5. phase diagrams

**phase** – a region in a material that differs in structure and function from other regions

**phase diagrams** – graphical representations of what phases are present in a materials system at different conditions (temperature, pressure and composition)

(1) phase diagrams of pure substances
pure substance exist as **solid**, **liquid** and **vapor** phases depending on the conditions of temperature and pressure

- water
  - two-phase equilibrium line
  - triple point

![Pressure-temperature (PT) phase diagram for water](image)

**Water**
- two-phase equilibrium line
- triple point

<table>
<thead>
<tr>
<th>Pressure of H₂O (torr)</th>
<th>Temperature of H₂O (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>760</td>
<td>100</td>
</tr>
<tr>
<td>4.579 torr</td>
<td>0</td>
</tr>
<tr>
<td>Solid</td>
<td>Frozen</td>
</tr>
<tr>
<td>Vapor</td>
<td>Liquid</td>
</tr>
</tbody>
</table>

- Vaporization line
- Freezing line
- Solid
- Liquid
- Vapor
- Triple point at 0.01°C
- 4.579 torr
• iron  
three distinct solid phases: $\alpha$Fe, $\gamma$Fe, $\delta$Fe  
three triple points

(2) **Gibbs phase rule**  
$$P + F = C + 2$$  
$P$: number of phases that coexist in a system  
$C$: number of components  
$F$: degrees of freedom  
ex. water  
triple point   $3 + F = 1 + 2 \iff F = 0$  
L-S freezing curve   $2 + F = 1 + 2 \iff F = 1$  
degrees of freedom indicate number of variables that can be changed without changing number of phases
(3) cooling curves used to determine phase transition temperature vs. time data of cooling molten material is recorded and plotted

BC – plateau or region of thermal arrest

- cooling curve for pure Fe
(4) binary isomorphous alloy systems

**binary alloy** – a mixture of two metals

**isomorphous system** – two elements completely soluble in each other in liquid and solid state usually satisfy one or more **Hume-Rothery solid solubility rules**

- copper-nickel system

```
<table>
<thead>
<tr>
<th>Temperature (℃)</th>
<th>Liquidus</th>
<th>Solidus</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1455</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Composition of liquid + solid phases at any temperature can be determined by drawing a tie line**

ex. at 1300℃ an alloy of 53% Ni + 47% Cu in liquid + solid phase

composition of liquid phase: 45% Ni

composition of solid phase: 58% Ni
points of change of slope of cooling curves (thermal arrests) are noted for metal alloys, solidification begins at a specific temperature (L) and ends at a lower temperature (S) the freezing temperature of a metal alloy is the temperature at which the solidification process is complete
(5) **lever rule**

The lever rule gives the weight % of phases in any two phase regions.

\[ X_s + X_l = 1 \]

\[ X_s = 1 - X_l \]

Consider 1 g of alloy, weight balance of B:

\[(1 \text{ g})(\%w_0) = (1 \text{ g})(X_l)(\%w_l) + (1 \text{ g})(X_s)(\%w_s)\]

\[ w_0 = X_l w_l + X_s w_s \]

\[ w_0 = (1 - X_s)w_l + X_s w_s \]

\[ w_0 = w_l - X_s w_l + X_s w_s \]

Wt fraction of solid phase = \[ X_s = \frac{w_0 - w_1}{w_s - w_1} \]

Wt fraction of liquid phase = \[ X_l = \frac{w_s - w_0}{w_s - w_1} \]
the weight fraction of liquid phase is the ratio of $OS/LS$
the weight fraction of solid phase is the ratio of $LO/LS$

ex. Cu-Ni alloy contains 47 wt% Cu and 53 wt% Ni at 1300°C

a. what is the wt% of Cu in liquid and in solid phases?
b. what wt% of this alloy is liquid?

\[
\begin{align*}
\text{a. from the phase diagram,} \\
\text{wt\% of Ni in liquid is 45\% and in solid is 58\%} \\
\text{wt\% of Cu in liquid is 55\% and in solid is 42\%} \\
b. \\
X_L = \frac{w_s - w_0}{w_s - w_1} = \frac{58 - 53}{58 - 45} = \frac{5}{13} = 0.38 \quad 38\% \\
X_S = \frac{w_0 - w_1}{w_s - w_1} = \frac{53 - 45}{58 - 45} = \frac{8}{13} = 0.62 \quad 62\%
\end{align*}
\]
ex. calculate the wt% liquid and solid for Ag-Pd phase diagram shown below at 1200°C and 70 wt% Ag.

\[ X_l = \frac{w_s - w_0}{w_s - w_1} = \frac{64 - 70}{64 - 74} = \frac{6}{10} = 0.6 \quad 60\% \]

\[ X_s = \frac{w_0 - w_1}{w_s - w_1} = \frac{70 - 74}{64 - 74} = \frac{4}{10} = 0.4 \quad 40\% \]
(6) nonequilibrium solidification of alloys slowly solidified alloys usually have a cored structure

70% Cu-30% Ni alloy

rapid cooling (nonequilibrium) delays solidification

homogenization: as-cast ingots are heated to elevated temperature to accelerate solid-state diffusion and to eliminate the cored structure. Temperature of homogenization must be lower than lowest melting point of any of the alloy components.
(7) binary eutectic alloy systems in some binary alloy systems, components have limited solid solubility – eutectic system ex. Pb-Sn system

- terminal solid solutions with restricted solid solubility $\alpha$ (Pb-rich) and $\beta$ (Sn-rich) phases
- eutectic composition freezes at lower temperature than all other compositions, this lowest temperature is called eutectic temperature
eutectic reaction

\[ \text{eutectic temperature} \]

\[ \text{liquid} \rightarrow \alpha \text{ solid solution} + \beta \text{ solid solution} \]

cooling

eutectic reaction is an invariant reaction – degree of freedom \( F = 0 \)

- slow cooling of a Pb-Sn alloy of eutectic composition

- eutectic composition

- 40% Sn - 60% Pb

- 70% Sn - 30% Pb

- 90% Sn - 10% Pb
• slow cooling of 60% Pb – 40% Sn alloy

\[ \begin{align*}
  \text{a. liquid at 300}^\circ\text{C} \\
  \text{b. at about 245}^\circ\text{C first solid solution } \alpha (12\% \text{ Sn}) \text{ forms – primary or proeutectic } \alpha \\
  \text{c. slightly above 183}^\circ\text{C composition of alpha follows solidus and composition of Sn varies from 12\% to 19.2\%, composition of liquid phase varies from 40\% to 61.9\%} \\
  \text{d. at eutectic temperature, all the remaining liquid solidifies}
\end{align*} \]
ex. make phase analysis at the following points in Pb-Sn phase diagram:
(a) at eutectic composition just below 183°C
(b) point c at 40% Sn and 230°C
(c) point d at 40% Sn and 183°C + ΔT
(d) point e at 40% Sn and 183°C – ΔT

(a) \( \alpha \) phase (19.2% Sn) + \( \beta \) phase (97.5% Sn)

\[
\text{wt\% (}\alpha\text{)} = \frac{97.5 - 61.9}{97.5 - 19.2} = 45.5% \\
\text{wt\% (}\beta\text{)} = \frac{61.9 - 19.2}{97.5 - 19.2} = 54.5%
\]

(b) \( \alpha \) phase (15% Sn) + liquid (48% Sn)

\[
\text{wt\% (}\alpha\text{)} = \frac{48 - 40}{48 - 15} = 24% \\
\text{wt\% (L)} = \frac{40 - 15}{48 - 15} = 76%
\]

(c) \( \alpha \) phase (19.2% Sn) + liquid (61.9% Sn)

\[
\text{wt\% (}\alpha\text{)} = \frac{61.9 - 40}{61.9 - 19.2} = 51% \\
\text{wt\% (L)} = \frac{40 - 19.2}{61.9 - 19.2} = 49%
\]

(d) \( \alpha \) phase (19.2% Sn) + \( \beta \) phase (97.5% Sn)

\[
\text{wt\% (}\alpha\text{)} = \frac{97.5 - 40}{97.5 - 19.2} = 73% \\
\text{wt\% (}\beta\text{)} = \frac{40 - 19.2}{97.5 - 19.2} = 27%
\]
ex. an alloy of 70% Pb + 30% Sn is slowly cooled from 300°C, calculate the following:

(a) wt% of the liquid and proeutectic α form at 250°C

(b) wt% of the liquid + proeutectic α form just above eutectic temperature (183°C)

(c) wt% of the α and β phases formed by the eutectic reaction

(a) α phase (12% Sn) + liquid(40% Sn)

\[
\text{wt\% (α)} = \frac{40 - 30}{40 - 12} \quad \text{wt\% (L)} = \frac{30 - 12}{40 - 12}
\]

\[
= 36\% \quad = 64\%
\]

(b) α phase (19.2% Sn) + liquid (61.9% Sn)

\[
\text{wt\% (α)} = \frac{61.9 - 30}{61.9 - 19.2} \quad \text{wt\% (L)} = \frac{30 - 19.2}{61.9 - 19.2}
\]

\[
= 74.7\% \quad = 25.3\%
\]

(c) α phase (19.2% Sn) + β phase (97.5% Sn)

\[
\text{wt\% (α)} = \frac{97.5 - 30}{97.5 - 19.2} \quad \text{wt\% (β)} = \frac{30 - 19.2}{97.5 - 19.2}
\]

\[
= 86.2\% \quad = 13.8\%
\]
ex. a Pb-Sn alloy contains 64 wt% proeutectic $\alpha$ and 36 wt% eutectic $\alpha + \beta$ at 183°C - $\Delta T$

calculate the average composition of this alloy

assume $x$ wt% Sn in this alloy

since 64 wt% proeutectic $\alpha$ exists, the alloy must be hypoeutectic and $19.2 < x < 61.9$

$$\frac{61.9 - x}{61.9 - 19.2} = 64\%$$

$x = 34.6$

this alloy consists of 34.6 wt% Sn and 65.4 wt% Pb

- in a binary eutectic reaction two solid phases ($\alpha$ and $\beta$) can have various morphologies
- structure depends on factors like minimization of free energy at $\alpha/\beta$ interface
- manner in which two phases nucleate and grow also affects structures

ex. lamellar eutectic structure of Pb-Sn alloy
(8) binary peritectic alloy system

peritectic reaction – liquid phase reacts with a solid phase to form a new and different solid phase

\[
\text{liquid } + \alpha \xrightarrow{\text{cooling}} \beta
\]

peritectic reaction occurs when a slowly cooled alloy

ex. Fe-Ni phase diagram

\(\delta\) phase – Ni in BCC-Fe

\(\gamma\) phase – Ni in FCC-Fe

Fe-4.3 wt% Ni passes through peritectic temperature of \(1517^\circ\text{C}\)

liquid (5.4 wt% Ni) + \(\delta\) (4.0 wt% Ni) \(\xrightarrow{\text{cooling}}\) \(\gamma\) (4.3 wt% Ni)
ex. Pt-Ag phase diagram

the peritectic reaction occurs at 42.4 wt% Ag and 1186°C

ex. make phase analysis at the following:

a. at 42.4% Ag and 1400°C
b. at 42.4% Ag and 1186°C + ΔT
c. at 42.4% Ag and 1186°C − ΔT
d. at 60% Ag and 1150°C

a. phases present
   composition: liquid α
   amount of phases:
   
<table>
<thead>
<tr>
<th>composition</th>
<th>liquid</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>55% Ag</td>
<td>55-42.4</td>
<td>7% Ag 55-42.4</td>
</tr>
<tr>
<td>42.4 –7</td>
<td>55 – 7</td>
<td>55 - 7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

= 74%  = 26%
b. phases present in liquid composition 66.3% Ag 42.4 – 10.5
amount of phases 66.3 – 10.5
= 57%

α 10.5% Ag 66.3 – 42.4
= 43%

66.3 – 10.5


c. phase present β only composition 42.4% Ag
amount of phase 100%


d. phases present in liquid composition 77% Ag 48% Ag
amount of phases 60 – 48
77 - 48
= 41%

β 48% Ag 77-60
77 – 48
= 59%

very slow cooling of an alloy of peritectic composition through the peritectic temperature
surrounding or encasement – during rapid solidification of alloy through peritectic reaction, the $\beta$ phase created surrounds primary $\alpha$

$\beta$ creates diffusion barrier resulting in coring

cast 60% Ag-40% Pt hyperperitetic alloy
(9) binary monotectic systems

monotectic reaction – liquid phase transforms into solid phase and another liquid

cooling

\[ \text{L}_1 \xrightarrow{\text{cooling}} \alpha + \text{L}_2 \]

two liquids are immiscible

ex. Cu-Pb system at 955°C and 36% Pb

Cu-rich portion

Pb-rich portion
(10) invariant reactions
zero degree of freedom at the reaction points

<table>
<thead>
<tr>
<th>Name of reaction</th>
<th>Equation</th>
<th>Phase-diagram characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eutectic</td>
<td>$L \xrightarrow{\text{cooling}} \alpha + \beta$</td>
<td>$\alpha \xrightarrow{L} \beta$</td>
</tr>
<tr>
<td>Eutectoid</td>
<td>$\alpha \xrightarrow{\text{cooling}} \beta + \gamma$</td>
<td>$\beta \xrightarrow{\alpha} \gamma$</td>
</tr>
<tr>
<td>Peritectic</td>
<td>$\alpha + L \xrightarrow{\text{cooling}} \beta$</td>
<td>$\alpha \xrightarrow{\beta} L$</td>
</tr>
<tr>
<td>Peritectoid</td>
<td>$\alpha + \beta \xrightarrow{\text{cooling}} \gamma$</td>
<td>$\alpha \xrightarrow{\gamma} \beta$</td>
</tr>
<tr>
<td>Monotectic</td>
<td>$L_1 \xrightarrow{\text{cooling}} \alpha + L_2$</td>
<td>$\alpha \xrightarrow{L_1} L_2$</td>
</tr>
</tbody>
</table>
(11) phase diagrams with intermediate phases and compounds

**terminal phases** – phases occur at the end of phase diagrams

**intermediate phases** – phases occur in a composition range inside phase diagram. ex. Cu-Zn diagram has both terminal and intermediate phases.

- **α** and **η** – terminal phases

- **β**, **γ**, **δ**, **ε** – intermediate phases

- five invariant peritectic points + one eutectic point
an intermediate phase called **mullite** is formed, which includes the compound \(3\text{Al}_2\text{O}_3.2\text{SiO}_2\)
in some phase diagrams, intermediate compounds are formed – stoichiometric percent ionic/covalent bond depends on electronegativity

ex. Mg-Ni phase diagram contains two intermetallic compounds:

MgNi$_2$ - congruently melting compound

Mg$_2$Ni - incongruently melting compound
(12) ternary phase diagrams

three components phase diagrams constructed by using a equilateral triangle as base
• pure components at each end of triangle binary alloy composition represented on edges
• temperature can be represented as uniform throughout the whole diagram – isothermal section

to determine the composition of a ternary alloy:
• draw a perpendicular line from a pure metal corner to the side of the triangle opposite that corner
• measure the distance from the side to the corner along the perpendicular line
ex. determine the wt% of metals A, B, C for ternary alloy at points $x$ and $y$ on the following phase diagram

draw three perpendicular lines AD, BE, CF for point $x$
(i) on AD line $\implies$ 40% A
(ii) on BE line $\implies$ 40% B
(iii) on CF line $\implies$ 20% C

for point $y$
(i) on AD line $\implies$ 20% A
(ii) on BE line $\implies$ 30% B
(iii) on CF line $\implies$ 50% C
ex. Fe-Cr-Ni phase diagrams.

- isothermal reaction at 650°C for this system
- the most important stainless steel has a composition essentially of 74% Fe, 18% Cr, and 8% Ni