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PHASE DIAGRAMS
LEARNING OBJECTIVES

- Explain about alloy formation
- Interpret a phase diagram
- Describe phases in a phase diagram
- Use phase rule, tie line and lever rule to predict and calculate the composition and weight fraction of phases
- Distinguish different isothermal reactions in phase diagrams
CHAPTER OUTLINE

- Phases and the Phase Diagram
- Solubility and Solid Solutions
- Determination of Phase Diagrams
- Isomorphous Binary Phase Diagram
- Binary Eutectic Phase Diagram
A material can exist in many forms depending on: temperature, pressure and composition.

The properties of a material also depend on the microstructure, which in turn depends on the type, number and form of phases present.

In order to understand phase transformations, a means of representing which phases are stable at what temperatures is required.

This information is easily understood graphically in what is known as a “phase diagram”. A phase diagram is simply a chart which shows which phase(s) are stable under which conditions.
(a) The three forms of water – gas, liquid, and solid – are each a phase. (b) Water and alcohol have **unlimited** solubility. (c) Salt and water have **limited** solubility. (d) Oil and water have virtually **no solubility**.
Three variables need to be specified in order to specify that a system is in equilibrium:

- Temperature
- Pressure
- Composition

Equilibrium conditions:

- The system is at a minimum free energy
- Characteristics of the system will not change with time
If the temperature, pressure or composition change, the free energy will change.

With pressure assumed constant at atmospheric value: hence phase diagrams indicate any structural change due to variations in temperature & composition.

If the type, form and number of these phases are changed, then the properties are changed.
Phase diagrams are used to map out the existence and conditions of phases.

Q: What is a phase?
A: A phase (Liquid, Solid, Gas) is:

- Homogeneous portion of a system (in crystal structure)
- Has uniform chemical composition and physical properties
- Recognizable and separable

![Phase Diagram of Water](image)
There are 3 types of phase diagrams based on the number of independent chemical components into:

- Single component systems (unary phase diagram)
- Two component systems (binary phase diagrams)
- Three component systems (ternary phase diagrams)

Q: What is a component?
A: A component which can be a pure metal or a compound (in ceramics) is a pure substance required to express composition of phases in the system
Binary phase diagram in which both constituents have complete solubility and form continuous solid solution.
Solid solution is made of two parts:

- Solvent (matrix) or major part which dissolves the solute
- Solute is the minor part of the solution which is dissolved (impurity)

There is a difference between solution and mixture:

- A solution is a single *homogeneous* phase of variable composition
- A solution maintains the original crystal structure
- A solution contains randomly dispersed impurities (substitutional or interstitial)
- A mixture is *heterogeneous* (more than one phase present)
Solid solutions

Crystal structure is maintained

substitutional impurity atom

interstitial impurity atom
Several methods are used to determine the data for constructing phase diagrams:

- Metallographic methods
- X-ray diffraction (XRD)
- Thermal Analysis (the most widely used)

**Thermal Analysis**

- Information is obtained from cooling curves
- This is achieved by melting mixtures of known compositions and then measure the temperature of these mixtures while cooling to room temperature
DETERMINATION OF BINARY PHASE DIAGRAM

- Liquidus
- Solidus
- T1
- T2
- 1085°C
- 1455°C
- Cu
- %
- Ni

- Liquid phase
- Solid phase
- Freezing Point
- Phase change start temp.
- Phase change finish temp.
DETERMINATION OF BINARY PHASE DIAGRAM

LCT = Lower Critical Temperature
UCT = Upper Critical Temperature
TA = Melting Temperature of Alloy A
TB = Melting Temperature of Alloy B
DETERMINATION OF BINARY PHASE DIAGRAM
1. PHASE RULE

- The phase rule (Gibbs phase rule) is based on thermodynamics and predicts the number of phases that will coexist within a system at equilibrium.

- It is given as:

\[ P + F = C + N \]

P: number of phases present
C: number of components
N: number of non-compositional variables; N=1 or 2 (temperature and pressure). Since P = const, N is usually = 1
F: number of degrees of freedom (variables that can be changed independently without changing the number of phases which coexist at equilibrium)
1. PHASE RULE

- **F = 0**  
  Invariant point  
  At double (triple) point

- **F = 1**  
  At phase boundary

- **F = 2**  
  Inside phase

\[
F = 1 + 1 - 2 = 0 \\
F = 2 + 1 - 2 = 1 \\
F = 2 + 1 - 1 = 2
\]
The tie line is used to determine the composition of phases.

Example:
At $C_o = 40$ wt% Ni

- **At point A**: Only L exists,
  \[ C_L = C_{\text{liquidus}} = 31.5 \text{ wt}\% \text{ Ni} \]
- **At point C**: Only $S(\alpha)$ exists,
  \[ C_\alpha = C_o = 40 \text{ wt}\% \text{ Ni} \]
- **At point B**: Both L & S exist
  \[ C_L = C_{\text{solidus}} = 31.5 \text{ wt}\% \text{ Ni} \]
  \[ C_\alpha = C_{\text{solidus}} = 55 \text{ wt}\% \text{ Ni} \]
The lever rule is used to calculate the amount or weight fraction of each phase.

To explain the lever rule, we consider a simple balance. The composition of the alloy is point C, and the compositions of the two phases are $C_1$ and $C_2$.

The amount of the phases present are determined by the weights needed to balance the system.

Fraction of phase 1 (left)  
$$= \frac{(C_2 - C)}{(C_2 - C_1)}$$

Fraction of phase 2 (right)  
$$= \frac{(C - C_1)}{(C_2 - C_1)}$$
Assume \( C_o = 40 \text{ wt}\% \text{Ni} \)

At point A: Only L exists,
\[ W_L = 100\%, \ W_\alpha = 0 \]

At point C: Only S exists,
\[ W_\alpha = 100\%, \ W_L = 0 \]

At point B: Both L & S exist

\[ W_L = \frac{S}{S + R} \times 100\% \]

\[ = \frac{55 - 40}{55 - 31.5} \]
\[ = 0.65 = 65 \text{ wt}\% \]

\[ = 1 - W_L \]
\[ = 0.35 = 35 \text{ wt}\% \]
Binary phase diagrams are categorized as:

- Binary isomorphous (complete liquid and solid solubility)
- Binary eutectic with limited solid solubility
- Binary eutectic with no solid solubility
- Eutectoid binary diagrams
- Peritectic Binary diagrams
- Phase diagrams with Intermediate phases
There is complete solubility between the 2 components.

Complete solid solution usually occurs when the 2 components:

1. **Have the same crystal structure**
2. **Have similar atomic radii** (difference not more than 15 %)
3. **Have similar valences**
MICROSTRUCTURE DEVELOPMENT

Equilibrium Solidification

![Equilibrium Solidification Diagram](image-url)
Equilibrium Solidification
Equilibrium Solidification

Microstructure Development

- Liquid phase (L)
- α phase (fcc)
- Solid solution of Cu and Ni
- Cu and Ni composition diagram
  - Liquid phase - Solution of Cu and Ni
  - Temperature: T1, T2, T3
  - Composition: C0, C1, CS
  - Solidus: 1455°C, 1085°C
Equilibrium Solidification
Adding Ni increases the mechanical properties of Cu by solid solution strengthening.
Non-Equilibrium Solidification

Average solid composition: \( C_{s1} \)

Average solid composition: \( C_{s2} \)

Average solid composition: \( C_{s3} \)

Average solid composition: \( C_0 \)
Determine the composition of each phase in a Cu-40% Ni alloy at 1300°C, 1270°C, 1250°C, and 1200°C. (Figure below)

The vertical line at 40% Ni represents the overall composition of the alloy:

• **1300°C**: Only liquid is present. The liquid must contain 40% Ni, the overall composition of the alloy.

• **1270°C**: Two phases are present. The liquid contains 37% Ni and the solid contains 50% Ni.

• **1250°C**: Again two phases are present. The tie line drawn at this temperature shows that the liquid contains 32% Ni and the solid contains 45% Ni.

• **1200°C**: Only solid $\alpha$ is present, so the solid must contain 40% Ni.
The binary eutectic phase diagram explains the chemical behaviour of two immiscible (unmixable) crystals forming a completely miscible (mixable) melt.
Eutectic is a “Greek” word, which means “most fusible”

Eutectic reaction occurs when one liquid phase transforms to 2 solid phases at a constant temperature.

$L \rightarrow S_1(\alpha) + S_2(\beta)$

For the Pb-Sn diagram, eutectic reaction occurs at $T = 183^\circ C$

$L (61.9\%) \rightarrow \alpha (19\%) + \beta (97.5\%)$
SOLIDIFICATION IN EUTECTIC SYSTEMS

\[ \text{Liquid} \]

\[ \text{Liquidus} \]

\[ \text{Eutectic point} \]

\[ \alpha + L \]

\[ L + \beta \]

\[ \alpha \text{ phase: solid solution of Pb in fcc Pb} \]

\[ \beta \text{ phase: solid solution of Pb in tetragonal Sn} \]

\[ \alpha + \beta \]

\[ \text{solvus} \]

\[ \text{solubus} \]

\[ \text{Pb} \]

\[ \text{Sn} \]

\[ 0 \quad 10 \quad 20 \quad 30 \quad 40 \quad 50 \quad 60 \quad 70 \quad 80 \quad 90 \quad 100 \]

\[ 0 \quad 50 \quad 100 \quad 150 \quad 200 \quad 250 \quad 300 \quad 350 \]

\[ \alpha \]

\[ \alpha \]

\[ \alpha \]

\[ \alpha \]
SOLIDIFICATION IN EUTECTIC SYSTEMS

- Liquid
- Liquidus
- Solidus
- Eutectic point
- α phase: solid solution of Sn in fcc Pb
- β phase: solid solution of Pb in tetragonal Sn
- α + L
- L + β
- α + β
- Solvus
- Pb
- Sn
- Wt%
SOLIDIFICATION IN EUTECTIC SYSTEMS

**Diagram:**
- **Liquidus** and **Solidus** curves.
- **Eutectic point** where **α** and **β** phases form.
- **α phase:** solid solution of Pb in fcc Sn.
- **β phase:** solid solution of Sn in tetragonal Pb.

**Inclusions:**
- Micrograph of a material.
- Photo of layered material.
SOLIDIFICATION IN EUTECTIC SYSTEMS

- Liquid
- Eutectic point
- Liquidus
- Solidus
- Solvus
- α phase: solid solution of Sn in fcc Pb
- β phase: solid solution of Pb in tetragonal Sn

Diagram showing the solidification process of a eutectic system with phase diagrams and micrographs.
Melting points of Lead (Pb) and tin (Sn) are 327°C and 231°C respectively. The system is completely soluble in LIQUID but partially soluble in SOLID. The maximum solubility of Sn in Pb is 19%Sn, while maximum solubility of Pb in Sn is 2.7%Pb. The eutectic reaction occurs at 183°C of composition 61.9%Sn.

i. *Construct the phase diagram of this system*
Determine (a) the solubility of Sn in solid Pb at 100°C, (b) the maximum solubility of Pb in solid Sn and of Sn in solid Pb, (c) phases present if a Pb-40% Sn alloy is cooled to room temperature, (d) compositions of these phases, (e) the amount of \( \beta \) that forms if a Pb-40% Sn alloy is cooled to room temperature.
EXAMPLE: MICROSTRUCTURE DEVELOPMENT

The diagram illustrates a phase diagram for a binary system with a solid solution. The axes are labeled as follows:

- Y-axis: Temperature (°C)
- X-axis: Weight percent tin

Key features include:

- Liquidus and Solidus curves
- α, β phases
- α + L, α + β, L + β phases
- Solvus lines

Points of interest:

- C₀
- C₁
- C₂
- Pb
- Sn

The diagram shows the phase changes and compositions at various temperatures and compositions.
Example: Microstructure Development

a. Solubility of tin (Sn) in lead (Pb) at 100°C therefore is 7%.

b. Maximum solubility of Pb in Sn is 97.5% at 183 °C

Maximum solubility of Sn in Pb is 19% at 183 °C

c. Phases Present at room temperature

\[ \alpha + \beta \]

d. Composition of Phases (tie line)

\[ C_\alpha = 2 \text{ wt\% Sn}, \quad C_\beta = 99 \text{ wt\% Sn} \]

e. Amount of \( \beta \) phase

\[
W_\beta = \frac{10 - 2}{99 - 10} \times 100\% = 0.11 \times 100\% = 11\%
\]
• Binary eutectic phase diagram with no solid solubility

- This type of eutectic system occurs when the components A and B are insoluble in each other.
- No solid solution will form.
- A close example is the Al-Si eutectic system, in which only one solid solution on the Al-rich side forms but no solid solution is formed on the Si-rich side of the diagram.
• The eutectoid reaction occurs when a single-phase solid transforms directly to two solid phases:

\[ S \rightarrow S_1 + S_2 \]

• **Eutectoid reaction**

  • *Invariant point with 3 solid phases in equilibrium*
  • *Similar to eutectic reaction but it involves only solid phases*
In the eutectic system described above, the two solid phases (α and β) which are in equilibrium with liquid are called *terminal solid solutions*.

Some binary systems, however, have *intermediate solid solutions* and which are separated from the composition extremes (0% and 100%).

Example: in the Cu-Zn phase diagram shown below

- α and η are terminal solid solutions.
- β, β’, γ, δ and ε are intermediate solid solutions
In binary systems, intermetallic compounds with precise composition form, instead of intermediate phases.

An intermetallic compound is represented on the phase diagram as a vertical line (specific composition)

Example:

Mg-Pb phase diagram shown below
Figure 9.18 The magnesium–lead phase diagram. (Adapted from Phase Diagrams of Binary Magnesium Alloys, A. A. Nayeb-Hashemi and J. B. Clark, Editors, 1988. Reprinted by permission of ASM International, Materials Park, OH.)