There is a strong correlation between microstructure and mechanical properties. And the development of microstructure of an alloy is related to the characteristics of its phase diagram.

It is a type of chart used to show conditions at which thermodynamically distinct phases can occur at equilibrium.

Provides valuable information about melting, casting, crystallization, and other phenomena.
What is a Phase?

- The term ‘phase’ refers to a separate and identifiable state of matter in which a given substance may exist.
- Applicable to both crystalline and non-crystalline materials.
- An important refractory oxide silica is able to exist as three crystalline phases, quartz, tridymite and cristobalite, as well as a non-crystalline phase, silica glass, and as molten silica.
- Every pure material is considered to be a phase, so also is every solid, liquid, and gaseous solution.
- For example, the sugar–water syrup solution is one phase, and solid sugar is another.
Phase Equilibria: Solubility Limit

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 $C_0 < 65$ wt% sugar: syrup
- If $C_0 > 65$ wt% sugar: syrup + sugar.

Sucrose/Water Phase Diagram

- $L$ (liquid)
- $S$ (solid sugar)
- $L$ (liquid solution i.e., syrup)

**Temperature (°C)**

**Solubility Limit**

$C_o$ = Composition (wt% sugar)
Microstructure

- the structure of a prepared surface of material as revealed by a microscope above 25× magnification
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 $\beta$).

Aluminum-Copper Alloy

Adapted from chapter-opening photograph, Chapter 9, Callister 3e.
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 $D$.

Adapted from Fig. 9.1, *Callister 7e.*

**Diagram:**
- **L** (liquid) + **S** (solid sugar)
- **A** ($20^\circ C, 70$) 2 phases
- **B** ($100^\circ C, 70$) 1 phase
- **D** ($100^\circ C, 90$) 2 phases

Water-sugar system

$C_o =$Composition (wt% sugar)
PHASE EQUILIBRIA

- **Free Energy** -> a function of the internal energy of a system and also the disorder of the atoms or molecules (or entropy).
- A system is at **equilibrium** if its free energy is at a minimum under some specified combination of temperature, pressure, and composition.
- A change in temperature, pressure, and/or composition for a system in equilibrium will result in an increase in the free energy.
- And in a possible spontaneous change to another state whereby the free energy is lowered.
Pressure-Temperature Diagram (Water)

- Each of the phases will exist under equilibrium conditions over the temperature–pressure ranges of its corresponding area.
- The three curves ($aO$, $bO$, and $cO$) are phase boundaries; at any point on these curves, the two phases on either side of the curve are in equilibrium with one another.
- Point on a $P–T$ phase diagram where three phases are in equilibrium, is called a **triple point**.
Phase Equilibria

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

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

Adapted from Fig. 9.3(a), Callister 7e.
(Fig. 9.3(a) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH (1991).
Phase Diagrams: 
# and types of phases

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

• Examples:
  $A(1100°C, 60)$:  
  1 phase: $\alpha$

  $B(1250°C, 35)$:  
  2 phases: $L + \alpha$

Adapted from Fig. 9.3(a), Callister 7e.  
(Fig. 9.3(a) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH, 1991).
Phase Diagrams: 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)

Adapted from Fig. 9.3(b), Callister 7e.
(Fig. 9.3(b) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH, 1991.)
Phase Diagrams: weight fractions of phases

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

- Examples:

  $C_o = 35$ wt% Ni

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

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

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

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

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

Adapted from Fig. 9.3(b), Callister 7e.
(Fig. 9.3(b) is adapted from Phase Diagrams of Binary Nickel Alloys, P. Nash (Ed.), ASM International, Materials Park, OH, 1991.)
The Lever Rule

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

How much of each phase?
Think of it as a lever (teeter-totter)

\[ M_\alpha \cdot S = M_L \cdot R \]

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

\[
W_\alpha = \frac{R}{R + S} = \frac{C_0 - C_L}{C_\alpha - C_L}
\]

Adapted from Fig. 9.3(b), Callister 7e.
Ex: Cooling in a Cu-Ni Binary

- 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; $\alpha$ phase field extends from 0 to 100 wt% Ni.
- Consider $C_O = 35$ wt% Ni.

Adapted from Fig. 9.4, Callister 7e.
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 ($\%EL, \%AR$)

--Peak as a function of $C_O$

Adapted from Fig. 9.6(a), *Callister 7e.*

--Min. as a function of $C_O$

Adapted from Fig. 9.6(b), *Callister 7e.*
Binary-Eutectic Systems

2 components

has a special composition with a min. melting T.

Ex.: Cu-Ag system
• 3 single phase regions $(L, \alpha, \beta)$
• Limited solubility:
  $\alpha$: mostly Cu
  $\beta$: mostly Ag
• $T_E$: No liquid below $T_E$
• $C_E$: Min. melting $T_E$
  composition
• Eutectic transition

$L(C_E) \iff \alpha(C_{\alpha E}) + \beta(C_{\beta E})$

Adapted from Fig. 9.7, *Callister 7e.*
EX: Pb-Sn Eutectic System (1)

- For a 40 wt% Sn-60 wt% Pb alloy at 150°C, find...

  --the phases present: $\alpha + \beta$

  --compositions of phases:

  $C_\alpha = 11$ wt% Sn
  $C_\beta = 99$ wt% Sn

  --the relative amount of each phase:

  $W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_\alpha}{C_\beta - C_\alpha} = \frac{99 - 40}{99 - 11} = \frac{59}{88} = 67$ wt%

  $W_\beta = \frac{R}{R+S} = \frac{C_\alpha - C_\alpha}{C_\beta - C_\alpha} = \frac{40 - 11}{99 - 11} = \frac{29}{88} = 33$ wt%

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

For a 40 wt% Sn-60 wt% Pb alloy at 200°C, find...

--the phases present: $\alpha + L$

--compositions of phases:

$C_O = 40 \text{ wt}\% \text{ Sn}$
$C_\alpha = 17 \text{ wt}\% \text{ Sn}$
$C_L = 46 \text{ wt}\% \text{ Sn}$

--the relative amount of each phase:

$W_\alpha = \frac{C_L - C_O}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17}$
$= \frac{6}{29} = 21 \text{ wt}\%$

$W_L = \frac{C_O - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 79 \text{ wt}\%$

Adapted from Fig. 9.8, Callister 7e.
Microstructures in Eutectic Systems: I

- $C_o < 2$ wt% Sn
- Result:
  - at extreme ends
  - polycrystal of $\alpha$ grains
    i.e., only one solid phase.

Adapted from Fig. 9.11, Callister 7e.
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

Adapted from Fig. 9.12, Callister 7e.
Microstructures in Eutectic Systems: III

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

Adapted from Fig. 9.13, Callister 7e.
Lamellar Eutectic Structure

Adapted from Figs. 9.14 & 9.15, *Callister 7e.*
Microstructures in Eutectic Systems: IV

- $18.3 \text{ wt}\% \text{ Sn} < C_0 < 61.9 \text{ wt}\% \text{ Sn}$
- Result: $\alpha$ crystals and a eutectic microstructure

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

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

Adapted from Fig. 9.16, Callister 7e.
Hypoeutectic & Hypereutectic

Adapted from Fig. 9.8, Callister 7e. (Fig. 9.8 adapted from Binary Phase Diagrams, 2nd ed., Vol. 3, T.B. Massalski (Editor-in-Chief), ASM International, Materials Park, OH, 1990.)

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.

- Alloying to produce a solid solution usually
  - increases the tensile strength ($TS$)
  - decreases the ductility.

- Binary eutectics and binary eutectoids allow for a range of microstructures.