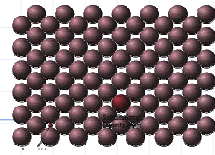
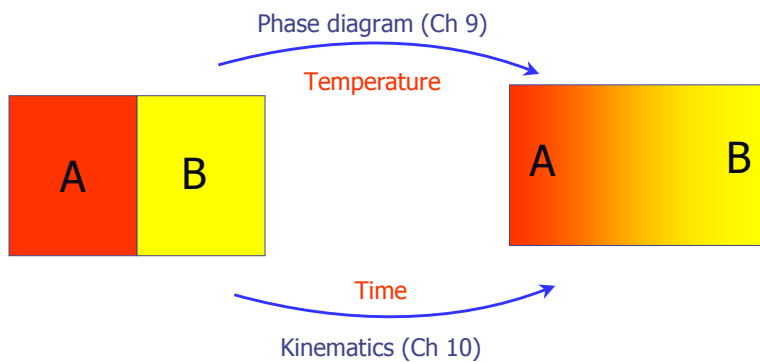


# Phase Equilibria & Phase Diagrams



## Motivation



New structure, concentration (mixing level)  
(at what temperature? for how long? )

## Goals for this unit

- Learn definitions and basic concepts of phase equilibria and phase diagrams
- Interpret equilibrium phase diagrams
  - binary isomorphous (complete ss)
  - binary eutectic (limited ss or no ss)
  - Intermediate compounds/phases
  - phases present
  - their compositions and amounts (i.e., the “phase assemblage” of the system)

ss: solid solution

## Phase Diagrams - Introduction

- Many materials systems can exist in a variety of forms depending on the temperature, pressure and overall composition (**allotropy**)
- A “phase diagram” is a *graphical representation* which details the form(s) the material takes under specific conditions
- Assumes the system has achieved chemical equilibrium (“equilibrium diagrams”)

## Definitions and Basic Concepts

- Equilibrium
  - thermodynamic definition: a system is at equilibrium if its free energy is at a minimum
  - characteristics of the system do not change with time, i.e., the system is stable
- If you change the temperature, pressure, or composition, the free energy will change
  - the specific phase(s) present may (or may not) change but the “phase assemblage” **will!**

## Definitions

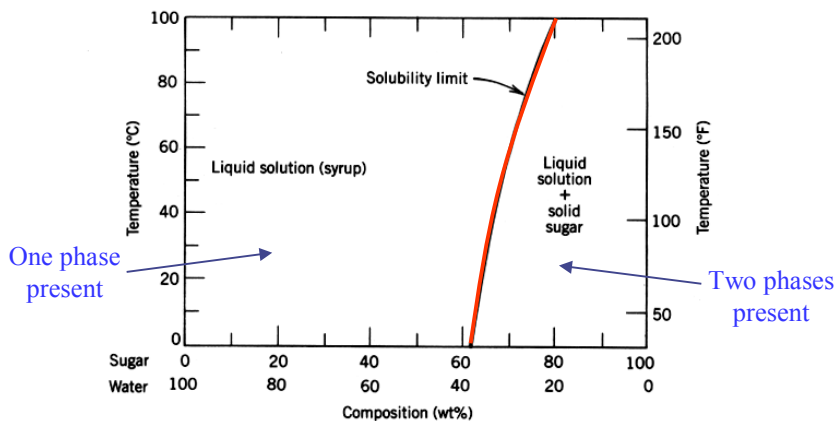
- Component (elements or compounds)
  - pure substance(s) required to express composition of phases in the system
- Phase (solid, liquid, gas)
  - Homogeneous portion of a system
  - uniform chemical and physical properties
  - several phases may be present simultaneously
  - in principal, phases are recognizable and separable
- System variables
  - Composition (in terms of components), temperature “T” and pressure “p”

## Phase Equilibria

- o Most systems we work with are solid systems:
- o Sometimes (usually) the kinetics (rate of reaction) of the system will not allow a phase change to take place completely, or instantly, under certain conditions
  - example: glass of ice water in the sun when it's 75°F outside (stays at 32°F until all ice is melted)
- o Consider glass, stable form is quartz
  - This is a **metastable state** - persists indefinitely
  - Same with diamond and graphite

## Definitions & Basic Concepts: *Solubility*

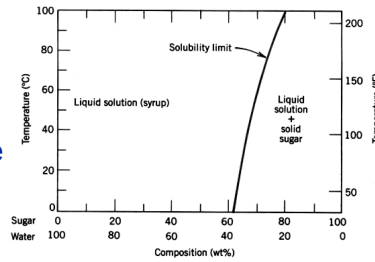
- o Solubility limit - Sugar in Water



Phase Diagram

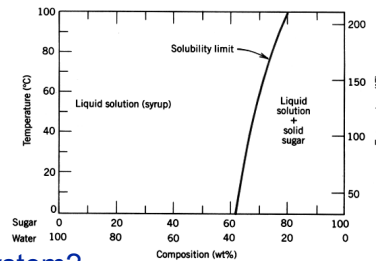
## Phase composition

- A particular phase can have variable composition (i.e., can be a solution)
- Solute and solvent
  - Solvent (component present in greatest amount)
  - Solute (present in minor concentration)
- Solubility Limit
  - maximum allowed concentration of solute in solvent
  - depends on species, temperature and pressure



## Definition – Phases

- This phase diagram is a two-component system, sugar(dextrose) and water.
  - Q. What are the phases in this system?
  - A. liquid (“*syrup*” or *sugar -in-water sol’n*) and a solid (*pure crystalline sugar*)
  - Note: **Solution vs. Mixture!**
    - A mixture is **heterogeneous** (more than one phase present)
    - A solution is a single **homogeneous** phase of variable composition.
- A two-phase mixture is present in the system (“syrup”+sugar)



## Phases

### Phase Characteristics:

A phase **does not** have to be **BOTH** physically and chemically distinct

Q. What is an example of a physically, but not chemically distinct phase?

- A. **Water, ice, steam or Diamond, graphite**

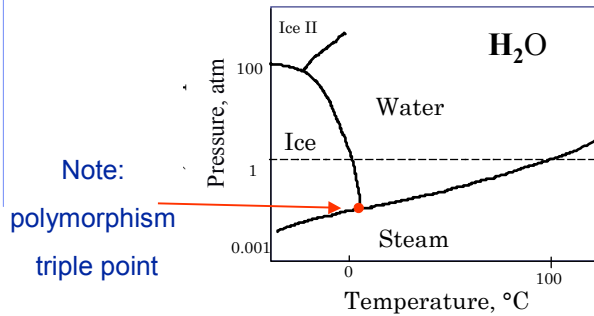
Q. What is an example of a chemically, but not physically distinct phase?

- A. **Oil and water (both are liquids)**

## Equilibrium Diagrams

- Represents phase relationships as a function of temperature, pressure and composition (equilibrium phases and microstructure)
  - But many useful diagrams are constructed for **constant pressure of 1 atmosphere**, so only composition and temperature are variables
- Phase diagrams provides us with information needed for the control of phase and microstructure in the materials we make

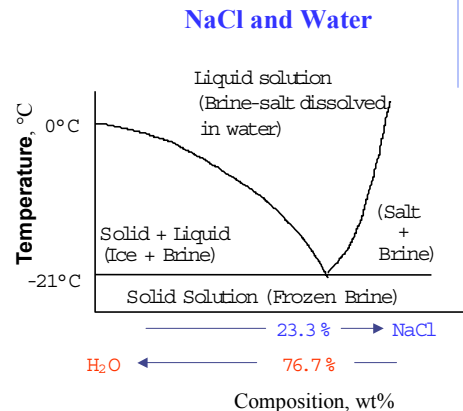
## Single Component Systems (fixed composition)



**Variables:** - Pressure “p”  
- Temperature “T”

## Two Component Systems (P=1 atm)

- o Melting temp of ice changes with % salt
- o Four phase fields
  - Liquid (Brine)
  - Solid and Liquid (Ice & Brine)
  - Solid and Liquid (Salt & Brine)
  - Solids (Ice and Salt)
- o Composition of brine changes
- o Questions
  - What is min temp at which salt works?
  - At any given temp is there an optimal amount of salt?



## The Phase Rule

- Gibbs Phase Rule
  - After J. W. Gibbs - 19th century physicist
- Based on thermodynamics
- Predicts the number of phases that will coexist within a system at **EQUILIBRIUM**
- Does not apply in non-equilibrium situations!

## The Phase Rule

$$P + F = C + N$$

- P = number of phases present
  - C = the number of components  
(minimum # needed to describe system)
  - N = number of noncompositional variables
  - N = 1 or 2 for T (*temperature*) and p (*pressure*)  
N = 1 If p=const or T=const
- (HINT: p is usually constant so N is usually 1)



## The Phase Rule

$$P + F = C + N$$

P = Phases

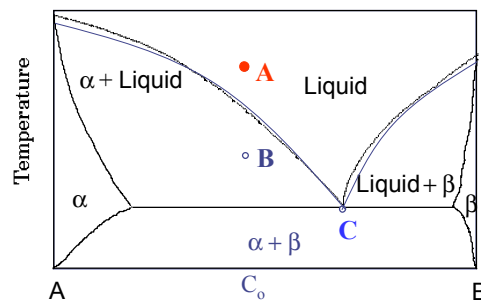
C = Number of components

N = 1 (usually for temperature)

F = number of degrees of freedom

No. of externally controllable variables (*e.g. T, p, and composition of a phase*), which can be changed independently without altering the number and kinds of phases which coexist at equilibrium.

## Phase Rule - Example



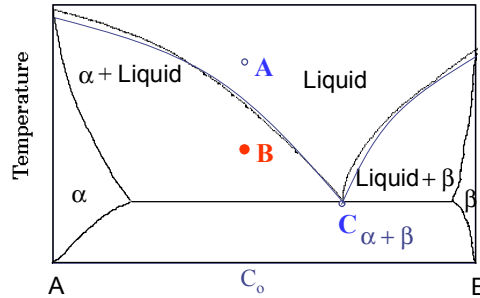
Point: **A**  $P + F = C + 1$  (N = 1, p = const.)

C = 2 (A and B) P = 1 (liquid)  $\rightarrow F = C + 1 - P = 2 + 1 - 1 = 2$

To completely describe the characteristics of this alloy:

- you must describe 2 parameters T and composition
- you can change 2 variables without changing the # of phases at equilibrium

## Phase Rule - Example



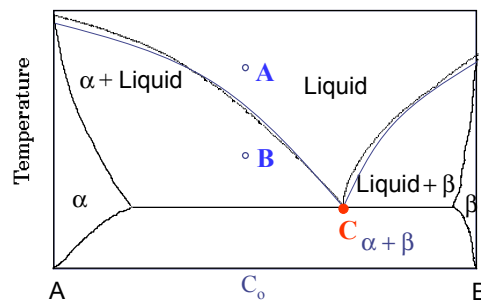
Point: B  $P + F = C + 1$  ( $N = 1, p = \text{const.}$ )

$C = 2$  (A and B)  $P = 2$  (liquid and  $\alpha$ )  $\rightarrow F = C + 1 - P = 2 + 1 - 2 = 1$

To completely describe the characteristics of this alloy:

- you must describe 1 parameter ( $T$  or composition of one of the phases)
  - you can change 1 variable without changing the # of phases at equilibrium
- (note only the nature of the phases is important - not relative amount)

## Phase Rule - Example



Point: C  $P + F = C + 1$  ( $N = 1, p = \text{const.}$ )

$C = 2$  (A and B)  $P = 3$  (liquid and  $\alpha$  and  $\beta$ )  $\rightarrow F = C + 1 - P = 2 + 1 - 3 = 0$  To completely describe the characteristics of this alloy:

- you do not need to describe  $T$  or composition
- you cannot change any variables without changing the number of phases present

## Equilibrium phase diagrams - binary systems

- I. Binary isomorphous (complete ss)
- II. Binary eutectic with no ss
- III. Binary eutectic with limited ss
- IV. Eutectoid
- V. Peritectic
- VI. Intermediate Phase
- VII. General

## I. Binary Isomorphous Systems “complete ss”

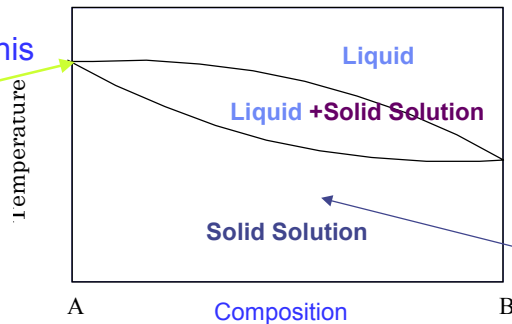
- Complete liquid and solid solubility of both components
- Common in some alloy systems  
e.g. Ni-Cu
- Seen in some salt systems  
KCl- KBr
- Solid phase is a “solid solution”
  - it’s like a liquid solution e.g. water and alcohol
  - not like a liquid mixture e.g. oil and water

## Solid Solutions

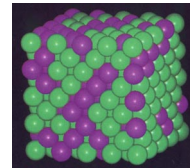
- How do they form:
  - Usually by introducing solute atoms into the solvent lattice
- **Why are solid solutions important?**
  - tailor mechanical, electrical, magnetic properties
- Complete solid solution sometimes occurs when solute and solvent have:
  - same crystal structure and similar atomic radii

## Solid Solution Phase Diagram

What is this point?

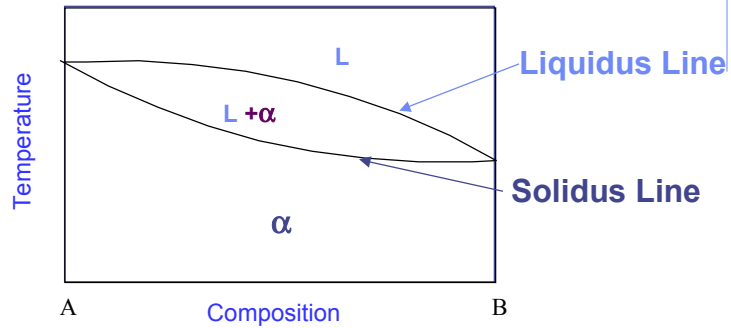


Liquid: AB  
SS: AB



- Complete Solid Solubility  
note that solid and liquid are each homogenous
- Q: Number of phases in each phase field

## Solid Solution Phase Diagram



- o Note solid solution phase is called  $\alpha$
- o Liquidus line- First solid appears on cooling
- o Solidus line- Last liquid disappears on cooling

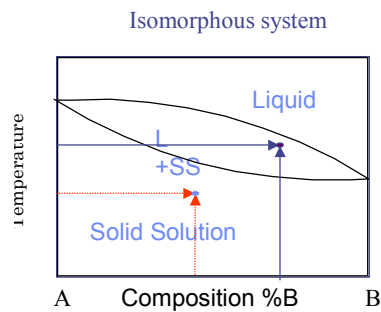
## Interpretation of Phase Diagrams

### To determine phases present:

1. Locate
  - Temperature
  - Composition

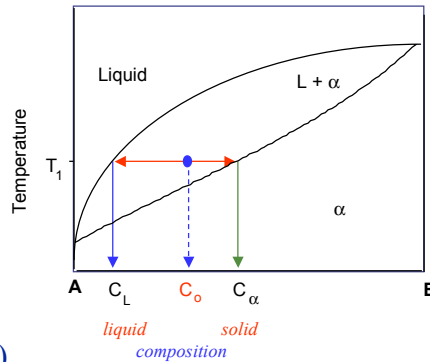
### 2. Phase Field is labeled

- Liquid and S.S. ( $\alpha$ )
- - - Solid Solution,  $\alpha$   
"Only"



## Phase Compositions

What is the phase assemblage  
For a composition of 35% B  
at a temperature of  $T_1$  ?



- Phases present (by inspection)
- solid solution  $\alpha$  and liquid
- Phase compositions (ends of the tie line)
  - $\alpha$  -- 45% B, 55% A
  - liquid -- 10% B, 90% A

## Phase Amounts- Inverse Lever law

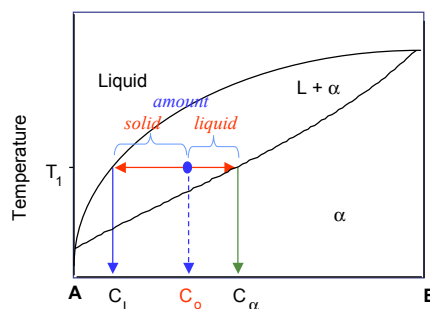
**How much liquid  
and how much  
solid?**

Use Inverse Lever Law

**At  $T_1$  and  $C_o$ :**

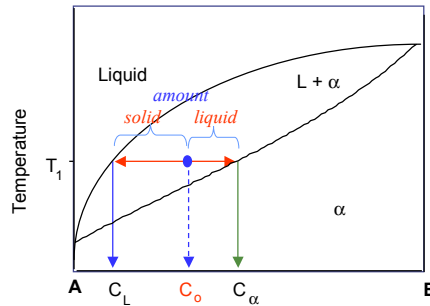
$$\text{Fraction of liquid} = \frac{C_o - C_\alpha}{C_L - C_\alpha} \quad \text{Fraction of solid} = \frac{C_L - C_o}{C_L - C_\alpha}$$

- Valid for two phase region only



## Phase Amounts- Inverse Lever law

$$\begin{aligned} C_o &= 35\% \text{ B} \\ C_L &= 10\% \text{ B} \\ C_\alpha &= 45\% \text{ B} \end{aligned}$$



### Phase Amount

- Calculate length of tie line and length of each segment
- e.g. For an overall composition of 35% AB at  $T_1$   
liquid amount  $= (45-35)/(45-10) = 0.286$  (28.6%)  
solid amount  $= (35-10)/(45-10) = 0.714$  (71.4%)

## Common Mistakes

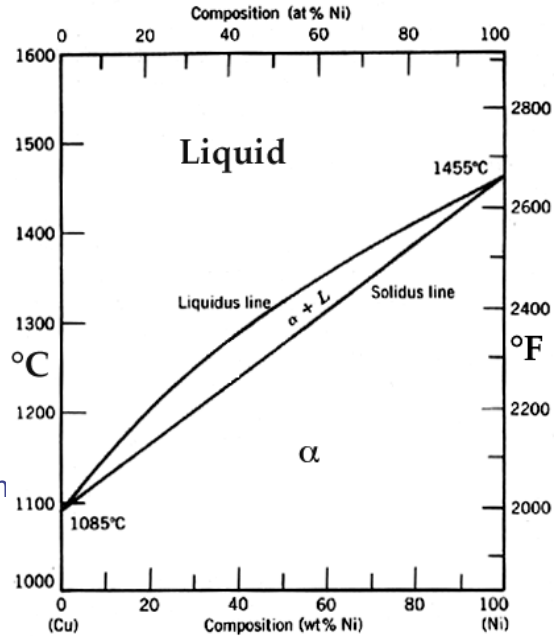
- Mixing up phase **composition** and phase **amount**
- Taking the fraction of the tie line for the wrong phase (take the length **opposite** the phase you are interested in)
- **Weight** fraction vs. **mole** fraction
- note how the composition axis is labeled!
- you may have to convert from weight to mole fraction or even to volume fraction

## Example

50-50 w% Cu-Ni

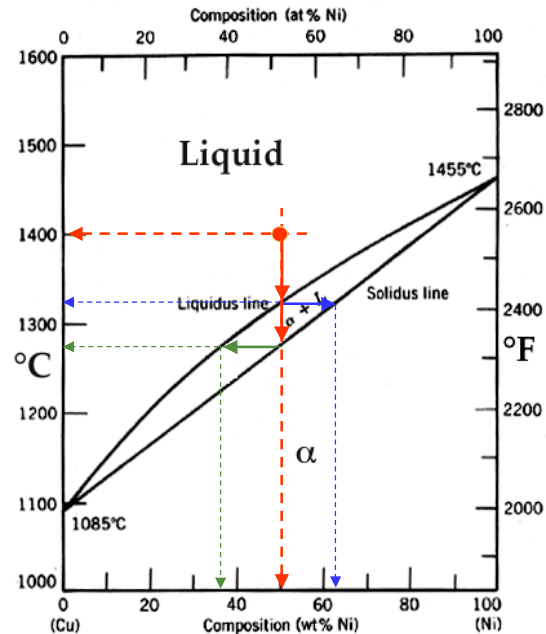
Cooling from 1400°C

- What T does 1st solid form?
- What is the comp. of the solid phase?
- At what T does the last liquid solidify?
- What is the composition of the liquid phase?



## Example

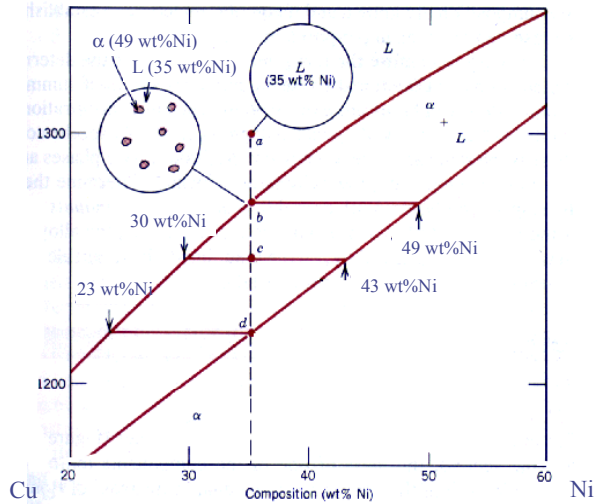
- 1st solid at 1320°C
- Composition of solid 62w% Ni, 38w% Cu
- Last liquid at 1275°C
- Composition of liquid: 37% Ni, 63% Cu
- Ni rich solid forms leaving Cu rich liquid





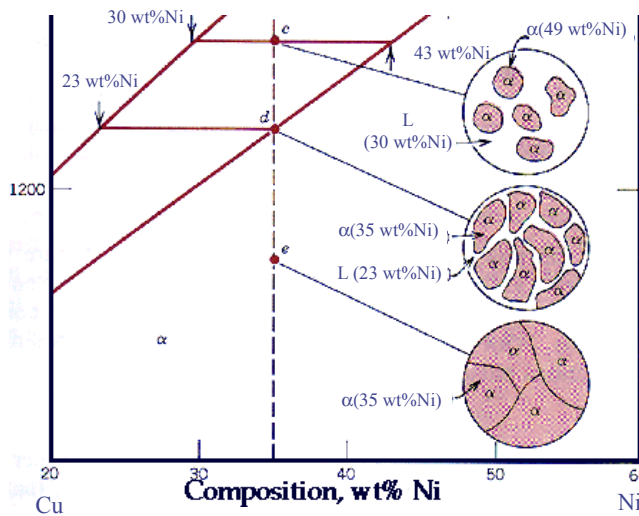
# Microstructure Development

Cu-Ni phase diagram



# Microstructure Development

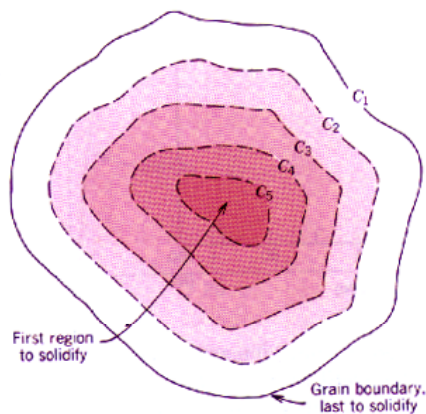
Cu-Ni phase diagram



# Microstructure Development

- Notice that composition of solid changes continuously as it forms
- Adjustments in composition is often limited by diffusion (dependent on rate of cooling)
- Most cooling processes are fast
  - nonequilibrium solidification
  - "segregation"
  - "cored" structures

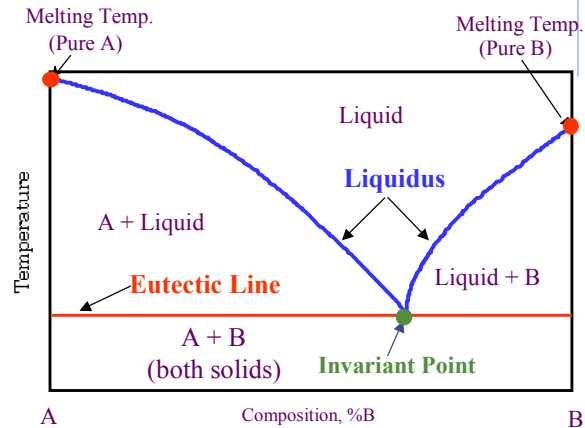
## "Cored" Microstructure



- Interior is rich in higher melting component
- Exterior is rich in lower melting component

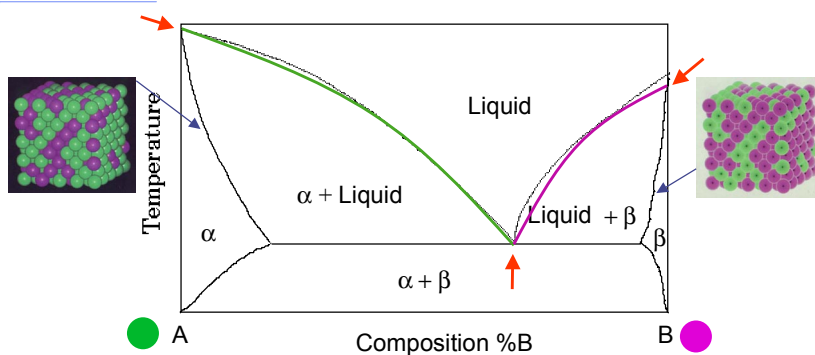
## II. Simple Binary Eutectic: *No Solid Solubility*

- o Liquidus - first solid appears on cooling
- o Eutectic Line - line of 3 phase equilibrium
- o Invariant Point - where 2 liquidus lines and eutectic line meet



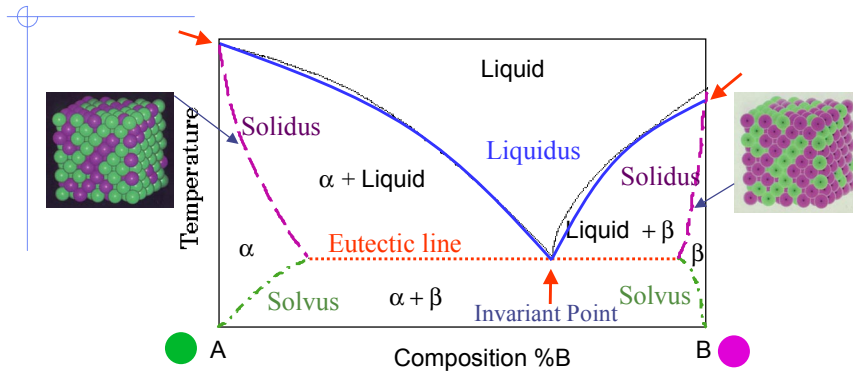
$$T_{m(\text{eutectic})} < T_{m(A)} \text{ or } T_{m(B)}$$

## III. Simple Binary Eutectic: *Limited Solid Solubility*



- o Limited Solid Solubility
  - alpha is solid A with small amount of solid B dissolved in it
  - beta is solid B with small amount of solid A dissolved in it
- o Components have different solid solubilities

## Binary Eutectic

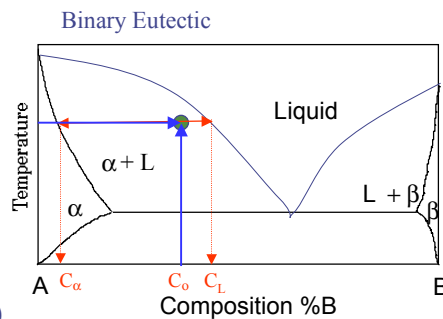


- o **Eutectic (occurs at eutectic temperature)**
  - Line of three-phase equilibrium
- o **Limit of solid solubility**
  - solidus (between solid and liquid and solid solution)
  - solvus (between single solid solution and mixture of solid solutions)

## Interpretation of Phase Diagrams

### To determine phases present

- Locate
  - Temperature
  - Composition
- Phase field is labeled

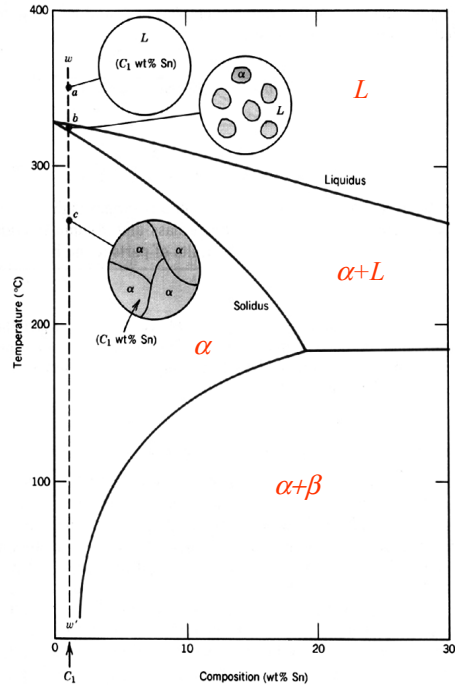


At  $T_1$  and  $C_o$  (approx. 35%B)

- Composition of Liquid is  $C_L$  (approx. = 45% B) , amount (~ 20%)
- Composition of Solid is  $\alpha$  - (approx. = 10%B) , amount (~ 80%)

## Microstructure

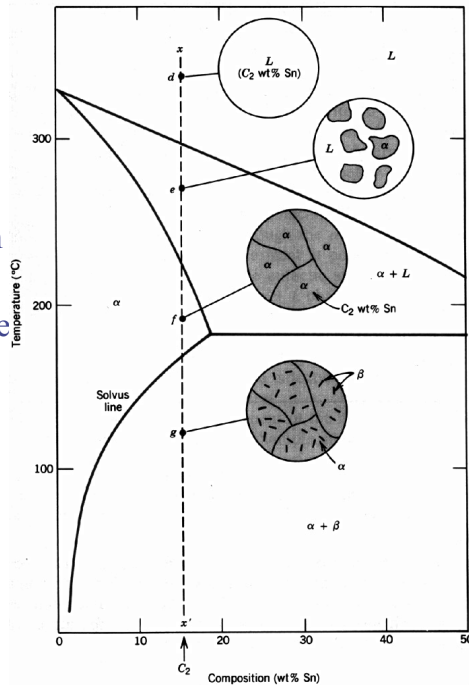
- Close to end-member
- Liquid above liquidus
- Solid  $\alpha$  precipitates crossing two phase boundary
- Solid  $\alpha$  forms complete solid solution region
- No other phase forms



Material Sciences and Engineering

## Microstructure

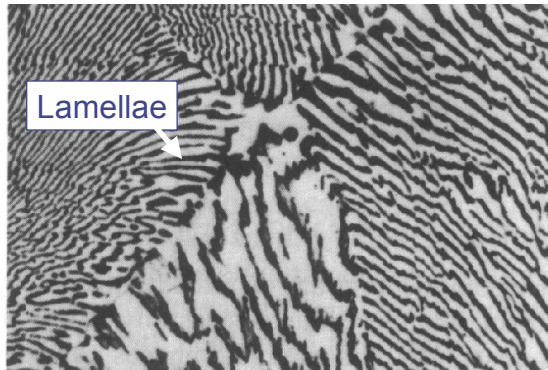
- First solid ( $\alpha$ ) forms at liquidus
- Solid grows- changes in composition
- Crosses solvus - become pure  $\alpha$
- Crosses two-phase boundary - ( $\beta$  precipitates)



Material Sciences and Engineering

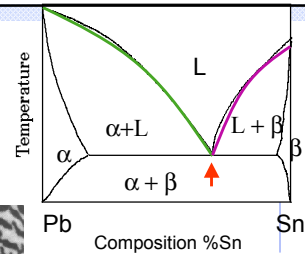
## Eutectic Microstructure

(forms when eutectic liquid freezes)



Alternating Pb-rich  $\alpha$ -phase (dark layers)

and a Sn-rich  $\beta$ -phase (light layers)



Chk textbook P. 317

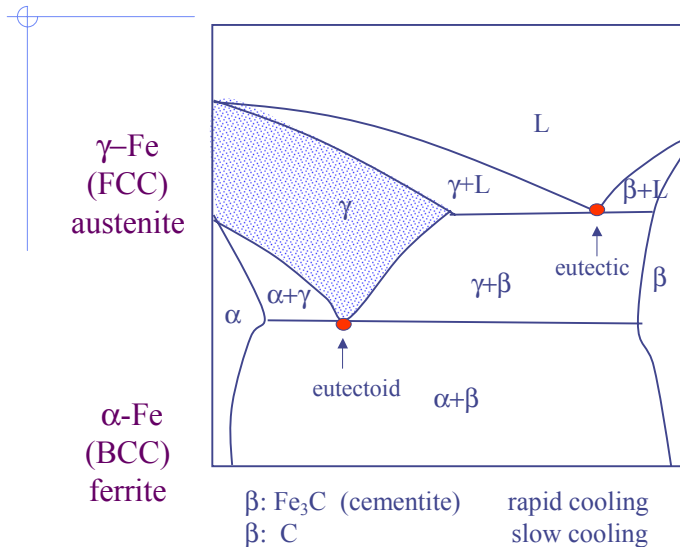
## IV. Eutectoid Binary Diagram ( $\gamma$ -Fe $\rightarrow$ $\alpha$ -Fe)

### o Eutectoid Reaction

- Invariant point with **three** phases
- Upon cooling, a solid phase transforms into two other solid phases
  - e.g.  $\gamma$  (eutectoid)  $\leftrightarrow$   $\alpha + \beta$
- It's like a eutectic only involving solids



## Eutectoid Binary Diagram



## Unit Review

- Explain basic concepts of phase equilibria and phase diagrams
  - Solubility limit, phases, microstructure
- Equilibrium phase diagram topics:
  - binary isomorphous, binary invariant points
  - phases present - their composition and amounts
  - microstructural development
- The phase rule is  $p+f=c+n$
- READ Class Notes & Shackelford, 2001, Ch 9, pp 304-321, 331-348