CHAPTER 9: PHASE DIAGRAMS

ISSUES TO ADDRESS...

• When we combine two elements...
  what equilibrium state do we get?

• In particular, if we specify...
  --a composition (e.g., wt%Cu - wt%Ni), and
  --a temperature (T)
  then...
  How many phases do we get?
  What is the composition of each phase?
  How much of each phase do we get?

Phase A

• Nickel atom
• Copper atom

Phase B
Some Definitions

- An alloy is a combination, either in solution or compound, of two or more components (elements), at least one of which is a metal.

- An alloy with two components is called a binary alloy; one with three is a ternary alloy; one with four is a quaternary alloy.

- The result is a material with properties different from those of its components.
COMPONENTS AND PHASES

- **Components:**
  The elements or compounds which are mixed initially (e.g., Al and Cu)

- **Phases:**
  The physically and chemically distinct material regions that result (e.g., a and b).

Aluminum-Copper Alloy

![Image of the material with labeled phases](image-url)

- **α** (darker phase)
- **β** (lighter phase)
THE SOLUBILITY LIMIT

- **Solubility Limit:**
  Max concentration for which only a solution occurs (remember **HUME ROTHERY RULES**).

Example: Water – Sugar System

**Question:**
What is the solubility limit at 20°C?

**Answer:** 65wt% sugar.
- If \( C_0 < 65\text{wt\% sugar} \): syrup
- If \( C_0 > 65\text{wt\% sugar} \): syrup + sugar.

- **Solubility limit increases with T:**
e.g. at \( T=99\text{°C} \), solubility limit is \( \sim 80\text{wt\%} \).
**EFFECT of T and COMPOSITION**

- Changing T can change number of phases: path A to B.
- Changing $C_0$ can change number of phases: path B to D.

Water-Sugar ($C_{12}H_{22}O_{11}$) system

![Diagram of phase behavior](image)
Phase Diagrams

- A phase diagram shows what *phases* are present and where the process *boundaries* are within the composition space.

- Equilibrium phase diagrams represents relations between temperature, pressure, *compositions* and *quantities* of phases at equilibrium.

- Phase diagrams allows to predict phase transformations which occur during *temperature change* (e.g. upon cooling).

The following type of *binary* (contains only two component) systems will be discussed below:

- complete solubility: *isomorphous*
- *eutectic*
- with *intermediate phases* or compounds
- involving *eutectoid* and *peritectic* reactions

Special attentions will be paid on the *iron-iron carbide* system
Binary Isomorphous Systems

• Isomorphous system is characterized by *complete* liquid and solid *solubility* of the components
• For this course:
  --binary systems: just 2 components.
  --independent variables: T and C₀ (P = 1atm is always used).

Phase Diagram for Cu-Ni system

- **B** - $\alpha$ and L
- **A** - $\alpha$ (FCC solid solution)
- **C** - L (homogeneous liquid solution)

Phase boundaries: *liquidus* and *solidus* lines
• **Rule 1:** If we know $T$ and $C_o$, then we know:
  - the number and types of phases present.

• **Examples:**

  A($1100^\circ$C, 60 wt%):
  1 phase: $\alpha$

  B (1250, 35):
  2 phases: L + $\alpha$
**Rule 2:** If we know \( T \) and \( C_0 \), then we know: the composition of each phase

- **Examples:**
  - at \( T_C = 1350 \, ^\circ\text{C} \), **only one**, Liquid phase exists with composition: 35 wt % Ni – 65 % Cu
  - at \( T_A = 1175 \, ^\circ\text{C} \), again **only one**, solid phase exists with composition: 35 wt % Ni – 65 % Cu
  - at \( T_B = 1250 \, ^\circ\text{C} \), **two phase** (L and \( \alpha \)) exist with compositions: L – 32 wt% Ni - 68%Cu \( \alpha - 43 \, \text{wt}\% \text{Ni} - 57\% \text{Cu} \)

*Tie line* is an *isotherm* in the two-phase region. Intersects of this line with phase boundary lines (e.g. liquidus and solidus) give the compositions of the corresponding phases (e.g. liquid and solid solutions)
**PHASE DIAGRAMS: Weight Fractions of Phases**

- **Rule 3:** If we know \( T \) and \( C_0 \), then we know:
  - the amount of each phase (given in wt%).

- **Examples:**
  
  \( C_0 = 35\text{wt}\%\text{Ni} \)

  At \( T_C \): Only Liquid (L)
  \[
  W_L = 100\text{ wt\%}, \ W_\alpha = 0
  \]

  At \( T_A \): Only Solid (\( \alpha \))
  \[
  W_L = 0, \ W_\alpha = 100\%
  \]

  At \( T_B \): Both \( \alpha \) and L

  \[
  W_L = \frac{S}{R + S} = \frac{43 - 35}{43 - 32} = 73\text{wt \%}
  \]

  \[
  W_\alpha = \frac{R}{R + S} = 27\text{wt\%}
  \]

**Lever rule:** The fraction of one phase is computed by taking the length of the tie line from the overall alloy composition to the phase boundary for the other phase, and dividing by the total tie line length.
Microstructure Development: Equilibrium Cooling

Example: Cu-Ni system
- **slow cooling** along the line with $C_o = 35\text{wt}\%\text{Ni}$.

- Solidification in the solid + liquid phase occurs gradually upon cooling from the liquidus line.
- The composition of the solid and the liquid change gradually during cooling ($B \rightarrow C \rightarrow D$, as can be determined by the tie-line method.)
- Nuclei of the solid phase form and they grow to consume all the liquid at the solidus line.
**Microstructure Development: Non-Equilibrium Cooling**

**Example:** Cu-Ni system; **Rapid cooling** along the line with $C_o = 35\text{wt}\%\text{Ni}$.

- Solidification in the solid + liquid phase still occurs gradually.
- The composition of the liquid phase evolves by **relatively fast** diffusion, following the equilibrium values that can be derived from the tie-line method.
- However, diffusion in the solid state is **slow**. Hence, the new layers that solidify on top of the grains have the equilibrium composition at that temperature but once they are solid their composition essentially does not change. This lead to the formation of layered (cored) grains and to the **invalidity of the tie-line method** to determine the composition of the solid phase.
**CORED VS EQUILIBRIUM PHASES**

- $C_\alpha$ changes as we solidify.
- Cu-Ni case:  
  - First $\alpha$ to solidify has $C_\alpha = 46\text{wt}\%\text{Ni}$.
  - Last $\alpha$ to solidify has $C_\alpha = 35\text{wt}\%\text{Ni}$.

- Fast rate of cooling:  
  - Cored structure

- Slow rate of cooling:  
  - Equilibrium structure

\[ \text{Uniform } C_\alpha: 35\text{wt}\%\text{Ni} \]
MECHANICAL PROPERTIES: Cu-Ni System

- Effect of solid solution strengthening on:
  - Tensile strength (TS)
  - Ductility (% EL)

Tensile Strength exhibits a maximum!!

Opposite behavior for Elongation
BINARY-EUTECTIC SYSTEMS (1)

Such systems are characterized by limiting components solubility and existing of a special composition (eutectic) with a minimum melting point, $T_E$ (eutectic means easily melted).

Example I: Cu-Ag system

The specific features are:

- **3 single phase regions**: L, $\alpha$ and $\beta$
- **Limited solubility**:
  - $\alpha$: mostly Cu
  - $\beta$: mostly Ni

- **Solvus lines**, BC and GH, separates one solid solution from a mixture of solid solutions.
- **Solvus lines show limit of solubility**
Such systems are characterized by **limiting components solubility** and existing of a special composition (eutectic) with a **minimum melting point**, $T_E$ (eutectic means easily melted).

**Example I: Cu-Ag system**

- Point E is an **invariant point**
- $T_E$: No liquid below $T_E$
- $C_E$: Composition with **minimum melting** $T_E$

**Eutectic reaction:**

\[
L(C_E) \xrightarrow{\text{cooling}} \alpha(C_{\alpha E}) + \beta(C_{\beta E}) \]

\[
L(71.9\text{wt}\%\text{Ag}) \xrightarrow{\text{cooling}} \alpha(8.0\text{wt}\%\text{Ag}) + \beta(91.2\text{wt}\%\text{Ag}) \]

- line $\text{BEG}$ is the **eutectic isotherm**: 3 phases can be in equilibrium along eutectic isotherm
EXAMPLE II: Pb-Sn SYSTEM (1)

• For point B, i.e. alloy 40%Sn-60t%Pb at 150°C, find...
  - What phase(s) is (are) present?
  - Answer: α and β coexist
For point B, i.e. alloy 40%Sn-60t%Pb at 150°C, find...

- What are the compositions of the phases?
  - Answer:
    - $C_\alpha = 11\% \text{ Sn} - 89\% \text{ Pb}$
    - $C_\beta = 99\% \text{ Sn} - 1\% \text{ Pb}$

- What are the relative amounts of each phase?
  - Answer:
    - $W_\alpha = \frac{59}{88} = 67 \text{ wt \%}$
    - $W_\beta = \frac{29}{88} = 33 \text{ wt \%}$
MICROSTRUCTURES IN EUTECTIC SYSTEMS: Equilibrium Cooling (1)

- Composition range: a pure component (e.g. Pb) - its maximum solid solubility at room (20°C) temperature (e.g. point B with $C_B = C_1 < 2\text{wt\%}$)

- Result:
  
  $T > T_L = 330 \, ^\circ\text{C}$ – liquid alloy with $C_1$ comp

  $T_S < T < T_L$ – very narrow region: solid a phase in liquid (L) and compositions of phases are defined by tie-line method;

  $T < T_S$ - polycrystal of $\alpha$ grains with uniform composition of $C_1$. 
MICROSTRUCTURES IN EUTECTIC SYSTEMS: Equilibrium Cooling (2)

- Composition range: maximum solid solubility at room (20°C) temperature (C = 2wt%) and maximum solid solubility at eutectic temperature, T_E=183°C (C=18.3%) (e.g. point B with 2wt%<C_B=C_2< 18.3 wt% )

- Result:
  - T>T_L – liquid alloy with C_2 comp.;
  - T_{solidus} < T < T_L – solid α phase in liquid (L) and compositions of phases are defined by tie-line method;
  - T_{solvus} < T < T_{solidus} - polycrystal of α grains with uniform composition of C_2.
  - T < T_{solvus} - α polycrystal with fine β crystals; the compositions of phases are defined by tie-line method and the amount of each phase by Level rule.
MICROSTRUCTURES IN EUTECTIC SYSTEMS: Equilibrium Cooling (3)

- **Composition range**: $C = C_E$

- **Result**:
  - $T > T_E$: *liquid* with $C = C_E = 61.9$ wt% Sn
  - $T < T_E$: *alternating layers of $\alpha$ and $\beta$ crystals*.

Microstructure of Pb-Sn eutectic lamellae

\[ L(61.9\text{wt}\%\text{Sn}) \xrightarrow{\text{cooling}} \alpha(18.3\text{wt}\%\text{Sn}) + \beta(97.8\text{wt}\%\text{Sn}) \]
\[ Eutectic \quad L + \alpha \quad 200 \quad T(\degree C) \]

<table>
<thead>
<tr>
<th>Composition, wt% Sn</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L )</td>
<td>C3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ 0 \quad 80 \quad 100 \quad \beta \]

\[ \alpha \quad + \beta \quad 18.3 \quad C_3 \quad 61.9 \quad \alpha \quad \beta \]

- **Composition range:**
  \[ 18.3\text{wt}\%Sn < C_3 < 61.9\text{wt}\%Sn \]
  (e.g. point B with \( C_B = C_3 \) 40wt% Sn)

**Results:**
- **Just above \( T_E \):**
  - \( \text{solid primary} \ \alpha \) phase in liquid
    - \( C_\alpha \approx 18.3\text{wt}\%Sn \)
    - \( C_L \approx 61.9\text{wt}\%Sn \)
    - \( W_\alpha = \frac{S_1}{R_1 + S_1} \approx 50\text{wt}\% \)
    - \( W_L = (1 - W_\alpha) \approx 50\text{wt}\% \)
- **Just below \( T_E \):**
  - \( \alpha \) crystals and \( \alpha \) eutectic microstructure
    - \( C_\alpha \approx 18.3\text{wt}\%Sn \)
    - \( C_\beta \approx 97.8\text{wt}\%Sn \)
    - \( W_\alpha = \frac{S_2}{R_2 + S_2} \approx 73\text{wt}\% \)
    - \( W_\beta \approx 27\text{wt}\% \)
HYPOEUTECTIC & HYPEREUTECTIC

(Pb-Sn System)

Eutectic alloy

Hypoeutectic: less than eutectoid alloy

Hypereutectic: (illustration only)

Eutectic micro-constituent
**Equilibrium Diagrams with Intermediate Phases**

**Example: The Copper-Zinc System**

- $\alpha$ and $\eta$ are **terminal solid solutions**: exist near the concentration *extremities* of the phase diagram
- $\beta, \gamma, \epsilon, \delta$ are **intermediate solid solutions** (or *intermediate phases*)
- New types (not eutectic) of *invariant points* (e.g. $E$, $P$) and corresponding reactions are shown below
Eutectoid and Peritectic Reactions

- **point E** (74 wt%Zn at 560°C): again (as in eutectic) **three phases** are in equilibrium ($\delta, \gamma, \varepsilon$)
  - but in this case upon cooling a **solid** phase transforms to two **solid** phases, so-called a **eutectoid reaction**:
    \[
    \delta \text{ (74wt%Zn)} \xrightleftharpoons{\text{cooling}} \gamma \text{ (69.5wt%Zn)} + \varepsilon \text{ (78.6wt%Zn)}
    \]

- **point P** (78.6 wt%Zn at 598°C): **three phases** are in equilibrium ($\delta, L, \varepsilon$)
  - in this case upon **heating** a **solid** phase transforms to liquid and another **solid** phases: a **peritectic reaction**:
    \[
    \delta \text{ (76wt%Zn)} + L \text{ (88wt%Zn)} \xrightleftharpoons{\text{heating}} \varepsilon \text{ (78.6wt%Zn)}
    \]

How many peritectics do we have for copper-zinc system?
Equilibrium Diagrams with Intermediate Compounds

Example: Magnesium-Lead System

- Mg₂Pb is an intermetallic compound with a distinct chemical formula (not a solution)
- for this specific example, the intermediate compound exists by itself only at this precise composition (region of its existence has infinite width-just a line!!)
- the phase diagram in Mg-Pb system can be thought of a two simple eutectic diagrams joined back to back, one for Mg- Mg₂Pb system and other Mg₂Pb-Pb system
Types of Phase Transformations

- **γ solid solution** at 1310°C and C = 44.9 wt% Ti melts without changing of the composition – *congruent transformation*
- melting of pure metals, allotropic transformations are *congruent*

- **P melting at 598°C**: ε ⇒ δ+L (peritectic reaction) occurs with *changing of phase* composition – *incongruent phase transformation*
- Eutectic, eutectoid and peritectic reactions are examples of incongruent transformations
IRON-CARBON
(Fe-C) System
**Iron** are alloys with less than 0.008 wt% of carbon

**Steels** are carbon-iron alloys with carbon in the range 0.008 wt.% to 2.14%.

**Cast irons** contain 2.14 – 6.7 wt% of carbon

Iron and carbons combined to form Fe-Fe$_3$C at the 6.67 % C end of the diagram.

**Eutectoid:** 0.76 wt% C, 727°C

\[ \gamma \leftrightarrow \alpha(0.022 \text{wt% } C) + Fe_3C \]

**Eutectic:** 4.30 wt% C, 1147°C

\[ L \leftrightarrow \gamma(2.14 \text{ wt% } C) + Fe_3C \]
PHASES in Fe-C SYSTEM

- **δ–iron**: exists between 1394°C and 1538 °C. It may exist in combination with the melt to ~ 0.5 %wt C, with austenite to ~ 0.18 %wt C and in a single phase state to ~0.10 %wt C. Delta iron has the B.C.C. crystal structure and is magnetic.

- **Austenite- (γ) gamma-iron**: interstitial solid solution of carbon (up to 2.14wt%) dissolved in iron with a (F.C.C) structure. Stable up to 1394 °C. Non-magnetic phase.

- **Ferrite - (α) alpha-iron**, which is an interstitial solid solution of a small amount (up to 0.022wt%) of carbon dissolved in iron with a B.C.C. crystal structure. Possesses polymorphic transformation to γ–iron at 912°C. It is the softest structure on the iron-iron carbide diagram. Magnetic below 768°C.

**Cementite - iron carbide**: chemical formula, $Fe_3C$, contains 6.67 % wt C. It is a typical hard and brittle interstitial compound of low tensile but high compressive strength. Its crystal structure is orthorhombic. Metastable phase: at~700 °C slowly (several years) decomposes to α-iron and carbon.
Three significant regions can be made relative to the steel portion of the diagram: the eutectoid $E$, the hypoeutectoid $A$, and the hypereutectoid $B$. 

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**Steel Microstructure**

- **α-ferrite**
- **austenite**
Iron-Carbon Alloy: Eutectoid Composition

- **Eutectoid invariant point:**
  - 0.76 wt% C, 727°C

- **Eutectoid Reaction:**
  - \( \gamma \leftrightarrow \alpha(0.022\text{wt\% C}) + \text{Fe}_3\text{C} \)

- **Pearlite** (\(\alpha + \text{Fe}_3\text{C}\)): eutectoid mixture containing 0.76 %wt C and is formed at 727°C under slow cooling. It is very fine plate-like or lamellar mixture of ferrite (0.022 wt% C) and cementite (6.7 wt% C). The structure of pearlite includes a white matrix (ferritic background) which includes thin plates of cementite.
Iron-Carbon Alloy: Hypo-eutectoid Composition

- Hypo-eutectoid compositions: 0.022-0.76 wt% C (less than eutectoid)

Hypo-eutectoid Steel

Pro-eutectoid $\alpha$ (before eutectoid)

Pearlite
Iron-Carbon Alloy: Hyper-eutectoid Composition

- **Hypo-eutectoid compositions:**
  - 0.76 – 2.14 wt% C
  - (more than eutectoid)

Hyper-eutectoid Steel

- **Pro-eutectoid Fe₃C**
  - (before eutectoid)

- **Pearlite**
Computation of the Relative Amounts of Different Phases in Fe-Fe₃C System

- **Hypo-eutectoid** composition: $C'_o ; T < T_E$
  - Phases: $\alpha$-Fe and pearlite
  - The fraction of pro-eutectoid $\alpha$-Fe:
    \[ W_\alpha = \frac{U}{T + U} \approx \frac{0.76 - C'_o}{0.76 - 0.02} = \frac{0.76 - C'_o}{0.74} \]
  - The fraction of pearlite:
    \[ W_\alpha = \frac{T}{T + U} \approx \frac{C'_o - 0.02}{0.76 - 0.02} = \frac{C'_o - 0.02}{0.74} \]

- **Hyper-eutectoid** composition: $C'_1 ; T < T_E$
  - Phases: Fe₃C and pearlite
  - The fraction of pro-eutectoid Fe₃C:
    \[ W_{Fe3C} = \frac{V}{V + X} = \frac{C'_1 - 0.76}{6.7 - 0.76} = \frac{C'_1 - 0.76}{5.94} \]
  - The fraction of pearlite:
    \[ W_{Fe3C} = \frac{X}{V + X} = \frac{6.70 - C'_1}{6.7 - 0.76} = \frac{6.70 - C'_1}{5.94} \]
ALLOYING STEEL WITH MORE ELEMENTS

In general, alloying elements that added to improve some specific steel properties, also **effect** the positions of **phase boundaries** and regions shape on the phase diagram.

**Example:** addition of ~1 wt% of Ti increases $T_E$ almost twice!!
Result: Pearlite = alternating layers of $\alpha$ and Fe$_3$C phases.

- Eutectic (A):
  $L \Rightarrow \gamma + Fe_3C$

- Eutectoid (B):
  $\gamma \Rightarrow \alpha + Fe_3C$

IRON-CARBON (Fe-C) PHASE DIAGRAM
HYPEREUTECTOID STEEL

Fe-C System

Co
Fe₃C (cementite)

1600
1400
1200
1000
800
600
400
200
0

γ
(austenite)

γ+L

γ+Fe₃C

α+Fe₃C

L+Fe₃C

γ+L

γ+Fe₃C

α+Fe₃C

Fe₃C (cementite)

1148°C

T(°C)

γ
γ
γ
γ

Fe₃C

γ

Fe₃C

Fe₃C

w₁Fe₃C = r/(r+s)
w₁γ = (1- w₁Fe₃C)

w₁α = S/(R+S)
w₁Fe₃C = (1-w₁α)

w₁pearlite = w₁γ

pearlite

= w₁γ

Hypereutectoid steel

60µm

C₀, wt% C

HYPEREUTECTOID STEEL

Fe-C System
HYPOEUTECTOID STEEL

(Fe-C System)

Fe₃C (cementite)

1600
1400
1200
1000
800

L

γ
(austenite)

γ+L

γ+Fe₃C

α+Fe₃C

Fe₃C (cementite)

w_α = S/(R+S)

w_γ = (1-w_α)

w_{pearlite} = w_{Fe₃C} = (1-w_α)

w_α = S/(R+S)

w_γ = (1-w_α)

w_{pearlite} = w_{Fe₃C} = (1-w_α)

727°C

1148°C

Hypoeutectoid steel

C₀, wt% C
Note that this diagram has both stable and metastable features. For example, the stable phase in equilibrium with iron is carbon, but since it is easier to nucleate Fe₃C, it is the phase that is usually found in equilibrium with iron.

The Fe₂,₂C phase, or Hagg carbide is found in purified iron which has been carburized below 350°C.
SUMMARY

• **Phase diagrams** are useful tools to determine:
  --the number and types of phases,
  --the wt% of each phase,
  --and the **composition** of each phase

for a given T and composition of the system.

• Binary **eutectics** and binary **eutectoids** allow for a range
  of microstructures with different properties