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:

\[
\text{Solution} \quad \overset{\text{dissolving}}{\rightleftharpoons} \quad \text{Solid} \quad \overset{\text{precipitation}}{\rightleftharpoons} \quad \text{Salty water} \quad \overset{\text{the solution}}{\rightleftharpoons} \quad \text{Solid salt} \quad \overset{\text{the precipitate}}{\rightleftharpoons} \]

The same concepts apply to solids: solid solution, saturation, solubility, precipitation.
Phase diagrams are used to map out the existence and conditions of various phases of a given 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 contain two constituents, such as binary alloys, phase diagrams are often expressed in the temperature-composition plane.
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 $C_0$ starts on cooling at $T_1$. The first solid formed has a composition of $C_{S1}$ and the liquid $C_0$. On further cooling the solid particles grow larger in size and change their composition to $C_{S2}$ and then $C_0$, following the solidus whereas the liquid decrease in volume and changes its composition from $C_0$ to $C_{L3}$ following the liquidus. The solidification completes at $T_3$. 
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

\[ W_1 \cdot L_1 = W_2 \cdot L_2 \]

\[ W_1 + W_2 = 1 \]

Weight fractions: \[ W_1 = \frac{L_2}{L_1 + L_2} \]
At temperature $T_1$, alloy $C_0$ is in the dual phase region, comprising the liquid phase and the $\alpha$-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
- $\alpha$-phase: Cu-55%Ni

$$W_L = \frac{C_s - C_0}{C_s - C_L} = \frac{55 - 50}{55 - 30} = 0.2 = 20\%$$

$$W_\alpha = \frac{C_0 - C_L}{C_s - C_L} = \frac{50 - 30}{55 - 30} = 0.8 = 80\%$$

or

$$W_\alpha = 1 - W_L = 1 - 0.2 = 0.8 = 80\%$$
Cooling Curves
determination of Phase diagrams

1085°C
(thermal arrest)

1455°C

Solidus

Liquidus

T1

T2

1085°C

Cu

% Ni

I

II

III
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: $\text{L} \leftrightarrow \alpha + \beta$

Pb has a fcc structure and Sn has a tetragonal structure. The system has three phases: L, $\alpha$ and $\beta$. 
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.
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: $L \rightarrow (\alpha + \beta)$ (eutectic reaction)
The amounts of $\alpha$ and $\beta$ increase in proportion with time.
Solidification finishes at the same temperature.
At point 3: $\alpha + \beta$
Further cooling leads to the depletion of Sn in $\alpha$ and the depletion of Pb in $\beta$.

The cooling curve of this alloy is similar to cooling curve II shown in slide 9.
(1) Pb-Sn eutectic

(2) Nucleation of colonies of $\alpha$ and $\beta$ laminates

Eutectic structure of intimate mix of $\alpha$ and $\beta$ 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.
Eutectic laminate of \( \alpha \) and \( \beta \) Cu-Ag alloy

Cooling curve
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.
Alloy $C_o$ starts solidification at $T_1$. The first solid formed has composition $C_{S1}$. On further cooling to $T_2$, 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 $T_2$ is, thus, somewhere between $C_{S1}$ and $C_{S2}$: $C_{S2^*}$. The same situation continues throughout the process. Under equilibrium condition solidification completes at $T_3$. However, under non-equilibrium condition, the average composition of solid at $T_3$ 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 $T_4$.

Non-equilibrium solidification lowers effective melting temperature.
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:

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

Coring leads to increase of weight fraction of eutectic products.
Supercooling window caused by rising $T_m$, resulting in unstable interface.
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 denticite 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.