

- Introduction
- Solubility Limits
- Phases
- Phase Equilibrium
- Interpretation of Phase Diagrams
- Binary Isomorphous Systems (Cu-Ni)
- Development of Microstructure
- Mechanical Properties
- Binary Eutectic Systems
- Development of Eutectic Alloy Microstructure

Components and Phases

• Components:

The elements or compounds that are mixed initially (AI and Cu).

• Phases:

A phase is a homogenous, physically distinct and mechanically separable portion of the material with a given chemical composition and structure (α and β).



Phase Equilibria: Solubility Limit

- Solution solid, liquid, or gas solutions, single phase
- Mixture more than one phase
- Solubility Limit:

Maximum concentration for which only a single phase solution exists.

Question: What is the solubility limit for sugar in water at 20°C?

Answer: 65 wt% sugar.

At 20°C, if C < 65 wt% sugar: syrup At 20°C, if C > 65 wt% sugar: syrup + sugar

Sugar/Water Phase Diagram



Equilibrium

- A system is at equilibrium if its free energy is at a minimum, given a specified combination of temperature, pressure and composition.
- The (macroscopic) characteristics of the system do not change with time the system is stable.
- A change in T, P or C for the system will result in an increase in the free energy and possible changes to another state whereby the free energy is lowered.

One Component Phase Diagram



Phase Diagrams

- Indicate phases as a function of Temp, Comp and Pressure.
- Focus on:
 - binary systems: 2 components.
 - independent variables: T and C (P = 1 atm is almost always used).



Effect of Temperature & Composition (C_o)

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



Determination of phase(s) present

Rule 1: If we know T and C_o, then we know:
 --how many phases and which phases are present.



Solidus - Temperature where alloy is completely solid. Above this line, liquefaction begins. Liquidus - Temperature where alloy is completely liquid. Below this line, solidification begins. 9

Phase Diagrams: <u>composition</u> of phases

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



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:

 $C_0 = 35 wt\% Ni$



$$W_{L} = \frac{C_{\alpha} - C_{0}}{C_{\alpha} - C_{L}} = \frac{43 - 35}{43 - 32} = 73 \text{ wt \%}$$
$$W_{\alpha} = \frac{C_{0} - C_{L}}{C_{\alpha} - C_{L}} = 27 \text{ wt \%}$$



Ex: Equilibrium Cooling of a Cu-Ni Alloy



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- Development of microstructure during the non-equilibrium solidification of a 35 wt% Ni-65 wt% Cu alloy outcome:
- Segregationnonuniform distribution of elements within grains.
- Weaker grain boundaries if alloy is reheated.



Cored vs Equilibrium Phases

- C_{α} changes as it solidifies.
- Cu-Ni case: First α to solidify has C $_{\alpha}$ = 46wt%Ni. Last α to solidify has C $_{\alpha}$ = 35wt%Ni.
- Fast rate of cooling: Cored structure

• Slow rate of cooling: Equilibrium structure



 Coring can be eliminated by means of a homogenization heat treatment carried out at temperatures below the alloy's solidus. During the process, atomic diffusion produces grains that are compositionally homogeneous.

Mechanical Properties: Cu-Ni System

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



Binary Isomorphous Systems

Cu-Ni system:

- The liquid L is a homogeneous liquid solution composed of Cu and Ni.
- The α phase is a substitutional solid solution consisting of Cu and Ni atoms with an FCC crystal structure.
- At temperatures below 1080 C, Cu and Ni are mutually soluble in each other in the solid state for all compositions.
- The complete solubility is explained by their FCC structure, nearly identical atomic radii and electro-negativities, and similar valences.
- The Cu-Ni system is termed isomorphous because of this complete liquid and solid solubility of the 2 components.



What is a solid solution?

When foreign atoms are incorporated into a crystal structure, whether in substitutional or interstitial sites, the resulting phase is a solid solution of the matrix material (solvent) and the foreign atoms (solute)

Substitutional Solid Solution: Foreign (solute) atoms occupy "normal" lattice sites occupied by matrix (solvent) atoms, e.g. Cu-Ni;Ge-Si

Interstitial Solid Solutions: Foreign (solute) atoms occupy interstitial sites, e.g., Fe-C

Criteria for Solid Solubility

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

	Crystal Structure	electroneg	<i>r</i> (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- 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 soluble in one another for all proportions.

Isomorphous Binary Phase Diagram

- Phase diagram: Cu-Ni system.
- System is:
 - -- binary
 - 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.



Importance of Phase Diagrams

- There is a strong correlation between microstructure and mechanical properties, and the development of alloy microstructure is related to the characteristics of its phase diagram.
- Phase diagrams provide valuable information about melting, casting, crystallization and other phenomena.

Microstructure

- In metal alloys, microstructure is characterized by the number of phases, their proportions, and the way they are arranged.
- The microstructure depends on:
 - Alloying elements
 - Concentration
 - Heat treatment (temperature, time, rate of cooling)

Eutectic

- A eutectic or eutectic mixture is a mixture of two or more phases at a composition that has the lowest melting point.
- It is where the phases simultaneously crystallize from molten solution.
- The proper ratios of phases to obtain a eutectic is identified by the eutectic point on a binary phase diagram.
- The term comes from the Greek 'eutektos', meaning 'easily melted.'



- The phase diagram displays a simple binary system composed of two components, **A** and **B**, which has a eutectic point.
- The phase diagram plots relative concentrations of A and B along the X-axis, and temperature along the Y-axis. <u>The eutectic point is the point where the liquid phase</u> <u>borders directly on the solid α + β phase; it</u> represents the minimum melting temperature of any possible A B alloy.
- The temperature that corresponds to this point is known as the **eutectic temperature**.
- <u>Not all binary system alloys have a eutectic point</u>: those that form a solid solution at all concentrations, such as the gold-silver system, have no eutectic. An alloy system that has a eutectic is often referred to as a eutectic system, or eutectic alloy.
- Solid products of a eutectic transformation can often be identified by their lamellar structure, as opposed to the dendritic structures commonly seen in non-eutectic solidification. The same conditions that force the material to form lamellae can instead form an amorphous solid if pushed to an extreme.

Binary-Eutectic Systems

T(°C)

1200

1000

T_E 800

600

400

200

0

α

2 components

has a special composition with a min. melting T.

L (liquid)

<u>779°C</u>

 $\alpha + \beta$

40

71.9 91

60 C_F 80

C, wt% Ag

100

+ α

1

20

8.0

Cu-Ag system

- 3 single phase regions (L, α, β)
- Limited solubility:
 - α : mostly Cu
 - β : mostly Ag
- T_E : No liquid below T_E
- C_E: Composition at temperature T_E
- Eutectic reaction

$$(C_E) \xrightarrow{\sim} \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

 $L(71.9 \text{ wt\% Ag}) \xrightarrow[heating]{\text{cooling}} \alpha(8.0 \text{ wt\% Ag}) + \beta(91.2 \text{ wt\% Ag}) 24$

Copper-Silver Phase Diagram

Composition (at% Ag)

0 20 40 60 80 100 2200 1200 2000 Α Liquidus 1000 Liquid 1800 Solidus F 1600 $\alpha + L$ α $\beta + L$ 779°C (TE) E Temperature (°C) 800 Temperature (°F) B G $(C_{\alpha E})$ 1400 91.2 71.9 β (C_E) $(C_{\beta E})$ 1200 600 1000 Solvus $\alpha + \beta$ 800 400 C 600 H 400 200 0 20 40 60 80 100

Composition (wt% Ag)

(Ag)

(Cu)

Eutectic Reaction

- Solvus (solid solubility line) BC, GH
- Solidus AB, FG, BEG (eutectic isotherm)
- Liquidus AEF
- Maximum solubility: $\alpha = 8.0$ wt% Ag, $\beta = 8.8$ wt %Cu
- Invariant point (where 3 phases are in equilibrium) is at E;
 C_E = 71.9 wt% Ag, T_E = 779C (1434F).
- An isothermal, reversible reaction between two (or more) solid phases during the heating of a system where a single liquid phase is produced.

Eutectic reaction

$$\mathsf{L}(\mathsf{C}_{\mathsf{E}}) \underbrace{\longrightarrow} \alpha(\mathsf{C}_{\alpha\mathsf{E}}) + \beta(\mathsf{C}_{\beta\mathsf{E}})$$

$$L(71.9 \text{ wt\% Ag}) \xrightarrow[heating]{\text{cooling}} \alpha(8.0 \text{ wt\% Ag}) + \beta(91.2 \text{ wt\% Ag})_{26}$$

Pb-Sn Phase Diagram



Solidification of Eutectic Mixtures

- Mixtures of some metals, such as copper & nickel, are completely soluble in both liquid and solid states for all concentrations of both metals. Copper & nickel have the same crystal structure (FCC) and have nearly the same atomic radii. The solid formed by cooling can have any proportion of copper & nickel. Such completely miscible mixtures of metals are called isomorphous.
- By contrast, a mixture of lead & tin that is eutectic is only partially soluble when in the solid state. Lead & tin have different crystal structures (FCC versus BCT) and lead atoms are much larger. No more than 18.3 weight % solid tin can dissolve in solid lead and no more than 2.2% of solid lead can dissolve in solid tin (according to previous phase diagram).
- The solid lead-tin alloy consists of a mixture of two solid phases, one consisting of a maximum of 18.3 wt% tin (the **alpha** phase) and one consisting of a maximum of 2.2 wt% lead (the **beta** phase).

(Ex 1) Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 150°C, determine:
 - -- the phases present



(Ex 2) Pb-Sn Eutectic System

- For a 40 wt% Sn-60 wt% Pb alloy at 220°C, determine:
 - -- the phases present:



$$W_{L} = \frac{C_{0} - C_{\alpha}}{C_{L} - C_{\alpha}} = \frac{23}{29} = 0.79$$

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Pb-Sn

- For lead & tin the eutectic composition is 61.9 wt% tin and the eutectic temperature is 183°C -- which makes this mixture useful as solder.
- At 183°C, compositions of greater than 61.9 wt% tin result in precipitation of a tinrich solid in the liquid mixture, whereas compositions of less than 61.9 wt% tin result in precipitation of lead-rich solid.

Microstructural Developments in Eutectic Systems - I

- For alloys where C₀ < 2 wt% Sn
- Result at room temperature is a polycrystalline with grains of α phase having composition C₀





Microstructural Developments in Eutectic Systems - II



Microstructures in Eutectic Systems - III



Lamellar Eutectic Structure

A 2-phase microstructure resulting from the solidification of a liquid having the eutectic composition where the phases exist as a lamellae that alternate with one another.

Formation of eutectic layered microstructure in the Pb-Sn system during solidification at the eutectic composition. Compositions of α and β phases are very different. Solidification involves redistribution of Pb and Sn atoms by atomic diffusion.



Pb-Sn Microstructures

The dark layers are Pb-rich α phase, the light layers are the Sn-rich β phase.










Microstructures in Eutectic Systems - IV

Pb-Sn

system

- For alloys with 18.3 wt% Sn < C_0 < 61.9 wt% Sn
- Result: α phase particles and a eutectic microconstituent



(part 2)

- Equilibrium Diagrams with Intermediate Phases or Compounds
- Eutectoid and Peritectic Reactions
- Ceramic Phase Diagrams
- The Gibbs Phase Rule
- The Iron-Iron Carbide Phase Diagram
- Development of Microstructures in Iron-Carbon Alloys
- Hypoeutectoid Alloys
- Hypereutectoid Alloys
- Influence of Other Alloying Elements

Intermetallic Compounds



Note: intermetallic compounds exist as a line on the diagram - not a phase region. The composition of a compound has a distinct chemical formula.

Cu-Zn System (Brass)





Eutectic, Eutectoid, & Peritectic

- Eutectic liquid transforms to two solid phases
 - $L \quad \underline{cool}_{\overline{heat}} \alpha + \beta \qquad (For Pb-Sn, 183^{\circ}C, 61.9 \text{ wt\% Sn})$
- Eutectoid one solid phase transforms to two other solid phases
 Solid₁ ↔ Solid₂ + Solid₃

$$\gamma \underset{heat}{\underline{cool}} \alpha + Fe_3C$$
 (For Fe-C, 727°C, 0.76 wt% C)

Peritectic - liquid and one solid phase transform to a 2nd solid phase
 Solid₁ + Liquid ↔ Solid₂

$$\delta + L = \frac{\delta \delta \delta}{\delta \delta} \epsilon$$
 (For Cu-Zn, 598°C, 78.6 wt% Zn)



Ceramic Phase Diagrams

MgO-Al₂O₃ diagram:



APPLICATION: REFRACTORIES

- Need a material to use in high temperature furnaces.
- Consider Silica (SiO₂) Alumina (Al₂O₃) system.
- Phase diagram shows: mullite, alumina and crystobalite (made up of SiO₂) are candidate refractories.





Composition, w/o SiO₂

SiO₂

[Al₂O₃]

Ceramic Phases and Cements

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Gibbs Phase Rule

- Phase diagrams and phase equilibria are subject to the laws of thermodynamics.
- Gibbs phase rule is a criterion that determines how many phases can coexist within a system at equilibrium.

P + F = C + N

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P: # of phases present
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- F: degrees of freedom (temperature, pressure, composition)
- C: components or compounds
- N: noncompositional variables

For the Cu-Ag system @ 1 atm for a single phase P:

N=1 (temperature), C = 2 (Cu-Ag), P= 1 (α , β , L) F = 2 + 1 - 1= 2



This means that to characterize the alloy within a single phase 4 field, 2 parameters must be given: temperature and composition.

- If 2 phases coexist, for example, α +L, β +L, α + β , then according to GPR, we have 1 degree of freedom: F = 2 + 1 2 = 1. So, if we have Temp or composition, then we can completely define the system.
- If 3 phases exist (for a binary system), there are 0 degrees of freedom. This means the composition and Temp are fixed. This condition is met for a eutectic system by the eutectic isotherm.

Iron-Carbon System

- Pure iron when heated experiences 2 changes in crystal structure before it melts.
- At room temperature the stable form, ferrite (α iron) has a BCC crystal structure.
- Ferrite experiences a polymorphic transformation to FCC austenite (γ iron) at 912 °C (1674 °F).
- At 1394°C (2541°F) austenite reverts back to BCC phase δ ferrite and melts at 1538 °C (2800 °F).
- Iron carbide (cementite or Fe₃C) an intermediate compound is formed at 6.7 wt% C.
- Typically, all steels and cast irons have carbon contents less than 6.7 wt% C.
- Carbon is an interstitial impurity in iron and forms a solid solution with the α , γ , δ phases.



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Though carbon is present in relatively low concentrations, it significantly influences the mechanical properties of ferrite: (a) α ferrite, (b) austenite.

4 Solid Phases

• α-ferrite

- solid solution of carbon in a iron,
- BCC structure
- carbon only slightly soluble in the matrix
 - maximum solubility of 0.02%C at 723°C to about 0.008%C at room temperature.
- Austenite (γ)
 - solid solution of carbon in γ -iron
 - FCC structure: can accommodate more carbon than ferrite
 - maximum of 2.08%C at 1148°C, decreases to 0.8%C at 723°C
 - difference in C solid solubility between γ and α is the basis for hardening of most steels.

δ-ferrite

- solid solution of carbon in δ–iron
- BCC crystal structure
 - maximum solubility of ferrite being 0.09%C at 1495°C

Cementite (Fe₃C)

- intermetallic Fe-C compound
 - Fe₃C : 6.67%C and 93.3%Fe.
- orthorhombic crystal structure: hard and brittle

Iron carbide (Cementite or Fe₃C)

- Forms when the solubility limit of carbon in α ferrite is exceeded at temperatures below 727 °C.
- Mechanically, cementite is very hard and brittle.
- For ferrous alloys there are 3 basic types, based on carbon content:

□ Iron (ferrite phase): <0.008 wt% C room temp

- □ Steel (α + Fe₃C phase): 0.008 to 2.14 wt% C
- **Cast iron: 2.14 to 6.70 wt% C**

Iron-Carbon (Fe-C) Phase Diagram



Eutectoid reaction:

- $\gamma \leftrightarrow \alpha + Fe_3C$
 - formation of the pearlite structure
 - nucleating at γ grain boundaries
 - growth by diffusion of C to achieve the compositions of α and Fe₃C (with structural changes)
 - · α lamellae much thicker



Pearlite



Redistribution of carbon by diffusion Austenite – 0.76 wt% C Ferrite – 0.022 wt% C Cementite – 6.70 wt% C





Proeutectoid

- Formed before the eutectoid
- Ferrite that is present in the pearlite is called eutectoid ferrite.
- The ferrite that is formed above the T_{eutectoid} (727°C) is proeutectoid.







compositions between 0.76 and 2.14 wt% carbon are hypereutectoid (more than eutectoid).



Hypereutectoid Steel (1.2 wt% C)







Example Problem

For a 99.6 wt% Fe-0.40 wt% C steel at a temperature just below the eutectoid, determine the following:

- a) The compositions of Fe₃C and ferrite (α).
- b) The amount of cementite (in grams) that forms in 100 g of steel.



Solution to Example Problem

a) Using the RS tie line just below the eutectoid

 $C_{\alpha} = 0.022 \text{ wt\% C}$ $C_{Fe_3C} = 6.70 \text{ wt\% C}$

b) Using the lever rule with the tie line shown

$$W_{\text{Fe}_{3}\text{C}} = \frac{R}{R+S} = \frac{C_0 - C_{\alpha}}{C_{\text{Fe}_{3}\text{C}} - C_{\alpha}}$$
$$= \frac{0.40 - 0.022}{6.70 - 0.022} = 0.057$$

Amount of
$$Fe_3C$$
 in 100 g
= (100 g) W_{Fe_3C}
= (100 g)(0.057) = 5.7 g



Alloying steel with other elements changes the Eutectoid Temperature, Position of phase boundaries and relative Amounts of each phase



Working with Phase Diagrams

- Overall Composition
- Solidus
- Liquidus
- Limits of Solid Solubility
- Chemical Composition of Phases at any temperature
- Amount of Phases at any temperature
- Invariant Reactions
- Development of Microstructure
- Chemical Activity

Determination of Phase Diagrams

- Cooling Curves
- Differential Scanning Calorimetry
- Thermomechanical Analysis
- Differential Thermal Analysis
- Metallography/Petrography
- Energy Dispersive X-ray Spectroscopy
- Electron Microprobe Analyzer
- X-ray Diffraction
- Transmission Electron Microscopy

Cooling Curves





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Using Phase Diagrams to determine Heat Treatability

- Heat Treatment is based on "controlling" the solid state transformation rate
 - Heat treatment of steels: control of the eutectoid reaction
 - Age hardening (precipitation strengthening) of aluminum alloys: control of precipitation reaction

Heat Treatment of Steels

- The eutectoid reaction
- Martensite
- Austenite
- Pearlite
- TTT diagrams
Summary

- Phase diagrams are useful tools to determine:
 - -- the number and types of phases present,
 - -- the composition of each phase,
 - -- and the weight fraction of each phase
 - For a given temperature and composition of the system.
- The microstructure of an alloy depends on
 - -- its composition, and
 - -- rate of cooling equilibrium

Review

- Heating a copper-nickel alloy of composition 70 wt% Ni-30 wt% Cu from 1300°C. At what temperature does the first liquid phase form?
- Solidus Temperature where alloy is completely solid. Above this line, liquefaction begins.
- <u>Answer</u>: The first liquid forms at the temperature where a vertical line at this composition intersects the α -(α + *L*) phase boundary--i.e., about 1350°C;



- (b) What is the composition of this liquid phase?
- <u>Answer</u>: The composition of this liquid phase corresponds to the intersection with the (α + *L*)-*L* phase boundary, of a tie line constructed across the α + *L* phase region at 1350°C, 59 wt% Ni;



- (c) At what temperature does complete melting of the alloy occur?
- Liquidus Temperature where alloy is completely liquid. Below this line, solidification begins.
- <u>Answer</u>: Complete melting of the alloy occurs at the intersection of this same vertical line at 70 wt% Ni with the (α + *L*)-*L* phase boundary--i.e., about 1380°C;



- (d) What is the composition of the last solid remaining prior to complete melting?
- <u>Answer</u>: The composition of the last solid remaining prior to complete melting corresponds to the intersection with α -(α + λ) phase boundary, of the tie line constructed across the α + λ phase region at 1380°C--i.e., about 78 wt% Ni.



THE LEVER RULE: A PROOF

- Sum of weight fractions: $W_{L} + W_{\alpha} = 1$
- Conservation of mass (Ni): $C_0 = W_L C_L + W_\alpha C_\alpha$
- Combine above equations:

$$W_{L} = \frac{C_{\alpha} - C_{o}}{C_{\alpha} - C_{L}} = \frac{S}{R + S}$$

$$W_{\alpha} = \frac{C_{o} - C_{L}}{C_{\alpha} - C_{L}} = \frac{R}{R + S}$$

• A geometric interpretation:



moment equilibrium:

$$W_{L}R = W_{\alpha}S$$

$$k$$

$$1 - W_{\alpha}$$

solving gives Lever Rule