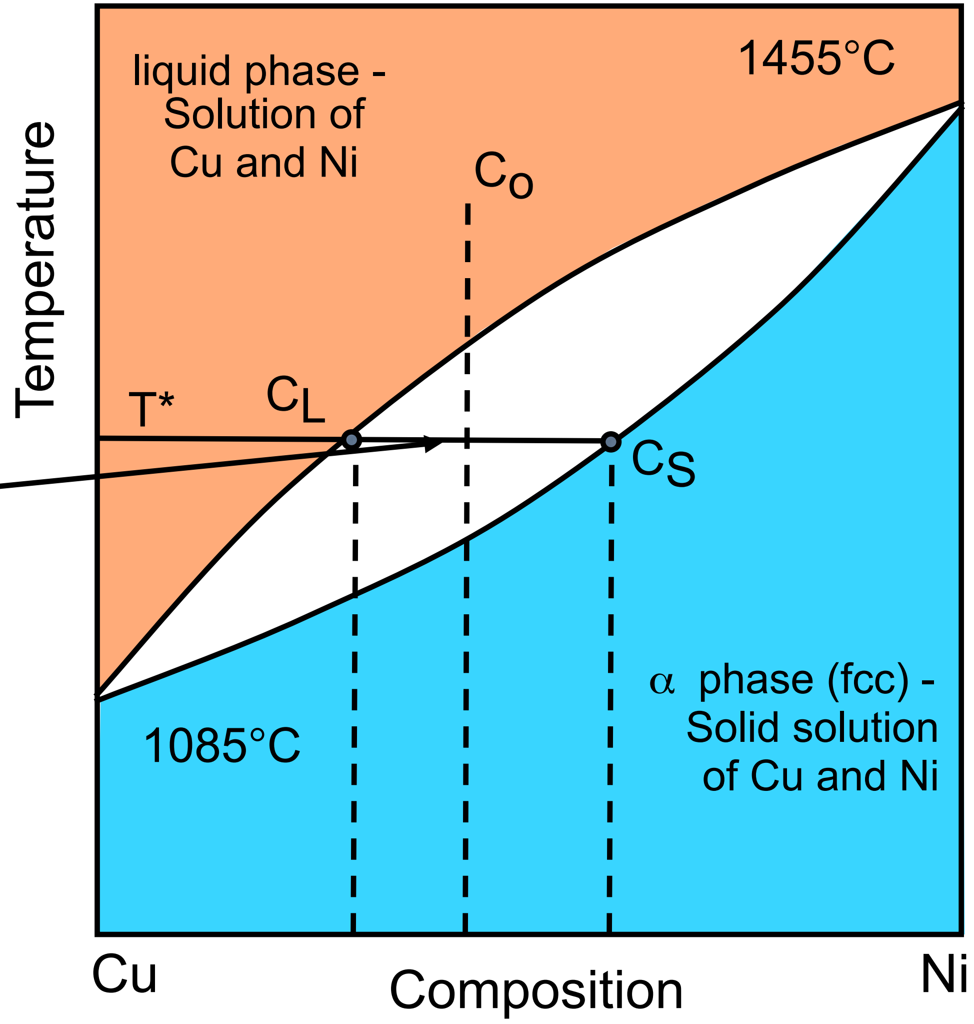
The simplest type of binary phase diagrams is the isomorphous system, in which the two constituents form a continuous solid solution over the entire composition range. An example is the Ni-Cu system.

Solidification of alloy C_o starts on cooing at T_1. The first solid formed has a composition of C_{s1} and the liquid C_o. On further cooling the solid particles grow larger in size and change their composition to C_{s2} and then C_o, following the solidus whereas the liquid decrease in volume and changes its composition from C_o to C_{L3} following the liquidus. The solidification completes at T_3.



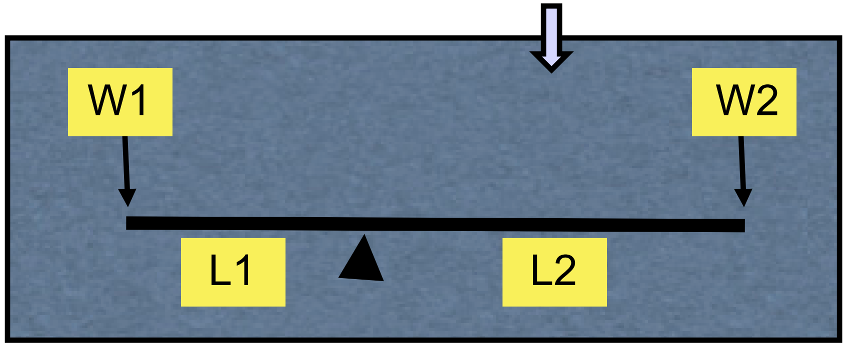
Binary Phase Diagrams

The simplest type of binary phase diagrams is the isomorphous system, in which the two constituents form a continuous solid solution over the entire composition range. An example is the Ni-Cu system.



Compositions of phases is determined by the **tie line**

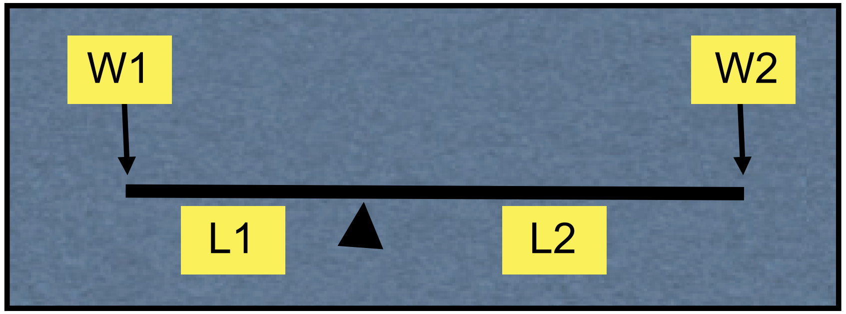
The relative fractions of the phases are determined by the **lever rule**



Lever Rule

$$W_1 \bullet L_1 = W_2 \bullet L_2$$

$$W_1 + W_2 = 1$$

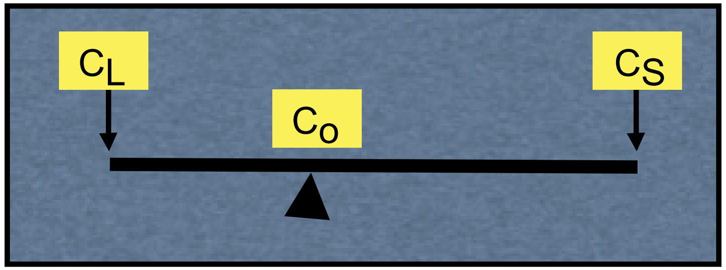


Weight fractions: $W_1 = \dfrac{L_2}{L_1 + L_2}$

Example

At temperature T_1, alloy C_o is in the dual phase region, comprising the liquid phase and the α-phase.

(i) Determine the compositions of the two phases;
(ii) Determine the weight fractions of the two phases



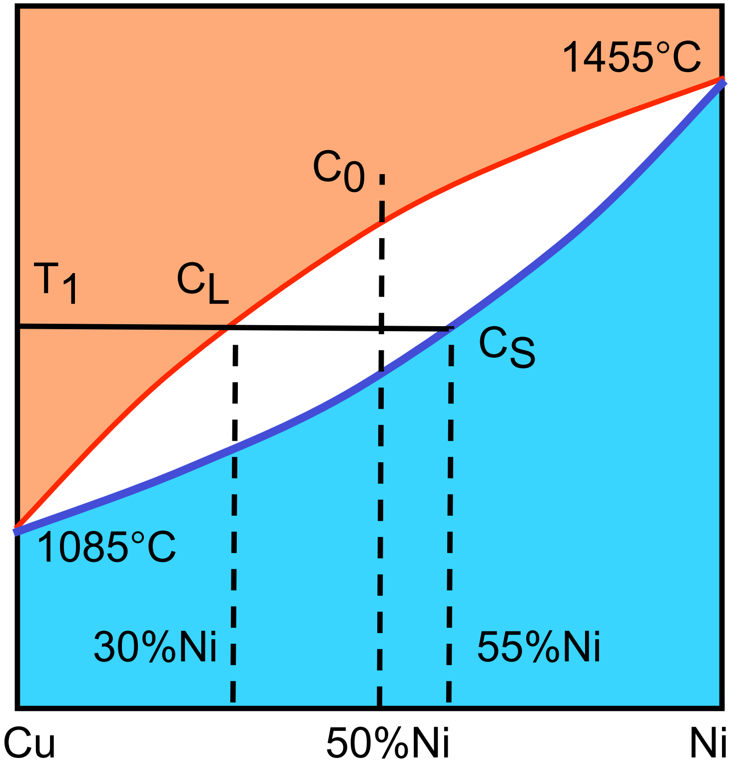
Read from the tie line:
Liquid phase: Cu-30%Ni
α-phase: Cu-55%Ni

$$W_L = \frac{C_s - C_o}{C_s - C_L} = \frac{55-50}{55-30} = 0.2 = 20\%$$

$$W_\alpha = \frac{C_o - C_L}{C_s - C_L} = \frac{50-30}{55-30} = 0.8 = 80\%$$

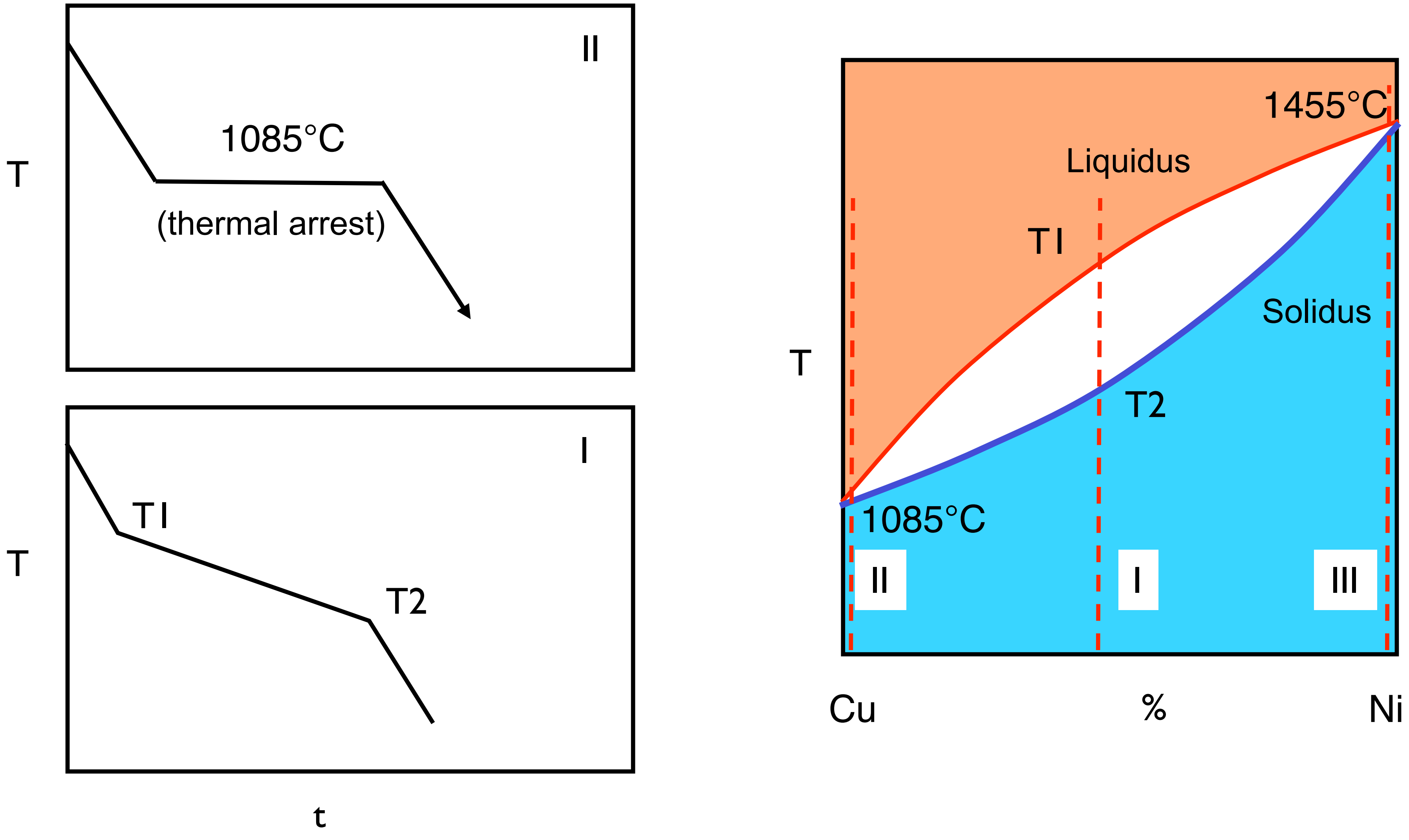
or

$$W_\alpha = 1 - W_L = 1 - 0.2 = 0.8 = 80\%$$



Cooling Curves

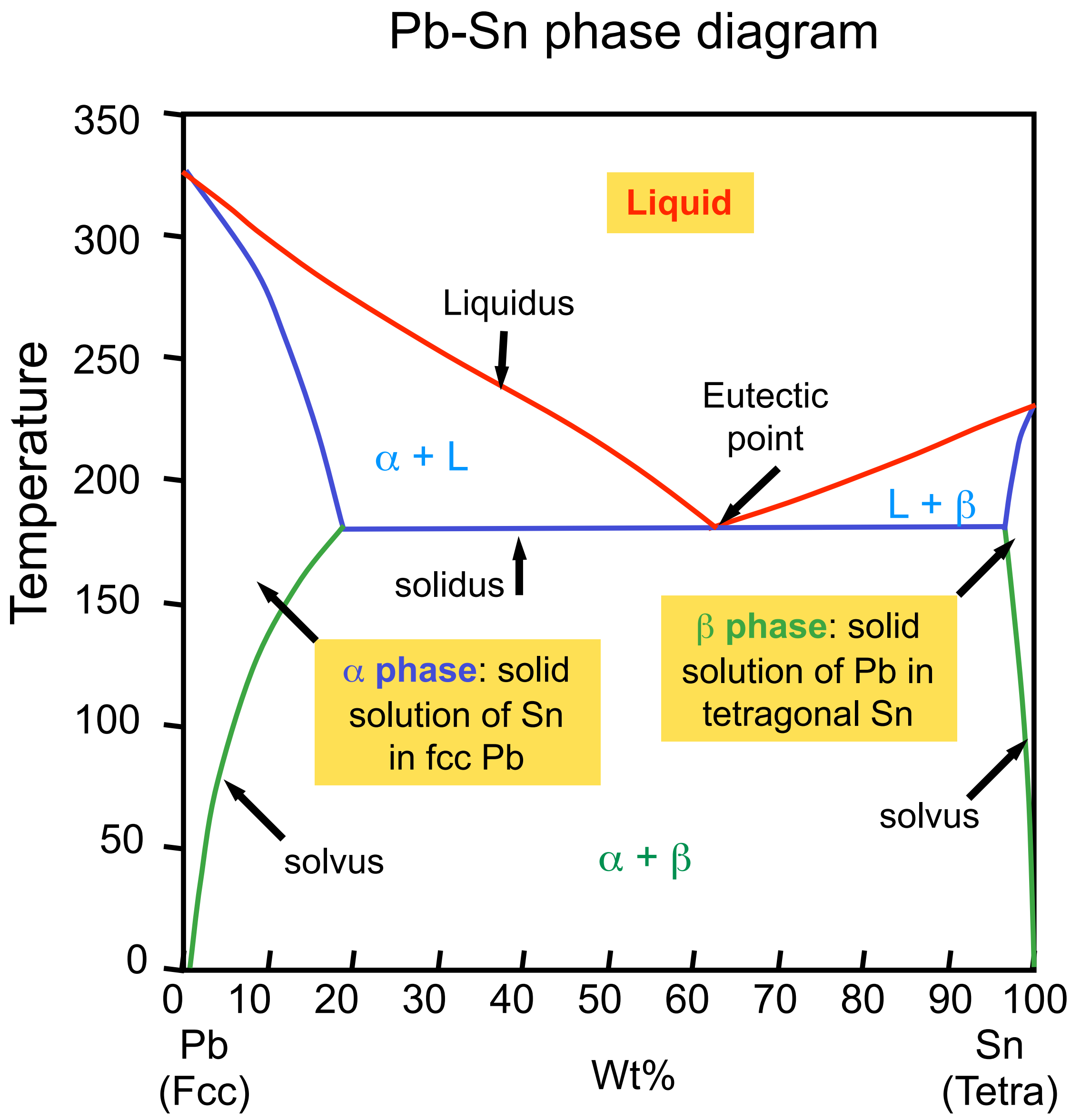
determination of Phase diagrams



Eutectic Systems

The Pb-Sn system is characteristic of a valley in the middle. Such system is known as the **Eutectic** system. The central point is the Eutectic point and the transformation though this point is called Eutectic reaction: **L**✦α+β

Pb has a fcc structure and Sn has a tetragonal structure. The system has three phases: L, α and β.

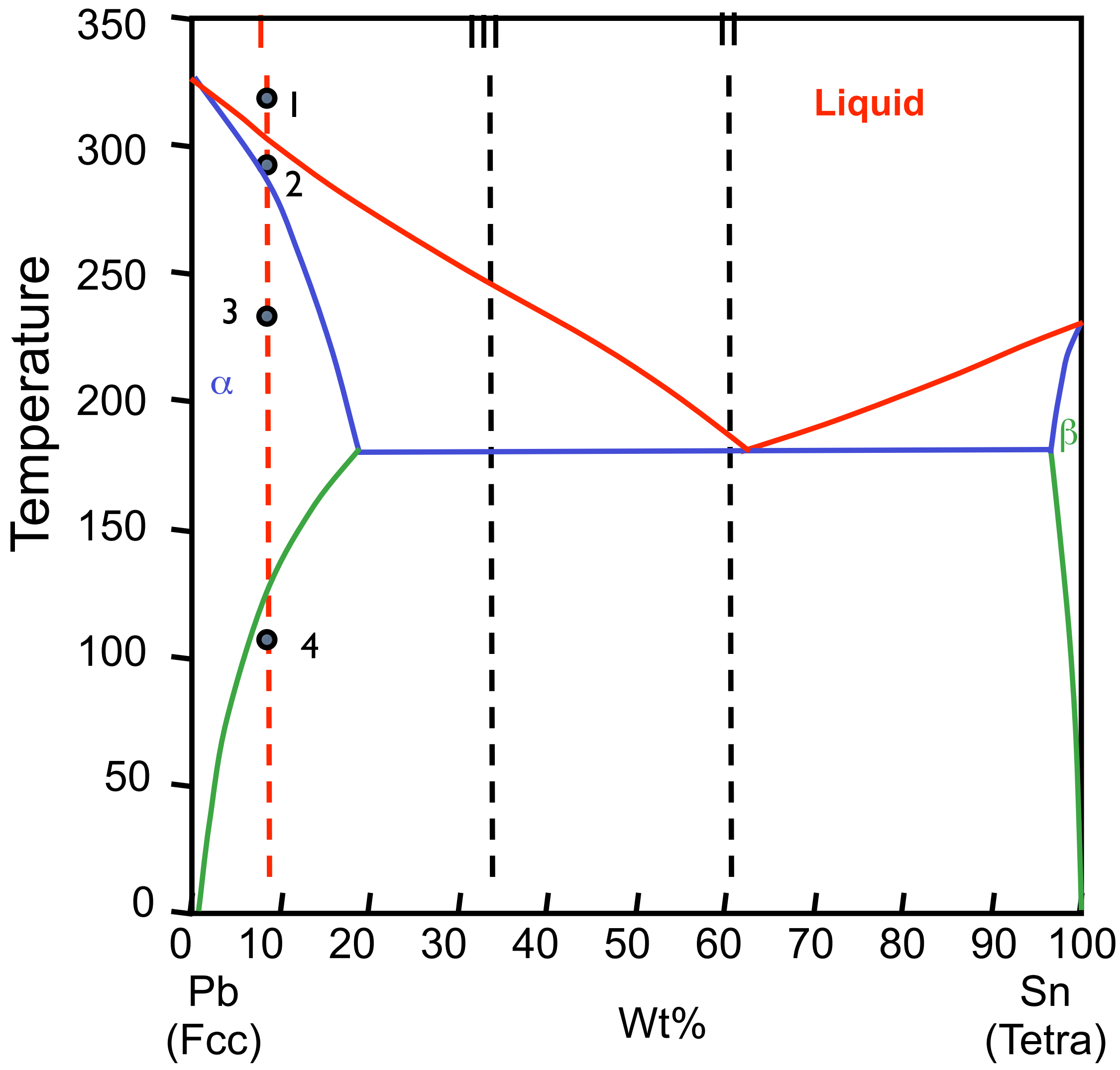


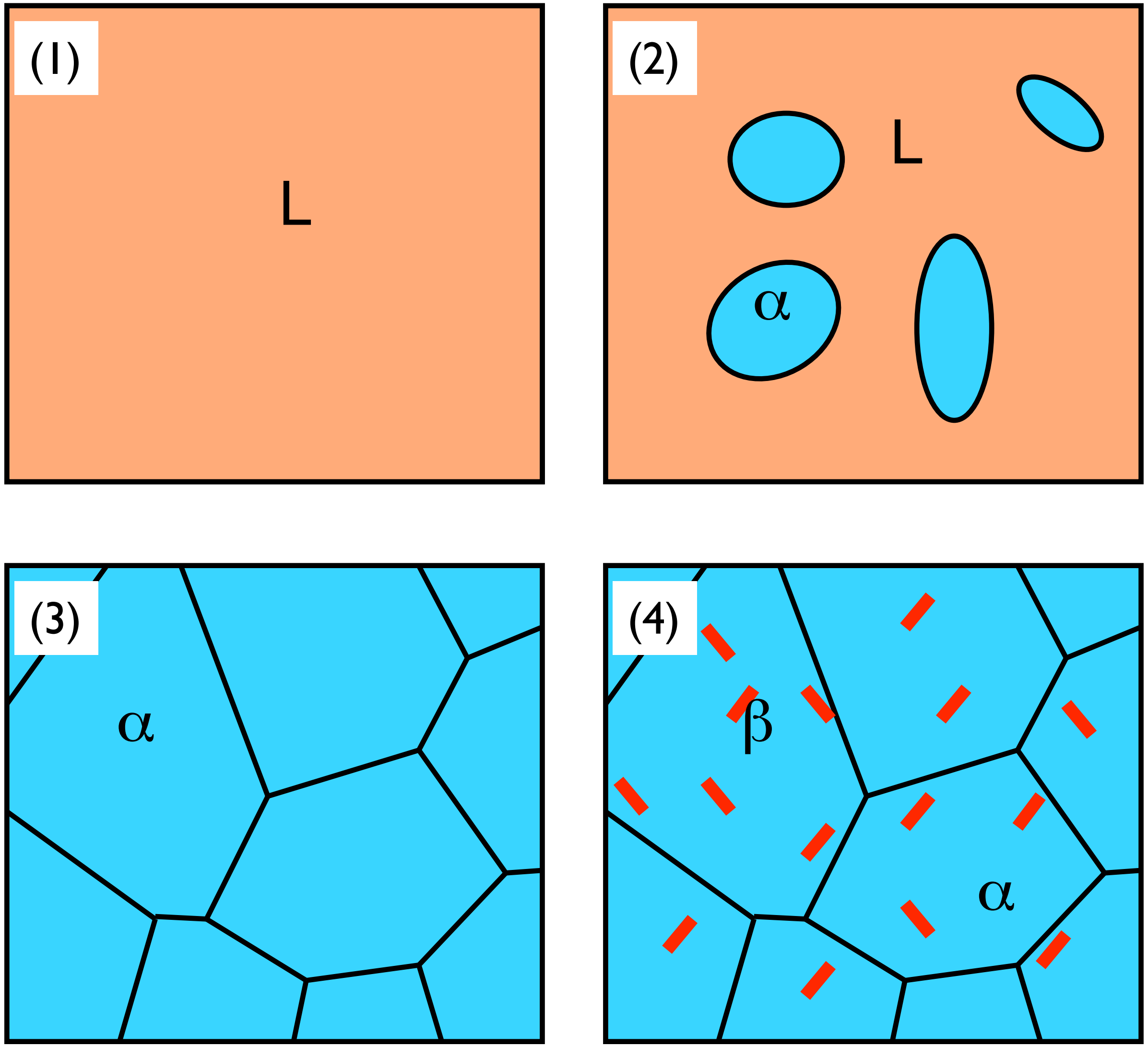
Solidification of Eutectic Systems

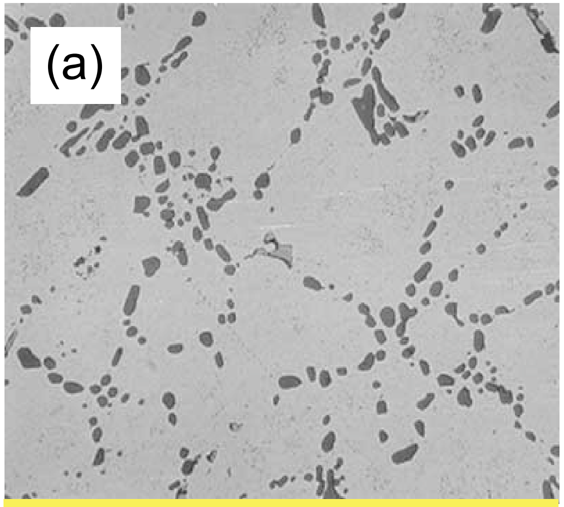
Alloy I:
At point 1: Liquid
Solidification starts at liquidus
At point 2: L+α
The amount α ↑ with ↓ T
Solidification finishes at solidus
At point 3: α
Precipitation starts at solvus
At point 4: α+β
Further cooling leads to formation and growth of more β precipitates whereas Sn% in α decreases following the solvus.

The cooling curve of this alloy is similar to cooling curve I shown in slide 9.

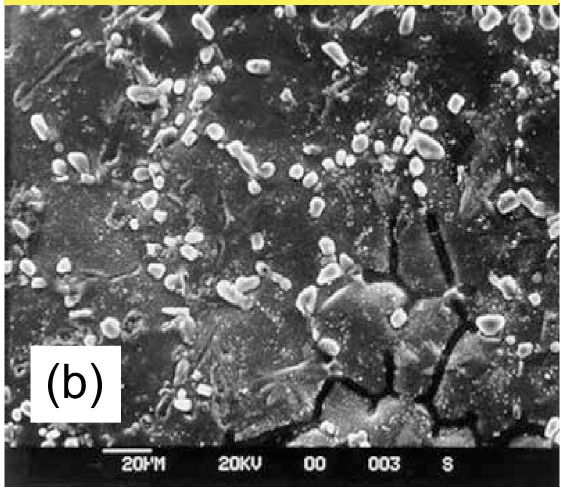
Pb-Sn phase diagram







Precipitates in a Al-Si alloy;
(a) optical microscopy,
(b) scanning electron
microscopy of fracture surface

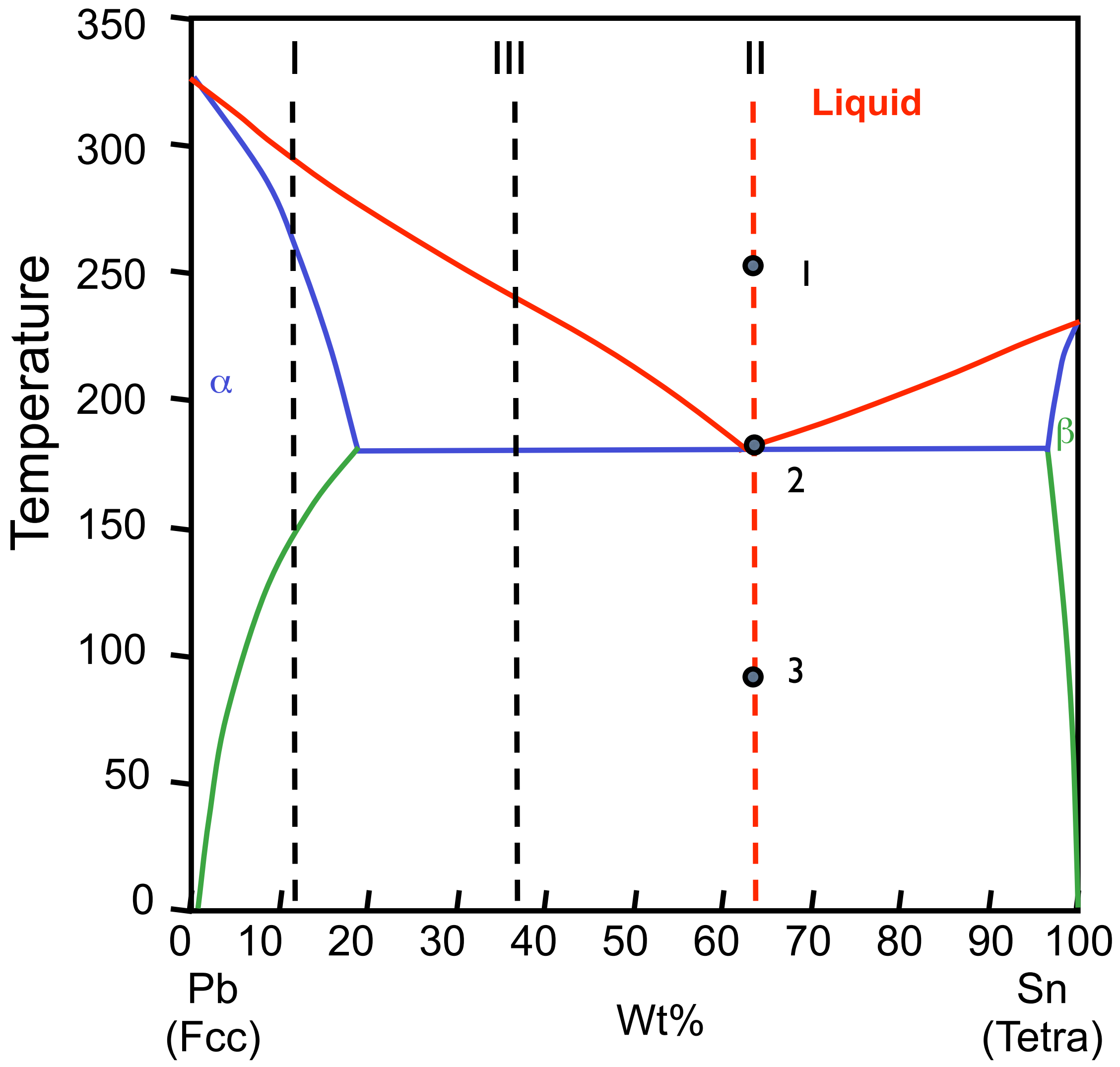


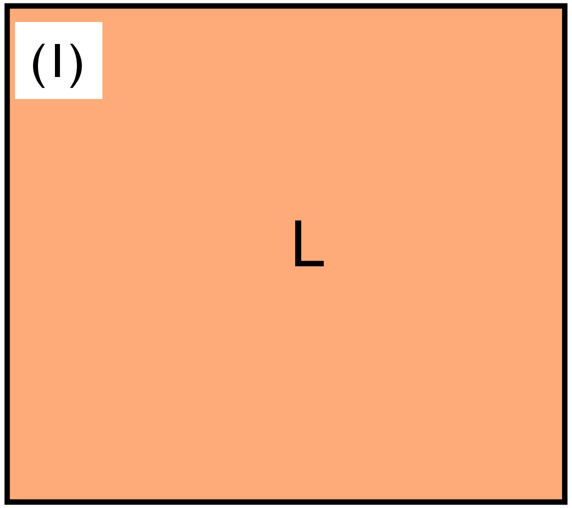
Solidification of Eutectic Systems

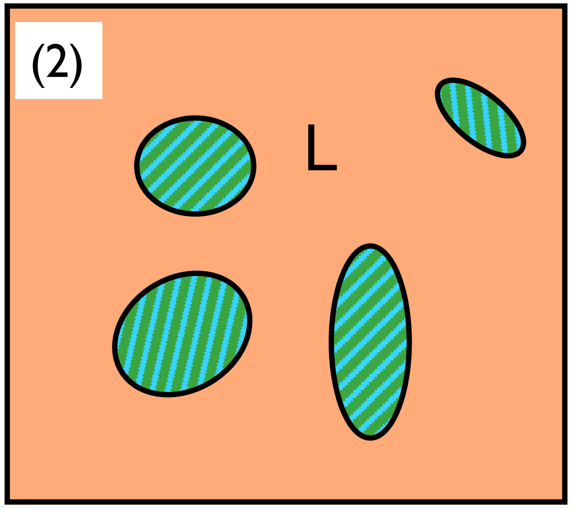
Alloy II:
At point 1: Liquid
Solidification starts at eutectic point (where liquidus and solidus join)
At point 2: L✦(α+β) (eutectic reaction)
The amounts of α and β increase in proportion with time.
Solidification finishes at the same temperature.
At point 3: α+β
Further cooling leads to the depletion of Sn in α and the depletion of Pb in β.

The cooling curve of this alloy is similar to cooling curve II shown in slide 9.

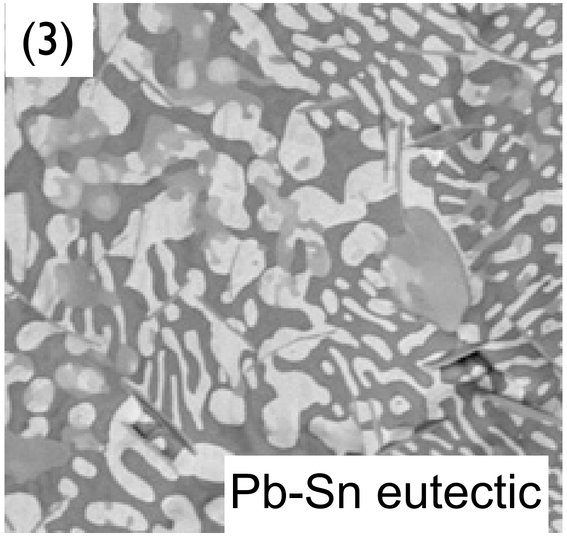
Pb-Sn phase diagram







Nucleation of colonies of α and β laminates

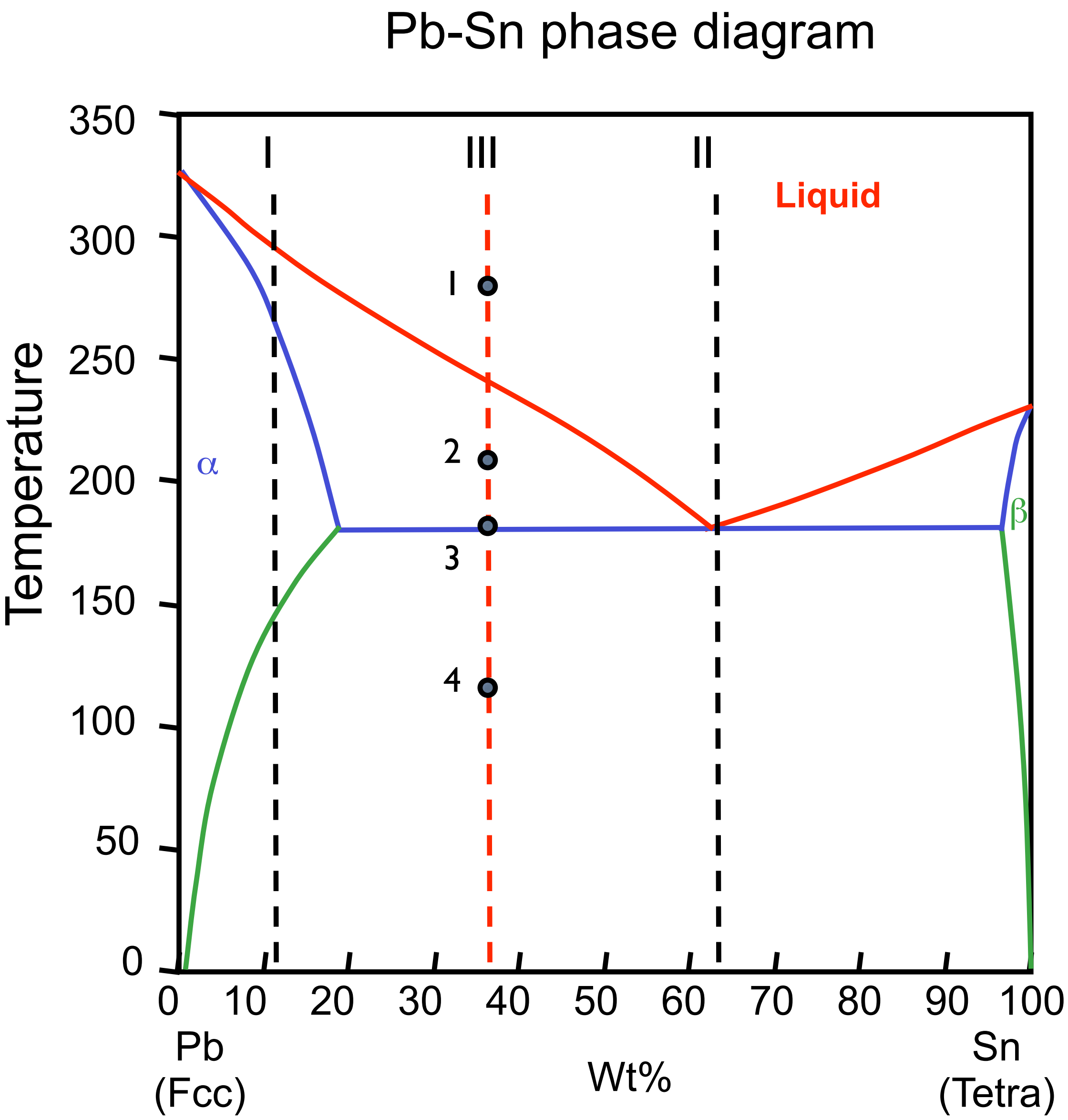


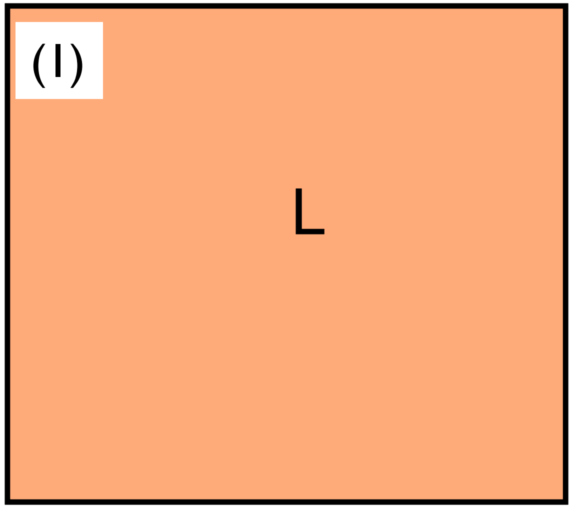
Eutectic structure of intimate mix of α and β to minimise diffusion path

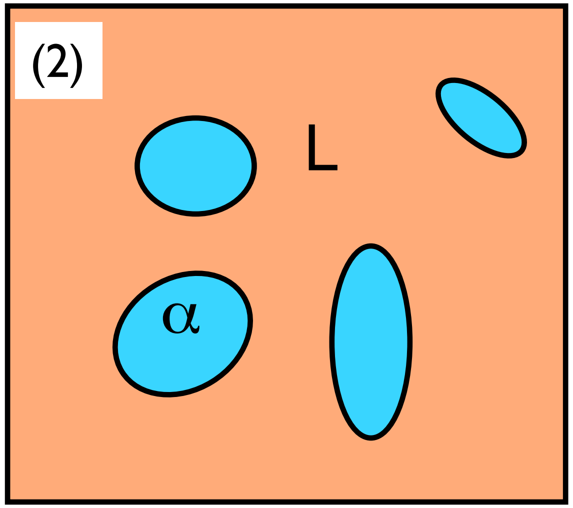
Solidification of Eutectic Systems

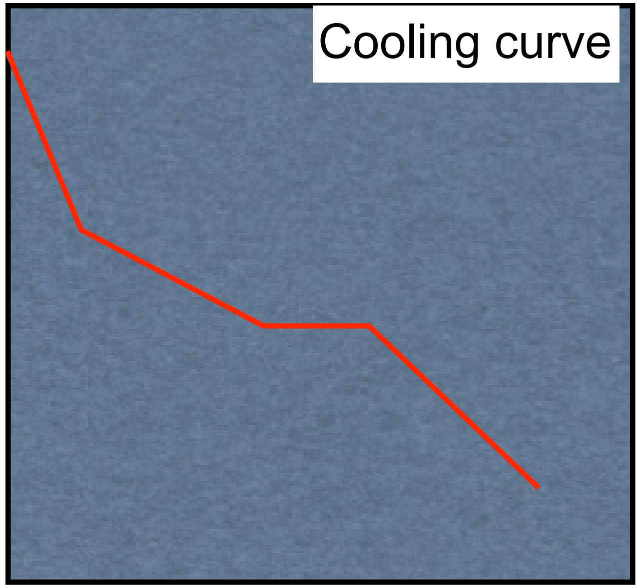
Alloy III:
At point 1: Liquid
Solidification starts at liquidus
At point 2: L✦L+α (pre-eutectic α)
The amount α ↑ with ↓T
At point 3: L✦ (α+β) (eutectic reaction)
Solidification finishes at the eutectic temperature
At point 4: α+β (pre-eutectic α + (α+β) eutectic mixture)
Further cooling leads to the depletion of Sn in α and the depletion of Pb in β.

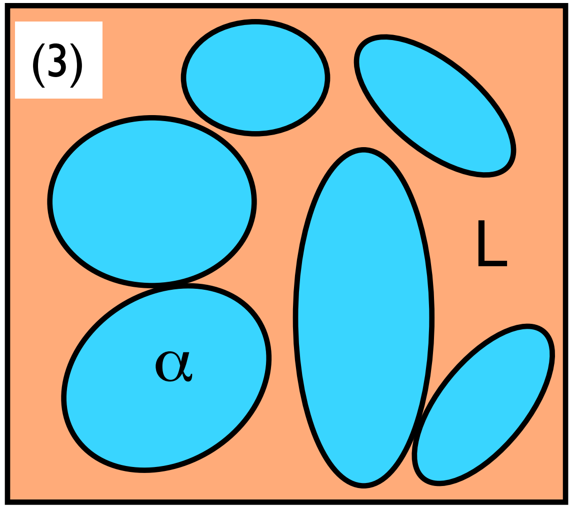
The cooling curve of this alloy is a combination of the two cooling curves shown in slide 9.

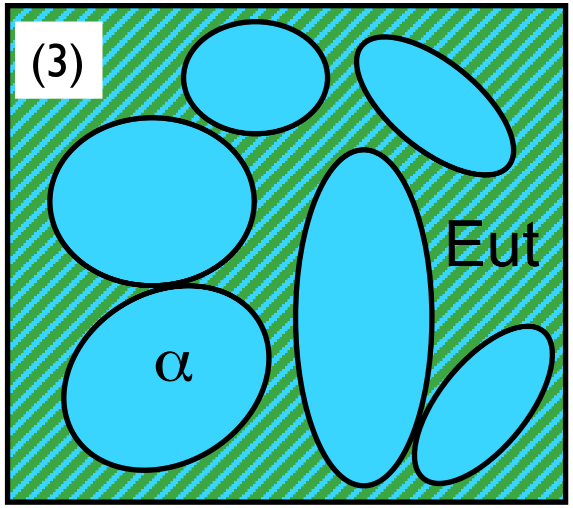


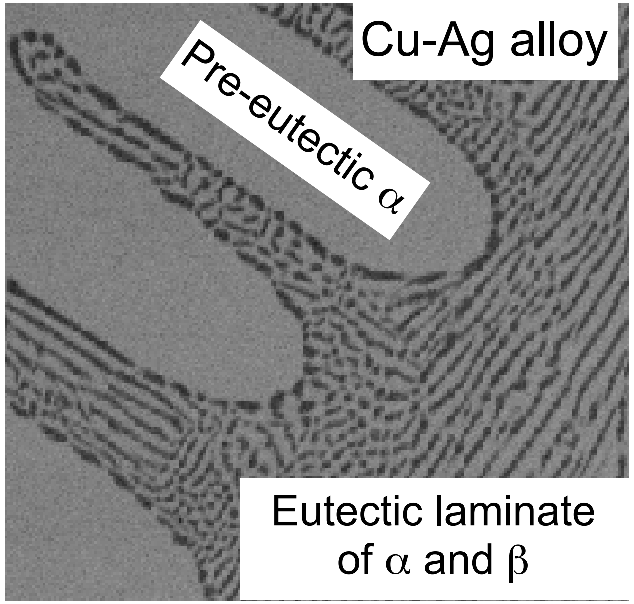

(1)
L


(2)
L
α


Cooling curve

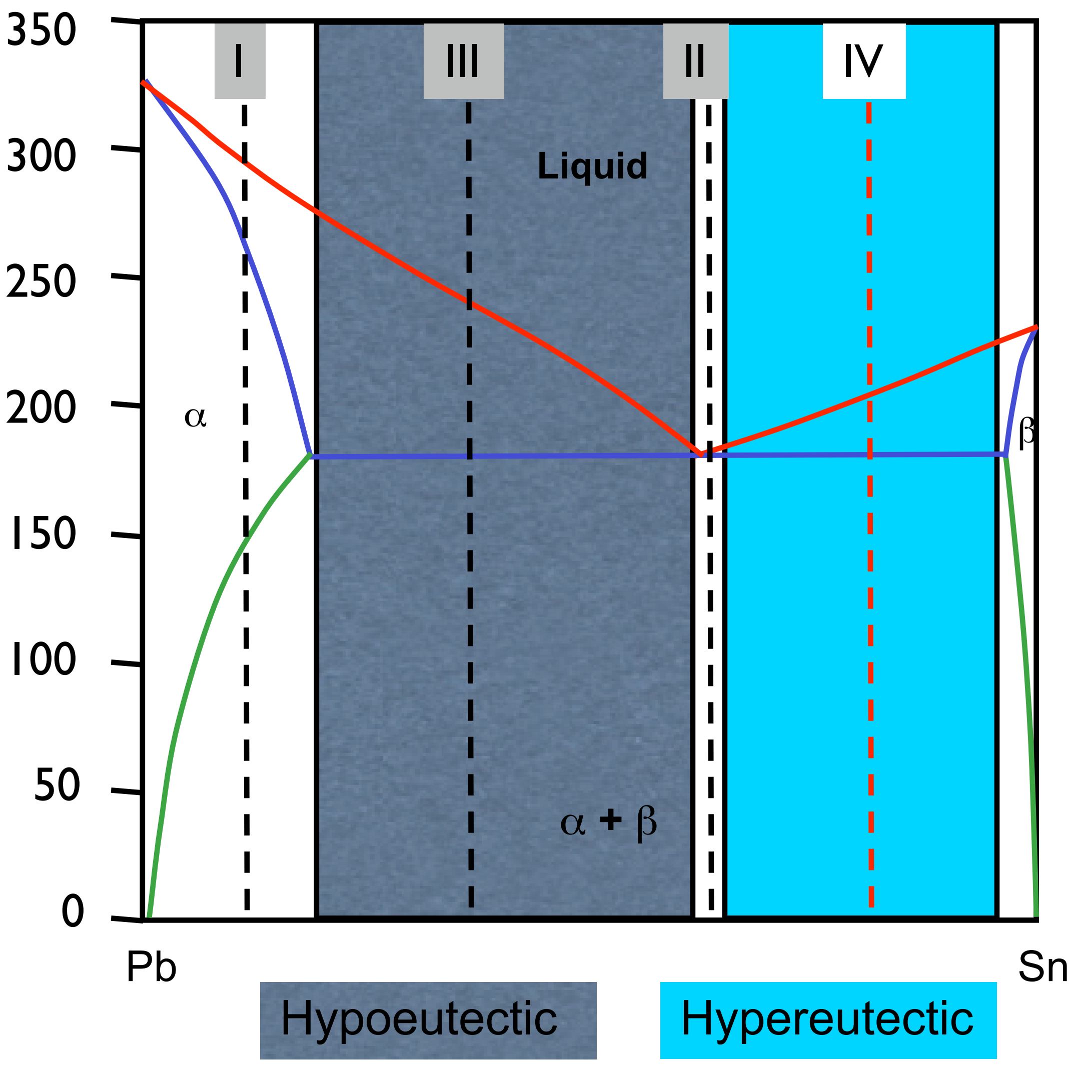

(3)
L
α


(3)
Eut
α


Cu-Ag alloy
Pre-eutectic α
Eutectic laminate of α and β

Solidification of Eutectic Systems

Can you describe the solidification process of alloy IV, including microstructure evolution, morphology of phases and cooling curve?

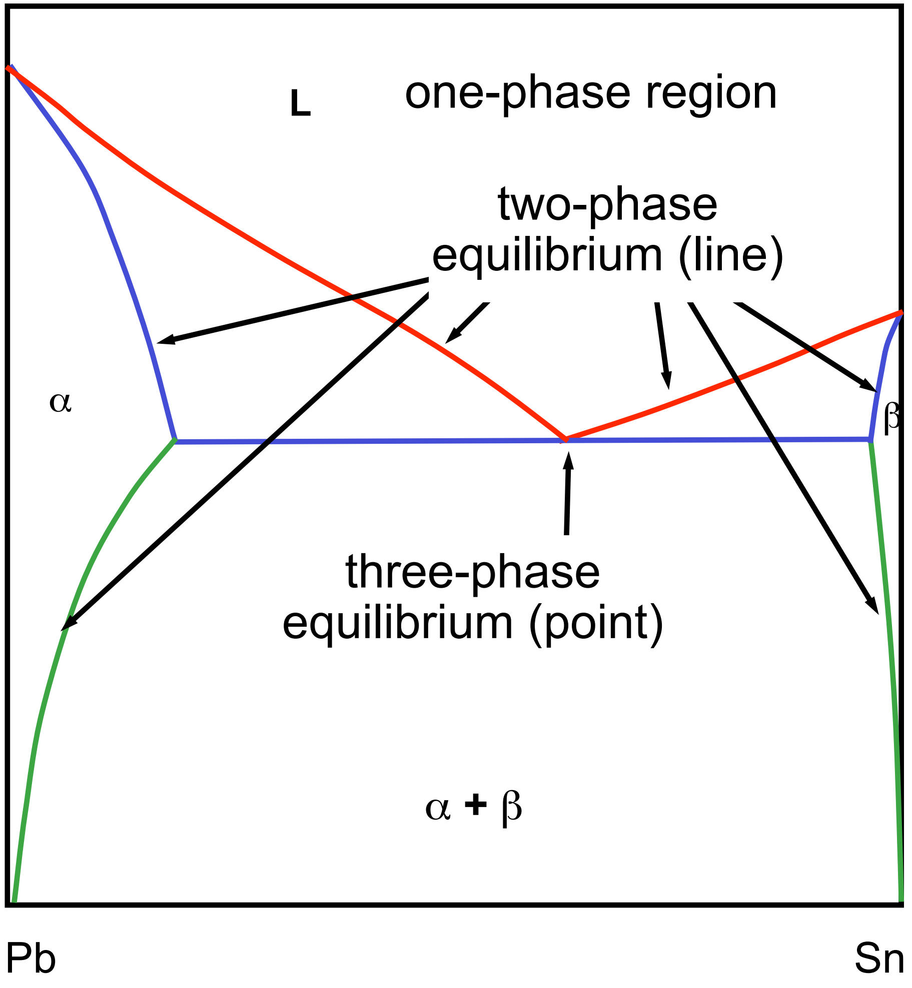


Gibbs Phase Rule

Gibbs phase rule **F =C+N-P**
F: degree of freedom
C: number of chemical variables
N: number of non-chemical variables
P: number of phases

Application of Gibbs phase rule:
For a binary system at ambient pressure:
C=2 (2 elements)
N=1 (temperature, no pressure)
For single phase: F=2: % and T (a region)
For a 2-phase equilibrium: F=1: % or T (a line)
For a 3-phase equilibrium: F=0, (invariant point)

May we have a 4-phase equilibrium, in a binary system, or in any system?

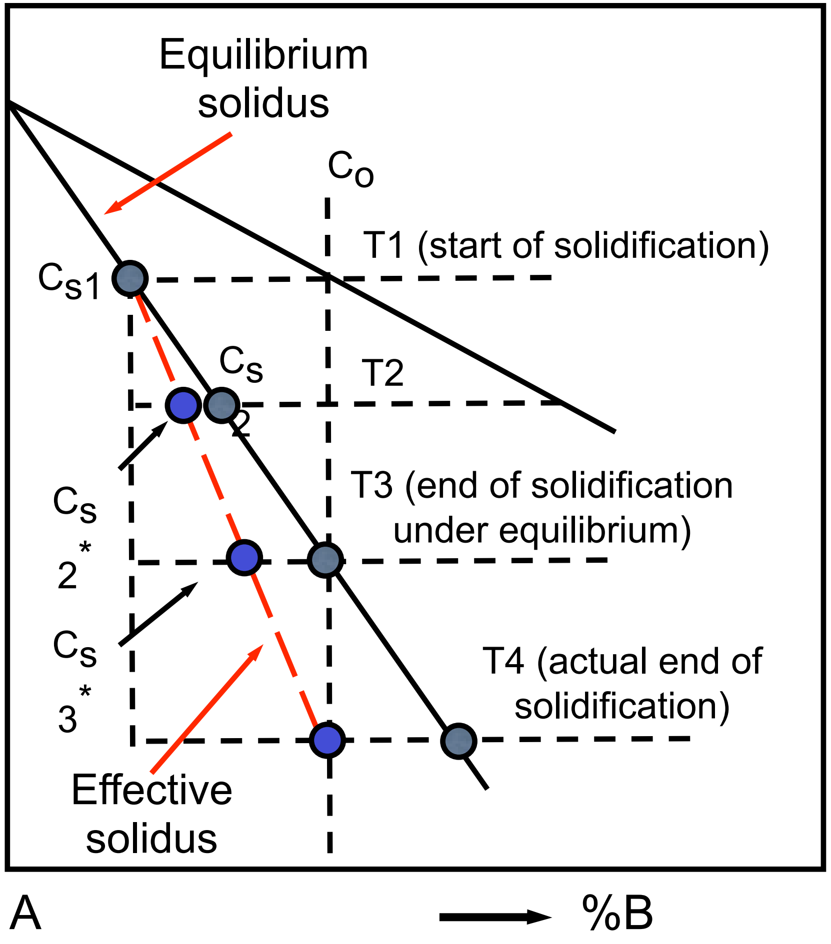


Non-Equilibrium Solidification

Some transformations do not cause changes in composition, such as the solidification of a pure metal, whereas some other do, such as the solidification of an alloy into a solid solution. The former is known as **congruent** transformation and the latter **incongruent** transformations. Congruent transformations are cooling rate insensitive and incongruent transformations are cooling rate sensitive – they rely on interdiffusion to proceed. Solidification under a fast cooling rate, where diffusion is insufficient to homogenise the composition simultaneously during the process is known as the **non-equilibrium solidification**. A common consequence of non-equilibrium solidification is **coring**.

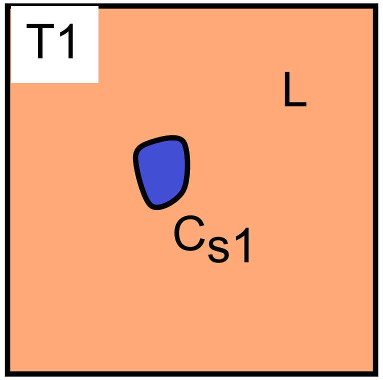
Coring

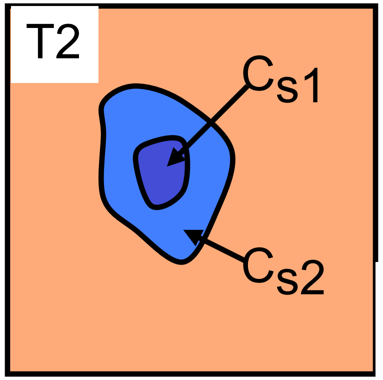
Alloy C_o starts solidification at T1. The first solid formed has composition C_{s1}. On further cooling to T2, an outer shell of composition C_{s2} is formed surrounding C_{s1}. Due to inadequate diffusion on fast cooling, a composition difference is created. The average composition of the solid composite at T2 is, thus, somewhere between C_{s1} and C_{s2}: C_{s2}^*. The same situation continues throughout the process.
Under equilibrium condition solidification completes at T3. However, under non-equilibrium condition, the average composition of solid at T3 is $C_{s3}^* < C_o$, indicating that solidification is not completed yet. Solidification actually ends when the average composition of solid equals C_o, i.e., at T4.



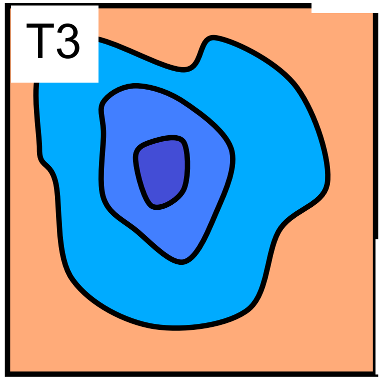
Non-equilibrium solidification lowers effective melting temperature.

Coring

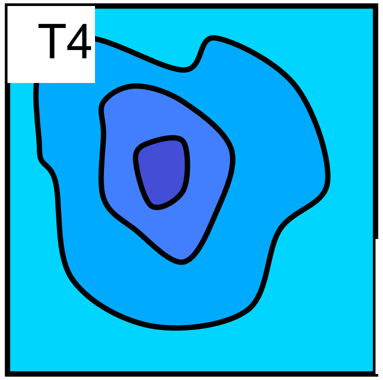




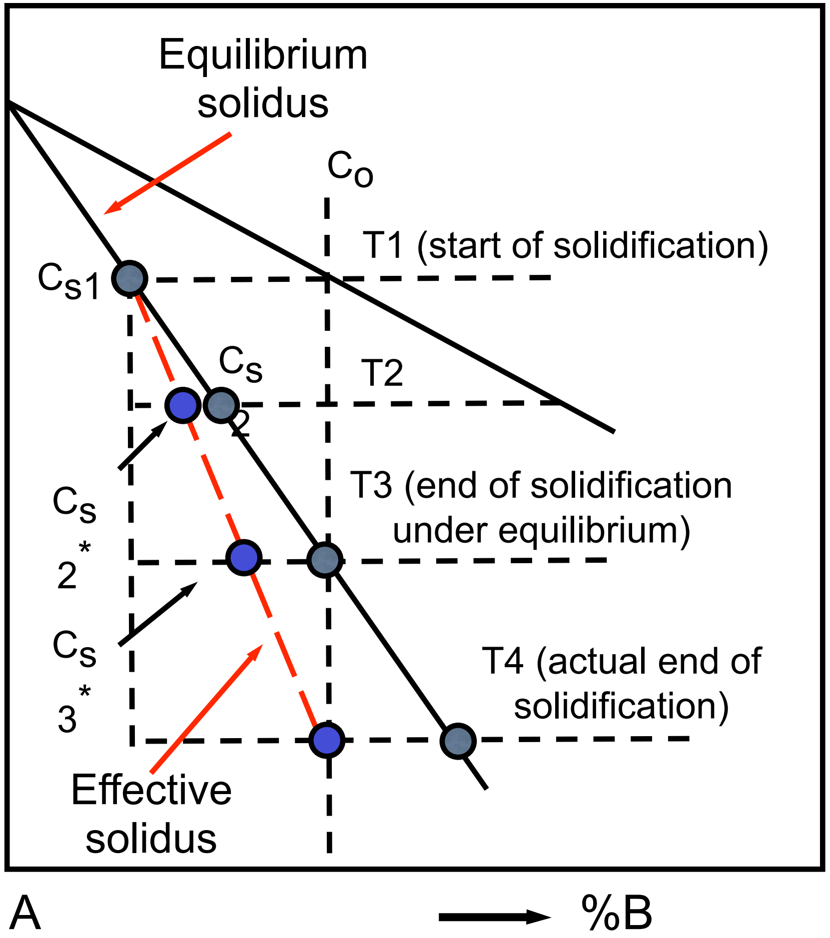
Average solid composition: C_{s2}*



Average solid composition: C_{s3}*



Average solid composition: C_o



The cored structure: composition segregation, enrichment of high-T_m constituent in the core

Coring in Eutectic Systems

According to the lever rule, the weight fraction of the eutectic products can be computed as:

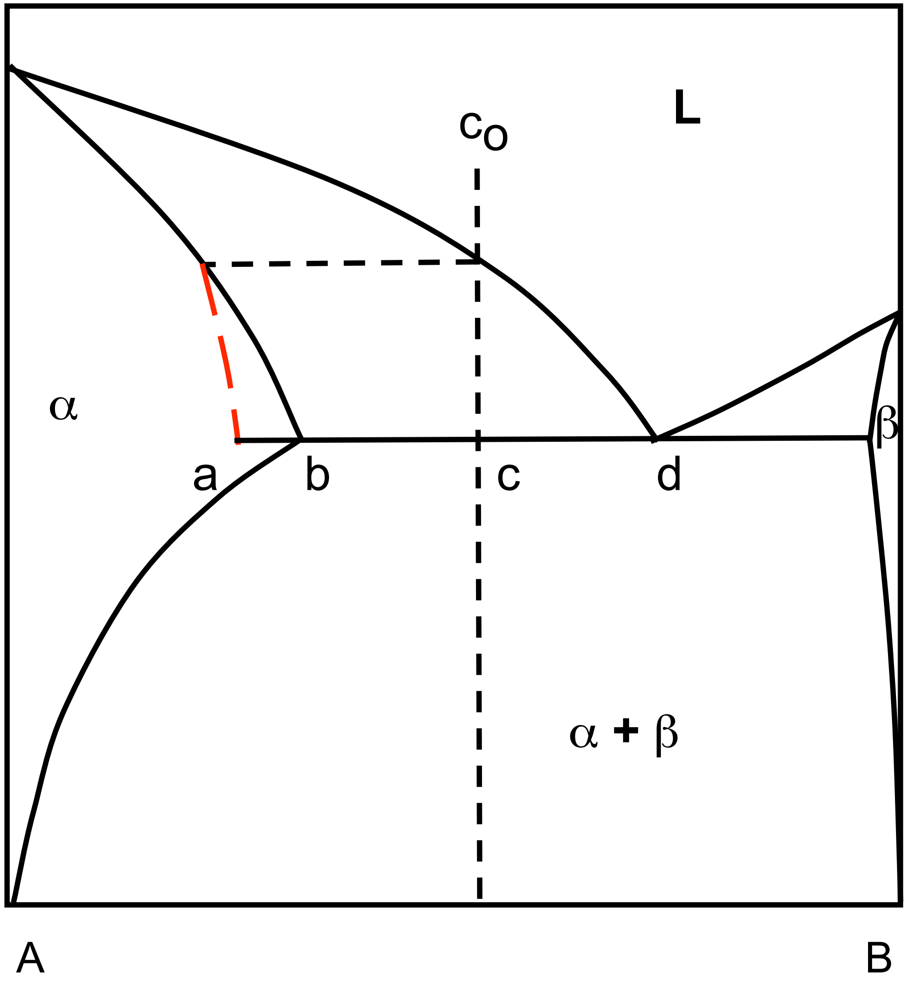
Under equilibrium condition:

$$W_{eut} = \frac{c-b}{d-b}$$

Under non-equilibrium condition:

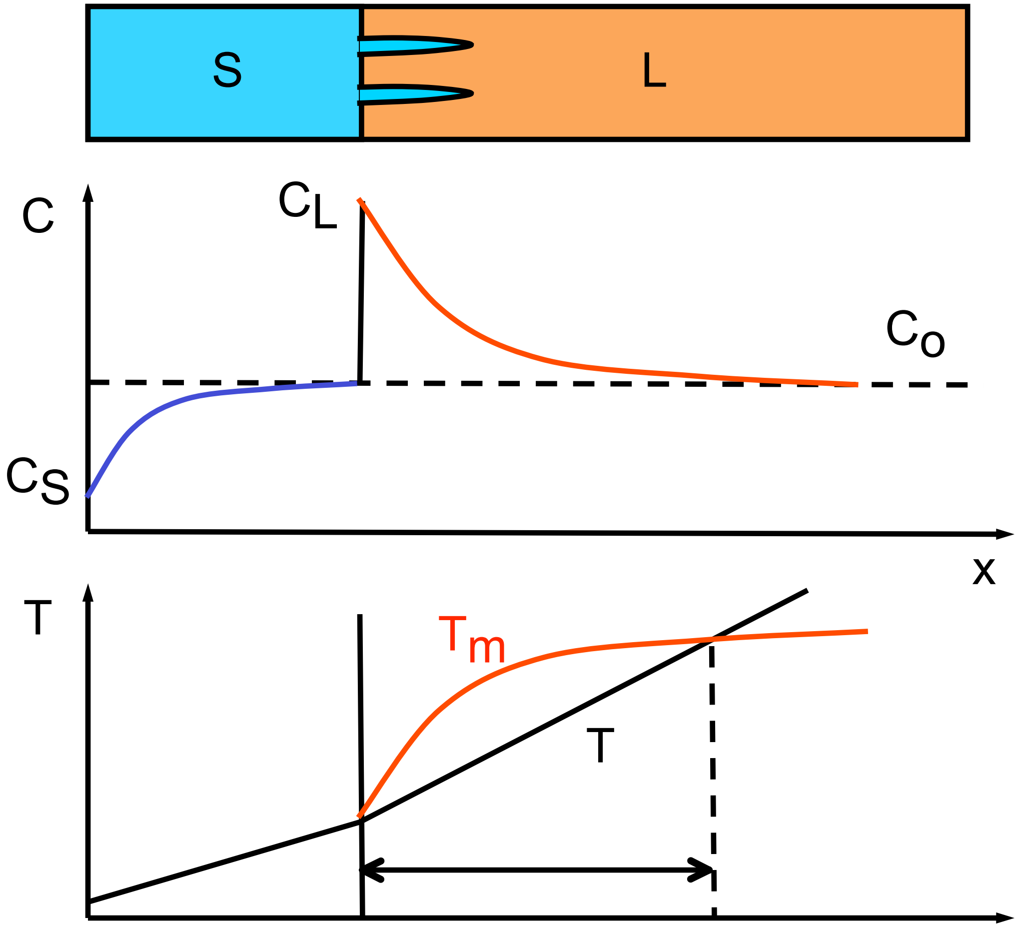
$$W_{eut}^{*} = \frac{c-a}{d-a}$$

$$W_{eut}^{*} > W_{eut}$$

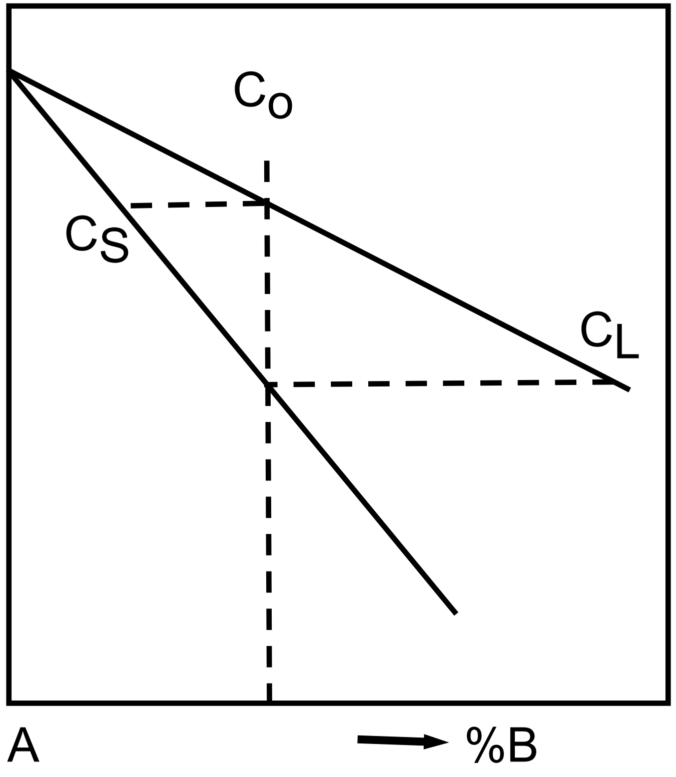


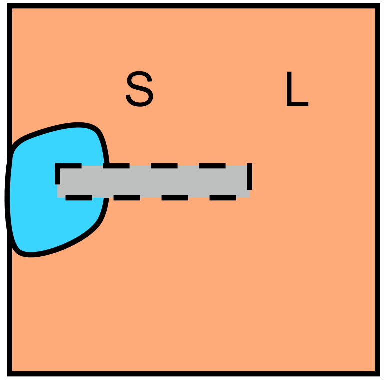
Coring leads to increase of weight fraction of eutectic products

Constitutional Supercooling



Supercooling window caused by rising Tm, resulting in unstable interface





Dendrite Structure of Metals

A consequence of constitutional supercooling and destabilisation of solid-liquid interface is the formation of dendritic structure, as commonly found in alloy castings. In such structure, gaps between dendrites and between dentitic fingers are regions rich of low-melting temperature phases and impurities. Dendritic branches themselves are often cored, too. This often require post-casting heat treatment to homogenise the structure.