PY2N20
Material Properties and Phase Diagrams
Lecture 5

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Phase Diagrams - Introduction

• How much can be done with pure elemental compounds?

• How many combinations of elements could be imagined? – $2^{100}$ ?

• How many of these combinations will have the structure (crystallographic, nanoscale, microscale, etc.) of the end members?

• How is mixing them going to affect the resulting mechanical, electronic and other physical and chemical properties?

• Can the properties of the end members be improved on?
When we combine two or more constituents (elements)...
what equilibrium state do we get?

In particular, if we specify... $c$, $p$, $T$, but also $H$, $E$
(all are intensive thermodynamic parameters)
- composition (e.g., wt% Cu - wt% Ni), and
- temperature ($T$)
then...

How many phases do we get?
What is the composition of each phase?
How much of each phase do we get?

Does this phase segregation really occur for $\text{Cu}_{1-x}\text{Ni}_x$?
Introduction

- **Solutions** – solid solutions, single phase
- **Mixtures** – more than one phase

**Solubility Limit:**
Max concentration for which only a single phase solution occurs.

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

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

• **Components:**
  The elements or compounds which are present in the mixture (e.g., Al and Cu)

• **Phases:**
  The physically and chemically distinct material regions that result (e.g., $\alpha$ and $\beta$).
Effect of $T$ & Composition ($C_o$)

- Changing $T$ can change # of phases: path $A$ to $B$.
- Changing $C_o$ can change # of phases: path $B$ to $D$.
Phase Equilibria

Simple solution system (e.g., Ni-Cu solution)

<table>
<thead>
<tr>
<th></th>
<th>Crystal Structure</th>
<th>Electroneg.</th>
<th>r (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>1.9</td>
<td>0.1246</td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>1.8</td>
<td>0.1278</td>
</tr>
</tbody>
</table>

- Both have the same crystal structure (FCC) and have similar electronegativities and atomic radii (W. Hume – Rothery rules) suggesting high mutual solubility.

- Ni and Cu are totally miscible in all proportions. Hence, the answer to the earlier question…is No…
Phase Diagrams

- Indicate phases as function of $T$, $C_o$, and $P$.
- For this course:
  - binary systems: just 2 components.
  - independent variables: $T$ and $C_o$ ($P = 1$ atm is almost always used).

Phase Diagram for Cu-Ni system

- 2 phases:
  - $L$ (liquid)
  - $\alpha$ (FCC solid solution)

- 3 phase fields:
  - $L$
  - $L + \alpha$
  - $\alpha$

wt% Ni

$T(°C)$
Phase Diagrams: Number and types of phases

- Rule 1: If we know $T$ and $C_0$, then we know:
  - the number and types of phases present.

- Examples:
  - $A(1100^\circ C, 60)$: 1 phase: $\alpha$
  - $B(1250^\circ C, 35)$: 2 phases: $L + \alpha$
Composition of phases

- Rule 2: If we know $T$ and $C_O$, then we know:
  - the composition of each phase.

Examples:

- $C_O = 35$ wt% Ni

At $T_A = 1320^\circ$C:
  - Only Liquid ($L$)
  - $C_L = C_O$ ( = 35 wt% Ni)

At $T_D = 1190^\circ$C:
  - Only Solid ($\alpha$)
  - $C_\alpha = C_O$ ( = 35 wt% Ni)

At $T_B = 1250^\circ$C:
  - Both $\alpha$ and $L$
  - $C_L = C_{\text{liquidus}}$ ( = 32 wt% Ni here)
  - $C_\alpha = C_{\text{solidus}}$ ( = 43 wt% Ni here)
Rule 3: If we know $T$ and $C_0$, then we know:
- the amount of each phase (given in wt%), via the so-called: ‘centre of gravity principle’ or the ‘lever rule’...

Examples:

$C_0 = 35\text{ wt\% Ni}$

At $T_A$: Only Liquid (L)
- $W_L = 100\text{ wt\%}$, $W_\alpha = 0$

At $T_D$: Only Solid ($\alpha$)
- $W_L = 0$, $W_\alpha = 100\text{ wt\%}$

At $T_B$: Both $\alpha$ and L

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

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

- Tie line – connects the phases in equilibrium with each other - essentially an isotherm

![Diagram showing tie lines and lever rule](image)

- How much of each phase?
  - Think of it as a lever

\[ W_L = \frac{M_L}{M_L + M_\alpha} = \frac{S}{R + S} = \frac{C_\alpha - C_0}{C_\alpha - C_L} \]

\[ W_\alpha = \frac{R}{R + S} = \frac{C_0 - C_L}{C_\alpha - C_L} \]
- Phase diagram: 
  Cu-Ni system.
- System is:
  - binary
    i.e., 2 components: Cu and Ni.
  - isomorphous
    i.e., complete solubility of one component in another; α phase field extends from 0 to 100 wt% Ni.
- Consider $C_0 = 35$ wt%Ni.

**Cooling in the Cu-Ni Binary System**

![Diagram of Cu-Ni phase diagram](image)
Cored vs Equilibrium Phases

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

- Fast rate of cooling: Cored structure
- Slow rate of cooling: Equilibrium structure
Mechanical Properties: Cu-Ni System

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

![Graph showing tensile strength and elongation as functions of composition.](image)

- Maximum as a function of $C_O$
- Minimum as a function of $C_O$
Binary Eutectic Systems

ευτηκτικός - from Greek ‘easiest to melt’
Binary-Eutectic Systems

Cu-Ag system

- 3 single phase regions 
  \((L, \alpha, \beta)\)
- Limited solubility:
  \(\alpha\): mostly Cu
  \(\beta\): mostly Ag
- \(T_E\): No liquid below \(T_E\)
- \(C_E\): Composition with min. melting \(T_E\)
- Eutectic transition
  \[ L(C_E) \leftrightarrow \alpha(C_{\alpha E}) + \beta(C_{\beta E}) \]
Pb-Sn Eutectic System (1)

- For a 40 wt% Sn-60 wt% Pb alloy at 150°C, find...
  - the phases present:
  - compositions of phases:
    \[ C_O = 40 \text{ wt\% Sn} \]
    \[ C_\alpha = 11 \text{ wt\% Sn} \]
    \[ C_\beta = 99 \text{ wt\% Sn} \]
  - the relative amount of each phase:
    \[ W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_O}{C_\beta - C_\alpha} \]
    \[ = \frac{99 - 40}{99 - 11} = \frac{59}{88} = 67 \text{ wt\%} \]
    \[ W_\beta = \frac{R}{R+S} = \frac{C_O - C_\alpha}{C_\beta - C_\alpha} \]
    \[ = \frac{40 - 11}{99 - 11} = \frac{29}{88} = 33 \text{ wt\%} \]

Adapted from Fig. 9.8, Callister 7e.
Pb-Sn Eutectic System (2)

- For a 40 wt% Sn-60 wt% Pb alloy at 220°C, find...
  - the phases present: $\alpha + L$
  - compositions of phases:
    
    $C_O = 40$ wt% Sn
    $C_\alpha = 17$ wt% Sn
    $C_L = 46$ wt% Sn

  - the relative amount of each phase:
    
    $W_\alpha = \frac{C_L - C_O}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17} = \frac{6}{29} = 21$ wt%
    
    $W_L = \frac{C_O - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 79$ wt%
• $C_o < 2 \text{ wt}\% \text{ Sn}$
• Result:
  - at extreme ends
  - polycrystal of $\alpha$ grains
    i.e., only one solid phase.
Microstructures in Eutectic Systems: II

- 2 wt% Sn < $C_o$ < 18.3 wt% Sn
- Result:
  - Initially liquid + $\alpha$
  - then $\alpha$ alone
  - finally two phases
    - $\alpha$ polycrystal
    - fine $\beta$-phase inclusions

![Pb-Sn phase diagram](image)
Microstructures in Eutectic Systems: III

- $C_o = C_E$
- Result: Eutectic microstructure (lamellar structure) - alternating layers (lamellae) of $\alpha$ and $\beta$ crystals.

Micrograph of Pb-Sn eutectic microstructure

Adapted from Fig. 9.14, Callister 7e.
Lamellar Eutectic Structure

Other possible eutectic structures are: rod-like, globular and acicular.
Microstructures in Eutectic Systems: IV

- 18.3 wt% Sn < $C_0$ < 61.9 wt% Sn
- Result: $\alpha$ crystals and an eutectic microstructure

![Pb-Sn system diagram]

- Just above $T_E$:
  $C_\alpha = 18.3$ wt% Sn
  $C_L = 61.9$ wt% Sn
  \[ W_\alpha = \frac{S}{R + S} = 50 \text{ wt\%} \]
  \[ W_L = (1 - W_\alpha) = 50 \text{ wt\%} \]

- Just below $T_E$:
  $C_\alpha = 18.3$ wt% Sn
  $C_\beta = 97.8$ wt% Sn
  \[ W_\alpha = \frac{S}{R + S} = 73 \text{ wt\%} \]
  \[ W_\beta = 27 \text{ wt\%} \]